# The 69th AES Annual Technical Conference Proceedings

San Francisco, CA June, 1982

Published by
American Electroplaters' Society, Inc.
1201 Louisiana Avenue, Winter Park, FL 32789

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Printed AES Press

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# Powder Coating
# Session J

## Metal Pretreatments for Powder Coating

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# METAL PRETREATMENTS FOR POWDER COATING

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## Abstract

Because of the unique nature of a dry powder paint film, special consideration must be paid to the pretreatment of metal prior to application of electrostatic powder paint.

This paper will describe the pre-paint treatment of various metals (steel, galvanized, aluminum), with emphasis on specific requirements in the case of powder coating applications. Case histories, examples, and slides will be used to demonstrate specific cases. The powder system, the substrate, the end product, and the exposure conditions materially affect the choice of pretreatment process.

A "total systems" approach should be used in choosing a processing line for pretreatment ahead of powder paint.

## Some Background on Powder Coating

Electrostatic powder application of paint film has enjoyed more than 10 years success in the U.S. and even longer overseas, particularly in Europe, where some of the early powder developments were commercialized. The advantages inherent in its use are many. When compared with "conventional" solvent-applied finishes, powder coating provides:

- Dramatic reduction in air pollution, since powders contain no solvents.
- Reduced fire hazard associated with its low flammability.
- Ability to apply uniform coatings of considerable thickness in one application.
- Highly efficient reclamation and re-use of oversprayed material.
- Good surface coverage with virtually no runs, tears, or sags.
- Elimination of messy, polluting water-wash systems to trap overspray.
- Energy savings by significant reduction in make-up air for spray booths.

Like any new technology in commercial development, powder coating was not without problem areas, however because of the many inherent advantages in the concept, paint vendors, equipment builders, and end users worked diligently to overcome the obstacles. Some of these early problem areas were:

- Need for completely new application equipment, necessitating high capital investment.
- Slow color changes.
- Poor powder storage stability.
- Difficulty in achieving thin coatings ( 1 mil).
- Poor coating deposition at inside corners and cavities (Faraday cage effect).
- Unavailability of metallic colors.

Industry has for the most part been successful in eliminating or reducing the severity of these problem areas, to the point where spray electrostatic powder application has taken its place as a definite finishing option in a wide variety of industries.

## Pretreatment Requirements for Powder

Years ago, when powder paints were applied to metal by hot dip, with film builds ranging from 5 to 15 mils or more, there was in most cases no need for any surface preparation other than oil and soil removal, because a thick, virtually impervious envelope was provided to protect the base metal. When spray electrostatic technique allowed for thinner films to be deposited with powder, it became clear that metal pretreatment was as important with powder coating as it was with liquid paints.

To complicate matters further, since the powder particles cannot by their nature "wet" the substrate as liquid systems can, the initial adhesion of coating to substrate is critical. Further, paint systems based on organic solvents can be more forgiving of a surface containing some oily residue by dissolving the contaminant into the paint film. Powder does not have this capacity. Thus, powder coatings have presented some unique situations in and of themselves as compared to solvent-borne paints.

## Soil Removal

Some of the simplest pre-cleaning methods involve degreasing with vapor or solvent. Systems like these tend to remove oil effectively from metal surfaces, but do a rather poor job of removing smuts, solid particles, or rust and scale.

If rust or scale are present, removal can be accomplished mechanically

with wire brushes, sanding discs, or the like. Abrasive blasting can also be used. Such impact pretreatment techniques involve the impingement of the surface with any one of a number of abrasive media, ranging from alumina or iron "shot", to glass beads, and even softer, natural abrasives such as nut shells, all available in a wide range of mesh sizes. Impact surfacing equipment has been dramatically improved over the past years, so that it can be automated and made virtually dust-free, with excellent media separation and recycling systems available. Impact or mechanical abrasion techniques have achieved some success in conjunction with powder coatings. Costs, however, can be higher than other methods, and a tendency for subsequent re-corrosion after sanding or blasting can be a major problem with cold-rolled steel.

In the majority of large commercial installations, oils and soils are usually removed with an alkaline cleaner. These proprietary chemicals are normally supplied as powders to be dissolved in water, but liquid versions are available. They are formulated with alkaline builders and synthetic detergents to optimize properties such as oil emulsification, saponification, dirt dispersion and suspension, water softening, and rinsability. Well formulated alkaline cleaners are available to remove not only organic residues (oils), but also smuts, and to a certain degree, rust or scale.

Acid pickling can be used to remove large deposits of rust or scale. Phosphoric acid formulations are often used for this purpose because of a reduced tendency for subsequent re-rusting, but other mineral or organic acids are sometimes substituted. Acids can be formulated with surfactants and water-miscible solvents to provide cleaning and de-rusting in one step.

No matter what the method of soil removal, a thorough cleaning job is essential to the subsequent performance of a powder coating. Residual grease and oil are detrimental to adhesion. Dirt, smut, fines, rust and scale readily lead to pinholes and blisters in the applied film because the water and oxygen (or other gaseous contaminants) come out thru the coating during the cure cycle. The choice of cleaning methods is made by considering production rates, part configuration, the types of soil to be removed, and the performance requirements of the finished piece.

## Simple Treatment Methods

If the powder coating to be applied is purely decorative, with little need for long-term resistance to a harsh environment, simple cleaning of the metal may be the only pre-paint handling required. For instance, vapor degreasing with chlorinated solvents gives good initial adhesion, but at some later time adhesion losses may occur if the workpiece is exposed outdoors or in a moist environment.

Alkali cleaning followed by a water rinse and dry-off is hardly used because of the concern for flash-rusting during drying.

Deoxidizing with a phosphoric acid formulation followed by a water rinse and dry-off can be an acceptable pretreatment for low-performance

decorative powder coatings. The tendency of steel to rust-blush during the drying step is reduced because of the passivating nature of the treatment. The phosphoric acid chemically modifies the steel surface, accomplishing a simple chemical conversion coating.

## Conversion Coating

A conversion coating is produced on the surface of a metal by the chemical reaction of a solution with the metal substrate. Components from the coating solution react with the metal surface to produce an insoluble, inorganic crystalline or amorphous coating on the metal. Conversion coatings increase the quality of a painted surface because:

- They convert the metal substrate to one which is much less reactive to subsequent corrosion.
- They provide "tooth" to the surface and serve as an absorptive base for improving the adhesion of an organic film to the substrate.
- They remove inorganic soils such as metal fines, light oxide films, and other surface contaminants.
- They serve as barrier film to stop possible chemical reaction (such as saponification) between organic films and the metal substrate.
- They impart an equal electrical potential to the metal surface, neutralizing any local anodic or cathodic "hot spots," thereby eliminating galvanic corrosion sites.

There are a variety of conversion coatings in common use ahead of powder coating. They range from iron and zinc phosphates on steel, to chromates or phosphates on galvanized or zinc substrates, to chromates or chrome-phosphates on aluminum.

There is a great possibility for variation of properties within a given generic coating type. For instance, an iron or zinc phosphate can be light or heavy in coating weight; the zinc phosphate crystal structure can be coarse or fine. Chromates on galvanized or aluminum can range from thin and iridescent thru a definite gold almost to a chocolate brown. Chrome phosphates on aluminum can likewise be thin and virtually colorless thru an iridescent green to a definite green hue.

The choice of pretreatment to be used ahead of powder coating is critical to the ultimate performance level of the finished product.

## Phosphate Coatings on Steel

Iron phosphates are applied on steel (and sometimes zinc and aluminum) surfaces from proprietary alkali-metal phosphate solutions. The actual coating deposited from an "iron phosphate" bath is a mixed oxide-phosphate

of the base metal. So, although technically there is little or no actual pure iron phosphate present on a zinc or aluminum surface after treatment in an "iron phosphate" bath, the generic name is still commonly used to describe the process on all three metals.

Coatings deposited from an iron phosphate bath are amorphous in nature, iridescent, slightly transparent, ranging in color from yellow-gold thru blue or violet, and are generally thin. A coating weight of 20 to 50 mg/ft$^2$ is common. Iron phosphate baths are relatively simple to control.

The adhesion of a powder coating to an iron phosphate is very good, and the corrosion resistance is much improved over a bare surface.

Zinc phosphate coatings are deposited on steel and galvanized surfaces (and less commonly, on aluminum) from solutions of zinc phosphate in combination with accelerators, refining agents, and various other proprietary ingredients formulated to modify the coating for optimum results. The coatings thus deposited are crystalline in nature, grey in color, and form an extremely adherent bond with the base metal.

The crystal size is dependent on such factors as growth rate, agitation, the effects of nucleating agents and foreign atoms in the crystal lattice. For example, crystal size can be reduced by pretreating the steel surface in a bath containing certain heavy metal salts, such as titanium phosphate, in colloidal suspension. In this pre-conditioning step, finely divided colloidal particles are deposited on the surface, serving as nucleation points for the subsequent deposition of a large number of very small crystals. Coatings of smaller more densely packed crystals provide optimum adhesion with an applied film. They likewise provide better corrosion performance because their low-porosity matrix, virtually void-free, prevents corrosive reactions from initiating.

Under most powders, the corrosion resistance of a zinc phosphate coating is excellent. The best adhesion results with time are realized if the coating weight and crystal size are kept low, say in the range of 100 to 300 mg/sq.ft.

Coatings for Galvanized and Aluminum

The application of powder coating to galvanized or aluminum is not as extensive as it has been to steel, but as powder technology increases to allow more wide-spread use of powder on these metals, the interaction of conversion coating and powder film will become more important.

If galvanized steel is coated as part of a larger assembly, the major surface area of which is cold-rolled steel (such as in an automobile body), or in a multi-metal pretreatment line, the galvanized is coated with the same type of conversion coating as is applied to the steel, usually zinc phosphate.

Where galvanized steel is the only metal being coated, as in a coil-coating application, a chromate coating is generally applied prior to the

application of the organic film. A chromate coating applied to a galvanized surface is colorless or nearly so, but contributes vastly to the adhesion and corrosion protection of the finished workpiece.

If passivated galvanized is to be subsequently powder coated, a chromate pretreatment is preferred over a zinc phosphate. Because of the more aggressive chemistry of the chromate bath, the passivating film interferes less with the conversion coating deposition. Phosphate coatings on passivated zinc are irregular and possess large differences in crystalline structure.

For hand treatment of zinc or galvanized surfaces, a phosphoric-acid based system with added fluorides has been effective.

The two types of aluminum pretreatment in common use are both based on solutions of hexavalent chrome (chromic acid). The chrome-phosphate baths are more reactive with aluminum surfaces and are thus used on aluminum extrusions which are generally more difficult to coat because of heavy oxides. For conventional rolled aluminum parts or fabrications either "gold" or "green" conversion coatings will give good performance as a pretreatment for powder films. Light coatings free of powder provide the best substrate for preventing corrosion and adhesion loss.

Pretreatment Equipment

Regardless of the type of metal to be treated, and for virtually any conversion coating used, the sequence of operations needed to optimize powder coating performance is essentially the same. A typical total system sequence is:

Clean
Rinse
Conversion Coating
Rinse
Passivating rinse

As noted earlier, the initial cleaning step is critical to insure complete soil removal and to allow complete contact of the subsequent coating solution with the metal surface. Cleaning is followed by a rinse to remove spent cleaner solution and loosened soil. Sometimes a second rinse is added to insure proper soil removal. If the subsequent coating stage will be a zinc phosphate, the second water rinse might contain the titanium phosphate colloid so important for the deposition of fine, densely packed crystals.

After the conversion coating has been applied (and rinsed to remove residual chemical), a passivating final rinse is typically applied. This rinse, normally a dilute solution of chromic acid, acts as a passivation treatment which enhances the corrosion performance of the system. Sometimes a rinse of distilled or deionized water following the passivating rinse is desirable to remove the excess soluble materials present on the surface and thereby reduce the incidence of film blistering in service.

Pretreatment can be accomplished by either spray or immersion systems. When comparing the two systems, some relative advantages become apparent. Conveyorized spray systems possess a significantly greater production capacity, and are therefore more commonly used in high-volume applications. Spray systems are likewise preferred because impingement of the various solutions aids cleaning and rinsing, and because the more rapid displacement of the coating solution at the metal interface reduces the required treatment time compared to immersion systems. Further, the lower chemical concentrations possible in spray baths reduce initial make-up costs; however, the lower initial capital costs of dip systems, coupled with the reduced maintenance costs of dip lines because of fewer moving parts, makes an immersion system a viable alternative for many small treatment lines.

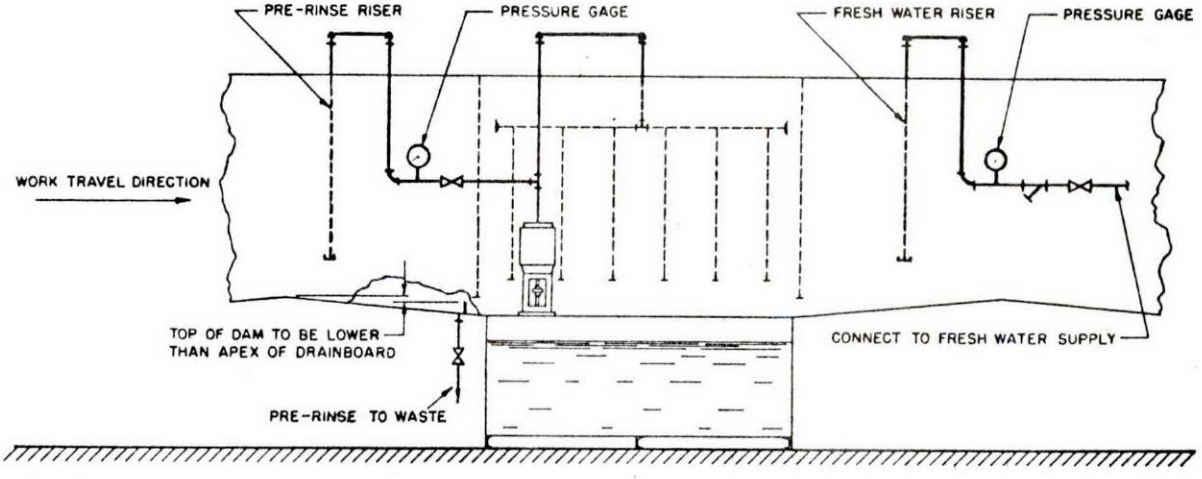
In instances where the workpieces are very large, or production very sporadic, or the work load is not otherwise conducive to continuous conveyorized operation, hand held spray wands (or even hand-wiping techniques) can be used to advantage.

## New Developments in Pretreatment Systems

Increasing energy costs and environmental pressures have prompted suppliers of pretreatment chemicals to develop new generations of materials in response.

Alkaline cleaners are now being formulated with completely biodegrada ble surfactants, and with non-phosphate or low phosphate builders.

New treatment facilities are being designed, and existing equipment retrofitted, with cascading rinse techniques or other methods for more efficient utilization of rinse waters. One such system is show here:




THREE-PHASE RINSE STAGE

Various new products are now available containing none of the undesirable, highly toxic compounds (such as those containing hexavalent chromium). Chrome-free final rinses have gained acceptance in many pollution-conscious areas. Non-chrome coatings for aluminum and galvanized are in common use, as are "no-rinse" products which are dried on the workpiece and thus generate no rinse effluents.

Major efforts have gone into the development of lower-temperature processes, especially in the cleaning and treatment stages, Significant savings in energy can be realized. For instance, an alkaline cleaner formulated to provide good cleaning at, say, 110°F, will consume less than half the energy of a system operated at the "normal" temperature of 160°. In addition, scaling of material onto the processing equipment is significantly reduced at lower temperatures.

Advances have been made in the area of automatic solution control. No matter what metal or pretreatment system, good chemical control and replenishment of each pretreatment stage is fundamental to continued successful operation. It is possible to automate many of the solution control procedures electrometrically, by conductivity, or pH, or redox potential. Such automation provides savings in labor and chemical costs and water consumption, as well as providing more consistent, reproducible bath conditions.

## Test Procedures and Results

Performance testing is important to determine the proper relationship between substrate, pretreatment, and organic film, as it relates to the desired properties of the end product. Thus, it is the responsibility of the user to establish a test program to define and insure the proper performance of the entire system. This "total systems" approach is essential to attaining an acceptable level of product quality, both at the outset and under continuous production.

Tests may vary depending upon the end use of the product, but generally performance testing can be accomplished by one or more commonly used test procedures.

SALT SPRAY TESTING is commonly used to study corrosion performance of finishes. ASTM B-117 describes apparatus and procedures for conducting the five percent salt fog test. Some people feel that salt spray testing of powder films does not correlate with outdoor exposure results as well as it might with other types of organic finishes. This can certainly be the case with the epoxy powders, which exhibit degradation on outdoor exposure to sunlight not predicted by salt spray testing.

HUMIDITY TESTING is used to study resistance of coatings to degradation by moisture. ASTM D 2247 describes apparatus and procedures for conducting the test, which exposes specimens to an environment of 100% relative humidity. Specimens are then evaluated for blistering, rusting, adhesion, specular gloss, and the like.

DETERGENT TESTING, performed in accordance with ASTM D 2248, measures

the ability of a film to withstand immersion in a hot solution of a synthetic detergent. It is normally used to test appliance finishes.

GRAVELOMETER TESTING, described by SAE Specification J 400, determines the chip resistance of a film when impinged with small stones under controlled conditions. Sometimes test pieces are subsequently tested in salt spray after gravelometer testing.

ADHESION TESTING is performed in many ways. Standard methods can include scratch, cross-hatch, impact (direct or reverse), mandrel bend, wedge impact, abrasion, tape, T bends, or ductility, alone or in combination with other exposures. These tests determine the degree of adhesion of the cured powder film to the substrate.

Whatever series of tests the manufacturer can determine as being the most pertinent to the use performance of his product, the expected results should be clearly defined and specified to all involved parties, especially including the suppliers of the powder, the pretreatment chemicals, the application equipment, and the raw metal stock. The material suppliers, in turn, will expect the manufacturer to exercise his own responsibility of using the materials in precisely the manner specified, maintaining the equipment in its proper order, and providing a sufficient number of adequately trained operators to carry out the process in the prescribed manner. It is not until all involved parties understand and accept their individual responsibilities that a true "total systems" approach can work effectively.

J-2

# Powder Coating Session J

## Powder Coating Increases its Role in Surface Finishing

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# POWDER COATING INCREASES ITS ROLE IN SURFACE FINISHING

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## Abstract

This paper presents the latest developments in powder coating materials, application equipment/systems, and comparative economics vs. alternate organic coating compliance technologies available for surface finishing of industrial products. Emphasis is placed on outlining the performance characteristics of the thermosetting epoxy, polyester, and hybrid powder coatings most widely in use today, along with highlighting the types of industrial products for which these powder coatings perform particularly well and economically in the surface finishing process. Examples of the recent trend in new powder coating application installations are also given.

## Introduction

After a decade of development and hard won acceptance, powder coating is now considered a mature finishing technology. Powder coating is a dry painting process in which no solvents, thinners, or liquid carriers are used. Because oversprayed powders are simply collected and reused, high material useage efficiencies of 95% or more are common for this unique new process. This fact, coupled with savings in energy consumption, labor costs, lack of solvent mixing as well as virtual elimination of volatile organic emissions and solid or liquid wastes, has made powder coating an economical and desirable high quality finishing process for a growing number of a wide variety of industrial products. Sales of electrostatic powder coatings surged ahead in 1981 or up almost 15% over the previous year exceeding 50 million pounds,according to industry market analysts. Powder coating is being given considerable attention including a number of new installations in California as a surface finishing process which is in compliance with the Bay Area's Regulation 8, Rule 19 and the South Coast Air Quality Management District's (Los Anglees) Rule 1107; these recent amended rules have a compliance deadline of January 1, 1983 for industrial finishers applying baked (194+ degrees F) coatings with minimum 59% and 62% volume solids respectively at 65% transfer efficiency to manufactured metal parts and products. Based on the current interest in new electrostatic spray powder coating installations including equipment and system purchase commitments made late in 1981 and early 1982, powder coating is indeed increasing its role in finishing.

## Powder Coating Materials

Powder coatings are available to the industrial finisher in two major types, namely the thermoplastics and the thermosets. A thermoplastic powder coating is one which melts and flows on the application of heat, but remains with the same chemical composition when it solidifies on cooling. Thermoplastic powder coatings are based on thermoplastic resins of high molecular weight as the properties of these coatings are dependent on the basic properties of the resin. These tough and resistant resins tend to be difficult; and also expensive to grind to the very fine particles necessary for the fusion of thin paint-like film thicknesses. Consequently, thermoplastic resin systems are used more as thicker film functional coatings of many mils thickness; and applied mainly by the fluidized bed application technique.

Typical examples of thermoplastic powder coatings would be:

Polyethylene

Polypropylene

Nylon 11 & 12

Polyvinyl Chloride

Polyester

Fluoropolymers

Since only 1% of the total electrostatic spray applied powder coating useage for metal products in the United States is represented by primarily polvinyl chloride, nylon 11 and fluoropolymer powders, our comments on these thermoplastics have been brief. The other major type of powder coating is, of course, the Thermosets which are capable of producing thin film paint-like surface coatings, and represent 99% of the electrostatic powder coating market. Thermosetting powder coatings are quite different from Thermoplastic powder coatings in that they are based on lower molecular weight solid resins, which on melting and flowing, chemically crosslink within themselves or with other reactive components to form a higher molecular weight reaction product. The coating film formed by this reaction is heat stable and will not soften back to a liquid on further exposure to heat as would a Thermoplastic. Powders based on these resin systems can be ground to fine particle sizes, i.e. in the range of 25-40u average, and also due to the rheological characteristics of these resin systems can produce thin paint-like 1-3 mil coatings.

The generic types of resins used in Thermosetting Powder Coatings are:

Epoxy

Polyester

Acrylic

It is this area of Thermosetting powder coatings that a large technological edpansion has occurred in the last few years.

Epoxy Resin Based Systems

Epoxy powders still are the most prominent type of thermosetting powder coating in the USA today due to their very wide range of formulation latitute. Epoxy powders are used for both thick film functional end uses and for thin film decorative uses. The two major thick film functional end uses for epoxies are in electrical insulation and corrosion protection. In the insulation end use, epoxy powders conform exactly to the contours of the electrical part, bonding to the surface of the part to become a permanent integral insulation that is void-free and of low bulk. Typical applications would be automobile alternators, electrical motors and in switch gear. In the area of corrosion protection, epoxy powders provide low cost, low maintenance and long lasting protection against most chemically aggressive environments making them suitable of exterior and interior coating of oil and gas transmission and distribution pipe. In the area of thin film surface coatings, i.e. 1-3 mil range, epoxy powders are formulated to produce highly attractive coatings of whatever gloss or surface texture is desired, while still retaining the inherent toughness, corrosion resistance, flexibility and adhesion characteristic of the epoxy resin family. Recent advances in epoxy crosslinking chemistry has given the formulator a wide range of film properties within the epoxy area, especially in the area of bake time and temperature. Epoxies are now available that can be baked at temperatures as low as 250 degrees F for a period of 20-30 minutes or for a very short time at much higher temperatures. A good example of a need for a fast curing thin film would be in the epoxy powder coating of insect screen wire.

Unfortunately, with this excellent combination of mechanical and resistance properties, epoxies do have one major disadvantage in the area of exterior weatherability. An epoxy will exhibit rapid chalking within a few months of exterior exposure, just as would a liquid epoxy coating. Although a weathered epoxy coating may look unslightly, it

still maintains its mechanucal and resistance properties. Thus, decorative epoxy powder coatings are restricted to internal uses or areas of very little UV exposure. However, this still leaves a lot of possible application areas. Because of its combination of toughness and resistance properties, epoxy powders are finding many uses in the Appliance industry. For example, white epoxy powder coatings have replaced porcelain on the interior of regriferators providing performance advantages and cost savings. The advantages come in the freedom from cracking, characteristic of porcelain, when handled roughly, and the cost savings in the type of substrate used in the liner construction. Porcelain requires low carbon steel which has to be thoroughly pickled through as many as fourteen stages, whereas powder coating can use Fe or Zn-phosphated cold rolled steel. Other areas of the appliance industry include the interior coating of dryer drums and wire racks for refrigeration. Another expanding use today is the coating of microwave oven cavities. - - Similarly, the properties of epoxy make them very suitable for many under hood automotive parts such as oil filters, and automotive springs, and many other end uses where exterior durability is not a prime requisite

Typical epoxy properties can be summarized:

Epoxy Properties

| | |
|---|---|
| -Hardness | HB - 5H |
| -Impact | 60 - 160 |
| -Salt Spray | 1000 Hrs. Min. |
| -Exterior Durability | Poor |

Epoxy-Polyester Hybrids

Recently there has been an upgrading of the epoxy powders by the utilization of a special hybrid binder system based on the direct reaction of new acid polyester with solid epoxy resins. Property-wise, these new hybrid powder coatings are more closely akin to epoxies than polyesters with a few notable exceptions. They show similar flexibility in terms of impact and bend resistance, but are slightly softer in film hardness. Their corrosion resistance is comparable to epoxies in many cases; oil filter is an example of a good application for a hybrid system. A major advantage of these hybrids, due to the influence of the polyester component, is a higher resistance to overbake yellowing in the cure oven this also translates to improved weatherability; these systems

will begin to chalk almost as fast as an epoxy, but after that, the deterioration is slower and the discoloration less severe. Another advantage of epoxy-polyester hybrid powder coatings is extremely good electrostatic spray characteristics. They have excellent transfer efficiency and penetrate well into corners and recesses, a property essential for the coating of radiators where good coverage is required between the fins.

The consideration of an epoxy-polyester hybrid should certainly be made along side that of epoxy, if one is considering a thin film decorative end use. Since epoxy and hybrid powder coatings readily meet the latest 240-336 hours (up from 96 hours) 5% salt spray test requirements to satisfy Detroit's objective of a 10 year service life for automobiles, both types are finding increasing use for decorating and protecting also battery trays, valve and regulator covers, fans, wiper motors, air conditioner components, air cleaner housings, engines, and transmission housings. General Motors now applies powder as a primer surfacer to their lightweight S truck bodies on a new line in Shreveport, LA; high material utilization and improved truck body corrosion resistance reportedly achieved on this line are encouraging factors for powder coating's growing use as an automotive primer surfacer.

Hybrid Properties

| | |
|---|---|
| -Hardness | HB - H |
| -Impact | 60 - 160 |
| -Salt Spray | 1000 M + |
| -Exterior Durability | Fair - Poor |

Polyester Resin Based Powder Coatings

The polyester powder coatings being used commercially in the United States represent two types. The primary type which has been in use for the past seven years is a urethane cured polyester comparable chemically to the exterior quality urethane paints which have been used on aircraft, buses, trucks, and railroad cars for the past ten to twelve years. They combine outstanding thin film appearance and toughness, with good weathering properties. Typical curing times for these types of systems range from 30 minutes at 320 F to 10 minutes at 400 F. These polyesters are true competitors to high quality liquid paints in respect to thin film appearance, i.e. in the 1-3 mil range and have found many uses in the Appliance and General Metal Finishing areas. One major use for

these polyesters is the coating of lighting fixtures where excellent reflectivity is required at a minimal film thickness. Other areas of use include office furniture, wheels, boat trailers, garden tractors and many others where exterior durability is required. In the Appliance industry, they are used as a procelain replacement on range side panels and meet all the requirements of this industry's exterior finishing specifications.

Polyester-Urethane Properties

| | |
|---|---|
| -Hardness | HB - 2H |
| -Impact | 60 - 160 |
| -Salt Spray | 1000 Hrs. |
| -Exterior Durability | Good |

The second type of polyester is based on technology developed in Europe and recently introduced in the U.S. market. These products can best be described as more exterior durable cousins of the epoxy-polyester hybrids previously described. The difference being that instead of using a conventional epoxy resin to co-react with the polyester, a very low molecular weight glycidyl or epoxy functional curing agent is used. In this way, the polyester constitutes a very high percentage of the resin and provides a high degree of exterior weathering durability. They are typically baked for 20 minutes at 350-375 F, but more recent formulations do give cures as low as 300 F. This could be an advantage over the urethane cure polyesters in certain applications. The primary attributes of this type of polyester, though, are their excellent mechanical properties at high film thicknesses, good edge coverage and very good application transfer efficiency performance. An ideal application for this type of polyester powder is the coating of air conditioner cabinets where a combination of good sharp edge coverage is required on the venting, with good exterior durability. Thicknesses of 3 to 5 mils offer excellent flow, gloss and toughness and exterior durability making them suitable for the coating of such items as outdoor furnuture, wrought metal architectural products, snow blowers, and prefabricated steel storage silos. However, these glycidyl polyester powders can be applied in the 1 - 2 mil range giving a little more textured surface appearance than the urethane cured polyesters, but again, advancement in this area is narrowing the difference with an emerging major new use for coating aluminum extrusions. Over-bake color stability is also excellent. Their adhesion and corrosion resistance properties are comparable to the urethane cured polyesters.

Glycidyl Polyester Properties

| | |
|---|---|
| -Hardness | HB - H |
| -Impact Resistance | 60 - 160 |
| -Salt Spray | 1000 Hrs. |
| -Exterior Durability | Good |

Acrylics

The other generic group of thermosetting powder coatings giving exterior durability is the acrylics. The major acrylic powder coatings sold in the U.S. are of the urethane cure type, although there are a few glycidyl or epoxy functional acrylics being imported from Japan. Acrylic-urethane powder coatings require similar bake temperatures to the polyester-urethanes with a minimum cure temperature around 340 F. They are also characterized by excellent thin film appearance and unlike liquid acrylic paints, retain a good level of film flexibility in the form of impact resistance with excellent film hardness making them good candidates for coating exterior appliance cabinets. The acrylic-urethane powder coating films show good resistance to alkali which is important should they come into contact with alkali oven cleaning compounds on range sides, and hot detergent on washing machine parts. These systems also demonstrate extremely good electrostatic spay properties making the application of thin film thicknesses very realistic and controllable.

Acrylic Properties

| | |
|---|---|
| -Hardness | 2 - 3H |
| -Impact | 40 - 100 Lbs. |
| -Salt Spray | 1000 Hrs. + |
| -Exterior Durability | Good |

The following table gives a generalized comparison of characteristics for each generic type thermosetting powder coating now used in the U. S. market:

Characteristics of Thermosetting Powder Coatings

| | |
|---|---|
| Epoxy | Tough<br>Chemically resistant<br>Poor exterior durability |

| | |
|---|---|
| Hybrid | Decorative film performance similar to epoxies<br>Some UV & overbake advantages<br>Good application transfer efficiency |
| Polyester-Urethane | Exterior durable<br>Thin film powder coating |
| Polyester-Glycidylester | Exterior durable<br>Slightly thicker film powder coating<br>Good application transfer efficiency |
| Acrylic-Urethane | Exterior durable<br>Thin film powder coating |

Application Equipment/Systems

Considerable progress has also been recently made in the development of better and more efficient electrostatic spray powder gun application equipment and recovery systems. New deflectorless electrostatic spray guns establish spray patterns by means of compressed air introduced around the periphery of the gun nozzle. This permits spray patterns to be completely controlled remotely and automatically. The pattern shaping air produces a swirling motion to the powder particles, thus reducing the forward velocity. The result is "soft" spray that reduces "bounce back" particles from the part. The ability to recover oversprayed powder is one of the major attractions of powder coating application. There is virtually no waste, as overspray is reclaimed for use. This aids in making powder coating economical and greatly reduces housekeeping problems compared to conventional liquid spray finishing systems. Early powder recovery systems use conventional dust collection equipment, such as cyclones and bag filers, to remove the powder from the high volume air stream exhausted from the booth. Today, cartridge type filters have largely replaced cyclone and bag houses for this purpose. In either case, the filter air is returned to the plant, eliminating the need for costly air makeup. Recent new types of booths have eliminated ducting between the booth and the cartridge collector by incorporating the filters within the booth. In most of these filter booths, the filters are arranged to be quickly and easily changed to facilitate

color change. A feed hopper can also be placed at the base of the spray booth and in this system design, a large portion of the oversprayed powder can be recycled with a reduction in need for utilizing conventional reclaim equipment. Another type of recovery system employs a moving filter belt in the floor of the spray booth. The high volume downdraft air required for safety passes through a filter belt with removes the oversprayed powder. The belt carries the powder to one end of the booth where a pickup head vaccums the powder from the belt. Powder is removed from the vaccum air stream by a small cyclone, a small cartridge filter, or a combination of the two. A feature of this system is that the powder is removed immediately from the high volume safety air flow. Since their introduction a few years ago, filter belt booths have undergone many refinements to minimize stree, wear and abrasion of the belts and to simplify belt changing when required. Microprocessor technology which has just been incorporated on a microwave oven powder finishing line this year, makes it possible to change all electrostatic powder gun parameters during the spray operation and pre-program almost unlimited spray pattern changes on line. The more sophisticated powder application system of the future will be fully automated employing robots, microprocessor and programmable controllers, and other automatic control devices. Such sophisticated automation will enhance transfer efficiency, provide for more flexibility in spray patterns as well as on/off powder deposition, improve uniform thin film powder coating control, reduce the need for manual reinforcing and air in rapid color changing.

## Comparative Economics

A model study approach, similar to the type under the Economic Analysis sections of EPA's Control Technical Guidelines (CTG's) For Surface Coating of Large Appliances, Metal Furniture and Miscellaneous Metal Products has been used to develop 1982 comparative economic data for powder coatings vs. conventional solvent borne vs. the other control water borne and high solids coating alternatives. This model coating line finishes formed sheet steel neither simple nor complex parts but both sides are automatically coated with manual touch-up. Two colors are used with a production rate of 1 MM sq. ft. of surface coated per month on a single 8 hour operating shift - 5 day week basis at a conveyor speed of 15 feet per minute. The model study covers only installation and operation of each respective control coating alternative designed to meet many recently enacted state 1982 and 1983 surface coating of appliance, metal furniture, and other metal product VOC emission regulations; it is assumed that most such retrofited coating operations can use existing pretreatment systems and

bake ovens with no or little modification.

Installed capital costs include 2 water wash down booths, 1 dry filter booth, 4 automatic and 2 manual electrostatic (ES) guns each for the water borne, and high solids coating application equipment; water borne also include safety interlocks and stand-offs while paint heating equipment and ES high speed atomizers are used with the high solids system. The powder coating equipment includes 2 powder spray booths each with automatic recovery systems, 4 automatic and 1 manual electrostatic powder deflectorless spray guns and 2 reciprocators. The study compares $8.25 and $10.00 per gallon 40% volume solids conventional solvent and water borne coatings, both reduced to 31% volume solids and applied at 60% utilization efficiency at 1 mil, with a $14.50 per gallon 62% volume high solids coating applied at 65% utilization efficiency at 1.2 mils and a $2.15 per pound polyester powder coating applied at 97% utilization efficiency at 1.5 mils. The following chart includes the respective capital, applied material and, most importantly, total annual operating costs for each of these technologies studied to coat 12 MM square feet of a formed metal product:

1982 Model Economic Analysis

| | Conventional Solvent | Water-Borne | High Solids | Powder |
|---|---|---|---|---|
| Capital Cost | - - - | $ 98,000 | $100,000 | $150,000 |
| Material Cost | $268,800 | 309,600 | 324,000 | 339,600 |
| Energy Cost (Gas) | 21,200 | 22,600 | 19,700 | 11,400 |
| Labor & Maintenance | 145,000 | 145,000 | 143,000 | 82,500 |
| Depreciation (10 yrs-St.Line) | - - - - | 9,800 | 10,000 | 15,000 |
| Total Annual Oper.Costs | $435,000 | $487,000 | $496,700 | $448,500 |
| Appl. Costs ($/sq. ft.) | $ .036 | $ .040 | $ .041 | $ .037 |

As shown in this model analysis, recent improvements in powder materials and equipment have reduced the costs of operating a powder coating system through on-line application of lower film thickness powder coatings, high 95-99% material utilization, lower labor and maintenance costs, less energy consumption and lower waste disposal costs. Recent actual powder coating operations are reporting a number of additional cost savings of which most are intangible and are not included in the above model analysis. These cost savings include less reject rates by as much as a factor of four, minimum operator training/supervision/OSHA complaints (better attitude), and less housekeeping problems/ clean-up costs. Longer term, powder coating's comparative future economics look even better. While rising petrochemical based resin costs will have a similar impact for all coatings in the fuutre, powder should be least affected due to its high material utilization and lack of solvents or thinners.

## Future Trends

The total number of electrostatic spray production scale powder application installations operating in the United States today approximate 700 including about 70 new additions in 1981. While powder will continue to enjoy good growth for surface finishing the many industrial products already described including use as a truck and perhaps long term an auto-body primer surfacer, two market segments indicate considerable promise for the futre. The first is powder coating job shops representing over 100 of the 700 ES powder installations now operating. Scott spreaders, automotive parts, aluminum and steel wheels, lighting fixtures, metal furniture, brass/ ornamental hardware, and many other industrial products are custom coated with decorative-protective pigmented and clear powder coatings. The growth in the powder job shop segment reflects in part the decision of a number of manufacturers, including those under compliance regulatory pressure, to arrange for custom powder coating their producrs before making the capital investment in a captive powder coating application facility. The second promising market segment for powder coating is building products. As already well established in Europe, highly exterior durable decorative powder coatings are beginning to be applied in this country to the interior and exterior of prefabricated building steel panels for storage of plastic raw materials and farm products. Another building product emerging use is powder coating aluminum extrusions. A major California aluminum extruder just chose to install a large automatic powder coating facility after comparing powder's economics and high quality performance properties with other coating technologies.

Thank you for the opportunity of sharing with you our enthusiasm about powder coating's future role in surface finishing. Should you desire to know more about powder coating, particularly as a prospective applicator or end-user, The Powder Coating Institute and/or any of its members are qualified to provide you information on powder coating materials, application and processing equipment, and custom powder coating services.

References


1. Gribble, P.R., "Powder Coating Materials, You and Your Supplier", AFP/SME Technical Paper FC81-447

2. Grove, J.P., "Powder Coating Systems: Review & Update", AFP/SME Technical Paper FC81-

3. Cole, G. E. Jr., "Promising Future For Powder Coatings", Plating & Surface Finishing, December, 1981

4. Cole, G. E. Jr., "Powder Coatings - - At the Turning Point", Modern Paint & Coatings, March 1972

5. Cole, G. E. Jr., "The New Economics of Powder Coating", PCI Technical Paper, 1982



ACKNOWLEDGEMENTS:

The author expresses his appreciation to the members of The Powder Coating Institute and to other surface finishing material and application equipment manufacturers who contributed to the preparation of this paper.

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# Powder Coating Session J

## Proper Pretreatment For Powder

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# PROPER PRETREATMENT FOR POWDER

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In the mid 1980's, industrial finishing will continue to undergo major changes - mainly because of energy and regulatory problems and the increased demand for better quality. Inevitably, these changes will affect production methods, but this is not necessarily bad and may even be beneficial to the finisher. Take powder coatings for example. Switching to powder coatings may eliminate or reduce many current finishing problems associated with solvent based paints, because powder coatings offer the following advantages:

Reduced costs - Very little waste since over spray can be reused.

Little Pollution - No solvents at all emitted into the air.

Less Disposal - Solvent free powder eliminates water pollution problems.

Energy-Low make-up air - Less oven air volume to replace; no after burner required.

Space-Single Booth application - Allows 1 to 5 mls (or more) in a single coat.

No Flash-off areas - Flash time needed to prevent solvent popping eliminated.

Shorter curing time - Powder can rise to fusing temperature faster than liquid paints.

Few Rejects - Rejects up to 15% are common with fluid paints. Powder's

ease of application results in 3% rejects.

These advantages, as well as others we can document, indicate that powder coatings will be one of the fastest growing finishing systems available. But even with these economic, environmental and handling advantages, powder coatings are superimposed organic films and are vulnerable to the same environmental assailants as are their liquid counterparts. Knowing this, the required preparation of metal surfaces for powder coatings can be summed up by the following statement made by a major powder coating manufacturer. "Improper phosphate coatings can cause the best powder to look terrible." The successful performance of any organic finish on any substrate depends upon the proper conditioning of the surface to receive the applied coating and this means proper pretreatment. Pretreatment is essentially five sided; (1) It removes soils and surface imperfections; (2) It creates bonding sites; (3) It establishes a corrosion barrier; (4) It neutralizes surface pH changes; and (5) It does all four functions economically.

Production metal is never clean and powder coatings possess poor wetting out ability. Thus, for proper bonding of powders, cleaning is essential. Any interference, whether planned or unplanned....chemical or physical.... will weaken the bond between the powder and substrate. Even though such a defect may be initially concealed and be visually acceptable, the soiled area will cause a rapid deterioration of the finish and eventually attack the substrate itself. If it is true that precleaning is essential to powder coatings, then it is also true that cleaning deserves the same scrutiny that other production operations get. If cleaning is thought of not as an unavoidable evil, but as an integral part of the finishing operation, and

if you begin giving it the attention you give other phases of the operation, don't be surprised if your overall costs begin to decrease.

The three parts of every cleaning puzzle are: (1) the substrate, (2) the soils, and (3) the cleaning solution. The difficulty in establishing a good low temperature cleaning process (or just a good cleaning process) lies in the almost infinite combination and variety of the first two parts. A recent study by Appliance magazine pointed out that almost all respondents mentioned various types of oils as the most common soils. True, many soils are oily or liquid but many are solid. Soils can also be ionic or nonpolar, reactive or inert and perhaps may be ground into the substrate surfaces. Liquid and solid soils are quite different in their physical and chemical properties and are consequently removed from surfaces by different mechanisms. The removal of organic (oily) soils by aqueous cleaners is achieved by a "rollback mechanism," which is caused by preferential wetting of the substrate. The thin liquid soil films are rolled up into droplets which now can be scrubbed from the surface. Solid particle soils are removed by absorption of wetting agents and other cleaner components in the particle/water interface. This reduces the work needed to remove solid soils and develops a network of like charges on the solid soil as well as the substrate which results in soil repulsion. Because of this wide range in the type and the extent of the soils, alkaline cleaners are the most effective and the most economical. For better cleaning with low temperature compounds, choose easy-to-remove rust preventive oils, stamping, drawing or machining compounds. You can even change scheduling to allow cleaning sooner after forming. When low temperature cleaners are developed,

their inorganic components are well set. The best possible wetting agent combination blended with select solvents and organic chelates offers effective organic soil removal along with removal of smuts and other electrostatically held films which interfere with powder bonding and phosphate performance and which affect the long term corrosion resistance of the entire finish. The lowering of cleaning temperatures, spray or tank, may demand higher chemical concentrations, both oz/gallon or % by volume and activity,but these costs are minimum when compared to energy and labor costs. Present cleaner contact times vary greatly but future exposure will increase, perhaps from 90 to 120 seconds for spray in order to offset the reduced temperature and in an effort to lower chemical concentrations.

As a general rule, when one solution parameter is reduced, another must be properly raised or chemical consumption and rejects will greatly increase. Low temperature spray cleaning is highly efficient, yet with modern part design, tank immersion may be required. In contrast to spray washing, tank immersion brings chemical solutions into intimate contact with all soiled metal surfaces. Thus, for parts that have spot welded overlaps or unusual designs, tank immersion systems may be required, or a combination of tank-spray may be demanded. Unfortunately, there is no one cleaner, spray or tank, that will remove all of the soils we encounter. A total system approach, cleaner vs. soil, spray vs. tank, low temperature vs. standard, is needed to determine the best combination. Ideally, the cleaner should reduce surface and interfacial tensions, provide alkalinity, buffer strong alkalies, soften water, chelate inorganic surface films and rinse freely.

The selection of a powder resin will depend on the end-use requirements of the coated substrate. Usually, thermoplastic powders derive their

physical and chemical properties by the nature of the polymer backbone as well as the molecular weight of the polymer. Likewise, the total finish obtains its backbone from the conversion coating.

Quality finishing demands a conversion coating, such as phosphating, which provides a bridge between metal and powder. These coatings increase the surface area for powder anchoring because they are slightly porous and paint penetrates and becomes an integral part of the coating. Phosphates have thermal expansion properties which are intermediate between the metal and the powder coating. Additionally, phosphates (as well as chromates and chrome-phosphates) insulate anodic and cathodic metal areas preventing anodic pitting and cathodic oxidation. These inert films stop reactions between metallic oxide alkali and many paints eliminating metallic soap formation which, like rust, forms a weak foundation.

Without question, in terms of simplicity, economy and environmental acceptability, iron phosphates are preferable. Traditionally, the best known of the iron oxide/iron phosphate compounds are the molybdenum accelerated cleaner/coater types which develop the attractive blue coating. In this same class, we should also mention the organic accelerated compounds, which produce a gray-gold coating. These iron phosphates offer the following production advantages:

1. One stage cleaning and phosphating permitting shortened time cycles. Additives are available for increased cleaning.

2. Low concentration use so that it is economical to discard solutions more frequently.

3. Less complicated controls.

4. Good adhesion with fairly good corrosion protection.

5. Low sludge formation.

6. Lower chemical costs.

With new and better detergent systems, lower temperatures can be achieved. With new and better activators, multimetal coating systems are in operation. With money tight, fewer stages or tanks are popular. And, coupled with powder, these three-step processes consisting of conditioning, rinsing and passivating will satisfy many needs. However, the quality of a three-step operation begins to deteriorate with the introduction of soil and necessitates that we accept a lesser quality or dump very frequently. We have investigated the use of filtration to maintain solution purity and with filtration the bath life can be increased several fold. This option removes sludge, grease and oils as well as some of the active surfactants and solvents. Here is where cleaning additives and sophisticated equipment will work together to reduce environmental problems. Where consistently higher performance is needed, then a four-step process is utilized. The first step does all or most of the cleaning and step two does the conversion coating. Quality is maintained and when stage one becomes contaminated and must be dumped, the clean stage two phosphate is pumped into one with a new solution made in stage two.

Remember, when one parameter is reduced, another must be increased. With a four-step process, we have increased the contact time and may be able to use lower concentrations for reduced rinse water overflow which lowers the pollution carryover load and we can also use lower temperatures for reduced energy consumption costs.

These moly and organic accelerated iron phosphates are capable of producing coating weights of 25-60 mgs/ft$^2$. Most metallic accelerated iron

phosphates give the higher weights at pH around 3.0-3.5 with a gradual decrease in coatings as the pH increases to above 5.0. However, oxidized accelerated iron phosphates can produce coating weights up to 90 mgs/ft. Unlike the moly accelerated coatings, these are not powdery and have greater protective and bonding qualities. But oxidized accelerated iron phosphates require higher temperatures of 140$^{o}$F or above and they are designed for use in five stage machine utilizing up front cleaning in order to maintain quality. With all amorphous phosphates, chrome sealing is essential for optimum quality. Iron phosphates are not as versatile as zinc phosphates and they rely heavily on the powder for long term severe finishing demands. Good rinsing is essential to prevent inter-pore contaminants remaining on the substrate.

For any given system, the solution concentration and pH are adjusted to fit the conditions encountered, such as soil load, metal mix, temperature and time available. The concentration is not too critical, but should be maintained close to the pretested or established limits. Automatic control based on conductivity should be used to maintain concentration and pH ranges. The pH may also require an additive such as phosphoric acid, or a replenisher which stabilizes the pH and/or accelerators and activators in the case of multi-metal systems.

Powder coatings have been recognized for their all-around high performance characteristics. But, most of the accumulated data is based on thick film coatings. This will, once again, put the burden of protection back on the conversion coatings.

The highest quality finish may therefore require a zinc phosphate. The gray crystalline coating is composed of black iron oxide with iron phosphate

formed in the first several seconds followed by the zinc phosphate crystalline growth. The iron oxide/iron phosphate base holds the crystals firmly making the entire coating an integral part of the metal.

Spray phosphating systems remain the most popular. With good impringement, spraying allows the effective use of low alkaline cleaners for tighter crystal formation by stopping crystal site elimination which can occur with highly alkaline cleaners. If crystal nucleating sites must be restored, cleaners with colloidal titanium can be substituted, or these nucleating agents can be used in an activating rinse just before zinc phosphate applications. Since zinc solutions are more acidic (usually operating at pH 2-2.2) they are capable of dissolving light oxides and pickling light smuts. Spraying, at low pressures, brings fresh phosphate solution to the surface allowing low concentration, low temperature processing ($110^{o}F$) with refined zinc phosphate crystal structures. And, always remember, the denser coatings with the smallest inter-crystalline zones are the most corrosion resistant.

Low temperature zinc phosphating is more sensitive and difficult to control, because at a low temperature, free acid generation is reduced. Lower free acid and temperature make the bath less reactive which tends to develop slower crystals and produce coatings that are softer and heavier. Control becomes important as the temperature of zinc phosphating baths is reduced. So, control is critical and these points are very important:

1. The critical control is the TA/FA ratio. The range of free acid needed depends on the metals coated, operating temperature and whether the process is spray or tank. Free acid control is accomplished by additions of nitrite accelerator and temperature regulation. Nitrite is added continuously at a precise rate. Nitrite,if not maintained, is reduced at

the rate of ½ of its concentration in about 1 hour operation. The total acid is maintained by continuous additions of zinc phosphate or replenisher. Automation is the key.

2. Avoid localized high temperature heating. A heater of low surface area has a high temperature gradient with the solution causing localized overheating which precipitates zinc phosphate heat sludge in addition to work sludge. Keep heat sources off of the bottom to avoid codeposition of sludge with the phosphate coating. Temperature control is a must.

3. Desludging or filtration keeps the iron phosphate sludge and zinc phosphate sludge by-products to a minimum for better quality and reduced costs.

4. Solution flow is important. Proper pressures create a wiping action that refines crystal structures. Selection of the best nozzles for spray is important. Zinc phosphates can coat "hard to reach surfaces" better than iron phosphates in spray washer applications.

A perfect phosphating system, iron or zinc, can be destroyed within 30 seconds. A poor rinse can cause many problems. Cleaner carryover, in a five stage system, changes the pH value of iron phosphates and neutralizes the free acid in zinc phosphates. Excess sludge is produced and the bath suffers zinc starvation causing open or sparse coating. Rinsing after phosphating tends to become acidic. Acidic mist and vapors can create flash rusting. Most blistering is nucleated by water soluble salts left on or in the conversion coating after the cleaning or phosphating steps. The phosphating solution must be completely removed with quality water.

Quality rinse water is low in harmful salts which may include these three: Approximately 100 ppm total chlorides and sulphates, 200 ppm total

alkalinity (as Ca $CO_3$) or 250 ppm of all three ($Cl^-$, $SO_4^{-2}$ 1 & 2). These harmful salts should be limited in all rinse waters, but more so in final rinses. However, powder coatings are slightly less sinsitive to water salts than others. Poor rinse water quality not only affects corrosion resistance but it also affects appearance.

In the 80's, many finishers may find the need to apply several types of paints. The pretreatment system chosen must accomodate a variety of paints, paint applications, metal mixtures and part design. Be wise! Choose the pretreatment that is the most versatile in future needs and the most enduring for quality finishing. With a look to the future, a properly planned finsihing system can increase production, reduce rejects and improve quality of U.S. goods and services while lowering production costs.

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# Powder Coating Session J

## The Status of Wastewater and Hazardous Waste Regulations For the Chemical Pretreater

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# The Status of
# Wastewater and Hazardous Waste Regulations
# for the
# Chemical Pretreater

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The subject of environmental control no doubt has caused many of you here today varying degrees of concern over the last several years. Questions such as "what must I do in order to be in compliance, both today and in the near future", "how do I go about it" and most importantly "how much will it cost", probably sound all too familiar.

My purpose today is to discuss a portion of the environmental requirements facing the Chemical Pretreater. Although I will limit discussion to industrial wastewater discharge and hazardous waste disposal, the requirements of environmental health and air emission legislation are of equal importance and should also be reviewed.

The Chemical Pretreater is generally required to comply with wastewater discharge and hazardous waste disposal regulations as a result of surface pretreatment operations.

Due to its fresh water rinsing requirements and the nature of the process chemicals used, unit operations performed during surface preparation of the product, will generate wastewater which may require treatment prior to leaving the plant. A careful review of the resulting wastewater quality is, therefore, essential in order to determine necessary treatment.

In the case of most metal pretreatment systems, alkali cleaning followed by a chromate conversion coating and a final chromic acid rinse will require wastewater treatment prior to discharge to either a POTW or running body of water. Other surface pretreatment systems usually also will generate wastewater normally requiring treatment prior to discharge.

In addition to the continuous rinse waste generated, the periodic disposal of concentrated process baths must also be considered.

Keeping in mind these waste producing processes, what specifically must be done in order to be in compliance with existing and future wastewater discharge and hazardous solid waste disposal regulations. Which of the bountiful regulations apply to you as a Chemical Pretreater.

Direct discharge of wastewater to a running body of water in most cases is the most complex and costly of the alternatives available for wastewater disposal.

The framwork for control of wastewater discharge was established by the Federal Water Pollution Control Act Amendments of 1972. The central mechanism of that legislation was to prohibit any discharge of pollutants into any public waterway unless authorized by a permit, with elaborate conditions to be set forth in the permit requiring adequate pollution control. The permit program was officially designated the National Pollutant Discharge Elimination System (NPDES).

Authority to issue these permits was initially vested in EPA, but the law provided for that authority to be transferred to state agencies meeting specified federal criteria. Thirty-two states, mainly in industrialized regions, have now taken over the permit program. In the remaining states EPA still runs the program. (Figure 1)

The 1972 Act established standards of pollution control to be met by 1977 by all dischargers, whether existing or new. It also established more stringent standards of control to be met by 1983. Both sets of standards included a combination of "technology standards" and "water quality standards".

The technology standards required every discharger to install by 1977 the "best practicable control technology" (BPT) and to install additional control equipment by 1983 representing the "best available technology economically achievable" (BAT). The 1972 Act also required that by the 1977 deadline each discharger must be in compliance with applicable water quality standards, which imposed a requirement for controls tighter than BPT in those localities where receiving waters were severely polluted.

The Act tightened this receiving water requirement for the 1983 deadline by specifying that no discharge should interfere with the use of any waterway for swimming or the protection of fish life, except in cases of extreme economic hardship.

The 1977 amendments to the Clean Water Act altered the 1983 requirements. Congress postponed the deadline to 1984 and replaced the single BAT limitation with a more complicated formula, applying a best conventional technology limitation (BCT) to certain conventional pollutants, a best available technology standard to toxic pollutants, and a best available technology limitation, subject to possible extension of the deadline to 1987, to certain other pollutants.

The statutory standards are applied to individual plants through a two-step process. First, EPA has conducted an extensive program of issuing effluent guidelines, which define the technology standards for various industrial categories and set numerical limits on the quantities of each pollutant which may be discharged by operating plants per unit of production.

In establishing the limitations, EPA took into account all information it was able to collect, develop and solicit with respect to factors such as age and size of plant, raw materials, manufacturing processes, products produced, treatment technology available and energy requirements and costs.

The limitations resulting for the chromating/phosphating/anodizing sub-categories under the Electroplating Point Source Category are shown in Figure 2.

These standards assume the application of the best practicable control technology currently available.

In order to fulfill the requirements of the Clean Water Act, EPA is currently preparing BAT standards for existing sources and NSPS for new facilities under a proposed new all encompassing category entitled "Metal Finishing".

This new category would combine "electroplating" with the mechanical products category and require compliance by July 1984. Finalization of this new regulation is expected in 1982.

As can be seen, discharge guidelines have been based on surface area treated rather than concentration in the past. This was a direct effort

by EPA to encourage in-process water conservation techniques and prevent compliance through the uncontrolled use of water for dilution advantage.

Initial indications from EPA announced during the 4th Annual EPA/AES Joint Seminar in January, 1982, shows a preference for excluding mass based or concentration/area guidelines from the proposed Metal Finishing category in favor of straight concentration limits.

Limits resulting from these guidelines are then specifically developed by the state NPDES program for each individual industry keeping in mind the water quality designated for the receiving body of water.

The EPA has also began an ambitious program of developing standards, including new source performance standards, to cover a list of 65 toxic pollutants, which were in turn subdivided into 129 substances. This effort was given further impetus by the 1977 amendments to the Clean Water Act, and these standards will be appearing in the Federal Register, in either proposed or final form, throughout the next two years. Detailed information as to the current status of such future regulations can normally be obtained from the staff of the Effluent Guidelines Division in EPA Headquarters in Washington.

Typical concentration requirements for discharge under the NPDES program for a metal pretreater is shown in Figure 3.

There is an alternative in most cases to the stringent and costly requirements of direct discharge just discussed. Industrial discharge to a Publically Owned Treatment Works is allowable and in most cases desirable after proper pretreatment of the wastewater.

Regulation which establishes mechanism and procedures for enforcing national pretreatment standards controlling the introduction of non-domestic wastes into a POTW were also established in 1977 under the Clean Water Act and finally promulgated on January 28, 1981 for new and existing point sources.

The intent of the regulation and the national pretreatment policy is to prevent introduction of pollutants into a POTW which will pass through or interfere with the works or contaminate the sludge.

These General Pretreatment Standards include discharge restrictions that apply to all users of a POTW who discharge non-domestic wastes as well as standards applicable to specific industrial categories. Discharge limits are based on the best available technology economically achievable.

Although portions of the revisions to these regulations have been suspended by the current administration pending review by the Office of Management and Budget, industry eventually will be required to identify themselves and their wastes to their POTW.

A baseline report will be required to be submitted to the POTW within 180 days of the effective date of a categorical standard and must include:

1). Description of processes.

2). Waste flow measurements.

3). Measurement of pollutants.

4). Certification of compliance with categorical standard.

5). Compliance schedule if standards are not being met.

To date, 21 industrial categories have been established for the purposes of developing discharge standards. Further, the EPA has also identified 65 toxic pollutants which may be discharged by these industrial categories requiring treatment.

Chemical pretreaters generally fall into only one of the 21 industrial categories formed.

Effluent discharged to a POTW from anodizing, chromating and phosphating operations falls within the Electroplating Point Source Category for which Pretreatment Standards were promulgated on January 28, 1981.

These standards which have gone into effect for non-integrated facilities, allows for a three year compliance schedule by industry (January 28, 1984). Integrated Electroplating Standards are currently under OMB review for economic impact.

For plants with a daily wastewater flow of 10,000 gpd or more, the promulgated standards specifically limit discharge of cyanide, lead, cadmium, copper, nickel, chromium, zinc and silver. (Figure 4)

Additionally, the regulations limit total metal discharge which is defined as the sum of the individual concentrations of copper, nickel, chrome and zinc.

For plants with a daily wastewater flow of less than 10,000 gpd, the standards limit lead, cadmium and cyanide only. (Figure 5)

Alternative mass-based standards which are equivalent to the concentration based standards are also established in this regulation. These optional standards may replace the concentration standards where mutually agreed to by the discharger and the POTW for dischargers with a daily volume of greater than 10,000 gallons.

A third option is available to dischargers with a daily waste volume greater than 10,000 gpd. If strong chelating agents are not present in the process, hexavalent chromium is reduced and neutralization is with lime, the concentration limits shown in Figure 6 can be applied if mutually agreed to by both the discharger and the POTW.

"Upsets" to a POTW has been defined by the regulations as an exceptional incident in which there is unintentional and temporary non-compliance due to factors beyond the control fo the industry. An upset does not include non-compliance to the extent caused by operational error, inproperly designed treatment facilities, inadequate treatment facilities, lack of preventive maintenance or careless or improper operation.

The pretreatment limitations set forth in the regulations are based on BPT control techniques which include cyanide oxidation, chrome reduction, metal precipitation via pH adjustment and solids removal.

As many of you are aware, these standards are not as stringent as indicated in discussions with local POTW's. Under the Clean Water Act, Congress specifically allows individual states and municipalities to set limits more stringent than federal standards. Concurrently, Congress also expressly forbids any state from adopting or enforcing a standard less stringent than a national standard. The federal EPA intends to enforce this policy directly via the issuance of NPDES permits to POTW and indirectly through available municipal funding.

Some relaxing of these standards is possible but not probable if a local POTW can document consistant removal of the pollutants in the POTW and is willing to grant removal credits to the industry.

Typical allowable industrial wastewater quality for discharge into a medium-sized POTW is shown in Figure 7.

Schematics of the wastewater treatment system necessary for compliance are shown in Figures 8 and 9.

The next topic of discussion today focuses on a piece of legislation which has already and will continue to have significant impact on both the methods and cost of conducting business.

The Resource Conservation and Recovery Act known to all as RCRA has arrived. Its provisions are far reaching and all encompassing for all types of industry.

Keeping the burden of RCRA on industry in mind, the federal EPA in their own distinguishable manner, predicts that approximately 67,000 hazardous waste generators, who will produce about 41 million metric tons of waste in 1980, would be affected.

Cost for compliance was estimated in 1980 at $740 million dollars annually nationwide to be shared by generators, treaters, haulers, storers and disposal site operators. According to EPA statistics, this total annual cost amount to less than .2% of the value of sales of the affected industries.

Future Phase II RCRA standards, which will establish the standards for permit issuance EPA reports, could conceivably double these total costs for compliance.

The Resource Conservation and Recovery Act of 1976 (RCRA) required the U.S. Environmental Protection Agency (EPA) to institute a national program of hazardous waste management. Specific regulations of the Act were set forth in the Code of Federal Regulations (40 CFR 250 and succeeding Parts) on May 19, 1980.

The program became effective November 19, 1980, six (6) months following the May 19, 1980 promulgation of Part 261. Under the regulation, a waste is identified as being hazardous if included in a comprehensive list of waste sources and waste streams or if it exhibits ignitable, corrosive, reactive or toxic characteristics as defined.

The actual control system began with notification to EPA by existing facilities engaged in generating, transporting, treating, storing or disposal site operation, as defined under Section 3010 of the Act. Notification submittal was required by August 18, 1980.

Generally, two mechanisms have been established for determining whether a waste material is hazardous for the purposes of the Act.

The first mechanism is a set of characteristics of hazardous waste which includes:

ignitability

corrosivity

reactivity

toxicity

radioactivity

Meaningful to the chemical pretreater is the toxicity requirement, which is intended to identify waste, which if improperly disposed of may release toxic materials in sufficient amounts to pose a substantial hazard to human health via leaching to groundwater or surface runoff.

Toxicity of a particular substance is determined via an extraction procedure which attempts to simulate sanitary landfill conditions by using a mild acid medium. (Figure 10)

Extract or leachate from such a procedure containing more than 100 times the current EPA National Interim Primary Drinking Water Standards will be the basis for classification of the substance as a hazardous waste and thus require ultimate disposal in a secure site. A tightening of these limits to 10 times the drinking water standard is being discussed within the EPA.

The second mechanism for determining whether a substance is defined as hazardous is the listing of specific hazardous waste materials and processes. Currently, approximately eighty processes have been identified as generating a hazardous waste material.

As a general rule, generators of waste determined to be hazardous as defined by the Act, must assure that their wastes are treated, stored, transported, and disposed of by permitted concerns only. EPA plans to focus a significant amount of its compliance monitoring and enforcement

effort on the generator. Failure to comply can result in both criminal penalties and civil fines.

Each state will be required to develop and implement a Hazardous Waste Management Program which follows the RCRA guidelines.

Figure 11 shows the listing of states currently approved by EPA for Hazardous Waste Management.

A three year implementation schedule is part of the proposed legislation. All states already request the use of manifest systems by industry. In some states, hazardous waste disposal sites are not available and therefore disposal requires costly interstate transport.

After receiving notification, the EPA will assign an identification number to the reporter which will be required in order to continue all hazardous waste activity such as generation, treatment, storage, transportation and disposal.

Accompanying the identification number from the EPA will be a permit application (EPA Form 3510-3), (5/80), which had to be submitted prior to the November 19, 1980 effective date of the regulations for those notifiers who acknowledged the treatment, transportation, storage and disposal of hazardous waste as defined.

Once a permit application is filed, the applicant must comply with the provisions of the Act including Interim Status Standards (ISS) for operation of a treatment, storage, or disposal facility by November 19, 1980.

Rather than expanding any further on whether a waste is hazardous under the regulations, a discussion of what is specifically excluded from RCRA may be helpful.

The following selected materials are not solid wastes for the purpose of the Act:

1). Domestic sewage.

2). Any mixture of domestic sewage and other wastes that passes through a sewer system to a publicly owned treatment works for treatment.

3). Industrial wastewater discharges that are point source discharges subject to regulation under Section 402 of the Clean Water Act. (i.e. Pretreatment Standards, NPDES Permit)

Point source discharge exclusion applies only to the actual point source discharge. It does not exclude industrial wastewaters while they are being collected, stored, or treated before discharge, nor does it exclude sludges that are generated by industrial wastewater treatment.

If a person generates, in a calendar month, a total of less than 1000 kilograms (2200 pounds) of hazardous wastes, those wastes are not subject to regulation under Parts 262 through 265 and Parts 122 through 124, and the notification requirements of Section 3010 of RCRA.

Special requirements for a hazardous waste that is used, re-used, recycled or reclaimed have also been included.

Except as otherwise provided, a hazardous waste which meets either of the following criteria is not subject to regulation under Parts 262 through 265 or Parts 122 through 124 and is not subject to the notification requirements of Section 3010 of RCRA:

a). It is being beneficially used or re-used or legitimately recycled or reclaimed.

b). It is being accumulated, stored, or physically, chemically or biologically treated prior to beneficial use or re-use or legitimate recycling or reclamation.

c). A hazardous waste which is a sludge, or which is transported or stored prior to being used, re-used, recycled or reclaimed is subject to certain partial regulations concerning the notification, generation, transportation, treatment and storage.

The following is a summary of the RCRA Section 3002 requirements for generators of a waste material determined to be hazardous: (Figure 12)

1. Obtain an EPA identification number if total waste determined to be hazardous exceeds 1000 kilograms per month (2200 lbs).
2. Obtain a facility permit if waste is accumulated on the generating property more than 90 days.
3. Use appropriate containers and labels for proper shipment.
4. Prepare and utilize a manifest for tracking hazardous waste.
5. Document via the manifest system that waste arrives at the designated facility.
6. Submit an annual summary of activities. (March 1, 1982)

A manifest system to tract the chain of custody of all hazardous wastes generated must be implemented. A chain of custody form will have to be used which includes: (Figure 13)

- document number
- name, address, telephone, and EPA Identification Number
- the transporter's name and EPA Identification Number
- disposal facility name, address and EPA Identification Number
- description and quantity of each waste

When possible, it is advisable to designate an alternate disposal facility; otherwise, the transporter will return your wastes if the designated facility is not able to accept your waste for any reason.

The form must also contain a clause that reads: (Figure 14)

> "This is to certify that the above named materials are properly classified, described, marked and labeled and are in proper condition for transportation according to the applicable regulations of the Department of Transportation and the EPA."

Before offering hazardous waste for transport, the waste must be packaged according to Department of Transportation regulations. These regulations are currently being re-written to conform with the EPA RCRA regulations and were not available at this time.

However, they are not expected to change significantly from the previous Department of Transportation regulations which essentially outline common sense and coventional practices for transporting wastes. Hazardous waste haulers are probably the best source of additional information.

Many existing hazardous waste storage, treatment and disposal facilities will require significant upgrading if they eventually are to receive a RCRA permit to operate.

Many of these operations may go out of business rather than upgrade, or discontinue operations unexpectedly due to accidents, permit violations or public pressure.

Prior to transport, both the generator and hauler must sign the custody forms. You will retain one copy, giving the transporter at least three copies.

Do not offer wastes to haulers who do not have an EPA Identification Number and do not sign custody forms without specifying a disposal facility by EPA Identification Number.

It is your responsibility to contact the hauler and the disposal facility if you have not received the disposer's signed copy of your chain of custody form within 35 days. The importance of checking out haulers and disposers is reemphasized here so that nuisances such as unreported shipments can be avoided.

When filing, keep in mind that the information stored may have to be retrieved at the end of each year to develop information needed for the annual hazardous waste report to EPA and/or the State. Chain of custody forms must be numbered serially - - you may initially want to file the forms serially, then file the forms by waste category after receipt of the disposal facility copy.

If after contacting your hauler and disposer you are still unable to obtain a signed copy of your chain of custody form within 45 days of shipment, you must file an Exception Report with the EPA Regional Administrator.

As a treater of hazardous wastes, you should have applied for a RCRA permit by November 19, 1980. The application will qualify you to receive "interim status" under RCRA. Interim status simply means your facility is temporarily permitted until EPA makes a request for a full permit application under Phase II of the regulations.

How does RCRA affect the individual chemical pretreater? Let us continue our discussion with a review of potentially hazardous waste producing process operations performed as part of the surface preparation of metal.

Operations within the chemical pretreatment industry which generate a potentially hazardous waste material, as defined by RCRA generally will be limited to: (Figure 15)

1. Surface Pretreatment
2. Industrial Wastewater Treatment

Surface Pretreatment

Surface pretreatment processes vary depending on the material being processed. Since many lines have multi-metal capabilities, overall facility waste output over a time period which reflects the use of the various pretreatment chemicals must be made. Regardless of the material processed, many present surface pretreatment operations can be broken down into cleaning, coversion coating and final acid rinsing operations. (Figure 16).

RCRA standards do not apply or affect wastewaters discharged directly to either a running body of water or a publicly owned treatment works. These discharges are specifically excluded from RCRA surveillance and compliance.

Discharge of either concentrated bath dumps or overflows as well as continuous rinse overflows to an on-site industrial wastewater treatment system is affected by RCRA treater regulations if the waste material being processed is hazardous as earlier defined.

RCRA generator requirements do apply for all off-site disposal via private haulers.

In the case of cleaner stage dump disposal, waste status determination is currently required due to either potential corrosive characteristics (i.e. pH less than 2.0 or greater than 12.5) or the presence of toxic metals such as cadmium and lead.

Off-site disposal of a conversion coating bath, however infrequent, should be carefully reviewed depending on the type of conversion coating in use. Chromate conversion baths will be classified hazardous under RCRA due to their corrosivity and the presence of chromium which is considered a toxic element.

Chromate conversion baths which also contain complexed cyanides will have additional cause for classification as a hazardous substance.

Other types of conversion coatings such as phosphate and complex oxide, are potentially hazardous due to either their corrosive nature or the presence of heavy metals considered toxic and should be reviewed accordingly.

Final acidulated rinses, usually do not exhibit corrosive characteristics at the time of dump for both chrome and non-chrome types. A chromic acid rinse dump would require classification as hazardous due to the listing of chromium as a toxic element.

Sludges resulting from the periodic clean-out of the conversion coating stages has traditionally been a problem both from a handling and disposal stand point.

Again, depending on the particular conversion coating in use, classification under RCRA may or may not be hazardous due to either corrosive or toxic characteristics. Leachate testing in most cases will be required to determine status for either off or on-site disposal.

Waste Treatment

Continuous waste overflows from the surface pretreatment processes just described, if not acceptable for direct or POTW discharge, must undergo a chemical/physical treatment process prior to discharge.

Properly designed treatment systems will normally also have the capability of processing periodic concentrated bath dumps at a reduced flow rate thus eliminating the need for private off-site disposal.

The typical conventional metal coating facility industrial wastewater treatment system may include part or all of the following unit operations:

a). Acidification for emulsified oil removal

b). Hexavalent Chromium Reduction

c). Neutralization (lime or caustic)

d). Metals precipitation

e). Solids removal

f). Sludge dewatering

As a result of these operations, a metal hydroxide/phosphate sludge is generated requiring ultimate off-site disposal. This sludge should be subjected to the EP Toxicity Test previously described to determine status as a hazardous or non-hazardous material. If determined to be hazardous, ultimate disposal in an approved secure landfill site will be necessary as well as compliance with the other annual reporting, manifest and storage requirements of RCRA.

It should be noted that dewatering of wastewater treatment sludges is recommended whenever possible due to the lowered leaching characteristics of a dewatered sludge at 25 to 30% by weight solids sludge compated to liquid sludges at 2-3% by weight solids composition using the EP Toxicity Test set up by RCRA. Depending on licensed haulers capabilities, dewatered sludge haulage normally will also result in an economic savings both in haulage and disposal costs.

Under the regulations, these types of wastewater treatment system will not be required to apply for a RCRA permit as a treater by November 19, 1980 unless a surface impoundment is part of the process. Once a permit is determined to be necessary and is applied for, a set of Interim Status Standards (ISS) must be adhered to by the treatment facility by the November 19, 1980 date. These standards include provisions, as previously discussed, for:

1. Waste Analysis Plan
2. Inspection Schedule
3. Personnel Training
4. Contingency Plan
5. Emergency Coordination
6. Closure Plan and Cost Estimate

Additional requirements for a ground water monitoring system have been included for implementation within one year of the effective date (November 19, 1980) for operators of hazardous waste treatment facilities which utilizes a surface impoundment (i.e. settling lagoon, sludge drying beds).

Any waste oils recovered or removed as part of the wastewater treatment process, as well as other plant waste hydraulic oils, are currently not included under RCRA as being hazardous. However, due to the problems associated with improper disposal of waste oils, segregated collection and disposal or reclaimation is recommended. Reclassification of waste oils as a hazardous waste material is expected to be in effect by early 1980.

The regulations just discussed are subject to a great deal of interpertation within industry, EPA and Federal and State environmental protection agencies.

Recent actions by the current administration indicates a lessoning of the burdens of these regulations on industry. However, it should also be understood that the responsibility of protecting the environment against abuse will remain with industry.

Familiarization with your individual State's hazardous waste management programs is essential as is detailed knowledge of your process and raw materials.

Advice? Conduct an in-plant survey of potential hazardous waste activity. Confirm hazardous waste characteristics outlined in RCRA through performance of the toxicity, corrosivity, reactivity and ignitable test procedures.

The task of explaining yet another environmental requirements for a no-return type investment to your corporation's board and/or stockholders is not envied.

Looking at the positive side, if that's possible after a talk of this nature, RCRA compliance, although costly and time consuming, will end an era of industry bad press frequently resulting from the actions of a few irresponsible firms involved with hazardous waste.

Industry-wide uniformity, which will hopefully result from the regulations, will no longer penalize the responsible industry.

Figure #1

## NPDES PERMIT STATES

CALIFORNIA
COLORADO
CONNECTICUT
DELAWARE
GEORGIA
HAWAII
ILLINOIS
INDIANA
IOWA
KANSAS
MARYLAND
MICHIGAN
MINNESOTA
MISSISSIPPI
MISSOURI
MONTANA
NEBRASKA
NEVADA
NEW YORK
NORTH CAROLINA
NORTH DAKOTA
OHIO
OREGON
PENNSYLVANIA
SOUTH CAROLINA
TENNESSEE
VERMONT
VIRGIN ISLANDS
VIRGINIA
WASHINGTON
WISCONSIN
WYOMING

Figure #2

MASS BASED
EFFLUENT GUIDELINES
CHROMATING/PHOSPHATING/ANODIZING
SUBCATEGORIES

| Effluent characteristic | EFFLUENT LIMITATIONS | |
|---|---|---|
| | Maximum for any 1 Day | Average of daily values for 4 consecutive days shall not exceed |
| | (Metric units) milligrams per square meters per operation | |
| Copper ..... | 90 | 45 |
| Nickel ..... | 90 | 45 |
| Cr Total ..... | 90 | 45 |
| Cr (VI) ..... | 9 | 4.5 |
| Zinc ..... | 90 | 45 |
| CN Total ..... | 90 | 45 |
| CN, A ..... | 9 | 4.5 |
| Fluoride ..... | 3600 | 1800 |
| Cadmium ..... | 54 | 27 |
| Iron ..... | 180 | 90 |
| Tin ..... | 180 | 90 |
| Phosphorus ..... | 180 | 90 |
| TSS ..... | 3600 | 1800 |
| pH ..... | Within the range of 6.0 to 9.5. | |

Figure #3

## TYPICAL NPDES PROGRAM DISCHARGE REQUIREMENTS METAL COATING INDUSTRY

| PARAMETER | MAX. ALLOWABLE CONCENTRATION | TYPICAL UNTREATED WASTE CONCENTRATION |
|---|---|---|
| pH | 6.0 to 9.0 | 3.0 to 5.0 |
| Chromium (hexavalent) | .05 mg/l | 70 to 80 mg/l |
| Chromium (total) | 0.1 mg/l | 100 to 110 mg/l |
| Aluminum | 5.0 mg/l | 25 to 30 mg/l |
| Fluoride | 2.0 mg/l | 40 to 60 mg/l |
| Phosphate (total) | 5.0 mg/l | 50 to 80 mg/l |
| Suspended Solids | 25.0 mg/l | - |
| Oil & Grease | 10.0 mg/l | 150 to 200 mg/l |
| Cyanide (total) | .01 mg/l | 5 to 10 mg/l |

Figure #4

CONCENTRATION
DISCHARGE LIMITS
P.O.T.W.
PHOSPHATING/CHROMATING/ANODIZING
SUBCATEGORIES

FLOW - GREATER THAN 10,000 GPD

| | Pretreatment standard (mg/l) | |
|---|---|---|
| Pollutant or pollutant property | Maximum for any 1 day | Average of daily values for 4 consecutive monitoring days shall not exceed - |
| CN,T ..... | 0.8 | 0.23 |
| Cu ..... | 4.5 | 1.8 |
| Ni ..... | 4.1 | 1.8 |
| Cr ..... | 7.0 | 2.5 |
| Zn ..... | 4.2 | 1.8 |
| Pb ..... | 0.6 | 0.3 |
| Cd ..... | 1.2 | 0.5 |
| Total metals ..... | 10.5 | 5.0 |

Figure #5

CONCENTRATION
DISCHARGE LIMITS
P.O.T.W.
PHOSPHATING/CHROMATING/ANODIZING

FLOW - LESS THAN 10,000 GPD

| | Pretreatment standard (mg/l) | |
|---|---|---|
| Pollutant or pollutant property | Maximum for any 1 day | Average of daily values for 4 consecutive monitoring days shall not exceed- |
| CN, A ..... | 5.0 | 1.5 |
| Pb ..... | 0.6 | 0.3 |
| Cd ..... | 1.2 | 0.5 |

Figure # 6

ALTERNATIVE CONTROL
DISCHARGE LIMITS
P.O.T.W.
PHOSPHATING/CHROMATING/ANODIZING

FLOW - GREATER THAN 10,000 GPD

| | Pretreatment standard (mg/l) | |
|---|---|---|
| Pollutant or pollutant property | Maximum for any 1 day | Average of daily values for 4 consecutive monitoring days shall not exceed - |
| CN, T ..... | 0.8 | 0.23 |
| Pb ..... | 0.6 | 0.3 |
| Cd ..... | 1.2 | 0.5 |
| TSS ..... | 20.0 | 10.0 |
| pH ..... | Within the range 7.5 to 10.0 | |

Figure # 7

## TYPICAL REQUIREMENTS FOR DISCHARGE OF INDUSTRIAL WASTEWATER INTO A MUNICIPAL TREATMENT FACILITY (POTW)

| PARAMETER | MAX. ALLOWABLE CONCENTRATION | TYPICAL UNTREATED WASTE CONCENTRATION |
|---|---|---|
| pH | 6.0 to 9.0 | 3.0 to 5.0 |
| Chromium (hexavalent) | .05 mg/l | 70 to 80 mg/l |
| Chromium (total) | 1.0 mg/l | 100 to 110 mg/l |
| Fluoride | 5.0 mg/l | 40 to 60 mg/l |
| Cyanide (total) | 0.1 mg/l | 5 to 10 mg/l |
| Suspended Solids | 25.0 mg/l | - |
| Oil and Grease | 100.0 mg/l | 150 to 200 mg/l |

FIGURE #8

# BATCH TREATMENT SYSTEM

## TYPICAL FIVE STAGE ALUMINUM PRETREATMENT PROCESS

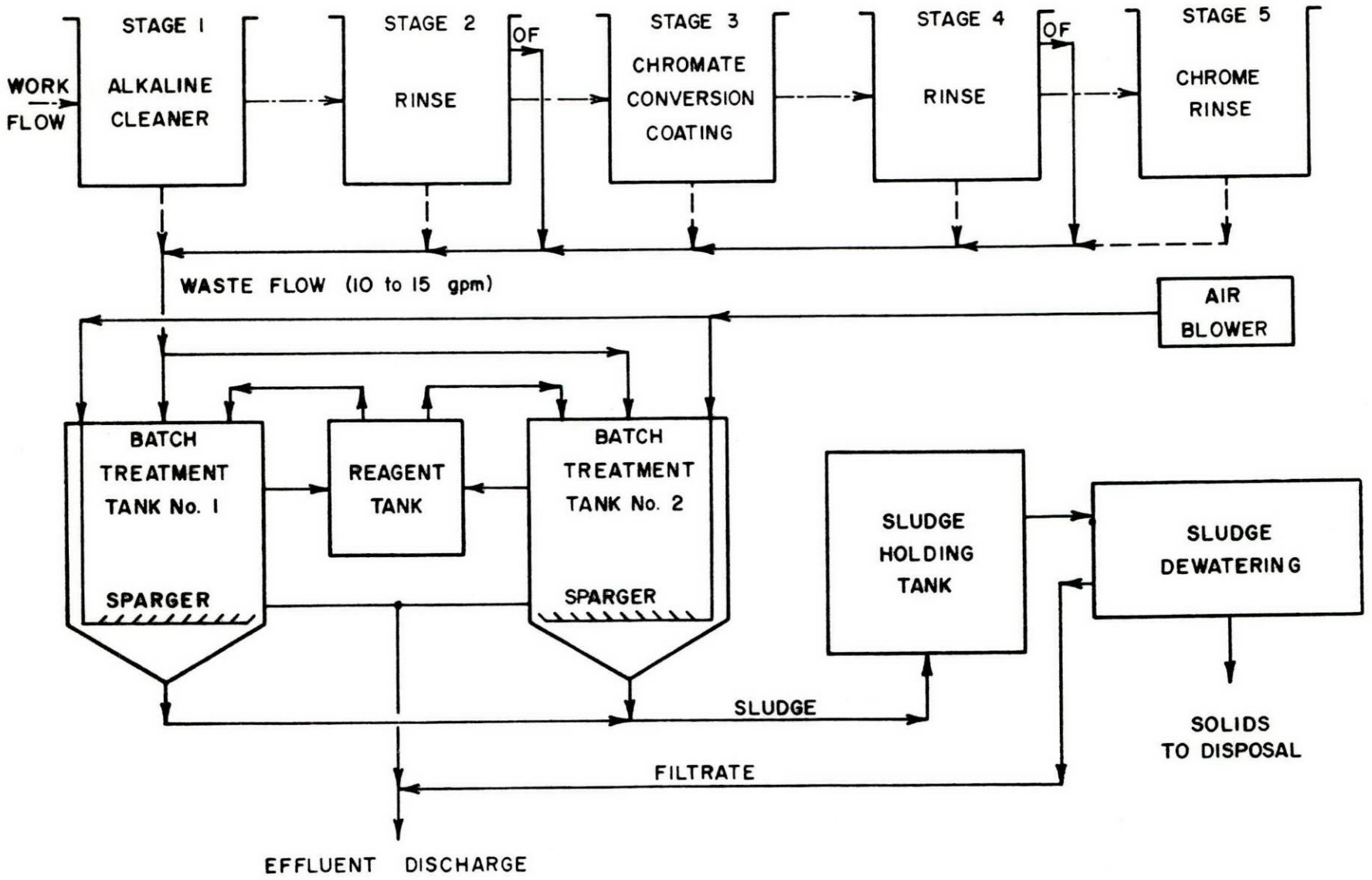


Figure #9

# CONTINUOUS TREATMENT SYSTEM

## TYPICAL FIVE STAGE ALUMINUM PRETREATMENT PROCESS

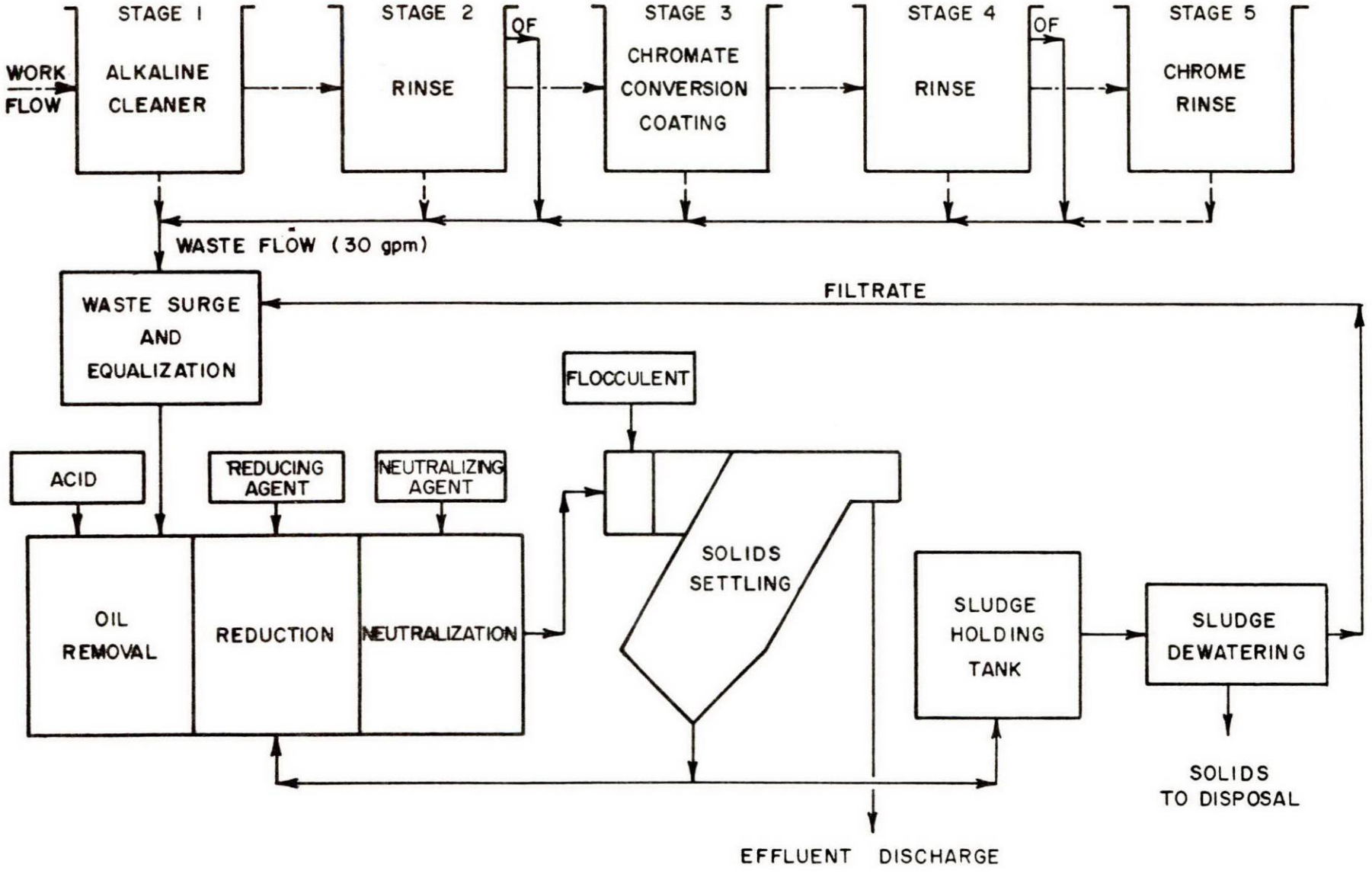


Figure #10

MAXIMUM CONCENTRATION OF CONTAMINANTS
FOR CHARACTERISTICS OF EP TOXICITY

| EPA HAZARDOUS WASTE NUMBER | CONTAMINANT | MAXIMUM CONCENTRATION (mg/l) |
|---|---|---|
| D004 | ARSENIC | 5.0 |
| D005 | BARIUM | 100.0 |
| D006 | CADIUM | 1.0 |
| D007 | CHROMIUM | 5.0 |
| D008 | LEAD | 5.0 |
| D009 | MERCURY | .2 |
| D010 | SELENIUM | 1.0 |
| D011 | SILVER | 5.0 |

* PARTIAL TABLE I, P 33122, MAY 19, 1980 FEDERAL REGISTER

Figure #11

## STATE RCRA AUTHORIZATION

| | |
|---|---|
| ARKANSAS | DELAWARE |
| UTAH | MASSACHUSETTS |
| NORTH DAKOTA | SOUTH CAROLINA |
| NORTH CAROLINA | MONTANA |
| LOUISIANA | MAINE |
| TEXAS | KENTUCKY |
| MISSISSIPPI | PENNSYLVANIA |
| OKLAHOMA | RHODE ISLAND |
| VERMONT | CALIFORNIA |
| IOWA | MARYLAND |
| GEORGIA | OREGON |
| ALABAMA | TENNESSEE |

Figure #12

RESOURCE CONSERVATION AND RECOVERY ACT

SECTION 3002

HAZARDOUS WASTE GENERATOR REQUIREMENTS

1. OBTAIN AN EPA IDENTIFICATION NUMBER.
2. OBTAIN A FACILITY PERMIT IF WASTE IS ACCUMULATED ON THE GENERATION PROPERTY MORE THAN 90 DAYS.
3. USE APPROPRIATE CONTAINERS AND LABELS FOR PROPER SHIPMENT.
4. PREPARE AND UTILIZE A MANIFEST FOR TRACKING HAZARDOUS WASTE.
5. DOCUMENT VIA THE MANIFEST SYSTEM THAT WASTE ARRIVES AT THE DESIGNATED FACILITY.
6. SUBMIT AN ANNUAL SUMMARY OF ACTIVITIES.

Figure #13

## RESOURCE CONSERVATION AND RECOVERY ACT
## WASTE MANIFEST SYSTEM

- DOCUMENT NUMBER
- NAME, ADDRESS, TELEPHONE, AND EPA IDENTIFICATION NUMBER
- THE TRANSPORTER'S NAME AND EPA IDENTIFICATION NUMBER
- DISPOSAL FACILITY NAME, ADDRESS AND EPA IDENTIFICATION NUMBER
- DESCRIPTION AND QUANTITY OF EACH WASTE

Figure #14

RESOURCE CONSERVATION AND RECOVERY ACT

MANIFEST FORM

"THIS IS TO CERTIFY THAT THE ABOVE NAMED MATERIALS ARE PROPERLY CLASSIFIED, DESCRIBED, MARKED, AND LABELED AND ARE IN PROPER CONDITION FOR TRANSPORTATION ACCORDING TO THE APPLICABLE REGULATIONS OF THE DEPARTMENT OF TRANSPORTATION AND THE EPA."

---

Figure 15

RESOURCE CONSERVATION AND RECOVERY ACT

SUMMARY OF POTENTIAL HAZARDOUS WASTE ACTIVITY

A. SURFACE PRETREATMENT

B. INDUSTRIAL WASTEWATER TREATMENT SLUDGES

Figure #16

## HAZARDOUS WASTE GENERATION
## SURFACE PRETREATMENT PROCESSES

| WASTE SOURCE | RCRA POTENTIAL STATUS: CURRENT DISCHARGE WASTE TREATMENT | RCRA POTENTIAL STATUS: DISCHARGE TO SEWER | RCRA POTENTIAL STATUS: OFF-SITE HAULAGE |
|---|---|---|---|
| 1. CLEANER STAGE(S) (OVERFLOW/DUMPS) | NOT INCLUDED | NOT INCLUDED | HAZARDOUS-CORROSIVE,TOXIC |
| 2. CLEANER RINSE(S) (OVERFLOW) | NOT INCLUDED | NOT INCLUDED | - |
| 3. CONVERSION COATING STAGE(S) (OVERFLOW/DUMPS/CLEANER) | | | |
| a). PHOSPHATE | NOT INCLUDED | NOT INCLUDED | HAZARDOUS-CORROSIVE,TOXIC |
| b). OXIDE | NOT INCLUDED | NOT INCLUDED | HAZARDOUS-CORROSIVE,TOXIC |
| c). CHROMATE | NOT INCLUDED | NOT INCLUDED | HAZARDOUS-CORROSIVE,TOXIC |
| d). NO RINSE | NOT REQUIRED | NOT REQUIRED | - |

## HAZARDOUS WASTE GENERATION
## SURFACE PRETREATMENT PROCESSES

| WASTE SOURCE | RCRA POTENTIAL STATUS | | |
|---|---|---|---|
| | CURRENT DISCHARGE WASTE TREATMENT | DISCHARGE TO SEWER | OFF-SITE HAULAGE |
| 4. CONVERSION COATING RINSE(S) (OVERFLOW/DUMPS) | | | |
| a). PHOSPHATE | NOT INCLUDED | NOT INCLUDED | - |
| b). OXIDE | NOT INCLUDED | NOT INCLUDED | - |
| c). CHROMATE | NOT INCLUDED | NOT INCLUDED | - |
| d). NO RINSE | NOT REQUIRED | NOT REQUIRED | - |
| 5. FINAL ACID RINSE(S) (OVERFLOW/DUMP) | | | |
| a). CHROMIC ACID | NOT INCLUDED | NOT INCLUDED | HAZARDOUS/ TOXIC |
| b). NON-CHROMIC ACID | NOT INCLUDED | NOT INCLUDED | HAZARDOUS/ TOXIC |

## HAZARDOUS WASTE GENERATION
## INDUSTRIAL WASTEWATER TREATMENT SYSTEM

| WASTE SOURCE | CURRENT POTENTIAL RCRA STATUS |
|---|---|
| 1. SLUDGE (LIQUID/DEWATERED) | |
| a). CHROME SURFACE PRETREATMENT PROCESSES | HAZARDOUS - EP TOXICITY |
| b). NON-CHROME SURFACE PRETREATMENT PROCESS | HAZARDOUS - EP TOXICITY |
| 2. WASTE OIL SKIMMINGS | NON - HAZARDOUS |

# Alternative Deposition Processes Session K

## PVD by Electron-Beam Processes

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# PVD by Electron Beam Processes

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Physical vapor deposition by electron beam evaporation has been used in manufacturing corrosion and oxidation resistant coatings, magnetic coatings, optical coatings and structural and electrically resistive elements. Electron beam evaporation process does offer high deposition rates, freedom from contamination, and deposition of virtually the entire periodic table of elements. The technology is commercially available. There is another technique in electron beam evaporation; it is referred to as hot hollow cathode evaporation. The main difference between the commercially available electron beam gun and the hot hollow cathode gun is the electron sources, which generate electrons with different characteristics.

Electrical characteristics of the two electron guns are shown in Table I.

Table I
Comparison of Electron Guns

| | Typical Values | | |
|---|---|---|---|
| Type | Voltage | Current | Vacuum |
| Filament Cathode | 8000 volts | ~1 amp | $10^{-5}$ Torr or better |
| Hot Hollow Cathode | 25 volts | 250 amp | $10^{-3}$ Torr or better |

The difference in the electron sources causes the electrons to have different current density and kinetic energy. The electrons fron the hot hollow cathode have the desirable density and kinetic energy to ionize the evaporant atoms. The ions are used to sputter-clean the substrate prior to deposition, resulting in an excellent adhesion between the coating and substrate. Thus, coatings from hot hollow cathode evaporation are used as a bonding aid. In comparing the two electron beam evaporation processes, the hot hollow cathode has the advantages of high adhesion and low substrate temperature; the disadvantages are a) it is a more complex process and b) some of the process equipment are not readily available.

The other principle technique used in physical vapor deposition is sputtering. Table II shows some of the differences between electron beam evaporation and sputtering. In general, electron beam evaporation processes are less complex and have a higher deposition rate.

Table II

Comparison of Evaporation with Sputtering

| | E-Beam Evaporation | Sputtering |
|---|---|---|
| Vacuum | $10^{-4}$ Torr or less | $10^{-2}$ Torr or less |
| Source | Molten | Solid |
| Adhesion | fair | good |
| Rate of Deposition | 50 mils/hr | 5 mils/hr |
| Material | All solid elements and some alloys | All solid elements, alloys and dielectrics |

In order to obtain the desired coatings, relationship between process parameters and coatings properties must be established. Some of the parameters and properties are listed in Table III.

Table III

Parameters and Properties

| Process Parameters | Coating Properties |
|---|---|
| Substrate Temperature | Microstructure |
| Substrate Bias Voltage | Crystallographic Orientation |
| Geometry | Density |
| Deposition Rate | Mechanical Behavior |
| Impurities | Electrical Behavior |
| Substrate Material | Chemistry |

For example, in the case of electron beam deposition of beryllium, film properties were measured as a function of substrate temperature; see Table IV. Microstructure of coatings also changes with the substrate temperature from extremely fine columnar grains at low temperatures to fine equi-axed at high temperatures. In the case of electron beam evaporation from a filament source, the substrate temperature has greater influence on the properties than other process parameters, such as deposition rate. B. A. Movchan and

Table IV

Properties of Beryllium Films versus Substrate Temperature

| Substrate Temperature During Evap. (°C) | Electrical Resistivity (micro-ohm cm) | Knoop Hardness No. (100gm load) | Fracture Strength (10001b per $in^2$) | Total Elougation (%) |
|---|---|---|---|---|
| 200 to 270 | | 488 to 490 | | |
| 300 to 345 | 9.62 to 12.9 | 267 to 326 | | |
| 350 to 425 | 8.85 to 9.22 | 250 to 230 | 19 to 21 | 0.1 |
| 480 to 550 | 4.2 to 4.9 | 204 to 233 | 39 to 43 | 0.3 |
| 625 to 685 | 4.5 to 4.8 | 168 | 40 to 52 | 0.45 |
| 760 to 790 | 3.7 to 4.0 | 170 | 40 to 44 | 1.0 |

A. V. Demchishin[1] have proposed a structural zone model for vacuum deposited films. Each zone is determined by the ratio of substrate temperature to the melting point of the deposited material; thus, the changes in the physical and mechanical properties are correlated to the micro-structural changes.

To illustrate the effects of substrate bias voltage on coating properties, the case of hot hollow cathode evaporation of silver is an excellent example. During the hot hollow cathode evaporation, the electrons evaporate and ionize the silver. When a negative potential is applied to the substrate, the silver ions are accelerated to the substrate. It is known that electric field and bombardment by charge particles influence the nucleation and growth process of the condensate. Since in hot hollow cathode evaporation, where the ratio of charged to neutral particles bombarding the substrate is several orders of magnitude greater than in conventional electron beam evaporation, the substrate bias voltage is a dominant parameter in controlling the coating characteristics. The changes in the nucleation and growth process caused correspondent changes in crystallographic orientation (Table V), microhardness (Table VI) and microstructure of the coating. The microstructure is altered by the substrate bias voltage. The fine columnar grains are changed to coarser grains with increasing bias voltage. The alteration in the morphology of the microstructure correlates with the changes in crystallographic orientation and microhardness. The effects of substrate bias voltage on the coating properties in the hot hollow cathode process are similar to the effects of substrate temperature in the conventional electron beam (filament source) process. This observation supports the theory that an increase in kinetic energy of the vapor ions is equivalent to a higher substrate temperature.

Table V

Effects of Substrate Bias Voltage on the Crystallographic Orientation of Silver Coatings Deposited From a Hot Hollow Cathode Source.

Substrate Material - Beryllium

| Substrate Bias Voltage (V) | I/Io Relative Intensities (111) | (200) | (220) | (311) |
|---|---|---|---|---|
| Ground | 100 | 19 | 10 | 15 |
| -2 | 100 | 12 | 13 | 10 |
| -5 | 100 | 25 | 5 | 12 |
| -20 | 100 | 50 | 37 | 47 |
| -40 | 50 | 100 | 1 | 5 |

Table VI

Microhardness of the Silver Coatings Deposited From a Hot Hollow Cathode Source versus the Substrate Bias Voltage.

| Substrate Bias Voltage (V) | KHN (25gm load) |
|---|---|
| Ground | 95 |
| -2 | 89 |
| -20 | 88 |
| -40 | 66 |
| -80 | 45 |
| Bulk Silver (worked) | 90 |
| Bulk Silver (annealed) | 25 |

Silver coatings deposited from a hot hollow are utilized in a variety of solid state bonding applications; as an example, to produce high-strength, leak-tight, and reliable steel-aluminum transitions joints.[2] The silver is used as a bonding aid; it is coated on the mating surfaces of the dissimilar metals. The mating surfaces are solid state bonded at low temperatures (200 to 450°C) for 10 minutes. The joint is stronger than the parent materials; in general, the weaker parent material fails first.

Electron beam evaporation process has become a common production technology; it is especially true in electronics and aerospace industries. Some of the applications[3] and the materials used are given in Table VII. The electron beam evaporation technology also has a future in depositing new and unusual materials, in order to meet new demands of materials requirements.

Table VII

Applications of Electron Beam Evaporation Technology

| Application | Material |
|---|---|
| Decorative | Cr, Au, Ag |
| Optical | Oxide, sulfides and fluorides |
| Electrical | Al, Ni, Cr, Fe |
| Mechanical | Cu, Al, TiC, TiN, Cr-Fe-Al |
| Corrosion-Oxidation Resistant | Ni-Co-Cr-Al-Y Alloys |

Feferences:

1. B.A. Movchan, A.V. Demchishin, Phys Met Metallogr.,28,83 (1968)
2. E.R. Naimon, J.H. Doyle, C.R. Rice, D. Vigil, and D.R. Walmsley Welding Journal, 60(11), 17(1981)
3. R.F. Bunshah and D.M. Mattox, Physics Today, 33(5), 50(1980)

K-2

# Alternative Deposition Processes Session K

## Thermal Spraying Coatings — The Process & Its Evolution

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# THERMAL SPRAY COATING
# THE PROCESS AND ITS EVOLUTION

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## ABSTRACT

Thermal spraying is a technique by which a material is melted and transported at high velocities to coat, and thus, to protect a surface. Application techniques vary from mundane oxy-acetylene torches to exotic plasma generators, of which the latter, may be operated in partical vacuum. This affords the deposition of dense, tightly adherent, coatings exhibiting improved properties and high integrity.

## INTRODUCTION

To protect various service components and extend their useful life, wear surfaces are often enhanced by the application of a more durable film or coating. Methods of applying these coatings has ranged from mundane brush-on to exotic ion sputtering. The gauntlet between is filled with a variety of processes, all competent of providing specialized coatings, with a myriad of applications. Some of these processes are considered a delicate art, while others are dubbed as calculated engineering sciences. In between this range are those which have been identified as both science and art. The thermal spray process falls within this latter group.

## THERMAL SPRAY PROCESSING

Conceived in 1902, the thermal spray process was recognized by the term "metallization" as the process was limited to the spray application of metals and their alloys. Metallization, or the American term "metallizing", used the heat of chemical combustion to melt the raw material while blasts of compressed gas atomized and propelled the metal onto the target.

German contributions of the 1920's, namely those of Bauerlin and Gerdien [1], provided theoretical concepts which eventually led to the development of the electric arc and plasma arc spray systems introduced in the 1950's. Electric heat sources provided the enthalpy necessary to plasticize and spray high melting ceramics, refractories and superalloys. New materials and coating requirements, coupled with advances in equipment design and capability began to evolve and become available to a wide range of industries. The point has been reached where thermal spraying is being performed by more people than ever before.

The list of materials being applied is endless. The only restriction being that the spray materials melt without significant disassociation within the flame or arc. Currently, the types of materials that can be sprayed consist of the following:

metals
metal alloys
ceramics
cermets
plastics
composites
refractories
mixtures of the above

Application techniques [2] for these materials are divided into two basic groups encompassing seven spray methods, namely:

| | |
|---|---|
| I Chemical Flame (Flame Spray) | 1. Molten Metal<br>2. Powder<br>3. Wire Metallization<br>4. Ceramic<br>5. Detonation |
| II Electric Heating | 1. DC Plasma Arc<br>2. Electric Arc |

Based upon service requirements, thermally sprayed coatings may be categorized [3] into six major groups. These include bonding materials; abrasive and abradable clearance control coatings; salvage and repair; environmental protection; instrumentation base; fretting and wear protection; and special purpose deposits.

Bonding materials are those that perform an anchorage function, aiding subsequent deposits to adhere. Clearance control coatings are those specifically designed for gas path seals. Abrasives cut while abradables sacrifice themselves to an intruding member. Salvage and repair type coatings are used to build up material worn or inadvertently machined away.

Specific materials, adversely affected by hostile environments, may be readily protected by more 'noble' outer claddings resistant to the adverse operating conditions. Coatings exhibiting resistance to wear and/or fretting are among the oldest used by man; these include carbides and hard-surfacing materials whose main attribute is to resist degradation to the host surface. A more complete breakdown is given in Table I. Noted are typical coatings and application methods as employed in routine tasks; specialty or developmental efforts are not included.

TABLE I
THERMAL SPRAY COATINGS APPLICATION AND USE

| SERVICE REQUIREMENT | COATING MATERIAL | DEPOSITION METHOD |
|---|---|---|
| BONDING | Nickel Aluminum | P/A;W;-P-F/S |
| | Molybdenum | P/A; W-F/S |
| CLEARANCE CONTROL | | |
| Abradable | Nickel Graphite | P-F/S |
| | Aluminum (99.0%+) | E-,P/A;W-F/S |
| | Silicon Aluminum (12 Si) | P/A; W-F/S |
| | Silver Copper Zinc Alloy | W-F/S |
| Abrasive | Aluminum Titania | P/A |
| | Cermet ($Al_2O_3$ + NiAl) | P/A |
| SALVAGE/REPAIR | Nickel Chromium | E-,P/A;W-F/S |
| | Nickel Chromium Aluminum | P/A; P-F/S |
| | Nickel Aluminum | E-,P/A;P-F/S |
| | Carbon & Stainless Steels | E-,P/A;W-F/S |
| ENVIRONMENTAL | Zinc | W-F/S; E/A |
| | Aluminum | W-F/S; E/A |
| | MCrAlX's | P/A |
| | Yttria Stabilized Zirconia | P/A |
| | Magnesia Stabilized Zirconia | P/A |
| INSTRUMENTATION | Nickel Chromium Alloy | W-F/S |
| | Nickel-Aluminum | P/A; W/F/S |
| | Nickel Chrome Silicon Boron Alloy | P/A |
| | Alumina | R-F/S |
| FRETTING/WEAR | Carbides (WC, TiC, $Cr_3C_2$) | P/A; D |
| | Refractory Oxides | P/A;R-P-FS;D |
| | Molybdenum | P/A; W-F/S |
| | Copper Nickel Alloy | P/A; D |
| | Copper Nickel Indium Alloy | P/A; D |
| | Nickel Chrome Silicon Boron Alloy | P/A; P-F/S |
| | Chrome Silicon Moly Cobalt Alloy | P/A |
| | Cobalt Chrome Nickel Tungsten Alloy | P/A |
| SPECIAL PURPOSE | | |
| Sacrificial | Molybdenum | W-F/S; P/A |
| Dynamic Balance | Nickel Aluminum | P/A |
| Speed Sensors | Nickel Iron Alloy (Mu Metal) | P/A |

| | | | |
|---|---|---|---|
| P/A | Plasma Arc | R-F/S | Rod-Flame Spray |
| W-F/S | Wire - Flame Spray | E/A | Electric Arc |
| P-F/S | Powder Flame Spray | D | Detonation Flame Spray |

## AVAILABLE THERMAL SPRAY APPLICATION METHODS

### Chemical

Thermal spraying using the heat resulting from a chemical reaction is usually referred to in the industry as either combusiton or oxy-fuel gas or flame spraying. The bulk of the commercial production is based on flame spraying, generallly using oxygen-acetylene mixtures as the fuel and powder or, more usually, rod or wire as the feed coating material. The equipment for flame spraying is relatively inexpensive and, consequently, capital costs are low. However, the process suffers from two major limitations preventing its acceptance as a universally accepted tool. Firstly, the flame temperature is insufficient to melt the more refractory metals and many ceramics. Secondly, the substrate tends to be heated by the flame and this may cause difficulty with workpiece temper and/or distortion, as well as precluding the use of low melting point substrates; e.g. plastics.

As noted previously, there are five basic flame spray application techniques: molten metal, wire metallizing, ceramic rod, oxy-fuel powder, and detonation. For all intents and purposes, only the latter four techniques are considered viable production applications.

### Molten Metal

Molten metal spraying is limited to the application of low melting point metals namely solders, tin, lead, cadmium, zinc, and aluminum. The latter four metals are used to protect ferrous alloys from the elements. Solders and tin are used primarily in foodstuff preservation; e.g., canning.

### Ceramic Rod and Wire Metallizing

Ceramic rod and wire metallizing closely resemble each other in that the equipment for the spraying of ceramics is basically the same as that used for wire except for slight modification in the design of the gun [4]. Consequently the two will be discussed as one subject. The overall facility is identical as shown in Figure 1. Major components include a spray gun, air and gas flow meters, and air and gas regulators. Accessory equipment includes compressed air, oxygen and fuel gas supplies. An air cleaner, inserted in the air line between the gun and air source, eliminates contaminants such as water moisture and oil which may inhibit flame efficiency.

The principle of operation is that the wire or rod is drawn through the rear of the gun by a pair of drive rolls which, in turn, are powered by an air turbine. The wire or rod is next

pushed through a nozzle where it is melted by a flame of burning gas as shown in Figure 2. The actual flame is used for melting and does not, in itself, spray the material. Thus it is necessary to surround the flame with a stream of compressed gas, the function of which is to disintegrate the film of molten material as it forms. This disintegration process atomizes the molten material and propels it to a targeted workpiece. Particle velocities in this process are approximately 800 ft/sec [5] which provides tenacious coatings whose densities are 90 to 95 percent of theoretical. Alumina ($Al_2O_3$), zirconia ($ZrO_2$) and chrome oxide ($Cr_2O_3$) are the refractory oxides most commonly used as flame sprayed ceramic coatings. Any metal that can be drawn into wire and with a melting temperature of less than 5200°F can be wire metallized.

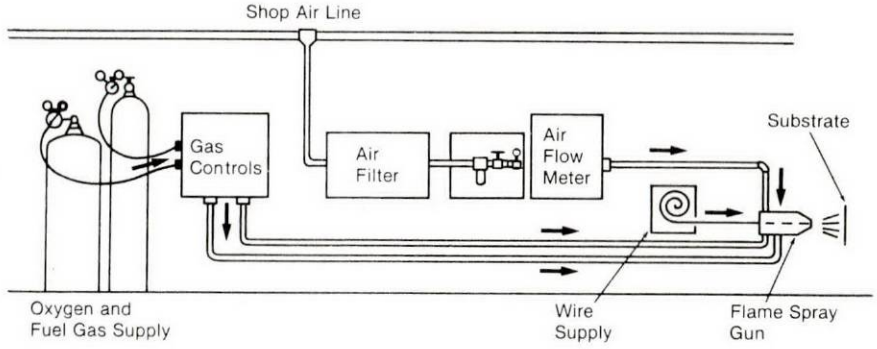



Figure 1: Typical wire/rod flame spray system

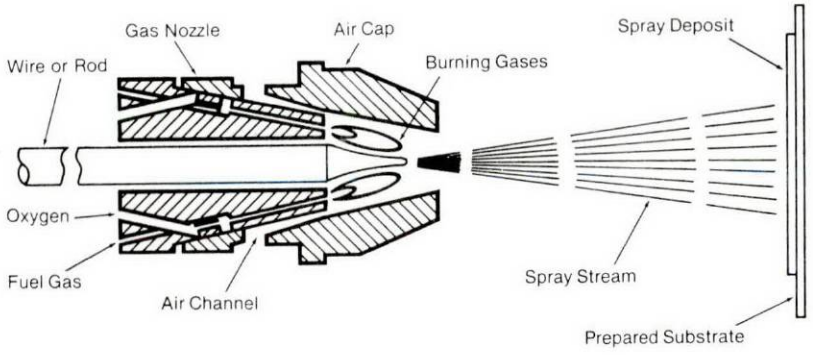



Figure 2: Cross section of a typical wire/rod flame spray gun

## Oxy-Fuel Gas-Powder

Powdered materials may be made to adhere to suitably prepared surfaces if they are suspended in a gaseous medium and heated to a temperature comparable to their melting points and subsequently projected forward. This aim may best be achieved by driving the suspended particles through a blowpipe flame; however, obtaining reasonable and consistent quality coatings was not always easy, and a good deal of development work, in the 1930's, had to be carried out before the method achieved the adaptability of the present process. Spray pistols, Figure 3, developed early in the process, maintained suitably balanced flames but suffered from erratic powder feed conditions. This was attributed to two major factors; namely, powder classification and powder feed mechanisms.

It must be emphasized that the type and size of the powder used in gas powder spraying is important. The particles suspended in the conveying gas must enter the center of the the heat source and, if the nozzles are properly constructed, most of the material is melted. The flame of a powder pistol must be larger and less intense than in the ceramic or wire systems for the flame is not only restricted on the outside by the stream of propellent gas, but expanded internally by the conveying gas.

Typically the velocity of the powder particles after leaving the nozzle is lower than in the wire method (80 to 120 surface feet per second) and in general are not further atomized in the process. It follows that the powder should be fine, usually within minus 140 plus 325 mesh, and as uniform as possible. The particle shape is not an important factor as all particles when molten tend to become, as in all other systems, spherical in flight. However, atomized and spheriodized powders tend to pack less and are easier to feed than mechanically pulverized ones.

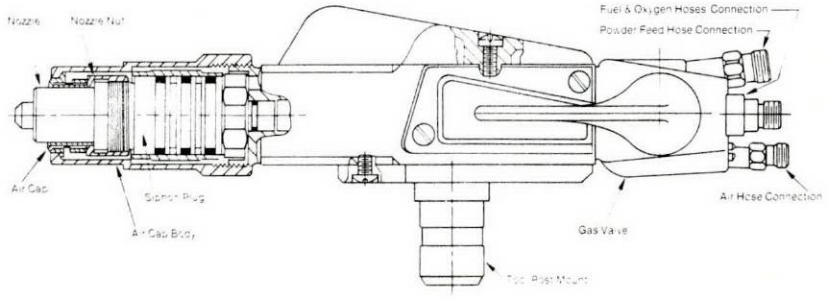



Figure 3: Flame Spray Powder Gun

## Detonation Flame Spraying

Concepts developed by F. Gfeller and B. Baiker [7], concerning flame propagaton in tubes were put to commercial use in the mid 1950's as a "flame plating" device. This process utilized explosions in a unique manner in that powdered material was sprayed through conveyance on detonation waves. The waves are produced by igniting a metered, measured mixture of acetylene and oxygen in a long tube, the open end of which is directed toward the workpiece.

As shown in Figure 4, the device is rather complex, consisting of numerous valves, an ignition system, and a long barrel attached to one end of a detonation chamber. The explosions within the chamber cause shock waves to pass down the barrel of the apparatus; and, as it is well known that, if such a wave can obtain ultrasonic speeds, high temperatures are generated. This searing heat, said to exceed 6000°F, plasticizes the powdered material, being propagated through the shock wave at 2400 fps, causing it to become embedded in the surface of the substrate. There, a microscopic welding action produces a tenacious bond at the splat-substrate interface. Immediately following an explosion, valves respond to cut off the fuel mixture, purge the system of combustion products with nitrogen and then back fill with the fuel mixture and powdered material. Again, ignition and the entire process is repeated - purge, backfill, ignition, purge.

The entire series of functions occurs four times per second and is successively repeated until the coating material is built up to the thickness specified for the particular application. The process is particularly useful for depositing hard-facing materials, such as tungsten carbide, which produce very dense coatings with excellent wear resistance. However, the process is more expensive and has more geometric limitations when compared to other thermal spray techiques [2].

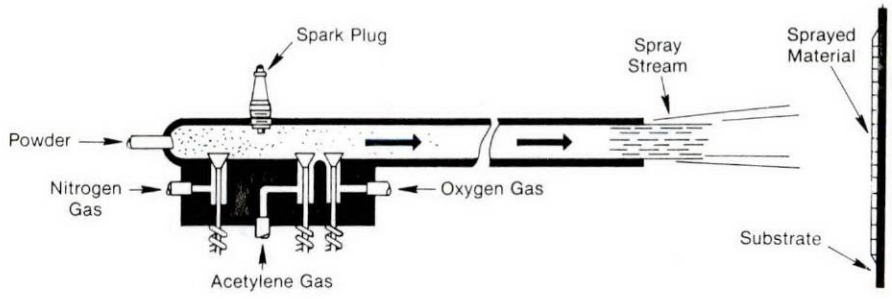



Figure 4: Detonation Flame Spray Gun [8]

## Electric Heating

As early as 1914, experiments were being conducted using electrical heating for spraying. Schoop and Bauerline [1] devised a spray gun where the metal to be sprayed was one pole of an electric arc and a carbon rod the other. An arc generated between the two poles melted the metal which was blown away by a jet of gas. A continuous feeding of the metal to the carbon rod was necessary to maintain the arc. Developments using electric energy for heat during spray were slow and far behind the advances made in the over-all field of electrical engineering. However, World War II and the subsequent prevelant adverse economic conditions accelerated attention to this low cost source of energy. Consequently, in the early 1950's, two "new" thermal spray process appeared on the commercial scene - plasma arc and electric arc.

Electric heating consists of an arc burning between two electrodes. Electrons emitted from the cathode (-) are accelerated by the applied potential. The electrons acquire high kinetic energy and collide with atoms and molecules of air. This causes ionization of the atoms and disassociation in diatomic gases. Recombination subsequently takes place and both heat and light are evolved. In this way, the electrical energy applied between the electrodes is converted to heat. Arc temperature is estimated to be 10,000 to 12,000°F. The thermal efficiency depends upon many factors but lies between 30 and 70 percent. In free-burning arcs, the heated gas expands laterally and this decreases the enthalpy. Increases in power only raises the arc temperature slightly. To achieve significantly higher temperatures, it is necessary to increase the current density and enthalpy. This can be accomplished by passing the arc through an anode (+) nozzle of a diameter smaller than that of the natural arc - an essential feature of the plasma gun.

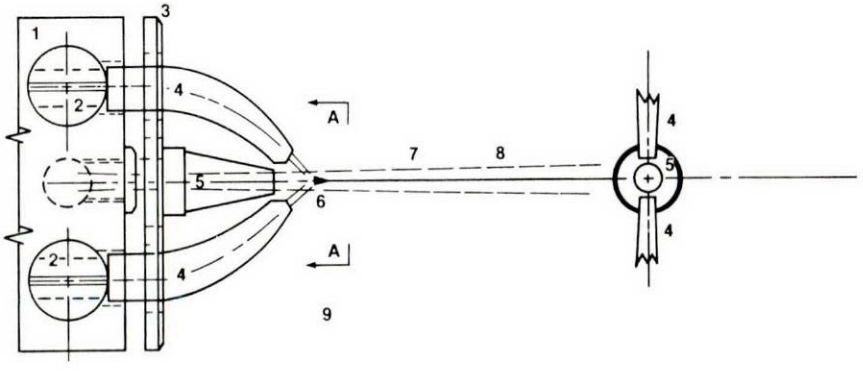
## Electric Arc

As defined by the American Welding Society [9] electric arc spraying is a method of thermally spraying metals in which two wires of either similar or dissimilar compositions are melted and the fused particles are projected onto a previously prepared surface to build-up an adherent coating. As described previouslly, the thermal energy required to melt the wires sufficiently is produced by means of an electric arc sustained between the two wires. A carrier gas, usually compressed air, is used to atomize the molten metal at the arc and propel the fine droplets, thus produced, onto the substrate to be coated.

The major components of electric arc thermal spraying systems consists of a power supply, wire feed unit, control unit and

spray gun. It is essential that the feed unit deliver the wires to the gun simultaneously and at a continuous rate in order not to lose point contact. At the gun, as shown in Figure (5), the wires are fed to and through electrical contact tips (anode and cathode) which also act to guide the wires to an intersecting point where they meet. Since the wires are electrically energized in the electrode tip, through which they pass, an electric arc is struck and maintained at the point of intersection by constant feeding. Located directly behind, and aligned with the arc, is a nozzle through which a high velocity of atomizing gas flows. While this gas is generally compressed air, cases arise - based on required coating attributes - where an inert gas may be utilized. This gas can eject the melting metal particles to velocities of 800 fps which is comparable to those recorded for ceramic rod or wire metallizing. Arc temperatures, as previously described, can exceed 10,000°F. Consequently, the moltent material is throughly heated, thus elevating the droplets to a super heated state. While in this condition, these particles can fuse to the minute protusions of a properly prepared surface, producing a high degree of metallurgical bonding of the coating to the substrate (adhesion) and also high intercoating strength (cohesion).

Generally speaking, electric arc sprayed coatings are more economically produced than those produced by other thermal spraying techniques. This is attributed to low costs of raw material, high efficiency, and economy of operation. But, however attractive the method appears, evident drawbacks include limited material availability, generation of voluminous dust, and geometric limitations due to equipment configuration.




1. Insulated housing for contact piece; 2. Contact piece; 3. Heat resistant protective plate; 4. Wire guides; 5. Atomizing air nozzle; 6. Arc point; 7. Metal particles; 8. Atomizing air stream; 9. Wires.

Figure 5: Schematic of Electric Arc Thermal Spray Gun

As discussed earlier, electric arc coatings are extremely tenacious and exhibit tensile strengths exceeding 7,000 psi (10) when applied over lightly roughened steel substrates. This high strength, owed to cohesive or interparticle attraction, permits coating buildup to thicknesses of 0.250 inches or greater. These attractive attributes along with the "highest degree of utilization of thermal efficiency..." (11) as compared to other spray processes have endeared the method to maintenance engineering. Tooling, powder plant machinery, chemical stirrer shafts, and any other on-site equipment that wears is often spray coated, refinished and returned to service faster and more economically by electric arc spraying than by purchasing, stocking and installing a new component.

DC Plasma Arc Spraying

Plasmas were used over fifty years ago to synthesize nitric oxide from air, but it was only during the 1950's that the technology was developed to make them commercially useful. To create plasma conditions, a suitable gas is passed through a high-current arc. At sufficiently high temperatures, the gas becomes ionized and collisions between electrons and ions generate radiant energy. In a plasma gun, the thermal balance in changed by constricting the arc, and this raises the temperature substantially, usually to 30,000 to 40,000°F.

A typical plasma spraying system is shown in Figure 6. The main component of the system is the plasma gun which is shown schematically in Figure 7. The electrodes are contained within the gun and are shaped to give the required constriction while the arc gas and the feed material are fed in through different orafices. Operation, including efficiency of the gun and quality of the deposit, depends on such factions as electrode design, powder size, substrate preparation, etc.

The extremely high temperatures in the plasma gun allow any material to be sprayed provided: (a) it melts without significant disassociation and (b) that a practical temperature interval exists between its melting and boiling points. The process is thus remarkably versatile and may be used to spray a vast array of powdered materials as previously listed in Table I.

Plasma deposits can vary in thickness from less than 0.001 inch to more than 0.100 inch, normally, however, they are in the 0.003 to 0.015 inch range. Due to the high particle temperatures and the rapid impingement to the target (to 1600 fps), the coatings are usually dense and adherent with porosities as low as 1.0% being common. Inert gas flooding during spraying minimizes oxidation. Within limits, the properties of the deposit can be varied to suit particular applications.

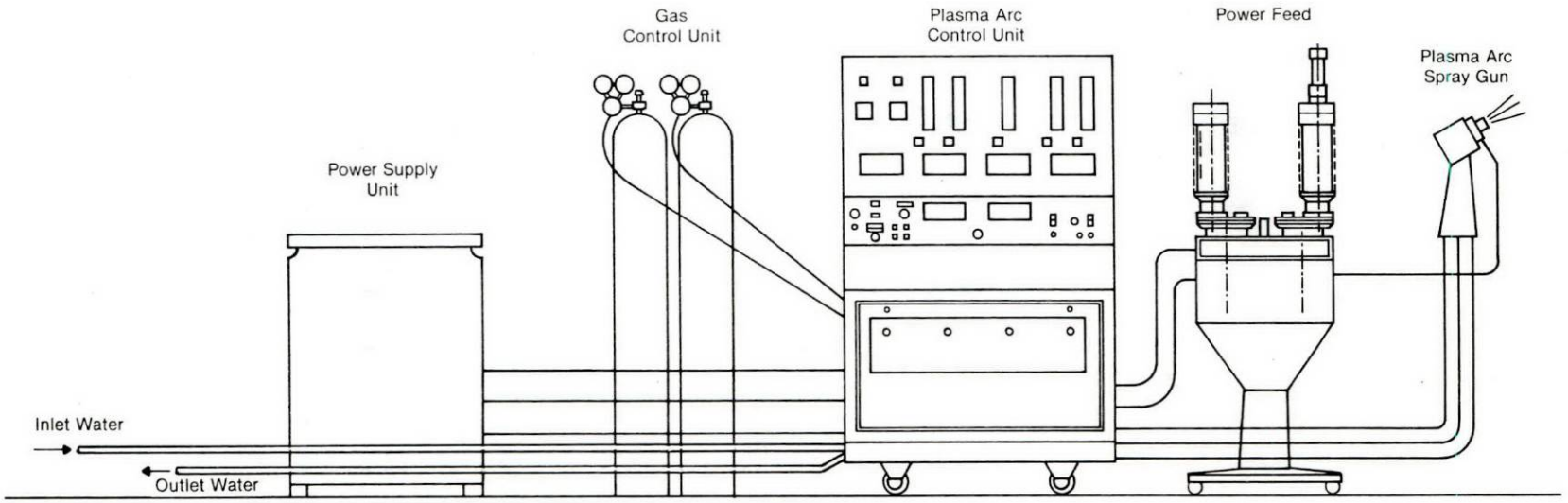



Figure 6: Typical plasma arc spray system

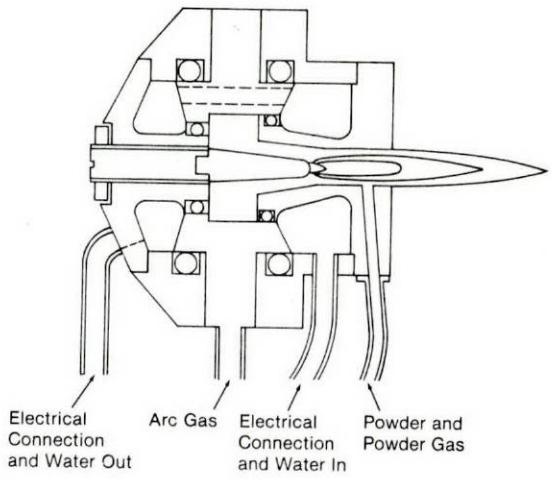



Figure 7: Cross Section of a Plasma Spray Gun

Vacuum Plasma Deposition

Several American and one European supplier have demonstrated a capacity to produce a marked improvement in plasma spray coating quality. This improvement results from installing the plasma generator within a chamber for operation under partial pressure conditions. This may be as low as 10 TORR. When generated in vacuum the plasma effluent physically changes becoming longer and thicker than that observed under normal, atmospheric conditions.

This new vacuum plasma deposition (VPD) process yields many benefits not readily evident. Since the vacuum chamber is evacuated of air, the only gases entering the system are those forming the plasma. These are usually inert. Hence, the coating is relatively oxide free and, since it can be preheated

without fear of oxidation, the substrate surface is likewise void of contamination. This nascent surface contributes to enhance coating adherence. Similarly, lack of intersplat oxides improves particle-to-particle cohesion and thus overall coating density. Porosity in as-sprayed MCrAlX and super alloy type overlays is usually less than one percent. This is true even in coatings applied at impingement angles of 45 degrees or less.

Operating a plasma device in a vacuum environment permits attainment of higher temperatures - both in the plasma stream and at the workpiece surface. The plasma generator employing varying power levels, in the 40 to 80 kW realm, yields an enthalpy greater than that developed at normal atmospheric pressure. This, coupled with the enlarged effluent, produces lengthened residence times for the spray particles. Consequently, a greater percentage of those particles are plasticized and deposited onto the substrate surface. Likewise, elevated substrate preheat temperatures reduces particle rebounding while promoting wetting by the impinging powdered materials. As a result, process efficiency is improved through greater deposition/utilization of the in-put material.

It should also be noted that effluent velocities are much greater in vacuum than in an air environment. Since the gas stream is moving at hgh speeds, often exceeding 3000 fps, it may be concluded that the particles entrained therein will likewise travel at rates greater than those anticipated for air spraying. Oxide-free splats, deposited at those resulting high velocities, will consequently wet and flatten to a higher degree than those atmospherically applied. This also contributes to increased process efficiency and deposit density.

Air sprayed coatings display high residual stresses, resulting from rapid solidification and cooling of the individual particles. Body stresses within a singular splat contribute to the whole or textural stresses within the entire deposit. Usually, the thicker a coating the greater the residual stresses. Hence, the serviceability of a coating decreases as its thickness increases. VPD coatings are low stressed. Since the application can be accomplished at hgh substrate temperatures, the deposit can be recrystallized and annealed in-situ; hence, stress relieved. Thus, thick deposits greater than 0.100 inches (2.54 mm), may be constructed without fear of spalling and/or delamination. Free standing structures suitable for load-bearing engineering components may also be developed.

The chemical integrity of coatings applied utilizing VPD has been analyzed and found to be equal to the in-put material. Elemental losses were not readily evident nor was oxide,

nitride or hydride formation. VPD preserves the chemical integrity of the original in-put spray material.

Materiallographic examination of a VPD applied MCrAlX coating reveals a homogeneous, coalescent structure relatively pore and oxide free, Figure 8. Absent is the inter-splat oxide lattice observed in the lamella structure typical of air sprayed deposits. The interface is clean, void of oxides and residual preparation media, and similar to evaporative Physical Vapor Deposited (PVD) coatings, but without the columna structure and leaders often observed in those overlays, (Figure 9).

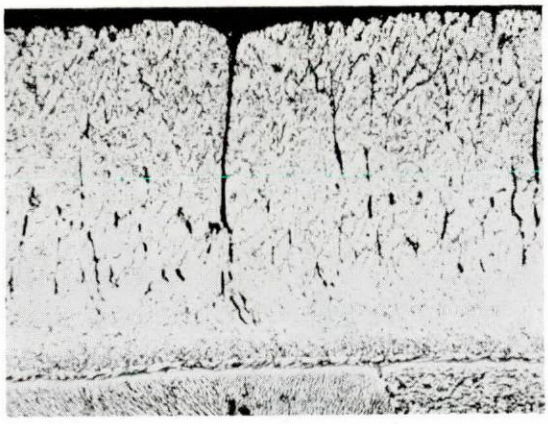
VPD systems are totally self-contained units, Figure 10, enabling the user to comply with existing and proposed EPA/OSHA standards. The noise level, at the glass viewing port, has been measured at less than 84 dBA. Dust particulates are entrapped by in-line filters and thus not discharged to either the working area or outside environment. Ultraviolet light is likewise confined thereby preventing needless exposure.

The efficiency of the VPD systems, when operating between 30 to 50 kilowatts, has been found to be equal to air spray systems operating at power levels in the 60 to 80 kW range. Thus, the use of high power levels in VPD spraying has been found to be unnecessary and wasteful - not only in the use of direct consumables but also in direct increased operating costs of attendant equipment; viz., pumps, cooling units, etc.

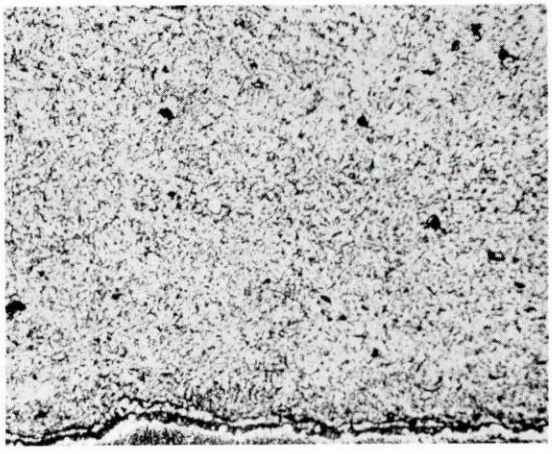


As-Polished MAG: 500X

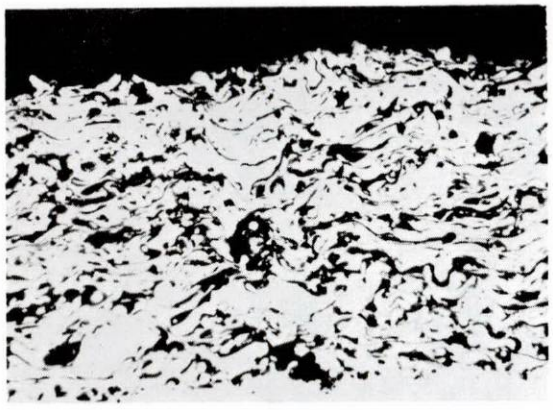
Figure 8: MCrAlX material as applied utilizing the VPD coating process. Note intimate coating to substrate interface (Arrows).



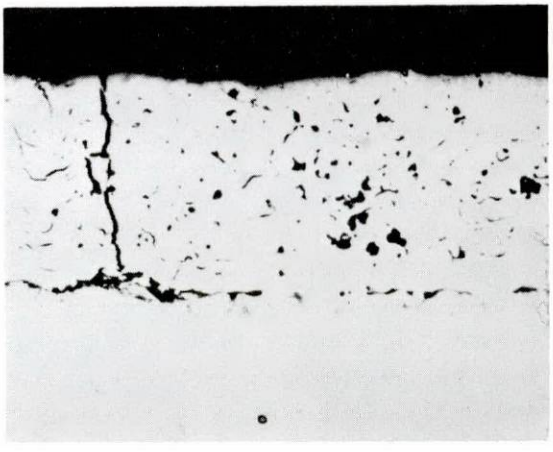
Left: Typical MCrAlX coating material as applied by the EB vacuum evaporative (PVD) process. Note numerous, deep leaders.



Right: MCrAlX coating material as applied by the VPD process. Note relative homogenity, and lack of oxides and voids.



Left: ACrAlX coating material as applied by standard plasma spray techniques and operated in a normal atmosphere. Note interparticle oxides and overall heterogeneousness.



Right: MCrAlX coating material as applied by the shrouded plasma process. Note coating cracks and interface voids and oxides.

Figure 9: The same MCrAlX composition as applied by various techniques. All photomicrographs MAG: 250X

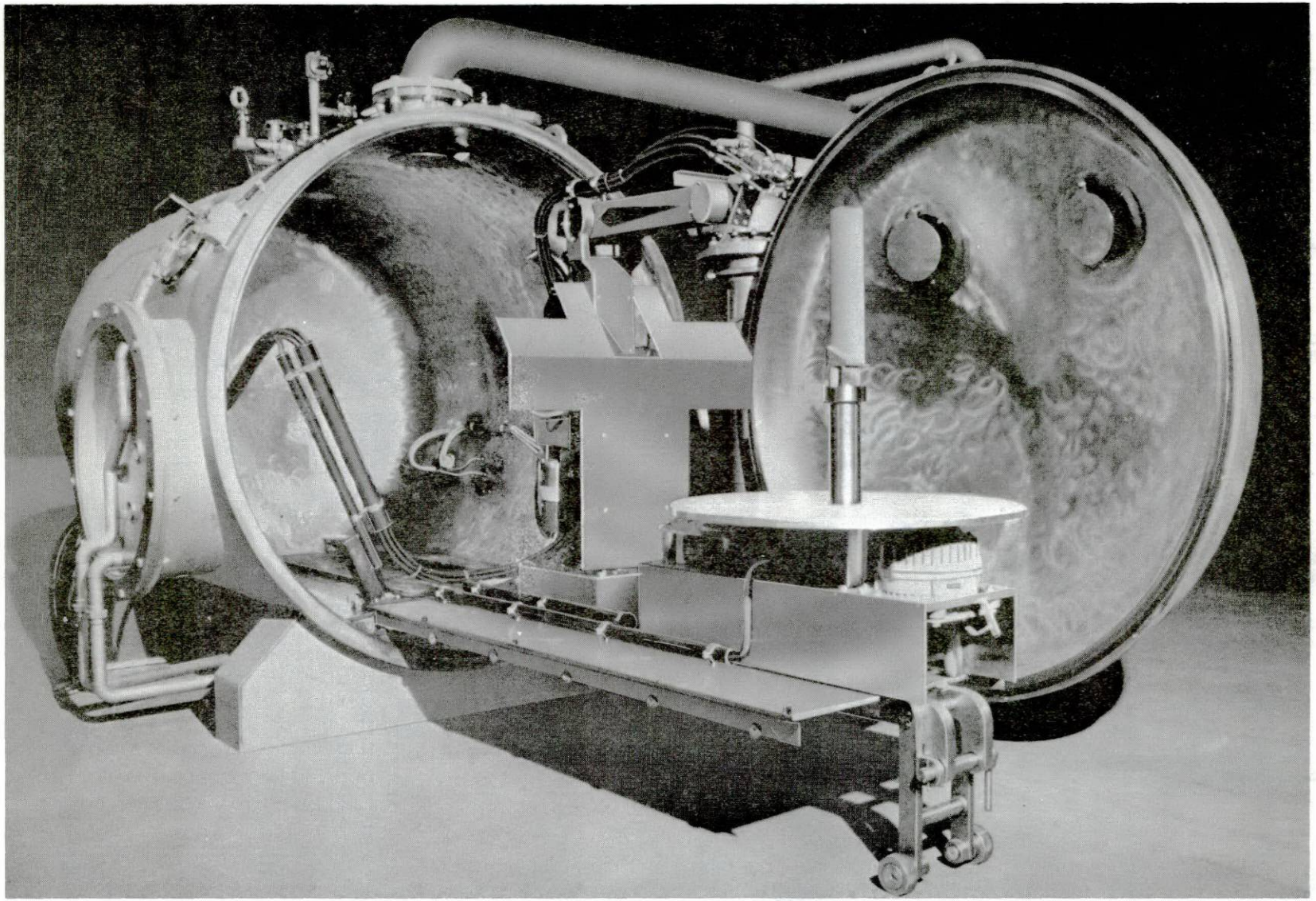


Figure 10: Self-contained VPD system showing a robotic gun manipulation system and Laval plasma generator.

## REFERENCES


1. Ballard, W.E. - "Metal Spraying and the Flame Deposition of Ceramics and Plastics"

2. Smart, R.F. and Catherall, J.A. - "Plasma Spraying"

3. Hermanek, F.J., March 1970 Metal Progress - "Coatings Lengthens Jet Engine Life"

4. Flame Spraying of Ceramics AWSC2. 13-70, American Welding Society, Miami, Florida

5. Welding Handbook, Sixth Edition, Section 2, "Welding Processes", Chapter 29

6. Thermal Spraying Terms and Their Definitions, AWSC2. 9-70 American Welding Society, Miami, Florida

7. British Patent 553,099 - Gfeller, F., Baiker, G.

8. UCAR Metal and Ceramic Coatings, Union Carbide Corporation Materials System Division, Coating Service, Indianapolis, Indiana

9. Electric Arc Spraying, Draft April 1974, Subcommittee, American Welding Society, Miami, Florida

10. Rondeau, H.S., "The Behavior fo Nickel Aluminum in the Electric Arc Process", Eighth International Metals Spray Conference, Miami, Florida, September 1976

11. Kretzschmar, E., "Variations of Metal Spraying and Problems of Atomization in Electric Arc Spraying" Seventh International Metal Spraying Conference, London, England, September 1973

K-3

# Alternative Deposition Processes Session K

## Is There a Planar Magnetron in Your Future?

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# IS THERE A PLANAR MAGNETRON IN YOUR FUTURE?

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## Abstract

This paper will discuss the planar magnetron process and some applications where the process is presently used.

Data will be presented to show two potential dual coating processes and one single layer process application. The first illustration will cover through-hole coatings on P.C. boards. The second illustration concerns use of sputtering onto almost any plastic or metal part to make it more easily plateable. The sputtered film is then built up by electroplating.

One other example will be covered where sputtering alone is a feasible process for EMI/RFI shielding material deposition.

## Introduction

Planar magnetron sputtering is a relatively new physical deposition process developed in the early 1970's. The high deposition rates which can be achieved with this process make it an attractive replacement for some electroplating techniques. The process advantages include elimination of effluent problems, competitive costs, wider range of materials for deposition and, in some instances, improvement of film characteristics.

## Planar Magnetron Sputter

Physical vapor deposition includes those coating processes such as evaporation and sputtering that are conducted in a vacuum system and use a physical process such as heating or ion bombardment to deposit a film. Evaporation occurs when a metal, alloy or other material is heated to its boiling point and the vapor produced then deposits on a surface in-line-of-sight with the heated material. This process is conducted in a vacuum to avoid reactions that can occur in air between metals and oxygen or nitrogen. Typical "heaters" include resistance heated strips, or electron beam and induction heated crucibles.

Ion plating is an evaporation process conducted in a partial pressure of an ionized inert gas. This procedure allows some ion bombardment cleaning before and during coating. It also adds energy to the depositing material and thus provides a higher adherence probability.

Sputtering is the ejection of atoms or molecules from a target of the coating material caused by bombardment by ions from a plasma. It is an old process first demonstrated in the 1800's.

Planar magnetron sputtering is a much more recent coating process that was originated in the 1960's. The first demonstration of a commercial cathode design was made by Van Vorous and Chapin in 1974. The initial designs for these cathodes are shown in Figure 1.

This first device used an electromagnetic field to trap the energetic ions and provide a large increase in sputtering rates over previous processes. Very soon the magnetic field was formed by permanent magnets of Alnico 5 made available in both rectangular and round cathodes.

Early cathodes were mounted inside a vacuum system. It became apparent an external wall mount design would be very useful and this construction was developed by Van Vorous. He followed this design, in quick succession with linear chamber system designs, load lock entry systems, radio frequency powered cathodes for non-conductors and improved cathode magnetics.

Several variations of the original magnetic block design then occurred as shown in Figures 2 and 3. All of these designs and the current flexible magnetic material design are still based on the same closed looping magnetic field structure demonstrated by Mullaly, Kay, Davidsee and other prior to 1970.

The most significant recent advances in planar magnetron design include huge cathodes, up to 10 feet in length, for applications and high inventory cathodes, such as those used by an automotive company for deposition of chromium onto grills and head light surrounds. This type of cathode is also decorative coaters and similar applications.

Table 1 illustrates some of the other areas of application where rapid growth has started in the industrial areas. Note that most of these areas of applications are classical physical deposition areas that have gone from evaporation to sputtering. The most active of these areas are automotive and architectural glass coating. For example, an automotive company has installed planar magnetron cathodes in their grill coating system. Virtually all decorative architectural glass and solar barrier glass coating systems now use planar magnetron cathodes. The next large growth will most certainly be to replace some or to work in conjunction with electroplating processes.

Table 2 lists present and future growth areas that include changes from chemical to physical coating processes. The next section of this paper addresses several of these process areas and describes the general type of sputter deposition systems that will be used for the coating process. (Table 3)

## Printed circiut boards

Several companies have demonstrated that planar magnetron deposition could have a major impact on the P.C. board industry. The magnetron cathode is being used to deposit copper on bare or pre-coated drilled boards for through-hole coating. The film is then built up by conventional copper electroplating. This process eliminates the need for the electroless plating steps or sensitizing layers. Sputtering could, of course, be used to build the entire copper layer, however, it does not allow a high enough deposition rate to be directly competitive with electroplating yet.

Through-hole coverage requires coating rates that exceed 10,000 angstroms per minute (0.00004 in/min). It also requires the use of an apposed cathode system design to obtain acceptable coatings with standard hole diameter-to-thickness ratios. Ratios up to 1:3.3 can be coated at a 12,000 angstrom per minute rate and 4 inch source to substrate spacing. The sputter film must also be of sufficient thickness so that the pulsed start of the electroplating process does not break the conductive path.

An apposed system design for this application is needed to achieve a "cloud effect" within the board hole. This effect occurs when the local area deposition material pressure reaches a point where a large amount of "scatter" is produced. In other words, the mean free path is very short and metal molecules collide with each other to produce non-cosine deposition.

Some other essential features of this type of system are low board heating, a high intensity ion source for board pre-cleaning, rugged vacuum system design, high throughput, ease of operation with microprocessor control and pricing competitive with electroplating processing.

All of these design features should be available in systems introduced late in 1982.

Another major criteria is the redesign of the planar magnetron cathode to substantially increase its deposition rate capability. This improvement is needed throughout the industrial coating area and should be a reality before the end of 1982.

## Starter coatings

Planar magnetron sputtering can be combined with electroplating in a variety of other industries. Examples would include flash sputter coatings on almost any plastic or metal followed by a buildup by chromium electroplating for plumbing fixtures, cosmetic containers or similar substrates.

Sputtering allows the use of almost any non-magnetic metal or alloy for the initial film. In the plumbing fixture example, the film would be chromium or other non-corrosive alloy, deposited over a plastic basecoat used for surface leveling. The film could then be electroplated up to the usual 1.5 mil chromium thickness.

The obvious advantages of this process are numerous. First, it provides a completely non-corrodible film versus the present use of corrodible base layers on fixtures. Second, several major steps are eliminated, thus reducing labor and materials costs, plus reducing effluent control problems. Third, in some instances, base materials could be changed to provide reduced coating thickness or improved operations, as in the replacement of die cast metals with engineering plastics. Fourth, the overall process allows a substantial reduction in energy requirements.

Existing decorative coaters using the evaporation process can be converted to planar magnetron sputtering for this under-coating process. New systems designed specifically for sputtering are also available. All of these existing design systems use either a central positioned co-axial planar magnetron or rod magnetron cathode.

An alternate construction is a wallmounted planar magnetron cathode such as shown in figure attached. All system designs require use of planetary (revolving) jiggery to insure overall coating. Most applications do not require a high degree of evenly deposited film. This is fortunate because both sputtering and evaporation processes are limited in their evenness by cosine law distribution, i.e., source to substrate distance.

EMI/RFI Shielding

There has been an explosive growth in the need for EMI/RFI shielding films on electronic device housings. This has occurred for several reasons. First, plastic has replaced metal in many housings as a cost reduction and design flexibility move. Plastic is not a conductor and thus cannot be used readily for shielding. Second, federal regulations require more attention to this problem. Last, the increased use of low signal micro-electronic circuits has increased the sensitivity of equipment to outside noise.

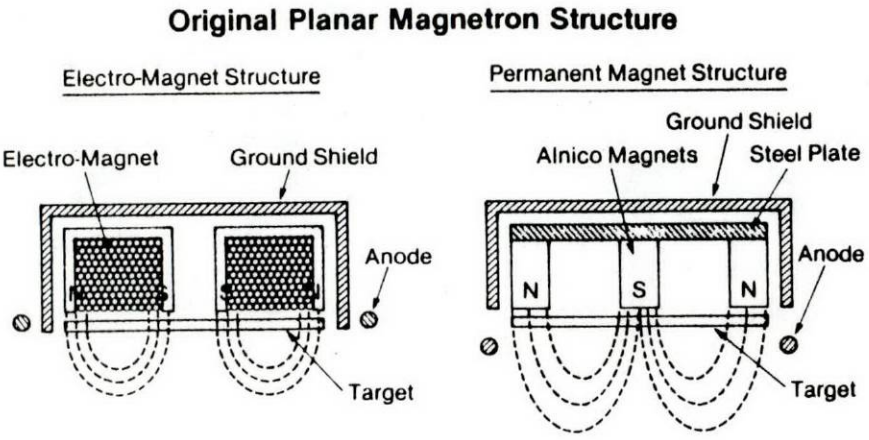
Present shielding films include conductive materials in the plastic, multiple layer electroplated films, plasma sprayed zinc, metal paints and evaporated coatings. All of these processes have some technical or cost problems. Evaporated films adhere poorly or are limited to pure metals that are not always desireable. Electroplating is expensive when multiple films are needed. Plasma sprayed zinc is both relatively expensive and has inconsistent adhesive characteristics.

Planar magnetron sputtering, combined with high intensity ion etching, eliminates many of these problems. It can be used with a wide range of materials, has good adherence features when used with ion etching, and is less costly than the other processes. Sputtering also reduces the amount of material required and used less energy to produce the coating, than some processes. It's disadvantages are higher initial cost for the equipment and some increased part shielding requirements.

This process would use the same type of batch coater discussed under the "Starter coatings" heading. Large coating systems are needed because of the large physical size of most substrates to be coated.

The future use of planar magnetron sputter deposition is only limited by the imagination needed to identify optimum applications and improve understanding of the process. It is probable that the industrial growth of this process over the next five years will equal or exceed its growth in micro-electronics. In all probability, there "will be a planar magnetron cathode in your future."

FIGURE - 1


Original Planar Magnetron Structure
Electro-Magnet Structure
Electro-Magnet
Ground Shield
Anode
Target
Permanent Magnet Structure
Ground Shield
Alnico Magnets
Steel Plate
Anode
N
S
N
Target

L-2

# Mechanical Finishing Session L

## Critical Relationships in Mass Finishing

John B. Kittredge
Kalamazoo, MI

A process that would help to reduce this cost and to assure greater reliability of quality in subsequent operations such as plating and finishing, certainly demands the attention of all profit minded companies. The use of the word imagineering in the introduction was not by accident. All of us upon graduation were given a base of knowledge on which to work. Inherent in each individual is that gift of imagination. Hence, if you and I as engineers are to do our best, we must build on our engineering base, and by using our imagination, we can become imagineers. This will allow us to manufacture for profit, not necessarily by traditional methods.

# CHEMICAL DEBURRING - DEBURRING AND SURFACE PREPARATION - ONE OPERATION

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## Abstract

This paper will describe the use of chemical deburring in removing the burr and eliminating any surface contamination from previous machining operations, the type of equipment tooling required, and changes required in manufacturing tolerance to accommodate this process. This process does require a standard precaution in the use of chemicals, but the profitability factor is most attractive. The author has found through years of manufacturing experience that most "plating problems" are a result of surface contamination. This method of deburring eliminates that possibility.

## Introduction

All parts to be plated must be deburred for dimensional accuracy or for cosmetic purposes. Surface preparation as cleaning, etc. is also a must for repeatable quality of part. The manufacturer's inability to produce consistant quality of parts in the processes of cleaning and deburring has been a constant source of rejects and added manufacturing costs. This paper challenges the manufacturer to deviate from the traditional and use some imagineering to solve this problem.

## Subject

Any mechanically produced surface is a contaminated surface. You do not cut metal, you swedge it, and in so doing there is minute entrapment of coolant and/or foreign particles. The more aggressive the metal remover, the greater degree of contamination entrapment. If this surface is then deburred for cosmetic purposes, we have now created a better seal for the entrapment of the contaminated surface.

With our ever increasing method of joining dissimilar materials, we now have an added problem of burrs and contamination on the same part. Add to this the ever increasing awareness and requirements of the surface integrity, our problem of quality control and manufacturing costs increase. Contrary to longstanding acceptance, surface finish is not a reliable indicator of surface integrity. Nine times out of ten a "poor plating job", plating that would peel, plating that would bleed after short term shelf life, or plating that would lose its color, has been the results of improper cleaning of contamination entrapment, allowing contamination to bleed out over a period of time.

Our approach to this problem was twofold. First, by using a chemical additive to a lined tumbling barrel and determining the amount of stock removal per minute, the life of the additive and the disposal of the additive after use were determined. We found that controlling the strength of the chemical additive that would allow stock removal rates of .0005 per minute were most acceptable on parts with broad tolerances, i.e., ±.010. Later on this process was advanced to established time cycles to predetermine amounts of stock removal; example, on a slot width having a tolerance of .004, manufacturing engineering would process part from split limit to .002 oversize. Deburring cycle would allow .002 stock removal to bring piece part into required tolerance. We found a greatly improved surface finish and a removal of the difficult ninety degree burr.

Our second approach was to debur the part and remove surface contamination using a chemical etcher. The machine was an all plastic vertical rotary etcher allowing us to place parts on an 18 inch diameter disc, rotated by a 3 inch diameter eccentric pulley. This disc was sprayed by two opposing forced streams of chemical. The eccentric movement of the disc assured blending of the chemical action. The disc was made of poly vinyl chloride (P.V.C.) and the clamping of the piece part was done by titanium fixturing. The etchant used was determined by the type of material to be deburred and a test piece attached to the rotating disc allowed you constant monitoring of the stock removal rate. Parts were processed by manufacturing engineers to allow burr removal, the removal of any machining contamination, and the assurance of size control. Example, a part having a root burr attachment of .003 thickness would require .004 stock removal per surface to assure burr removal. All slots and bores could be processed accordingly and chemically etched to required tolerance.

The author recognizes the disposal of chemicals varies from locality to locality and makes no recommendation for their disposal. The chemical additives to the tumbling barrel would certainly increase the initial cost but the manufacturer will have to determine the trade off between the reduced time and improved quality versus the added cost.

The use of the rotary chemical etcher seems to me well worth the investigation of all potential users. The ability to control stock removal rates, the quality improvement and the assured deburring action will relieve the reject and inspection burden. Many types of parts are now coming to the deburring department and plating department, those that have been produced by electrical discharge machining and electro-chemical machining, parts that are an assembly of brazing of all alloys, parts welded by laser and electron beam, and those of dissimilar and exotic metals. This ever increasing new technology demands the best of the manufacturing engineer and all manufacturing personnel. Deburring has long been recognized as the common cold of industry, a two billion dollar annual expense to industry.

L-1

# Mechanical Finishing Session L

## Chemical Deburring—Deburring and Surface Applications In One Operation

Jack McMillen
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FIGURE - 3

**Other Standard Magnetic Configurations**

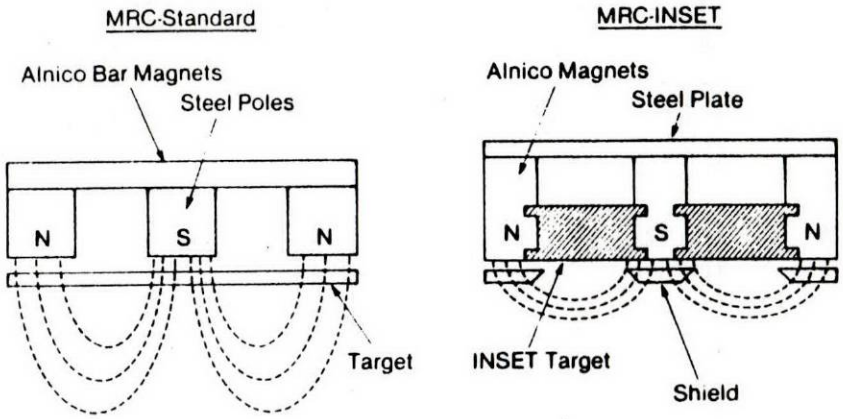
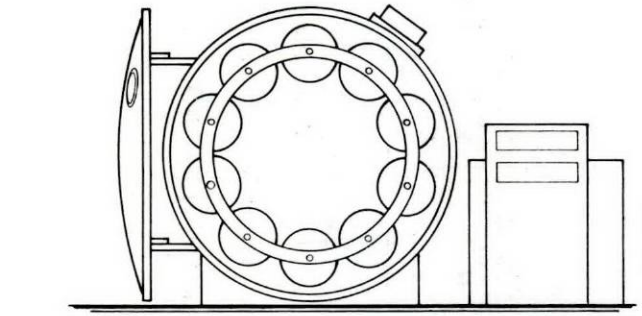


FIGURE - 4



**Production**
**Sputtering Metallizer**

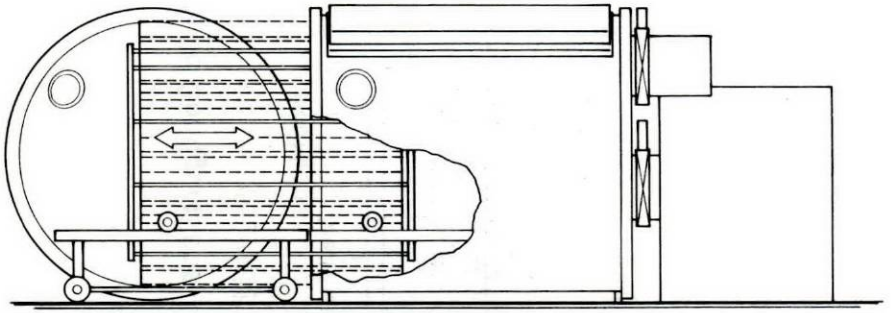


TABLE - 3

## Industrial Sputtering System Design

| | |
|---|---|
| Type A | Batch Metallizers with Planetary Motion Jigs |
| | *Used where one or two layer films must be deposited on simple or complex parts that require planetary motion for complete coverage.* |
| Type B | Batch Metallizers with Barrel Type Coating Jig |
| | *Used for complete coverage of small parts that cannot be readily jigged.* |
| Type C | Linear Chamber/Lock to Lock Systems |
| | *Used for one or two side coating without planetary motion to obtain good film property control and high throughput. Also used where one or more cathodes are required.* |

FIGURE - 2

**Change from Original Magnetics to FLEXIMAG™ Design**

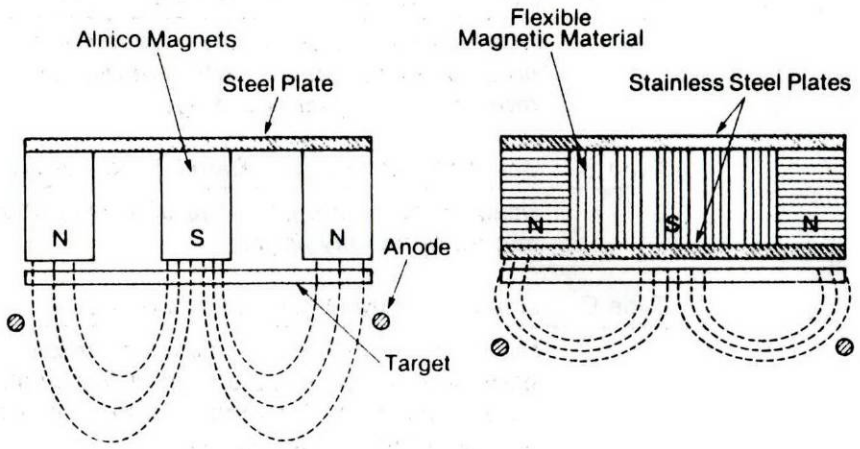


TABLE - 1

## Industrial Applications of Planar Magnetron Sputtering

**Decorative Films**
- Aluminum
- Chromium
- Alloys
- Color Films by Direct Reactive Deposition

**Architectural Glass**
- Single Layer
- Multiple Layer for Solar Applications

**Automotive**

**Displays**
- Liquid Crystal
- Plasma

**Video Discs**

**Hard Surface Films for Tooling**

**Thin Film Resistors**

**Aircraft Parts**

TABLE - 2

## Present and Future Growth Areas for Planar Magnetron Sputtering

**Automotive**
Chromium for Grills and Headlight Surrounds
Chromium on Interior Parts
Color Films and Improved Chromium-Like Films

**Aircraft**
Aluminum on Nuts and Bolts
Chromium-Like Films on Short-Run External and Internal Parts
Improved Alloy Films on Small Parts

**Architectural Glass**
Single Layer Films – Primarily Decorative
Three Layer Solar Heat Mirror Films

**Decorative**
Replace Aluminum and Chromium Evaporation
Use of Alloys or Reactive Films for Color Range Coating
Clear Hard Surface Wear Resistant Overcoat Films

**Replacement for Electroplating**
Substitute Method to Coat Small Parts
Flash Undercoat Film for Non-Conductive Substrates
Use of Alloys to Replace Pure Metals for Improved Properties

L-3

# Mechanical Finishing Session L

## Substrate Conditions Affecting Finish Quality

Ezra A. Blount
Somers, CT

to provide sufficient inhibition to prevent this from happening. This can be an insidious problem in plating quality and one that is very difficult to diagnose.

6. Parts and Equipment. Equipment controls the energy level in the mass finishing process. It provides for easy or difficult means to adjust the energy levels, hence will they or won't they ever be used?

Equipment provides the means of separation of media from parts. It can be done very gently or robustly or somewhere in between. As the separation step occurs and the media falls away from the parts, the parts are significantly more susceptible to part-on-part contact damage. Planning is required to prevent destruction of the benefits of the entire process at this stage.

Parts can cut, gouge and destroy the best polyurethane linings in very short order. This occurs primarily when parts are dumped or the surface of the media before they become dispersed in the media. Sharp parts can stick in the linings and small parts can get stuck in cracks, crevices and drains and these "hard spots" in the lining can destroy other parts.

Equipment sometimes provides the means for parts to be loaded into it (or, worse yet, it may not!) A skip hoist and dumper, a slowly moving conveyor, a tote pan full of parts dumped into a vibratory feeder or manual loading are common practices. For just a moment, think of a tote pan of parts dumped into the vibratory chamber on top of the media. For several minutes, the parts are not separated by the media at all, are in constant contact with one another, have a media-to-parts ratio of 0:1. Severe impingement damage can be put into the parts such that the balance of the cycle cannot possibly remove them.

Part-on-part damage can also occur when the parts tangle in the machine chamber or the improper ratio is used or scraps of contaminating steel is in the media mass. Care does help such situations.

7. People. What is it that can change to a "cheaper" media or compound or change the lubricating oils used on the part without telling anyone or run that die casting die or trim press an extra several thousand parts "to save money" or shorten the cycle ten or more minutes today to get to coffee on time or stuff a few extra hundred parts in the machine to increase productivity or shorten the leveling nickel time to "save money" or make any other of a thousand decisions? Certainly not the process! It's too darned dumb! People. The really big variable in mass finishing. Unknowingly, with the very best of intentions, people can make very sad mistakes that are often as difficult to eliminate. Knowledge and understanding will help eliminate this source of problems. Good record-keeping will be of great help in solving this kind of problem, too.

8. Other Relationships. Relationships exist when three or more of the elements interact. For example, the initial quality of a part, the ability of the electroplate to level and the time of the process are dependant one on the other. Therefore the cost of the process depends on these as well (6). The better the surface at the start of the process, the better the ability

of the electroplate system to level, the shorter will be the process time and therefore the lower will be the cost of the process.

## Summary

An understanding of some of the elements in the mass finishing process and the way they relate to one another and have an effect on one another is of help in improving the value and productivity of these processes. It is a means to reduce costs. It is a means to improve quality of the critical processes including those which precede plating.

Properly used and understood, mass finishing methods offer significant advantages over competitive methods for reliability, efficiencey, quality and quality control, reduction or headaches and rework for the manufacturing engineer. Take advantage of them and soothe a savage finishing problem. They really do work!

## References


(1) Kittredge, John B. Understanding Vibratory Finishing, Parts 1 - 4, PRODUCTS FINISHING, February - May, 1981.

(2) Preplate and Prepaint Mass Finishing, the new (1982) Illustrated Lecture Series, American Electroplaters' Society.

(3) Mass Finishing, Vol. 1, No. 1, Metal Finishing Suppliers' Association, Birmingham, MI.

(4) Kittredge, John B. The Mathematics of Mass Finishing. Technical Paper MR81-399, Society of Manufacturing Engineers, Section 4.

(5) Claus, Joseph J. Conditioning of Metallic Surfaces with 3-Dimensional Abrasives. Technical Paper MR81-410, Society of Manufacturing Engineers.

(6) Kittredge, John B. Mass Finishing: A Natural Way to Prepare Surfaces, PLATING AND SURFACE FINISHING, April 1981.

effluent. These are the two most carefully scrutinized when difficulty arises with compliance with local and State laws.

When metallic media such as steel is used, the solution provides the only barrier against corrosion. Modern mass finishing solutions provide excellent inhibition against corrosion in such instances even when the media is held for extended periods of inactivity.

2. Equipment and Media. The equipment provides the container in which the media is put. It provides power to the media mass so it can do the cutting or burnishing on the parts. Equipment is the source of materials handling for the process. It provides for any separation of media from parts and thereby controls the ease or complexity of this important step. Improper handling of media is often the cause of fracture of corners or large media pieces leading to premature media lodging problems and higher costs.

Media abrades against the lining of the machine, usually a polyurethane these days, to prevent destruction of the steel machine. The lining type and quality has a marked effect on machine life and maintenance costs.

Equipment provides the drainage capacity for the machines, if any. More of this later, but the drains are sometimes a means of screening out undersized media and metal fines or chips before they lodge in the parts or in the drains.

3. Equipment and Compound Solution. Equipment must be designed such that the compound solution used will not corrode it (or vice versa). Protective coatings or special alloy selection can be used. And the lining material must be compatible with the compound and its solutions.

Equipment provides the metering of the compound and water to the process. In critical situations, this metering must be very exact. Excessive concentrations of compound in water can be just as bad for some processes as too low concentrations. Either extreme should be avoided. And the equipment drains remove the spent and dirty solution from the machine. They must be of a proper design and in the proper location to do this with efficiency and to do it without clogging.

The solution has an influence on housekeeping of the area around some of these processes. Excessive foam, spatter, splash and spillage are not helpful in area tidiness.

4. Parts and Media. Obviously, the media is that material which cuts the metal and removes burrs or smoothes surfaces. Or, if a non-abrasive media is used, the media peens the edges and surfaces of the parts developing a luster on them.

Media size and shape is selected such that the media will have sufficient contact with all critical edges and surfaces of the parts and also, so the media can be separated from the parts at the end of the process cycle. Further, the media should show long life and never get stuck in the parts.

Parts have the unique ability to bring to the process all kinds of soil. Oily soils from stamping or machining, die lubes and greases, metal chips and other such contamination and whatever the plant can find, are soils to be cleaned from the parts. If the solution cannot cope with any one or more of them, the soils can easily transfer to the media causing it to glaze over and stop cutting.

Either from too frequent or too careless handling, media can become contaminated with other media. Preplate quality media in which ceramics or fast-cutting plastics have been mixed, will cause defects in the parts.

The so-called "Media-to-Parts Ratio" is a volumetric ratio of the mixture of these two elements. It controls the amount of contact one part will have with another from a statistical standpoint. While some effort is being made to obsolete this ratio (4), it is still a concept which is known and understood. At high ratios, fewer parts are mixed with more media and the part-to-part contact during the process is minimized. At lower ratios, part density is increased, improving productivity, but sometimes damaging critical parts. In this same context, media is the material often used to cushion and protect certain massive or delicate parts from one another. Smaller media and full media size blends help in this respect.

5. Parts and Compound Solution. The solution cleans the parts by cleaning the media. The speed of this operation after the parts are introduced into the system controls the residual soils on the surface of the parts -- whether they are removed or pounded into the part surface. Part color is a result of the efficiencey of this step. Darker parts result when soil removal is slow. Light part colors are the result of more efficiencey in the cleaning step. This is important to the plater in that soiled surfaces are those that produce imperfect after-plate quality such as adhesion problems, blistering, haze and related defects. Corrosion of parts will also produce such defects. The plater must also realize that the mass finishing processes are very efficient cleaning machines and that many parts are being cleaned in these processes today that cannot be as efficiently cleaned by any other means, including ultrasonics!

The solution system can create or minimize the surface contamination of parts as they leave the process. And, needless to say, surface contamination is not at all conducive to good electroplate adhesion or quality.

The relationships between parts and the solution cannot be overemphasized. They are the primary reasons people have some electroplate problems. The solution system is as critical to success as any other factor in the entire process.

And, the solution is water-based. Parts are generally metallic. Most of the mass finishing processes are performed with plenty of air surrounding them, often churning up the mixture of air and solution with the parts. And by the highly efficient scrubbing action available with mass finishing media, the metallic surfaces are made extremely active just as described for another effective scrubbing agent (5). The combination of active metal, oxygen and moisture makes corrosion have to occur if it can. It is up to the solution

types cut the edges and surfaces of the parts. Non-abrasive media is used to "burnish" or peen and thereby brighten metal parts as is common, for example, with die cast furniture hardware prior to plating. Media, unfortunately, takes many forms, a fact that makes it confusing to the novice.

1. Preformed Ceramics. These are the most popular types of media in use today because of their economy and good results. They are made in a great number of desireable sizes, from about 1/8" (3mm) up to over 2" (50mm), in a variety of useful shapes, including the angle cut cylinder, triangle and star, and in a variety of useful bodies or compositions from very fast cutting to very fine preplate quality for some applications specially on harder metals.

2. Preformed Plastics. Like the preformed ceramics, these products are available in a wide veriety of compositions, cut rates, surface finishes, sizes and shapes. Their preplate products are superior to the ceramics in developing preplate quality surfaces on even very soft metal surfaces. The plastics are used also when the ceramics would indent or impinge the softer metal surfaces and also when large burrs could be rolled over by the heavier and harder ceramics. Plastics are the first consideration for most high quality preplate work of softer metals up to and including the steels.

3. Preformed Steel. Case-hardened and stress-relieved steel media is very precise in both shape and dimension. It will not wear and therefore can not change in dimension during use. It can develop bright, lusterous surfaces on most of the metals in common use. The surfaces produced are attractive are are very acceptable for preplate applications when mirror-quality reflectivity is not required. Precise dimensions permit steel media to be used where conventional types would create awesome lodging problems.

4. Random Types. Random types are those which are not preformed or uniform in dimension, but are usually crushed or ground to size and coarse-graded by screening. The products include natural stone of all types, emery, fused aluminum oxides, ground corn cob meal, etc. Cob meal is often used as a drying media and sometimes to polish metals. Because of their tendency to lodge in parts, random shapes are often avoided when possible.

## Compound and Water

The third element critical to the mass finishing operation is the compound and water. These two combine to make a "solution" which is what is seen, felt and used by the media and parts. The solution is usually 99% or so water, hence the water is a vital portion of it. For example, if the compound is not designed to take care of the hardness in that particular water used in the plant, there is no way that a satisfactory result can be achieved.

Both liquid and dry compounds are popular today, with the liquid forms being used most often in the advanced, automatic metering systems available. Dry products do not offer any advantages from a chemical standpoint nor are they any more cost effective. In fact, with automatic feeding, the useage of the liquid compound is reduced to the minimum and waste is eliminated, further reducing their cost of operation,

Special compounds are available for special needs as required for ferrous or non-ferrous metals or when both types are present. Compound types include deburring, cleaning, burnishing, inhibiting, abrasive grinding, etc. The properties of compounds get further confused because of the limitations or requirements of certain types of mass finishing equipment. For example, foam and lubricity. Foam is essential in most barrel applications and high foam is used to help cushion the mass. Excessive foam in a vibratory machine however will stop the action even when steel media is used and it is sloppy. High lubricity is used to advantage in barrels to reduce the cut of abrasive or "dual purpose" media, but in a vibratory machine, lubricity will serve only to stop the mass action, materially extending the process time.

Parts

The final, and most important element in the mass finishing process is the parts. The uniformity or variability of the parts must be considered in any expectation of process cycle uniformity. (It usually is not!) The changes in amount or type of surface soils, burr sizes, surface roughness, physical defects caused by handling, etc. all add up to the degree of uniformity of of the part at the start of the process cycle. As these increase, so must the process time.

Relationships

The primary purpose of this paper is to discuss the relationships and interactions that take place in the mass finishing process. For example, what effects, if any, do the compound solution have on the media and vice versa?

1. Media and Compound Solution. If we can accept the fact that the compound solution is the sole source of cleaning power in the mass finishing system, it is easy to understand that control of the solution system is required in order to keep the media clean. And, if the media is not clean, the parts cannot be clean. And, dirty media, just like dirty sandpaper, will clog up and stop cutting. Logic tells us then that clean media is more efficient and it is!

Media cleanliness effects its rate of cut, the surface roughness it can develop and the cycle time of the process. If the media cuts at its maximum, time cycles can be reduced. Dirty media from too low a flow rate of solution and/or the wrong compound and/or too low a concentration of compound can slow down the metal removal rate remarkably. Such conditions can cause the media to "glaze" and stop cutting entirely.

These effects are much more often seen in vibratory finishing processes due to the sensitivity of them to the effects of the solution. Rotary barrels, centrifugal barrels and centrifugal disc machines are much more tolerant of non-exact solution systems.

The compound solution and abraded material from the media constitute the major portion of the effluent from the finishing process. Accordingly, these two are the problems or non-problems when dealing with compatibility of this

# CRITICAL RELATIONSHIPS IN MASS FINISHING

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## Abstract

Relationships between the key elements in mass finishing processes are discussed. The criticality of these relationships to surface roughness and to other results obtained by the electroplater is explained. An understanding of these concepts and their implementation are shown to be means to improve both the quality and the economy of mass finishing.

## Mass Finishing

"Mass Finishing" is a term which includes a variety of useful manufacturing processes which are ideal for the finishing of parts prior to electroplating. These prosesses include rotary barrel tumbling, centrifugal barrel finishing, vibratory finishing in a number of equipment configurations and centrifugal disc finishing. The differences and similarities between these processes are of interest to the user or the potential user. Advances in recent years have extended the technology of mass finishing greatly such that previous "failures" with these processes may well be highly successful today. Mass finishing, the industry, is coming of age.

Much detail of specifics regarding the equipment, media and compound have been published (1), (2), (3) and will therefore not be repeated here.

## Equipment

As stated, mass finishing involves several types of manufacturing equipment for deburring, cleaning and surface finishing a variety of parts. Several of the most popular types of equipment are the following;

1. The Rotary Barrel. This very simple machine tool has literally been around for ages. Octagonal in shape, equipped with a door for loading and unloading media, parts, water and compound and with a controlled rotational speed, the barrel is easy to use. It is not uncommon for a barrel to be loaded, sequentially, with several types of compounds and be flushed between each, before being unloaded and parts separated from media.

Cycles are generally long, labor skills and strength must be good to excellent and labor costs are generally higher than for other techniques. But the barrel is often the least costly type of mass finishing process for a great many types of parts.

2. The Centrifugal Barrel. This machine is designed to develop a much higher "gravity" or pressure on the rotating mass, thereby deburring, radiusing and smoothing surfaces at a much faster rate than would otherwise occur.

In the centrifugal barrel system, a turret rotates in one direction upon which are mounted small rotary barrels which rotate in the opposite direction. And since the designs permit the turret to rotate in the horizontal or the vertical plane, a very modest floor space is required and the output of these machines is very great. Small media is often used. Often no compound is needed. Both very delicate work and heavy grinding can be done with excellent speed.

3. The Tub Vibrator. Built somewhat like a bath tub mounted on coil springs but with an eccentric weight system mounted underneath or up on one side, the tub develops power and motion. Since the entire contents are active all of the time, it is faster than the rotary barrel by a factor of five to ten. Since the container is open, inspection of the contents during the process is easy. With a door in the end, the tub can be discharged to an external separation system. A media return conveyor transfers this material to an overhead storage bin for recycling to the next batch. Automation is therefore possible with tub vibrators.

4. The Round Vibrators. Round vibratory machines have an eccentric weight system located in the middle of the center section of the machine with weights on either end of the rotating shaft. The amount of each weight, the angle between them and the speed of rotation controls the action in the circular chamber.

There are three major modifications of the round vibrators. One is the "flat bottom" style in which there is no change in the elevation of the mass as it progresses around the circular chamber. Second is the style in which the mass is elevated about half way up to the built-in separation screen. Third is the large "diameter ratio" design which increases the overall machine diameter while decreasing the channel diameter for a given capacity. This version is primarily used with steel media when better control of the mass is required.

The round vibrators generally separate parts from media inside the machine eliminating the need for external media return conveyors and related hardware, but the flat bottom style can use those external separation systems. Equipment simplicity, excellent surface finishes, gentle handling, internal separation, adequate process speeds and easy machine adjustments have made the round machines the accepted norm in current vibratory finishing.

5. The Centrifugal Disc. These are the newest members of the mass finishing family. Essentially a vertical cylinder with a disc in the bottom rotated at a controlled speed, they are simple to control and are getting to be an important segment of the mass finishing field. With easy process controls such as speed of the disc, media size and load height and solution flow rate and retention, it is an impressive machine concept. The big surprise with this type of equipment is its ability to develop excellent surface finishes even at its very high metal removal rates.

## Media

Media is the material put into the equipment chamber into which parts are dispersed and which does the scrubbing on the parts. Abrasive media

# SUBSTRATE CONDITIONS AFFECTING FINISH QUALITY

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## Abstract

Finishers have long known that a high quality finish of any kind is dependent in part on the condition and properties of the underlying surface. Some problems involved in the application of various finishes indicate the need for finishers to have more detailed information not only about surface conditions, but about the substrate material being processed.

## Introduction

Conditions of the substrate surface, either in the form of surface contaminants, surface physical condition, and/or the nature of the substrate itself alter, limit, or dictate finishing operations required for a high quality finish. Surface roughness must be corrected by polishing, buffing, or mass finishing processes. It is axiomatic that surfaces must be clean before a sound electroplate or attractive or functional organic finish can be applied. Surface contamination requires cleaning by any number of chemical and/or mechanical processes. Some substrates are quite difficult to plate successfully, and special procedures must be devised. Generally, the application of a high quality finish requires that all surface impurities be removed. Some porous substrates can be "sealed" so that a final finish can be applied to the product in question.

Volumes could be written to enumerate the many problems encountered and solved by finishers in producing good finishes on a wide variety of substrates under many different conditions. Some illustrative examples of a few substrates and surface conditions to be avoided or corrected by various finishing procedures will be cited.

## Surface Problems Corrected by Mass Finishing

The polishing, buffing and mass finishing industries have for years stressed the fact that a little time and money spent on surface improvement before plating or organic finishing results in a much finer finish. Product appearance, service life are improved; potential corrosion sites are eliminated or reduced; product quality is enhanced. In many cases edge and surface finish improvement is essential to product performance. Literally thousands of examples can be cited to show product improvement brought about by polishing, buffing, or mass finishing processes. A few examples of metal surface defects corrected by mass finishing may be useful.

It is every chain manufacturer's dream to be able to blank components out of high carbon steel with a minimum of burr formation. If there is a burr, it is desirable that it be on the outside of the assembly or in a location so that it does not impair the operation of the assembled chain. However, tooling is difficult to maintain, and burrs are formed on chain

links, pins and guides. These burrs can cause automatic assembly equipment to jam, and impair operation of the assembled chain. Therefore, all chain parts are deburred by mass finishing equipment to generate radii of 127 micrometres (0.005 inch) on all edges. This makes possible easy assembly, and insures smooth chain operation without fatigue failure.

The slightest degree of burr on a stainless steel microminiature machined component for an aircraft altimeter will cause the part to wear, bind, or malfunction. Parts are deburred by mass finishing, maintaining dimensional tolerances of plus or minus 2.54 micrometres (0.0001 inch), with precise control of radii.

Coil springs of Swedish spring steel are mass finished to improve fatigue life and insure that there are no blemishes on the surface that may lead to failure by fatigue crack. Stress must be absorbed uniformly throughout the entire length of the spring.

Orthodontic braces made from stainless or marine steel are mass finished for radius generation, removal of any surface porosity or surface areas that might harbor harmful bacteria while braces are being worn.

Brass fuel flow nozzles are deburred and all edges radiused by mass finishing. Radii are critical, affecting part performance. An extra 76.2 micrometres (0.003 inch) radius on an edge would change fuel flow values by several percentage points, for example.

In the molding of rubber automobile tires, tread patterns are formed by placing low carbon steel parts called "sipes" in the mold. These sipes must be radiused precisely so that the tire tread, as molded, will have rounded base areas to prevent shearing of the tread and tire failure in service.

Flapper or reed valves to control flow of freon through air conditioners are blanked from Swedish spring steel. The part, in operation, flexes as much as 9,000 cycles per hour. Any sharp edges or burrs would prevent valves from seating and sealing, and lead to fatigue failure in service. Mass finishing is used to deburr and form a complete radius in critical areas.

High strength steel inner races for bearings require deburring and microfinish surface improvement to insure that balls or rollers inserted in the bearing are not scuffed, scarred, or caused to wear prematurely.

Cams and weights for automobile distributors are blanked from low carbon steel. Parts are mass finished to remove surface scale and burrs, produce a surface finish of 0.254 micrometres (10 microinches) or less, and an edge radius of 25.4 micrometres (0.001 inch).

Gears and sprockets machined from screw machine steel stock are deburred to insure smooth operation throughout the specified service life.

Sand cast steel flow control valves are deburred on all areas. A minimum radius of 1,270 micrometres (0.050 inch) is required on the inside

diameter opening to insure smooth operation with no seal leaks under high pressure.

Forged titanium aircraft compressor blades are mass finished to form a radius on all areas of the root, platform and air foil to prevent fatigue during the life cycle of operation. Degree of radius generation is critical and must be controlled carefully.

Surface Defects Affecting Electroless Nickel Quality

Physical defects in the substrate can greatly affect the purity of an electroless nickel deposit, and can lead to incomplete coverage and skipped plate (1). A deposit thickness adequate for sound parts is not sufficient for parts with surface defects. Some examples can be cited to show how manufacturing methods and raw material quality produce parts with surface defects which lead to electroless nickel coatings of less than the quality level required.

Anvil holders for use in a surgical apparatus are stamped from 0.3175 mm (1/8 inch) carbon steel stock and formed by means of conventional secondary operations. Specifications for finish require 5.08 micrometres (0.0002 inch) thickness of electroless nickel over the entire part with no exposure of steel substrate. Part must pass a copper sulfate immersion test and a steam-pack sterilization test. A cross-section of the anvil edge revealed that the shearing action in stamping caused a lapped-over recess. Even though the plating specification was increased to a thickness of 15.24 micrometres (0.00060 inch), nickel did not deposit into the full depth of the recess. In addition, a fissure in the surface permitted some plating to take place, but prevented complete coverage. In some cases the defect was sealed over with plate. The wide variation in defect size and geometry makes plating these parts with a predetermined specified thickness of electroless nickel difficult at best, in view of the 100 percent assurance level required for the surgical instrument.

Transistor headers composed of nickel alloy leads, a copper heat sink and steel base with glass seals require a 2.03 to 4.57 micrometre (0.00008 to 0.00018 inch) thickness of electroless nickel. Plate must withstand a 30 sec immersion in concentrated nitric acid with no discoloration or substrate attack. Plate must be a pure nickel-phosphorus alloy of maximum density. Fragile nature of the nickel alloy leads require that the parts be basket plated. Defect recesses were formed on the sheared edges of the steel base. Recesses caused formation of hydrogen gas pockets and insufficient plate thickness in recesses. Nitric immersion test produced dark streaks in areas leading from the recesses; parts were rejected. Parts are successfully plated in large quantities, but defects produce some rejects which are expensive and difficult to strip by reason of the various substrates in the assembly. Overall deposit thickness must be maintained at the higher level of the specification to compensate for the defects which occur in various areas of the part.

Small steel cans for transistor and diode devices used in electronics must be electroless nickel plated with 2.54 to 3.31 micrometre (0.00010 to

0.00013 inch) nickel thickness. There must be no staining or discoloration after 5 min immersion in 50 percent hydrochloric acid. Parts rejected due to stains indicate that the stains are the result of a basis metal defect, apparently an inclusion such as rolled-in mill scale, in the steel. Rolled-in foreign material is not an uncommon problem in thin metal stampings.

Plating bath parameters can be adjusted to maximize deposition into recesses. Surface tension of the solution and viscosity should be optimized when surface defects create a problem. The slowest rate of deposition coupled with maximum solution agitation will improve deposit quality and reduce rejects stemming from substrate defects.

Substrate and Surface Problems in Electroplating

A basic characteristic of electroplating is that the electroplate can not be any smoother than the surface upon which it is deposited--even with today's leveling plating processes. Hence, suitable polishing and buffing operations are required for brilliant deposits. The influence of a case-hardened, nitrided, carburized, steel substrate on plate deposition, and that of any of the "difficult-to-plate" metals is well known. The selection of proper solutions, preplate systems, and plating processes generally solves most problems in plating basis metals of this type.

Another basic requirement in electroplating is that the surface to be coated shall be scrupously clean. Over many decades this subject has been discussed; many tests for surface cleanliness have been devised. But as more sophisticated analytical instruments have been developed, we are finding that the surfaces that once were thought to be "clean" are now subject to question. These are basic generalities; some specific problems will be cited.

In the process of nickel-chromium plating molded plastics, generally the pre-etch and acid etch cycles remove minor surface soils so that good plated parts are obtained. If the molded plastic surface exhibits "splay" (equivalent to "cold shut" in zinc die castings), the parts can not be plated with an acceptable electroplate. Further, incoming parts must be inspected for surface roughness caused by pits in the molding dies. Such pits develop during die operation; dies must be removed from production and repolished to correct the condition.

Bumper stock is generally hot rolled steel of about 275 MPa (40,000 psi) yield strength. Incoming steel stock exhibiting a high yield strength and low elongation must be annealed. This process creates a blue scale or thin surface layer of pure iron which is insoluble in most pickling acids. Polishing of the front surface of the formed bumper removes this layer, but the scale remains on the back side. Following plating, plate peels from the back of the bumper as an "onion skin", causing a reject. When this surface condition is experienced, the back of the bumper must also be polished to remove the thin surface layer of insoluble iron.

Sometimes the polished surface of steel exhibits "steel slivers,"

which can cause poor corrosion resistance of the final plate. Process cycle can include anodic pickle in concentrated sulfuric acid to remove slivers. If a surface becomes magnetized, small slivers may persist and cause a rough plate. Sometimes the surface must be demagnetized to make possible the removal of such very small, smooth metal particles.

Polishing lines on polished parts must be oriented in the same direction to obtain the best appearance. Any orange peel not removed by polishing will show through the plate and produce a poor quality deposit, and possible rejection of the part.

Parts stripped for replating may have substrates which are attacked by the stripping solution. Although it is difficult to see the rough surface so produced, such a surface may require repolishing prior to replating.

Elongation or stretching of metal during forming creates microscopic cracks in the formed areas. When these areas are polished, more stock must be removed to remove the defects. A trained polisher can accomplish this by visual observation or with the aid of an eye piece or magnifier. Pits or cracks in the surface, which are not removed by mechanical polishing, create sites for corrosion both up through the electroplate and down into the formed part.

A rough surface, in addition to producing a rough deposit, sometimes causes the plate to show poor corrosion resistance because of thin plate. A rough surface has a greater surface area than a smooth surface of the same dimensions. Hence, the current and time calculated to produce the desired thickness of plate are too low to achieve the specified result.

The porosity of cast iron, possible slag inclusions, and the fact that the iron contains 4½ percent carbon lead to formation of surface smut and plate porosity. Such surfaces are difficult to plate in cyanide solutions. Even though the "skin" is removed by mechanical polishing and a smooth surface produced, parts electroplated in brass, for example, and then lacquered will show "spotting out" after processing. A nickel deposit on the cast iron can be applied first to seal the surface so that subsequent electroplates will be of good quality.

Parts machined from low carbon screw machine steel stock, processed through a thin nickel plate, final brass plate and lacquer, exhibited spotting out. Examination revealed surface tears and roughness from the machining operation. Use of sharper tools resulted in an improved steel surface, and eliminated the failures due to spotting out.

Straight pins formed by heading drawn wire, then barrel nickel plated, failed to pass specified corrosion resistance tests. Inspection of the wire stock with a 30-power binocular revealed draw marks on the wire. In the plating barrel, nickel did not deposit in the draw marks under plating conditions required to prevent buildup on the pin points. Close inspection of incoming material under 30-power magnification insured that only wire without draw marks was accepted for fabrication and finishing.

Surface smut on heat treated steel fasteners caused peeling and brittle plate when processed through a chloride zinc barrel plating cycle. As in many cases, inadequate cleaning in the heat treat cycle, with oil baked on the steel surface, was the cause of the problem. Problem was solved by installing a strong, periodic reverse electrocleaner followed by a relatively weak acid dip prior to barrel plating.

When leaded steel is improperly polished, lead smears may develop on the surface and lead to poor adhesion of a subsequent electroplate. The preplate cycle must be designed to overcome this problem, if the polishing operation can not be improved to correct it at the source.

Cold shuts in the surface of zinc die castings result from poor metal and/or zinc oxide from remelting of rejects. Die castings must be polished and buffed to remove cold shuts and hard blisters (caused by slag, poor quenching oil) from the surface. Insufficient buffing to remove surface defects tends to cover the surface blemishes. Even though the visual appearance is satisfactory, holes are only concealed and blistering of the electroplate results.

Quality of the die casting metal can be controlled by removing only 20 percent of a furnace charge for each run, then adding a new charge. Metal mix should contain 3.9 to 4.3 percent aluminum, 0.02 to 0.05 percent magnesium, balance pure zinc. Spectrographic analysis of each furnace melt must be carried out to be sure that impurities are within specified limits. Copper should be less than 0.25 percent, iron less than 0.08 percent, nickel less than 0.02 percent, lead less than 0.004 percent, tin less than 0.002 percent, cadmium less than 0.003 percent. Combined lead, tin, and cadmium should be less than 0.007 percent. Incorrect chemical composition of die castings not only results in plating problems, but causes below-specification mechanical strength of the castings, and failures in service.

Chromium is stripped from rejected parts before using them as additions to the zinc die cast furnace charge. Impurities in zinc die castings above the limits noted above cause delayed blistering of the resulting copper-nickel-chromium electroplate. Pits in die castings make parts difficult to plate, and lead to poor appearance of the plated part with poor resistance to corrosion in service.

Processing steps which improve the quality of the plate on die castings include the use of highly wetted cleaners in the correct sequence, the proper acid dip (buffered acid salt solution plus a wetter), a high current density copper strike. Best quality finish can be obtained with a high leveling copper, or a very bright copper to get good depth of color for the final nickel-chromium coating.

Incorrect gating of castings can produce a substrate which causes plating rejects. A blistered deposit resulted when die cast aluminum pistons were plated with copper, iron, and tin. The pistons were trimmed and machined routinely after casting. Although not visible, porosity in the metal in the gate area caused absorption of the machining oil. Oil

was not removed in the preplate cleaning cycle. Problem was solved by changing the location of the gate area in the casting.

Aluminum die castings and sand castings have a hard surface due to oxidation, and exhibit a dark color. Surface must be polished to a lighter color which indicates that the hard skin has been removed. Otherwise the resulting electroplate will be dull.

Mold release compounds containing silicone must be avoided. If the silicone enters the cleaning and plating system, all solutions will be contaminated and electroplates will blister and peel.

Preparation and polishing of the casting surface for plating should include removal of particles from the surface of sand castings. If not removed, they form corrosion sites under the electroplate.

Aluminum bumpers are polished, buffed, bright dipped and then anodized. The buffing compound can leave spots on the aluminum surface, preventing uniform bright dipping. A special cleaner must be formulated to remove spots from the aluminum surface.

Brass sand castings may exhibit markings or non-uniform areas on the surface--a condition somewhat similar to a cold shut on a zinc die casting. Such areas must be removed by polishing, else the design of the surface defect will appear in the final electroplate.

Surface Problems in Electropolishing, Chemical Polishing

Stainless steel of the 400 series (chromium-iron), or annealed stainless steel, may contain a surface temper oxide. This surface layer or film must be removed before electropolishing can be carried out successfully. If high quality steel is used in manufacturing parts to be electropolished, excellent results can be obtained. If, however, there are seams in the stainless steel containing slag particles, electropolishing will open up the seams to create a nonuniform surface.

Electropolishing of high carbon steel may cause a surface smut to develop because of the carbon content. Steel should be hardened to form cementite prior to electropolishing to eliminate this cause for rejects.

Chemical polishing of any metal with mercury contamination on the surface will result in a poor chemical polish, and lack of adhesion of any subsequent electroplate. Mercury contamination on parts to be processed through almost any finishing sequence is a serious hazard.

Substrate Conditions and Quality of Mechanical Plating

As in other plating processes, parts to be mechanically plated must have clean surfaces. Clean parts of hardened steel, die castings, brass and some stainless steels can be mechanically plated with zinc, tin, cadmium, tin-zinc or tin-cadmium. A nonmagnetic stainless steel can not be coated. Present state of the art limits part size to 203.2 mm (8 inches)

in length and 0.45 kg (1 lb.) in weight.

Sintered or powdered metal parts can be mechanically plated if the density of the part is 84 percent or more. Porosity of parts with lower densities causes entrapment of processing solution and subsequent bleed-out after plating and drying. A final dichromate film formed on the lower-density plated parts, for example, will disappear within 24 hours. Bright zinc surfaces of the less dense plated parts will turn dark. Parts with densities of less than 84 percent can be sealed by vacuum impregnation prior to processing, then mechanically plated successfully.

Surface Contamination from Buffing, Polishing

Certain buffing compounds tend to create a residue on a part surface which is incompatible with cleaners. During buffing, metallic soaps are produced on the surfaces of both ferrous and nonferrous parts. Products with this type of surface contaminant are difficult to clean and plate. Special cleaning processes must be developed to remove the metallic soap films so formed.

Buffing compound must be removed from a buffed surface within 24 hours or less to minimize subsequent cleaning and plating problems. On more sensitive metals, etching, staining or discoloration, pitting will occur, causing subsequent plating rejects. Treating buffed brass, zinc, aluminum or steel parts immediately in an air-agitated aqueous nonalkaline mixture of surfactants at pH 9 to 9.5 will prevent or minimize subsequent cleaning and plating problems.

Surface Conditions and Paint Finish Quality

A study of the surface attributes of autobody type cold rolled steel substrates which influence organic coating corrosion behavior has been conducted (2). Results indicate that high concentrations of carbon, retained on the steel surface after alkaline power wash, appear to be the most probable cause of poor corrosion performance of the painted metal parts.

Steel samples were evaluated for cleanliness, topography, surface reactivity, and surface chemistry. Techniques and equipment employed included profilometry, electron microscopy, electron scanning, chemical analysis, electron probe microanalysis, and X-ray diffraction. Electron spectroscopy measurements of a steel surface indicated that a steel surface, even if thoroughly cleaned by established cleaning methods, consists only to a small degree of iron atoms, while other elements like oxygen and carbon predominate. Electron probe analysis indicates that carbon appears to exist first, as a fine deposit uniformly spread over relatively smooth surfaces, and second, in high concentration in micro pits, crevices and cavities along with high concentrations of sodium, chlorine, sulfur and other contaminants.

High surface carbon levels, whether analyzed spectroscopically or chemically, consistently provide the signal for high probability of poor

system corrosion performance. Surface carbon and corrosion tendency as measured by salt spray creep correlate strongly with each other. Cavities, cracks and fissures can, of course, form corrosion sites under the paint film or final finish.

The pattern of corrosion failure demonstrates beyond reasonable doubt that random purchase of cold rolled steel holds a high probability for occasional weak to catastrophic failure in coating system performance. Cleaning processes which employ mechanical abrasion (with 400 grit nonwoven nylon abrasives, for example) prior to painting can significantly reduce the failure probability. Examination by microprobe, electron spectroscopy for chemical analysis, or similar micro analytical techniques are essential to the determination of "good" and "poor" surfaces. As in the case of electroplates, paint finishes applied can be of no better quality than the surface to be coated.

The surfaces of both wrought and cast aluminum alloys to be finished must be smooth, and should be cleaned either by vapor degreasing or alkaline cleaning methods prior to conversion coating with either an amorphous chromate or an amorphous phosphate (3). Surface inclusions or impurities can develop into corrosion sites under the final organic finish.

For aluminum surfaces, the etch rate or dissolution rate is the key factor which determines good cleaning prior to conversion coating (4). Etch rate--the amount of aluminum removed from the surface by the cleaner per unit of time--should be between 216 to 324 mg/sq. m (20 to 30 mg/sq. ft.). Less than 216 mg/sq. m (20 mg/sq. ft.) can leave soil and oxides on the surface; these will prevent good conversion coating and lead to premature failure of the paint finish. More than 324 mg/sq. m (30 mg/sq. ft.) may lead to smutty surfaces which are powdery--again preventing proper conversion coating and a sound organic finish with good service life.

Metal surfaces to be conversion coated and painted must be clean. The fact that they are water break free is a general indication of cleanliness. However, a water break free surface is not necessarily clean. A black residue on a cloth is an indication that the surface is not clean, preventing proper phosphatizing and good paint finish performance.

In addition to the removal of rust, polymerized oil spots, carbon smut, rolling and dry film lubricants from steel surfaces, surface carbon must also be removed if a good conversion coating and a paint finish of good quality is to be obtained. Surface carbon levels above 8.6 mg/sq. m (0.8 mg/sq. ft.) can be a cause for poor paint finish salt spray resistance.

Galvanized surfaces may have been passivated, or may show white rust. Both the passivated surface layer and the white rust must be removed. A water break free surface is a good indication of a clean surface. An etch rate in cleaning of 10.8 to 43.2 mg/sq. m(1 to 4 mg/sq. ft.) is acceptable.

Metal surfaces can be considered suitably free from surface contaminants for good conversion coating and paint finishing if they pass the following

tests:

Aluminum: Water break free surface
Etch rate of 216 to 324 mg/sq. m

Galvanized steel: Water break free surface
Etch rate of 10.8 to 43.2 mg./sq. m

Steel: Water break free surface
White cloth wipe test
Surface carbon value of less than 8.6 mg./sq. m

## Acknowledgment

Grateful thanks are extended to the following individuals for their kind and generous cooperation in providing information for this paper:

Edward A. Rodzewich, Amchem Products, Inc.
Robert Rieneke, Fisher Body Div., General Motors Corporation
Paul M. Johnson, Guide Div., General Motors Corporation
J. Bernard Hignett and Edward Tulinski, The Harper Company
Edward Bendziunas, Richard J. Heller, Spencer Henn, The Lea Mfg. Co.
Charles T. Schroeder, 3 M Company
William Innes and William Toller, MacDermid, Inc.
Ralph E. Pike, Consultant
Robert Groom, Reilly Plating Company
Robert J. Leipertz, Reynolds Metals Company
Jack Hyner and Stephen Gradowski, Whyco Chromium Company, Inc.

## References

1. "Electroless Nickel Performance as Related to Surface Defects," by Jack Hyner and Stephen Gradowski, Whyco Chromium Co., Inc., Electroless Nickel Conference II, Sponsored by Products Finishing magazine, 1981.

2. SME MR79-741, "Aspects of Substrate Influencing Industrial Coating Systems Corrosion Performance," by Ralph E. Pike, Consultant, 1979.

3. SME FC81-436, "Preparation of Aluminum for Organic Coatings," by Robert J. Leipertz, Reynolds Metals Company 1981.

4. "Surface Cleaning of Metals for Phosphating and Painting," by Edward A. Rodzewich, Amchem Products, Inc., SME Third Conference and Exposition for Coating and Finishing Technology, 1981.

L-4

# Mechanical Finishing Session L

## Surface Contamination: Its Sources, Effects and Methods of Removal

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# SURFACE CONTAMINATION: ITS SOURCES, EFFECTS AND METHODS OF REMOVAL

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## Introduction

The metal surface is a multilayered transition region between a gas and a solid. Figure 1 shows a conceptualized cross section of a metal surface. The first layer above the bulk material is a segregated layer which is enriched in elements which are driven to the surface from the bulk by thermodynamic forces in the natural process of energy minimization.

The oxidized layer consists of the reaction products of the segregated layer elements and oxygen from the atmosphere.

The chemisorbed layer contains strongly bonded contaminants from the environment, and the physisorbed layer consists of weakly bonded contamination from the environment. In reality, there is a significant intermixing of these surface layers.

A real metal surface has important chemical and topographical characteristics. A conceptual cross section of the surface of cold rolled autobody steel is shown in Figure 2. The bulk consists of iron, along with alloying and trace elements (Li, C, Na, Mg, Al, S, Mn). The surface region (10-80 angstroms deep) includes the layers discussed previously which are composed of iron oxides, segregated element oxides, and compounds of Ca, Na, Cl, S, and P.

The surface irregularities are typical of most cold rolled steel surfaces which have scratches, gouges, fissures and dents in which rolling oils, processing fluids, and other environmental contaminants can be trapped. Finally, the physisorbed layer contains $H_2O$, $CO_2$, $O_2$ and other contaminants.

It is clear that metal surfaces have a chemical nature that is very different from the bulk metal. Frequently these chemical differences are detrimental and must be removed by a cleaning process for optimum performance in coating, bonding, and other surface sensitive application areas. For example, printed circuit boards must be cleaned prior to the application of photo-resist masks and solder lines, otherwise poor adhesion of plating and discontinuous circuits occur. (1,2)

The purpose of this paper is to present our most recent findings relative to the surface chemistry of metals. The role of surface chemistry as it effects subsequent manufacturing operations will be discussed, and the alteration of surface chemistry by various chemical and mechanical surface treatments, especially treatment by 3-dimensional non-woven abrasives, will be emphasized.

## Experimental

Analysis of the surface chemistry of the metal samples evaluated for these experiments was done in our laboratory using a Physical Electronics Scanning Auger Microprobe (SAM) Model 545 with an attached 3M Secondary Ion Mass Spectrometer (SIMS) Model 610. The theory and use of these powerful analytical tools is adequately described in the literature (3, 4). For this paper, however, a brief explanation of the Auger Electron Spectroscope (AES) System and the SIMS system is in order.

In AES the surface is bombarded with 5 to 10 KeV electrons. The bombarding particles eject one of the core atomic electrons of elements in the near region of the surface. This vacancy is filled by one of the outer orbital electrons falling into this void. One mode of de-exciting the atom is the emission of an Auger electron. The energy of this electron is characteristic of the atom from which it is emitted. The spectroscopy is sensitive to $\pm$ 1 eV, and since the depth of Auger electron emission is limited to approximately 10 angstroms (Å), the system is an unambiguous method for determining surface chemistry composition.

In SIMS analysis, charged ions bombard the surface causing ejection of electrons and surface atoms - a small percentage of which are charged. By measuring the mass of these ejected ionized particles, surface atomic and molecular information can be determined. Because a few atomic layers are removed during analysis, SIMS is considered to be a destructive system, however, it is a very sensitive technique ($10^{-4}$ to $10^{-8}$ atomic fractions) and can basically detect all elements from hydrogen to uranium.

This AES/SIMS system has two features which make it a very powerful analytical tool. First, it has the capability of imaging and thus determining the location (distribution) of each element in the surface. Second, the SIMS ion gun can be used to sputter away the surface, effectively removing the surface atom layer, layer by layer, while simultaneously doing Auger analysis of the newly exposed surface. Thus a "depth profile" can be made to determine how the chemical composition changes as the ion beam sputters through the surface layers into the bulk composition.

The preparation and processing of the steel samples used in this experiment are described in previously published papers (5-7).

Likewise, the experimental conditions for the 2024-T3 and 7075-T6 aluminum alloys are presented in a paper prepared for a SAMPE conference (8).

The other aluminum alloys (2036-T4 and 5182-T0) involved were processed by running .050" and .040" x 36" x 72" sheets through a SOMACA Brand Printed Circuit Scrubber or through a Timesavers Flat Finishing Machine at 50 fpm. A Scotch-Brite Brand 7A-Medium Cutting and Polishing

Cleaning Brush (24) operating at 3500-4000 sfpm was used to abrade the surfaces. The power consumption of the brush during processing was about .25 HP per inch of working width. Tap water at a rate of approximately 8 gpm was sprayed on the brush and sheets during the processing. As the sheets exited the machines, they were dried using ambient room air through air knife dryers behind the machines. Some samples were cut for surface chemical analysis, other samples were sent for additional physical testing.

Finally, a coil of cartridge brass (70% copper, 30% zinc) was supplied by a customer. It was processed on the laboratory coil cleaning line using a Scotch-Brite Brand 7A-Very Fine Cutting and Polishing Cleaning Brush (24) running at 3500-4000 sfpm against feed direction, using about .15 HP per inch of working width. The coil was fed through the machine at 25 fpm while oscillating the brushing head at 220 cpm at 1/4" stroke and while a spray of tap water was directed at the brush and coil surface. Small samples were removed from the coil before and after processing so that analysis of surface chemistry could be made, and the coil was returned to the customer for solder wetability, bonding evaluations, and fabrication.

## Results and Discussion

### STEEL

Corrosion is a problem all of us share. It costs the world's economy billions of dollars each year. Recently a lot of attention has been focused on the corrosion performance of steel after painting, particularly in the steel used for our automobiles and appliances. Numerous investigations (9-16) have shown that the presence of carbon on the surface of steel sheet or coil can be directly correlated to its performance in accelerated corrosion testing. One possible source of this carbon is the rolling oils which are baked onto the surface. (11, 13, 14) This contamination is not removed by the conventional alkaline cleaning pretreatment applied as the first step in the zinc phosphate conversion coating of autobody steel. Our recent work has shown that abrasive brushing of the steel with 3-dimensional non-woven abrasives, as currently practiced in the making of Zincrometal (17, 18), uniformly removes about 0.5$\mu$m of the steel surface thereby eliminating the detrimental carbonaceous deposit. Elimination of the carbon layer by this means results in a decided improvement in the steel's corrosion resistance. (5, 7)

Surface carbon and salt-fog test data for samples taken from ten coils of steel are given in Table 1. C/Fe atom ratios were determined from Auger spectra obtained after sputter removal of approximately 30 Å of surface material to avoid possible contributions from weakly absorbed carbon. All but three lots of steel could be easily separated into good and bad quality groups based on all three measurement criteria. Steel lots with low surface carbon but intermediate or inconsistent corrosion performance were placed in the marginal group. Figure 3 presents typical

Auger scans for representative samples of the good and bad steels. Carbon, iron and oxygen make up 94 atom % of the surface composition. The concentration of carbon in the good steel at this 30 Å depth is considerably less than it is for bad steel.

Tables II and III are reproduced here to show the effects of various surface treatments on the surface chemistry of the steels. All steels were initially alkaline cleaned, and for purposes of this study was determined to be the starting point, thus it is identified as the treatment labelled "none".

The "activator" treatment indicates that the steels have been rinsed with a solution containing a commercially supplied powder. When mixed with water the solution becomes an alkali-metal phosphate containing titanium salts. It is a recommended pretreatment for conversion coating because it is believed to enhance corrosion resistance by providing nucleation sites for zinc phosphate crystal growth. Its chemistry is mainly sodium, phosphorus, and oxygen with some potassium and trace amounts of titanium.

The "abrasion" treatment indicates that the steels were brushed with a 3-dimensional abrasive product after an alkaline cleaning and water rinsing step.

The "abrasion plus activation" treatment involved the rinsing of the brushed steels with the chemical activator solution referenced earlier.

The data of Tables II and III show that only carbon and possibly nitrogen and manganese appear to chemically differentiate bad steel from good steel. For the case of the alkaline cleaned only (none) treatment the Auger data in Table II show the bad steel surface to have greater amounts of C and N but not Mn. The SIMS data in Table III substantiate these results and specifically show the N tied to C in the detection of the $CN^-$ mass fragment. Further, the SIMS data suggest that Mg and Si may also be in excess on the bad steel.

The two tables permit a comparison of the surface chemistry of the steel after treating with the 3-dimensional abrasive product. The values for the chemical elements on the surface of the two steels are almost identical after abrasion. Attention is also directed to the evidence showing the removal of Si and Mn as a result of this cleaning process.

In effect this means that there is much more consistent surface uniformity between the steels than has been possible before. The ability to produce a uniformity and similarity between steels, regardless of mill source, has tremendous implications for providing a more consistent protective coating.

The effect of chemical and mechanical preparation of the steel surface on the steel's accelerated corrosion performance was also studied at the time of these experiments. 240 hour salt-fog test data for

conversion coated and primer painted panels are shown in Figures 4 and 5. The average creepback measured to one side of a scribed line is given in Figure 4, as a function of preconditioning treatment, for the good (I), marginal (II), and bad (III) steel groups. Similarly, the corresponding average percent panel area showing rust is shown in Figure 5. From these data, it is quite evident that rust area is a much wider ranged response to salt-fog exposure in the present analysis. Reasons for the limited response found for creepback corrosion probably rest in the specific coating system used in this study as well as the short test duration. We, therefore, limit discussion of creepback to noting that only the bad steel group receiving no preconditioning treatment showed a significantly greater creepback, and preconditioning, either abrasively or chemically, served to limit the creepback to values characteristic of the better quality steels. The facial rusting data in Figure 5 shows that chemical activation is of no benefit to the bad steel group, although some benefit is realized with the better quality steels. Abrasive preconditioning, with its uniform action of removing about 0.5$\mu$m of surface material regardless of steel quality differences, results in a consistently moderate amount of rust occurence, an amount equivalent to that occurring with non-preconditioned good steel. Chemical activation of all steel after an abrasive treatment yields the same benefit in reduced rusting as results from chemically activating good steel. Thus, from a facial rusting standpoint, abraded steel, irrespective of the steel's initial surface quality, behaves as good steel both with and without the additional use of chemical activation.

Finally, an interesting pattern emerged when Auger carbon and sodium images of the chemical activator treated panels were compared. These scanning Auger images in Figures 6 and 7 show sodium not present in surface regions of high carbon concentrations. One must conclude that carbon inhibits the deposition of the nucleating agent and subsequent phosphate conversion coating film. It is thus necessary to remove the C before a uniform chemical activation treatment can be applied.

One final note on the steels, by way of a summary, is contained in evidence from both the AES and SIMS analyses. Abrasion not only reduces the amount of carbon but also significantly reduces the overall contamination level of all other elements normally found on good steel as well as those specific to bad steel. Whether the starting steel is good or bad, abrasion results in a nearly identical, consistent surface composition. This implies that bad steel is "bad" only because its surface is "bad", not its bulk. This surface uniformity effected by abrasion reflects itself in the consistency of the facial rusting response among the various quality steel groups in Figure 5.

## ALUMINUM

The surface contamination of a few aluminum alloys was studied to determine the influence of the surface chemistries on subsequent performance of the metal. Two quite different application uses of aluminum are focused on in this report. The first discusses the

preparation of 2024-T3 and 7075-T6 alloys for anodization and bonding as practiced in the aerospace industry. The second is concerned with the weldability of 2036-T4 and 5182-T1 aluminum for automotive body members.

The most widely used surface treatment of aluminum for adhesive bonding is the FPL (Forest Products Laboratory) etch. It is used as a final treatment as well as a pretreatment before anodization. The FPL etch contains significant quantities of $Na_2Cr_2O_7$ and there is a great deal of concern regarding the use of Cr-VI containing solutions both from the viewpoint of the health of the materials handler and also from the viewpoint of having to dispose of large amounts of hazardous waste. An initial evaluation of an alternative pretreatment method to the FPL etch was the basis from which the data and results of this study grew. The alternative pretreatment is the use of Scotch-Brite Brand 3-Dimensional Abrasive Products prior to anodization. (8)

Certain of the samples were subjected to AES and SIMS analysis. Auger spectra comparing brushed aluminum and FPL etched aluminum is contained in Figure 6 and reveals interesting contrasts and similarities. It is easy to note that all of the same elements are present on both surfaces except that there is no evidence of a copper signal on the brushed material. Special attention is called to the substantial reduction of the Mg signal on both the FPL etch and brushed samples. MgO formed by the segregration of bulk Mg to the outer layers is removed by both processes.

This conclusion is amply supported by the Auger and SIMS data listed in Tables IV and V. Table IV contains the elemental surface compositions of the various alloy surfaces as ratios with respect to the aluminum concentration and also includes a determination of the thickness of the oxide layer. It is the contrast between the oxide thicknesses which indicates the most striking differences between the types of aluminum and the types of pretreatments. In the as received state, the 7075-T6 alloy has an oxide layer about 50% greater than the 2024-T3 alloy. However, after treating the two types of aluminum with either the FPL etch or by brushing, the oxide forms a significantly thinner layer that is less than 200 Å in depth. Of these treatments, brushing limits the oxide layer growth to a thickness consistently below 100 Å.

Table V shows the composition of the first 20 Å depth for some selected elements from the SIMS analysis. (These are also shown as ratios with respect to aluminum concentrations.) In combination with Table IV, there is evidence that the FPL etched and brushed surface elemental compositions are similar with the following exceptions. The FPL etched surface seems to have a larger amount of Cu, Na and F while the brushed surface has a slightly larger amount of C (believed adsorbed from the atmosphere). Especially notable is the fact that the AES shows a significant amount of Cu on the FPL etched surface but none was detectable on the brushed surface.

After anodization and bonding, roller peel, overlap shear, and wedge test specimens were prepared and subjected to environmental exposure, durability, and bond strength evaluations. It is apparent from the data reported in reference 16 that the FPL etch surface is not a prerequisite for obtaining an anodized aluminum surface that is adequate for adhesive bonding. The indication is that pretreatment of the alloys with the 3-dimensional abrasive brushes creates a conditioned surface capable of being anodized and sufficiently bondable as to be equivalent to the present FPL etch method of pretreatment.

As more and more aluminum is being used in our automobiles in an effort to reduce weight and increase efficiency, the fabrication and joining of this metal has become increasingly important. Initial concern centered on the ability of the sheets to be spot welded, and within this framework, the ability of a weld tip to make 2,000 acceptable spot welds before failure or redressing was considered crucial. (19-22) Examples of good and bad spot welds are presented in Figure 9.

Aluminum sheets with the surfaces in the "as received" condition cannot be reliably resistance spot welded on a production basis.(20) However, sheets whose surfaces have been abraded with Scotch-Brite Brand products consistently passed the "Weld Reliability Test" and were able to do so even after 90 days of plant storage. (20) Table VI gives a comparison of how different surface preparations effected weldability performance.

Auger scans and depth profiles of the 5182-TO alloys are useful in determining the differences in surface chemistry for the "as received" and "brushed" aluminum. Figure 10 compares the elemental composition of the two surfaces as analyzed by AES. Specific notice is to be made of the magnesium signal dominant in the as received material over the brushed specimen. This suggests a heavy MgO layer on the as received sample which is removed by brushing the surface. From Figure 11, it is evident that a magnesium-aluminum-oxygen composition occupies the outer surface of the as received sample for a thickness of nearly 200 Å. After brushing, the oxide layer grows to a depth of only 25 Å.

It is the high electrical resistance of the Mg-Al-O compound ($1700_{\mu}\Omega$) which causes the poor weldability of the as received alloys and therefore promotes poor tip life. The thin oxide layer of the brushed metal has a low resistance ($250_{\mu}\Omega$) and contributes to the improved weldability and extended tip life.

The contamination of aluminum surfaces is a concern of many users. The sources of this contamination may come from the exterior environment of the metal, as was shown in the bonding example, or from the migrating of elemental species within the alloys, as evidenced by the weldability example. In either case it has been shown that processing the surface with a 3-dimensional abrasive product produces a substrate which is free from the detrimental contaminants and which promotes subsequent processing for improved performance.

BRASS

Another example of the surface conditioning capability of 3-dimensional abrasives on metals emanated from a request by a customer to evaluate the poor solderability of cartridge brass used in automotive radiators. The customer was experiencing an increase in bonding failures at the solder joints after the normal cleaning and surface preparation of the mill finished material. An evaluation was made on this material as well as on samples of the metal which were processed with 3-dimensional abrasive brushes. (23)

Detailed chemical analyses of the surface is shown in Figure 12 comparing the Auger spectra for the as-received and brushed cartridge brass. The as-received surface is seen to contain mainly zinc, oxygen, and carbon. Only a slight amount of copper (Cu) is evident. Thus, the major metallic compound on the as-received surface is ZnO, which, because of the lower surface energy, explains the extreme difficulty encountered in solder bonding to this surface. By comparison, the brushed surface is much richer in copper resulting in a higher surface energy allowing wetability by solder. We also note much less carbon on the brushed surface which should enhance bondability to this surface. One further note regarding the brushed surface is the absence of nitrogen indicating nylon brush fibers are not a source of contamination. Previous work using x-ray photoelectron spectroscopy suggests the carbon is due to hydrocarbons adsorbed from the ambient environment.

Since the chemical information contained in the Auger spectra reflects the chemical differences within the outer few atomic layers of the sample surface, it is of interest to know how the chemical concentration varies with depth into the sample surface. To determine this, the atomic layers were sequentially removed by ion sputter etching and simultaneously recording Auger spectra resulting in the concentration versus depth profiles shown in Figure 13. Here we see that the segregated zinc region on the as-received surface extends over 100 Å deep into the brass surface. Also, the oxygen concentration profile strongly correlates with the excess zinc concentration. In fact, there is nearly a 1:1 correspondence between the excess zinc concentration (i.e., the amount of zinc over and above the 18% measured bulk concentration) and the amount of oxygen which suggests the surface oxide is mainly ZnO. The preferential oxidation of zinc is in agreement with the fact that the heat of formation of ZnO is more than double that of CuO and $Cu_2O$. The oxidation of zinc would also be a good driving force causing zinc segregation. In any case, the thick oxide can be expected to cause difficulties in soldering, and joining in general, as well as cause accelerated die wear due to the abrasive nature of oxides. It is not surprising then to have greatly improved solderability when dealing with the brushed surface.

Poor solderability of cartridge brass is due to a relatively thick zinc-enriched surface region which appears to occur naturally as a result of surface oxide formation. Since zinc is an alloying constituent in

brass, it is not a contaminant per se, but its effect on solderability is just as detrimental as any externally deposited contaminant. Removal of the zinc-enriched surface oxide layer is readily achieved by brushing. The brushed surface is characterized by a uniformly thin, high copper surface oxide providing superior solderability.

## Summary and Conclusions:

Surface contamination of metals is a common concern of fabricating and production industry. The contamination may originate from the processing or storage environment, from the movement, migration and segregation of internal components to the interface, or from both. A cleaning method which can be applied to many surface contamination problems and which leaves the surface, at least initially, free from residual, inhibiting materials and reflecting a metal's bulk composition is the 3-dimensional abrasive surface conditioning system. With this method, the outer micron or so of a material surface is abraded away removing all contaminants, including segregates and their oxides.

## Acknowledgments:

The author wishes to extend his gratitude to other 3M employees who contributed to this work, particularly P. M. Winter, R. P. Wenz, A. V. Pocius, D. K. Charest, and H. A. Peterson.

## REFERENCES

1. E. Armstrong and E. F. Duffek, in Printed Circuits Handbook, 2nd Edition, (C. F. Coombs, Jr., Editor), pp. 6-7, 6-8, McGraw Hill, New York, 1979.

2. W. L. Hamilton, "Dry Film Photoresist Performance on Electroless Copper Surfaces," in Electronic Packaging & Production, June, 1981.

3. Characterization of Solid Surfaces, P. F. Kane and G. B. Larabee, Eds., Plenum Press, New York, 1974.

4. Methods of Surface Analysis, A. W. Czanderna, Ed., Elsevier, New York, 1975.

5. J. J. Claus, R. P. Wenz, and A. V. Pocius, "The Surface Chemistry and Corrosion Performance of Cold Rolled Steel Conditioned with 3-Dimensional Abrasives," presented at Finishing '79 Conference, October, 1979. (Available from authors, 3M, St. Paul, Minnesota, 55144).

6. R. P. Wenz and J. J. Claus, "Surface Chemistry, Corrosion Resistance, and the Zinc Phosphate Conversion Processing of Auto Body Steel," presented at the ACS Symposium, Las Vegas, August, 1980.

7. R. P. Wenz and J. J. Claus, "Influence of Abrasive Cleaning on the Corrosion Resistance of Coated Steel," presented at Corrosion '81, Toronto, April, 1981, paper #82.

8. A. V. Pocius and J. J. Claus, "Replacement of Sulfuric-Chromic Acid (FPL) Etch by 3-Dimensional Abrasive Surface Conditioning for Pretreatment of Aerospace Alloys before $H_3PO_4$ Anodization," to be presented at SAMPE Conference, Mt. Airy, Pennsylvania, October, 1982.

9. V. Hospadaruk, J. Huff, R. W. Zurilla, and H. T. Greenwood, "Paint Failure, Steel Surface Quality, and Accelerated Corrosion Testing," Paper No. 780186, National SAE Meeting, Detroit, March, 1978.

10. J. J. Wojtkowaik and H. S. Bender, "Interrelationship between Steel Surfaces, Phosphatability, and Corrosion Resistance," J. Coatings Technol. 50, 86-92, July, 1978.

11. R. A. Iezzi, "Studies of the Surface Characteristics of Cold Rolled Steel that Control Paint Performance," Ph.D. Dissertation, Lehigh University, April, 1979.

12. H. T. Greenwood and R. W. Zurilla, "Effect of Steel Surface Carbon Contamination on Salt Spray Performance,", American Iron and Steel Institute, Technical Session, May, 1979.

13. P. L. Coduti and D. E. Smith, "How Clean is Clean - Technical Evaluation of Cleanliness," Proceedings of the National Coil Coaters Association, September, 1979.

14. P. L. Coduti, "Effect of Residual Carbon on the Paintability of Steel Strip," Metal Finishing Magazine, May, 1980.

15. J. Westberg and L. Borjession, "Influence of Sheet Metal Surface Conditions on the Corrosion Properties of Automotive Paint Systems," Paper No. 278, Corrosion/80, Chicago, March, 1980.

16. J. J. Wojtkowaik, and H. S. Bender, "The Determination of Organic Contaminants on Cold Rolled Steel Surfaces," presented at the ACS Symposium, August, 1980.

17. A. W. Kennedy, "Zincrometal" Coil Coating's Answer to Corrosion," Modern Paint and Coatings, September, 1976.

18. Product Finishing, "Coil Coater Uses Abrasive Cleaning," Product Finishing Magazine, October, 1976.

19. C. A. Roest, "Resistance Spot Welding Aluminum," SME Technical Paper AD-75-745, 1975.

20. W. Dilay, E. A. Rigola, and E. J. Zubinksi, "Investigation of Resistance Welding of Aluminum Sheet," Technical Report No. SR-76-06, Ford Motor Company, January, 1976.

21. C. Wick, "Forming and Joining Aluminum Hoods," in Manufacturing Engineering, February, 1977.

22. "Abraded Aluminum Sheet Best for Resistance Welding," article in Iron Age, April 4, 1977, pp. 36-38.

23. R. P. Wenz, "Scotch-Brite Products for Removal of Surface Segregated Zinc on Cartridge Brass," from a Surface Research Note #8101, July, 1981. (Available from the author, 3M, St. Paul, Minnesota, 55144).

24. This brush is one of a family of 3-dimensional non-woven abrasive products manufactured by the Building Services and Cleaning Products Division of 3M, St. Paul, Minnesota, 55144.

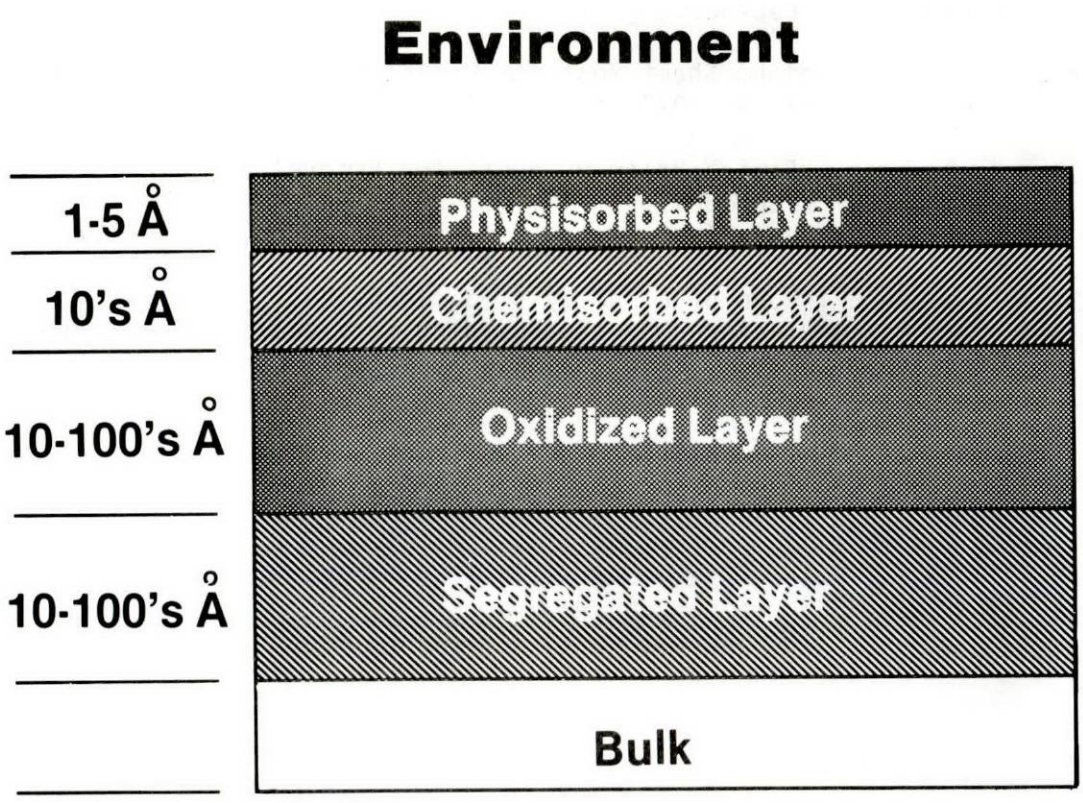



Figure 1. Conceptualized Cross-Section View of Transition Region of a metal surface.

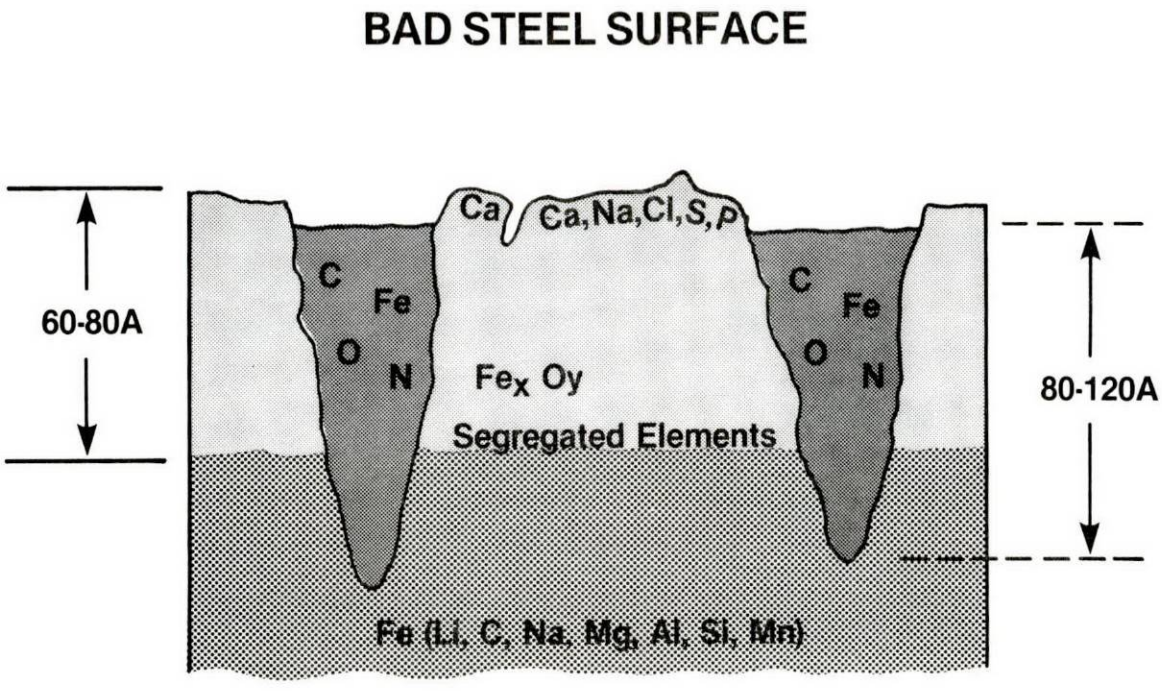



Figure 2. Conceptualized Cross-Section of Cold Rolled Auto Body Steel Surface.

Table 1. Overall quality ratings for steel groups based on surface carbon content and 240 hour salt-fog corrosion performance.

| Group | Lot | $\frac{C}{Fe}$ Atom Ratio @ 30 Å Depth [a] | Creepback (1/64 inch) | | Facial Rust (% area) | | Overall Rating |
|---|---|---|---|---|---|---|---|
| I | A | 0.1 ± 0.05[b] | 1.5 | ± 0.7[c] | 40 | ± 4[c] | Good |
| | B | 0.1 | 1.5 | | 50 | | |
| | C | 0.1 | 2.0 | | 55 | | |
| II | D | 0.1 | 1.5 | ± 0.6 | 65 | ± 10 | Marginal |
| | E | 0.2 | 1.5 | | 80 | | |
| | F | 0.2 | 3.0 | | 80 | | |
| III | G | 0.4 | 3.5 | ± 0.7 | 90 | ± 6 | Bad |
| | H | 0.5 | 3.5 | | 95 | | |
| | I | 0.8 | 3.5 | | 80 | | |
| | J | 0.9 | 4.5 | | 90 | | |

(a) From AES data obtained while scanning a 10 keV, 1.0 μA electron beam across a 500 μm x 500 μm area; atomic concentrations calculated using relative sensitivity factors, reference 10.

(b) Mean deviation of duplicate sampling.

(c) 80% confidence interval for data within the specified steel group.

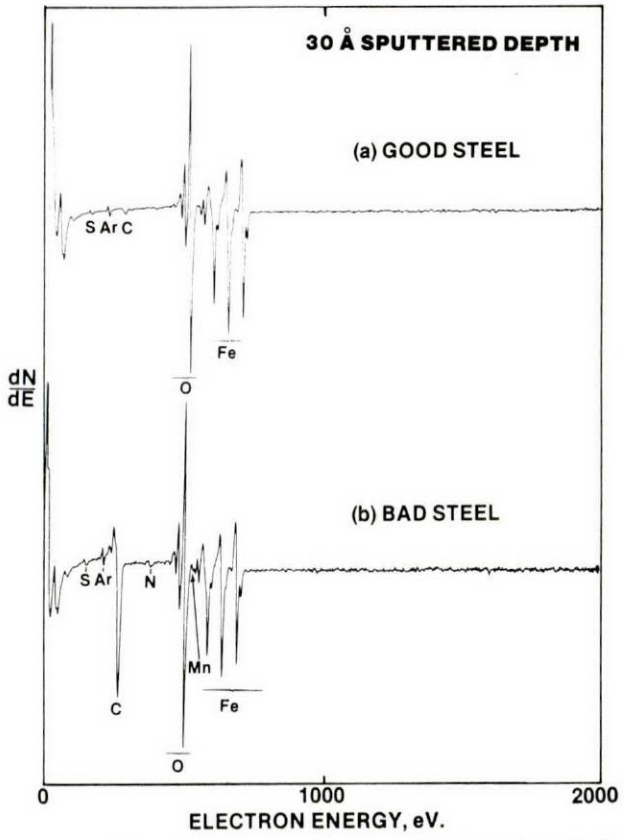



Figure 3. AES spectra obtained at sputtered depth of 30 A for (a) good steel (lot c) and (b) bad steel (lot J). 10 keV beam energy, 1.0μA beam current, 500 μm x 500 μm scanned area.

Table II - Summary of Auger Data[a] expressed at atom fractions[b] relative to Fe.

| Steel | Added Preconditioning[c] | C | N | O | Na | Si | P | Cl | K | Mn |
|---|---|---|---|---|---|---|---|---|---|---|
| Good (Lot C) | None | 1.1 | 0.03 | 1.7 | 0.13 | 0.12 | 0.01 | 0.04 | — | 0.06 |
| | Chemical Activation | 1.2 | 0.03 | 2.0 | 0.70 | 0.09 | 0.17 | 0.03 | 0.09 | 0.04 |
| | Abrasion | 1.0 | 0.02 | 1.2 | — | — | 0.03 | — | — | — |
| | Abrasion Plus Chemical Activation | 0.9 | 0.02 | 1.4 | 0.32 | — | 0.13 | | 0.04 | — |
| Bad (Lot J) | None | 7.6 | 0.13 | 1.7 | 0.11 | 0.17 | — | 0.03 | d | 0.06 |
| | Chemical Activation | 7.6 | 0.19 | 2.1 | 0.58 | 0.32 | 0.08 | 0.03 | d | 0.05 |
| | Abrasion | 1.0 | — | 1.3 | 0.06 | — | 0.03 | 0.01 | — | — |
| | Abrasion Plus Chemical Activation | 0.9 | — | 1.4 | 0.35 | — | 0.11 | 0.02 | 0.02 | — |
| Mean Deviation of Duplicate Sampling | | ± 0.1 | ± 0.01 | ± 0.2 | ± 0.05 | ± 0.03 | ± 0.01 | ± 0.01 | ± 0.02 | ± 0.03 |

(a) Obtained while scanning a 10 keV, 1.0 $\mu$A electron beam across a 500 $\mu$m x 500 $\mu$m area.

(b) Atomic concentrations calculated using relative sensitivity factors, reference 10.

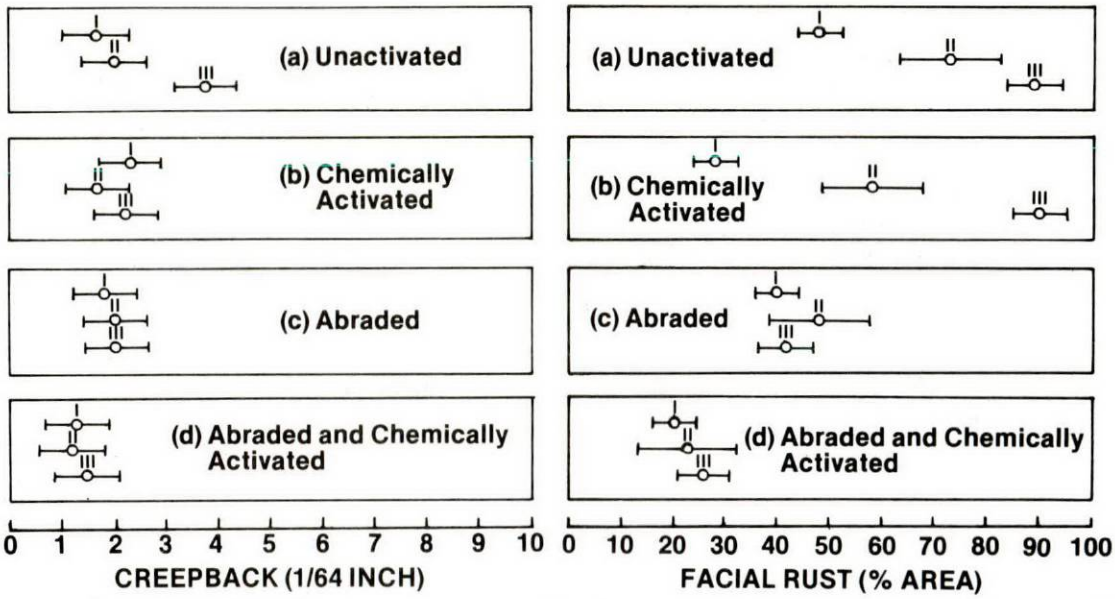
(c) Conditioning treatment in addition to standard alkaline precleaning and deionized water rinsing.

(d) Not detectable due to large C peak interference.

Table III - Summary of SIMS Data[a] expressed as secondary ion intensities relative to $Fe^+$.

| Steel | Added Preconditioning | $Li^+$ | $C^-$ | $CN^-$ | $O^-$ | $F^-$ | $Na^+$ | $Mg^+$ | $Al^+$ | $Si^+$ | $PO_2^-$ | $Cl^-$ | $K^+$ | $Mn^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Good (Lot C) | None | 0.11 | 0.08 | 0.18 | 2 | 0.3 | 18 | 0.19 | 0.24 | 0.08 | — | 0.08 | 0.7 | 0.4 |
| | Chem. Activation | 0.07 | 0.30 | 0.70 | 16 | 2.9 | 86 | 0.16 | 0.37 | 0.09 | 0.3 | 0.92 | 6.6 | 0.6 |
| | Abrasion | 0.02 | 0.03 | 0.07 | 1 | 0.1 | 6 | 0.02 | 0.09 | 0.02 | — | 0.07 | 0.3 | 0.1 |
| | Abrasion Plus Chem. Activation | 0.01 | 0.07 | 0.09 | 6 | 0.5 | 43 | 0.02 | 0.12 | 0.01 | 0.2 | 0.16 | 3.2 | 0.2 |
| Bad (Lot J) | None | 0.21 | 0.26 | 0.54 | 3 | 0.2 | 23 | 0.77 | 0.29 | 0.22 | 0.1 | 0.10 | 0.7 | 0.4 |
| | Chem. Activation | 0.29 | 0.68 | 1.57 | 11 | 1.0 | 92 | 1.71 | 0.49 | 0.45 | 0.2 | 0.25 | 4.7 | 0.3 |
| | Abrasion | 0.03 | 0.04 | 0.07 | 1 | — | 10 | 0.02 | 0.09 | 0.01 | — | 0.04 | 0.4 | 0.1 |
| | Abrasion Plus Chem. Activation | 0.03 | 0.10 | 0.13 | 7 | 0.8 | 57 | 0.02 | 0.08 | 0.02 | 0.2 | 0.11 | 3.2 | 0.1 |
| Mean Deviation of Duplicate Sampling | | ± 0.02 | ± 0.02 | ± 0.02 | ± 0.5 | ± 0.3 | ± 3 | ± 0.03 | ± 0.06 | ± 0.03 | ± 0.05 | ± 0.03 | ± 0.2 | ± 0. |

(a) Obtained while scanning a 5 keV, 600 nA $Ar^+$ ion beam across a 3 mm x 3 mm area.




Figures 4 & 5 - (Left) Average creepback measured to one side of a scribed line. (Right) Average percent panel area rusted, after processing and 240-salt hour salt-fog testing on good (I), marginal (II), and bad (III) steel for a) no preconditioning, b) chemical preconditioning, c) abrasive preconditioning, and d) abrasive followed by chemical preconditioning. Error bars indicate 80% confidence interval.

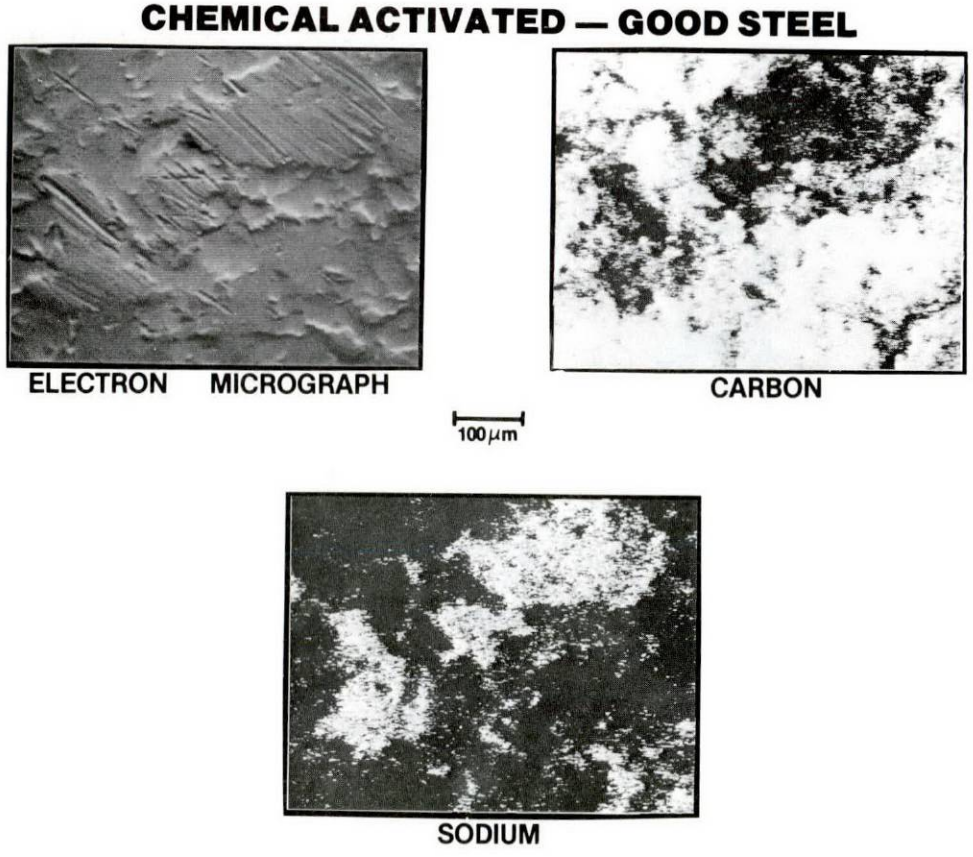



Figure 6 - Distribution of C and Na on chemical activated good steel.

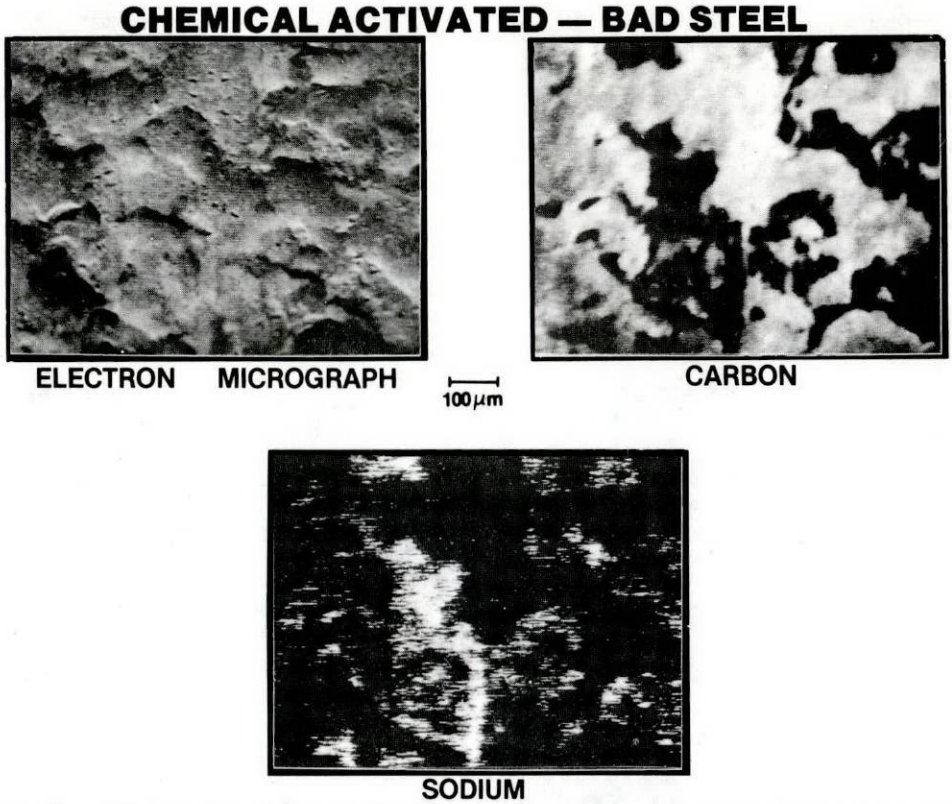



Figure 7 - Distribution of C and Na on chemical activated bad steel.

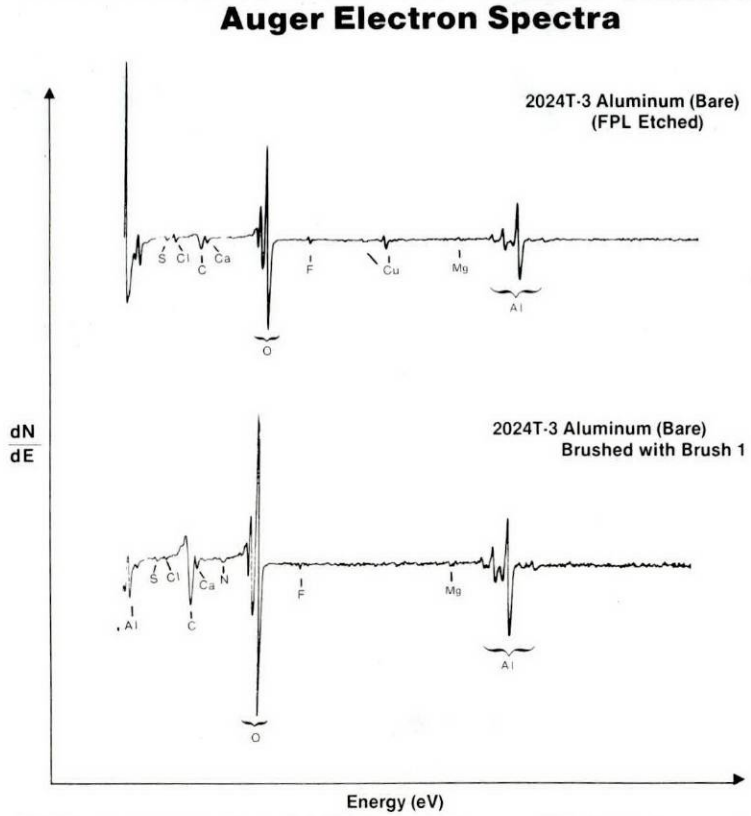



Figure 8 - (AES spectra for 2024T-3 alloy. 10 keV beam energy, 1.0 μA beam current. 500 μm x 500 μm scanned area).

Table IV

Auger Electron Spectroscopy Data on Variously Treated Aluminum

2024T-3 Bare Aluminum Alloy

| Surface Preparation | Oxide Depth (A) | C/Al | O/Al | Mg/Al | Cu/Al |
|---|---|---|---|---|---|
| None | 380 | 2.6 | 6.9 | 5.5 | — |
| FPL Etch | 165 | 0.2 | 3.0 | 0.03 | 0.2 |
| Brush 1 | 80 | 0.6 | 2.6 | 0.02 | — |
| Brush 2 | 65 | 0.3 | 2.5 | 0.05 | — |
| 7075T-6 Bare Aluminum Alloy | | | | | |
| None | 570 | 4.2 | 7.1 | 5.7 | — |
| FPL Etch | 110 | 0.2 | 2.8 | 0.02 | 0.07 |
| Brush 1 | 65 | 0.4 | 3.2 | 0.07 | 0.05 |
| Brush 2 | 55 | 0.5 | 3.2 | 0.08 | 0.05 |

Table V

Secondary Ion Mass Spectroscopy Data on Variously Treated Aluminum

(Data was collected in the first 20°A of surface)

2024T-3 Bare Aluminum Alloy

| | Elemental Ratios | | | | | |
|---|---|---|---|---|---|---|
| Surface Preparation | C/Al | O/Al | Mg/Al | Cu/Al | Na/Al | F/Al |
| None | 1.1 | 14.1 | 1.4 | 0.02 | 0.57 | 0.57 |
| FPL Etch | 0.04 | 0.67 | 0.04 | 0.002 | 0.61 | 0.24 |
| Brush 1 | 0.02 | 0.22 | 0.07 | 0.002 | 0.17 | 0.03 |
| Brush 2 | 0.03 | 0.37 | 0.06 | 0.001 | 0.15 | 0.04 |
| 7075T-6 Bare Aluminum Alloy | | | | | | |
| None | 0.16 | 5.6 | 3.4 | 0.006 | 0.47 | 0.88 |
| FPL Etch | 0.003 | 0.4 | 0.07 | 0.003 | 0.59 | 0.17 |
| Brush 1 | 0.006 | 0.35 | 0.19 | 0.002 | 0.16 | 0.07 |
| Brush 2 | 0.004 | 0.29 | 0.15 | 0.002 | 0.17 | 0.05 |

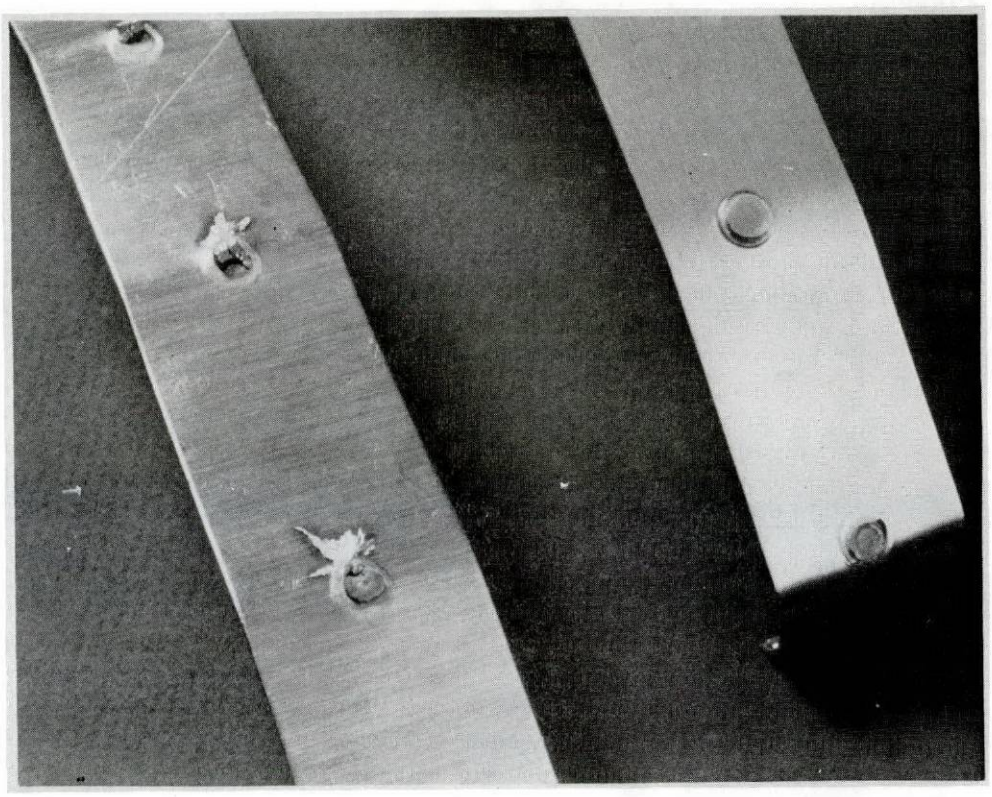


Figure 9 - Photograph of spot welds on aluminum

Figure VI - Effect of surface preparation on weldability.

**How Surface Condition Affects Welds**

| Surface Treatment | Weld Test Passed | Weld Test Failed | Average No. Spots | Range Spots |
|---|---|---|---|---|
| As Received | 1 | 5 | 954 | 25-2400 |
| Chemically Cleaned | 9 | 14 | 1748 | 500-4250 |
| Shot Blast | | | | |
| Glass Bead | 0 | 1 | | 1250* |
| Silicon Carbide | 1 | 0 | | 2750* |
| Aluminum Oxide | 1 | 0 | | 2750* |
| Plating | | | | |
| Zincate | 0 | 1 | | * * |
| Alstan 70 | 0 | 1 | | * * |
| Abrading | 30 | 0 | 2980 | 2200-4500 |

* Results of one test. * * Could not set up. Source-Ford Motor Co.

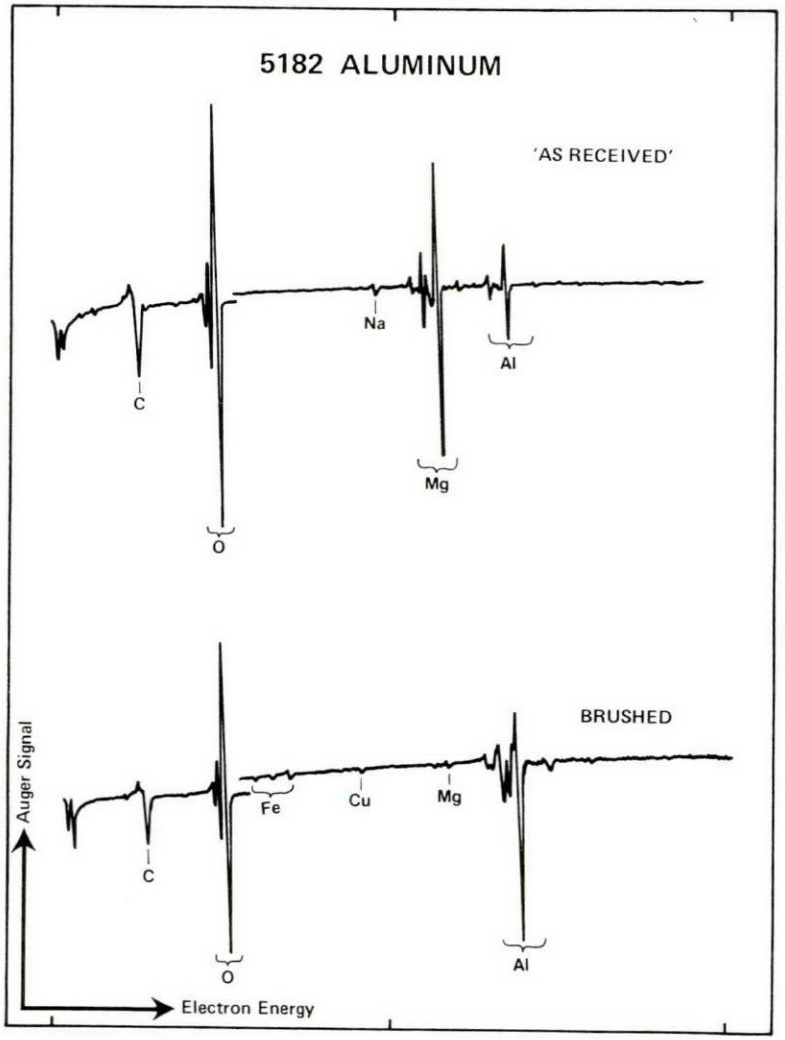



Figure 10 - AES Spectra for 5182-0 alloy

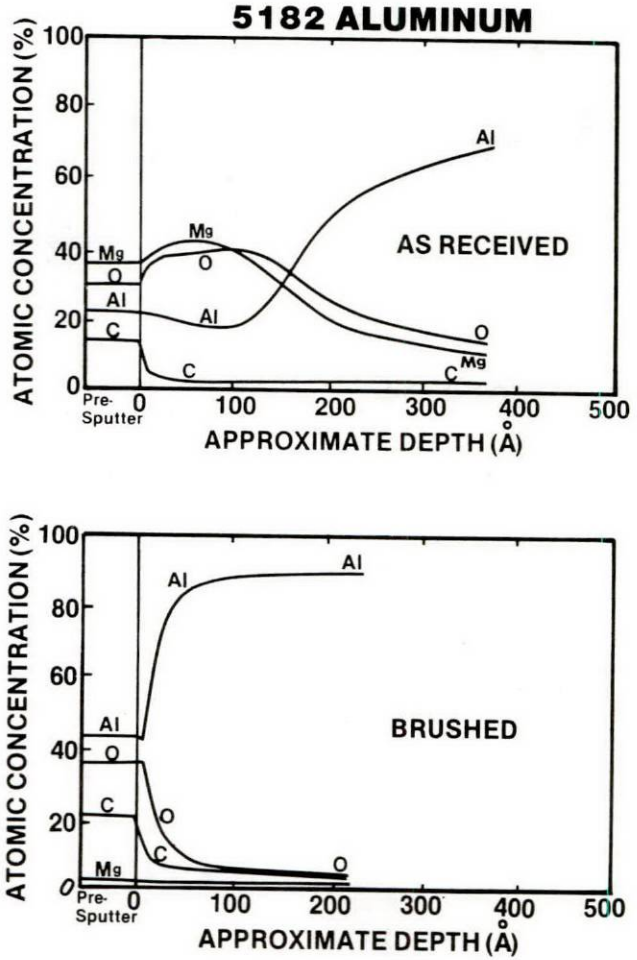



Figure 11 - Auger Depth Profiles of 5182-0 aluminum in "as received" and "brushed" states.

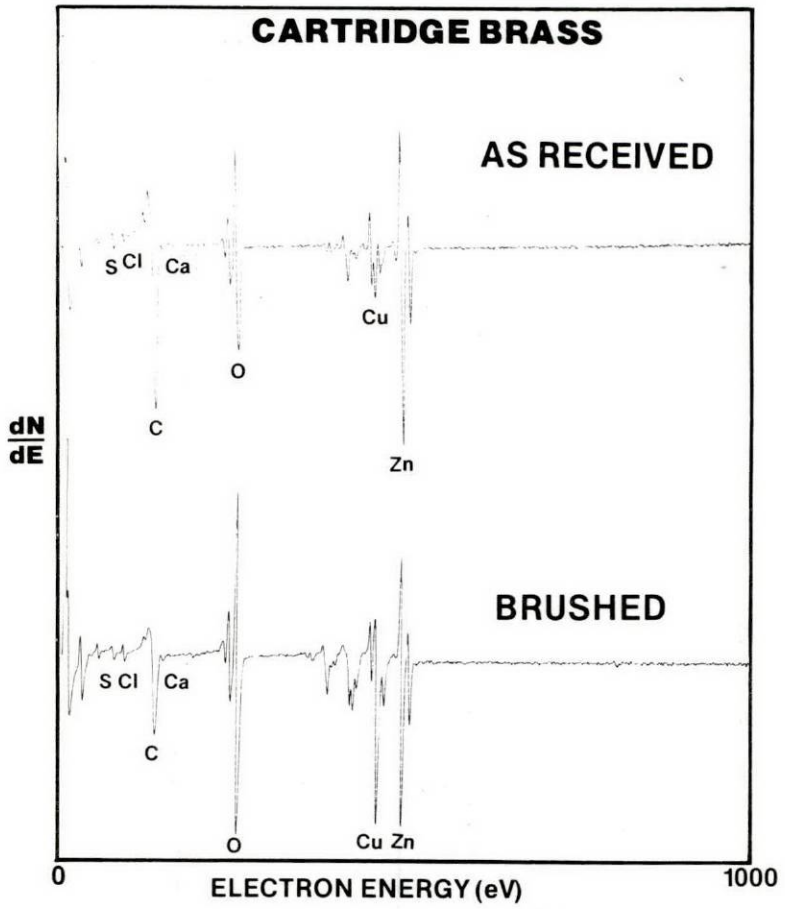
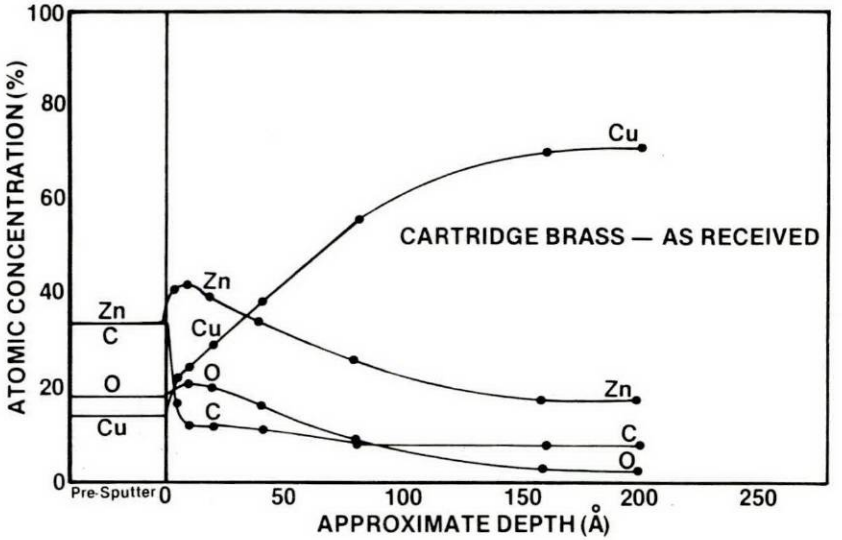



Figure 12 - Auger spectra of cartridge brass showing that brushing with "Scotch-Brite" enhances the copper concentration at the surface while also reducing overall carbon contamination.



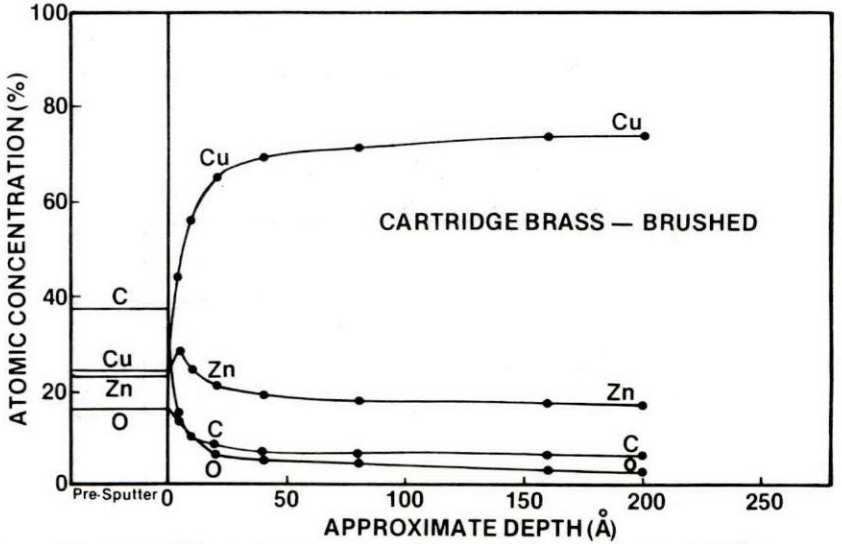




Figure 13 - Auger depth profiles of cartridge brass showing the "as received" surface enriched in zinc and oxygen, while brushing with "Scotch-Brite" substantially reduces the enriched layer thickness. The small residual enrichment left following brushing suggests natural oxidation may cause zinc enrichment.

L-5

# Mechanical Finishing Session L

## I Didn't Know That!

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# I DIDN'T KNOW THAT !

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"Process to print specifications", gets the engineer off the hook; "Burr-free surface required", is the Deburring Department's instructions; "Nickel-chrome plate .0005" + .0005", is the platers part. During the carrying out of these "finite" directions millions of dollars are spent each year. If the deburring foreman and the plating foreman better understand and appreciated each others problems and needs, many of these dollars need not be spent. Therein lies a tale !

Now we all know that an engineer designed the bumble bee. It is the production department, the deburring department and the finishing departments that fine-tuned and modified the original print so that the poor bumble bee can actually fly. In the original design the body was 6" long 3" in diameter with a wing span of 10 decimeters !

What problems? What needs? "All he has to do is take off that silly little burr or change the surface from looking like the Grand Canyon to something more like the Dakota Badlands" says the plater. Likewise we hear "I smooth the parts surfaces, take off all the rough spots and give it back to him all cleaned up. All he's got to do is hang it on a string and push the rectifier button".

So where are the problems? -- let us list and think about just a few

- Soils and oils
- Soap
- Brazing Fluxes
- Protective films
- Oxidized surfaces
- Weld scales
- Base metal particles
- Acid and alkaline films
- Dimensional variations
- Physical surface properties
- Imbedded particles
- Porosity
- Trapped media
- Peened down burrs
- Destruction of media

Cases of Guess What Happened?

Case 1

Thermo deburr is used to remove burrs from a brass valve assembly with many interesting holes. Parts are then sent to the plating room for zinc plating. Guess what happened? The plater, the first time around noticed the light discoloration and inspected parts on the rack as they came out of the acid before alkaline zinc plate. They looked O.K. then and after plate ! Guess what happened next ? Inside the valve assembly where there had been more severe thermo discoloration (oxide) the zinc blistered off during assembly testing. Next Step ? The plater had a part cut up and saw the problem so he worked out a longer, more concen-

trated, higher temperature pickel that removed the oxide. This required rearranging the plating cycle to put in a double pickle on his automatic. Next problem - Final inspection rejects the finished parts, because of over etching and dezincification of the brass ! The plater now goes to the thermo deburr department and raises all sorts of fuss. The thermo deburr department installs a bright dip so that parts are clean and oxide free--we have spent a lot of time but we got it done. Oh yes we spent some money too but that's over right? Wrong ! Parts are blistering again out of the zinc ! The plater is desperate ! Along comes old silver tongue Sam the chloride acid zinc salesman. He convinces the plater that for these parts acid zinc is what he needs and brings laboratory processed parts from his company's pilot line that do not blister. A panic panel of company big wigs vote the appropriation and zinc tanks are lined, titanium baskets purchased, all the good things needed are done and finally we get good parts--two weeks later the problem is back AND THEN--ONLY THEN do the thermo deburr foreman, plating foreman, and plating suppliers get together. The solution is simple. Do you know? Yep ! The bright dip installed early in this sad but true story was a chromate type, and the solution of the oxide problem had been replaced by a chrome contamination problem. There is a happy ending. A non chromate bright dip was substituted. Silly yes but sad the plater never really let the deburrer know his problems and needs ! It took 21 months to write off all the unnecessary equipment expenses of converting from alkaline to acid zinc !

Case 2

The plating foreman after a three month trial and error project had finally found a soak cleaner that would remove the-much-to-be-desired sulfonated cutting oil that allowed the cutting and milling department to machine brass fittings. An electropolish process for the copper tubing brazed to these fittings had been the project the year before. One little catch however, the tubing had a better finish than the fitting and the electropolish did nothing for the brass fitting--so here we go again ! It was decided to utilize the barrel burnishing department. The capacity was available and the burnishing foreman was pleased. The parts came out of the burnishing department "like jewelry". Everyone was pleased. Let's not agnoize the days, nights and weeks that followed. Let's just follow the parts and tell what we now know as what happened. The burnishing foreman worked out his cycle times, the correct media (Dear Plater ! they are not called rocks !) and tumbling speeds. The parts with a soap film then went to the automatic brazing equipment. The amount of brazing flux had to be increased, more heat was required, considerably more spitting occurred but good silver brazed joints were made in the joining of the copper tube and the fitting. The parts then went to the electropolish machine wherein the polishing action released trapped stearates that within 3 weeks contaminated the electropolish solu-

tion to the point that selective etching was occurring. The plater couldn't hide or level out the etching and the splattering that was showing up as "bumps" on the finished product. And just to make sure that "Murphy's Law" was in complete command, the 100% pure copper recovered from the electropolish had organics and zinc and silver metal in it so it no longer commanded top dollar in resale ! Oh yes the plater and the burnishing foreman got together. The plater gave the burnishing department a drum of his super soak cleaner; cycles were reevaluated and affected. During these weeks of Murphy mania all tubing was sent out to a buffer. That alone had added $2160/day to the cost of operation until the solution was found ! This is not a fabricated story, it really happened ! Are you starting to see the message I have for you? Let's look at some of the other items in my INCOMPLETE LIST.

Case 3

Did you hear the one about the process engineer who solved the problem of parts coming into the plating room with corrosion due to the inadequate attention to drying in that "black hole" they call the burnishing department? The deburring department promptly found a chemical company that supplied them with a rust preventative that worked on all base metals. A very small 5% by volume addition of this magic elexir added to a final rinse stopped the rust, water stains, etching, and psoriasis. Can you begin to imagine how expensive this "solution" was to the plater in his electroless nickel line before he was able to pin down why he kept "blowing" baths from the drag-in of residual acrylic lacquer (it had a little chrome in it too) !

Case 4

Oh yes and the plater who forgot to tell the tumbling room that the tote boxes with those innocent steel-copper assemblies were loaded with steel fines and, if he didn't wash the parts first he could spend days trying to find a media that didn't scratch the part. His media in the tumbling action was becoming embedded with steel particles. The result was not to dissimilar from what happens to highways when exposed to studded snow tires !

Case 5

And the frustrated tumbling foreman who couldn't seem to get any polishing on the new aluminum job be inherited--the hard anodized aluminum job !

Case 6

Here's a honey ! Hard spot in the copper stop off. This plater was doing copper stop off prior to selective carbonizing and it wasn't doing the job. He changed suppliers three times. Twice by slide-in conversion; once by making up a new bath to no avail. Switched his whole operation from cyanide copper to pyro copper before he found out that the burr removal operation that preceeded his operation was the culprit. How? Well the burr removal department got a new centrifugal deburr machine and these particular parts turned out to be a 20% savings when compared to his vibratory operation. A fact-

centrifugal deburring has an excellent bonus, it introduces compress strength properties to the surfaces so processed. No one told him there was a problem ! In fact he didn't even know what happened to the parts after they left his department.

Case 7

The case of the zinc diecast plater that accused his supplier of having shipped him a bad batch of cleaner, accused his bulk acid supplier of filling his storage tank with an oil contaminated muriatic acid and likewise accused his copper brightener supplier; his source of copper cyanide, sodium cyanide, and caustic soda of having slipped him some of that foreign junk. $150,000 worth of scrap parts later, the problem was traced to the burnishing room where a change in the hardness of the media had cut the processing time by 20 minutes per load in the vibratory machine. Oh yes and had produced a peening over and complete hiding of cold shot on the parts. Murphy, and his law had done it again. At the same time the burnishing deparmtnet made its changes, the diecasting department had instituted a "cost saving" program of using remelt of scrap parts !

Case 8

And don't ever forget, the plater gets the part last and so if the finished dimensions are wrong the plater did it ! Why all the fuss? The load was supposed to come out of the tumbler 5 minutes before lunch. They got two hours instead of one--they should be twice as good ! !

I gave this talk a title of "I Didn't Know That" and it has two meanings. The poor guy stuck with the problem really doesn't know why and the poor guy who did it to him doesn't necessarily know who and why he caused the problem. With the sophistication and growth of technology progressing moving at such a rapid pace in today's market one think has become evident. The days of "I'll run my department keep my nose clean, my operations up to snuff are no longer a policy for job security and serenity.

It is the rare, and I believe it, rare case when you find someone deliberately performing their job knowing it will provide defective parts. The fact is that it is ignorance. Not ignorance in the sense of intelligence but rather ignorance in the area of not being kept abreast of and aware of the effect their function provides as it contributes to the finished product.

Our hope with these cases today is to bring about an awareness that we all are an important part of the end product. No part of the many steps that go into this end product can be any better than the input of what has transpired by the time the part gets to your department. The subsequent operations are dependent upon what you do in your part of the operation.

What may seem to be a minor change to you in your operation can become a well intended but extremely costly addition to the next operation.

If you have ever in the past been able

to say in response to a production problem, "I didn't know that" you have also probably been able to say something like, "they never tell me anything"; they expect us to fix all the mistakes they make; "we are only a plating room, I'm not a miracle worker !"; the company treats our department like the "black hole"; etc. etc. Having made the statement you're right ! If you are then, content to crawl back in your "black hole" you're wrong ! The challenge is for you to educate the others as to your limitations and develope the atmosphere that through your willingness to try, they will become aware of and think about involving your department and your needs into their processing operations. It is a big challenge, something that won't happen overnight AND it won't even start to happen until you make the first step.

Remember the list this se sion started with?

- Soils and oils
- Soap
- Brazing Fluxes
- Protective films
- Oxidized surfaces
- Weld scales
- Base metal particles
- Acid and alkaline films
- Dimensional variations
- Physical surface properties
- Imbedded particles
- Porosity
- Trapped Media
- Peened down burrs
- Destruction of media

Let me leave you with just two thoughts. If machining operators have left a difficult soil from a "new improved" cutting oil. Who has the best technology and facilities to determine how to remove this soil? The tumbling and deburr department with the tubs, barrels, and bright dip tank or the plater who has 15 peddlers a day calling on him with "super cleaners"? You may be pleasantly surprised by the possible "ego trip" you give to the plater by asking his help.

If parts are coming to the plating room etch stained, oxidized, under size, or with media jammed in recessed holes, what do you think might happen if instead of rejecting or scrapping the travel ticket you go back to the deburr room, parts in hand and explain why you can't process the parts and could he help you?

Another possible ego trip? you bet !

Three billion dollars a year are being spent to remove burrs, a conservative estimate is 10% of these operations are being performed wrong the first time around ! Ninety-five percent of this $300,000 dollars can be eliminated if the right people are aware of the problem and needs of the "next department's operation".

"I didn't know that !" will not cease being the justification for these kind of energy and money loss until we collectively educate each other !

L-6

# Mechanical Finishing Session L

## Mechanical Finishing—From Craft to Technology

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# MECHANICAL FINISHING -- FROM CRAFT TO TECHNOLOGY

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## Abstract

While performing a vital function within industry, mechanical finishing has not developed as a full technology. Electroplating has. This paper discusses current trends in mechanical finishing in the U.S.A. and elsewhere, and offers some suggestions for its future development.

## Introduction

The cost of electroplating a car bumper, a lady's brooch, a bathroom faucet or a domestic doorknob is well known by the manufacturers of those products and, given accurate specifications, it is quite readily calculated by the electroplating technologists. Mechanical surface preparation costs of those products prior to electroplating are not as well known nor are they readily calculated or even estimated. Only half the respondents to a recent SME survey of deburring operations within the metalworking industry could offer reasonable estimates of the proportion of the total manufacturing costs attributable to deburring and surface conditioning. Only half of those respondents could analyze their mechanical finishing costs by labor, materials and overhead.

The survey covered automotive, heavy equipment, precision machined parts, household products, appliances, general metal goods and job shops. The questionnaire for this survey was sent to the chief production executives of companies ranging in size from 50 to 5,000 employees. The requested information concerned the burrs formed by all traditional machining and forming processes on all metals and plastics. Of the companies surveyed which did have some understanding of the cost of mechanical finishing, a very high proportion estimated that the total exceeded ten percent of the manufacturing cost of its product. For parts which were to be subsequently decorative electroplated, the mechanical pre-plate finishing averaged about 15 percent of total cost.

## The Present State Of The Craft

This table shows the mechanical finishing costs of some typical products as determined by the SME survey.

| PRODUCT | TOTAL COST A $ | MECHANICAL FINISHING COST B $ | $\frac{B}{A} \times 100$ |
|---|---|---|---|
| Car bumper | 28.50 | 4.50 | 15.8% |
| Bearing | .30 | .02 | 6.7% |
| Lady's brooch | 7.50 | 3.50 | 46.7% |
| Faucet | 3.00 | .60 | 20% |
| Aircraft compressor blade | 25.00 | 6.50 | 26% |
| Door knob | 4.00 | .28 | 7% |
| Dental Partial | 12.50 | 6.00 | 48% |
| Aircraft gear | 30.00 | 11.00 | 36.7% |
| Golf club head | 1.86 | .66 | 35.5% |
| Pocket knife | 7.90 | .60 | 7.6% |
| Carbide tool insert | 1.50 | .10 | 6.6% |
| Spring clip | .14 | .10 | 7.1% |
| Car door handle | 1.40 | .17 | 12.1% |

The technology of mechanical finishing is as important as that of electroplating. Indicators show that the importance of mechanical edge and surface conditioning will increase faster than the need for development of improved electroplating processes. It must ... The SME survey showed that the most common method of mechanical finishing is still manual -- filing, scraping, brushing and buffing. Fewer than half the companies surveyed had automated their finishing methods and few have quantitative standards. The science (and part) of edge and surface conditioning will surely not develop until it is accepted by U.S. industry as a technology of major importance.

As with so many fields of engineering, the U.S.A. has been, and still is, the leading developer of processes and automated machinery. It is a matter of some concern then to learn that similar surveys carried out in Japan and Europe reveal greater interest in and knowledge of mechanical finishing than was revealed by the survey conducted in the U.S.A. despite the fact that the mechanical finishing equipment and materials produced in the U.S.A. are unquestionably the best in the world. The use and application of the most modern finishing equipment is growing faster outside the U.S. than within. Several countries have more immediate and long-term research and are offering more training in better finishing methods. U.S. industry is not planning fully for the much needed development of our technology.

For the U.S. supply industry to be in advance of its user industry is an unsatisfactory and obviously unstable state of affairs. It can be resolved in one of two ways. The first possibility is that the U.S. suppliers of metal finishing equipment and materials will increasingly rely on the scientific progress and technical opinions of foreign user industries. The inevitable result -- the U.S. user industries will fall farther and farther behind and will surely lose all hope of profitable export markets.

The preferable alternative is for U.S. industry, immediately and as a whole, to explore the available expertise of its mechanical finishing technologists. It must collaborate with them in planning and supporting a long-term program of research and development. It is surely such action that has revitalized the electroplating industry.

Improved methods of electroplating have allowed lesser pre-plate surface condition to achieve acceptable final quality of many products. This has not produced the need for mechanical finishing, nor is it likely to. As consumer demand becomes more sophisticated and as performance standards of mechanisms become more stringent, there is increasing need for better mechanical finish on final and preplate surfaces.

Seventy percent of all metalworking companies still do some manual mechanical finishing and fewer than half of the metalworking companies have installed automatic mechanical finishing processes. This situation has changed little during the past five years in spite of the increased availability of automated equipment and the need for both economy and quality.

The standard mechanical finishing processes are mass finishing (tumbling barrels, vibratory, centrifugal disc, centrifugal barrel and spindle finishing) buff, brush and polish methods and the blasting techniques. Together, these must surely offer opportunities to mechanize more than 50 percent of all deburring and surface conditioning requirements of the metalworking industry. There is increasing need to handle higher precision parts, more fragile components and components of more complex shape. The standard processes have developed to meet these newer requirements and the capabilities of newer mechanical finishing processes have found greater application.

As is well known by the electroplating industry, today's requirements for decorative finishing are becoming ever-increasingly stringent. The product with an excellent surface finish is far more marketable than one with a mediocre surface. For functional surface finishing, improved standards have shown quite startling benefits. Fuel consumption of automobiles has been improved by five percent as a result of better surface conditions on moving parts. Improved edge and surface condition has been an important means of reducing effluent problems. The aerospace industry has found perhaps even greater benefits by improved finish on engine and frame parts. Not only does the well-finished component have higher efficiency, but also longer life and a reduced likelihood of premature fatigue failure.

## The Need For Development

It seems inconceivable that manual filing, polishing and buffing will be acceptable finishing techniques for the future. Not only are these manual methods far too expensive, they demand 100 percent inspection and are certain to produce inconsistent results. The consumer will become evermore discerning. It is reasonable to assume that the benefits of improved edge and surface condition for improved performance, efficiency and safety will become more fully appreciated. The need for more and better equipment and faster development of the technology is essential.

Ten years ago, the metalworking industry was hoping for dramatic changes in the forming processes. It was hoped electro-chemical machining, electrical discharge machining, precision casting and precision forging to size might produce parts which would not need further finishing. This has not occurred -- to the contrary -- the likelihood of its happening in the next few decades is (at best) remote. The industry also anticipated that all the improved coating techniques would result in reduced need for mechanical finishing. This has not happened either and almost certainly will not.

The metal forming processes are being developed to achieve parts of more consistent quality finish. This will mean that parts coming to equipment capable of accurate finishing will have truly uniform final condition. This greatly facilitates more highly automated finishing equipment so that we can (in the future) expect mechanical finishing to be built in line with the forming and coating processes. It will be program controlled and capable of handling a variety of different parts, either simultaneously or in quick succession.

Research and development is needed for precise, quick and economical measurement and control of edges and surfaces. The first step is to educate the engineer to realize that a drawing of a component without specifications for edge and surface conditions is as incomplete as one that does not specify dimension and tolerances or one that does not specify the final coating to be applied. It is, of course, fruitless to incorporate close specifications unless the results can be measured and controlled during the manufacturing process.

Mechanical edge and surface finishing will be a standard part of the production of most components for many years to come. The need for better edge and surface conditions will increase so there is need for engineers educated in the technology of mechanical finishing.

## The U.S.'s Position in the Technology of Mechanical Finishing

There is currently no formal undergraduate program available in the U.S.A. to train a mechanical finishing engineer. There is no requirement of the student of mechanical engineering or manufacturing engineering to take any courses in mechanical finishing. It seems almost incredible that no university in the country is encouraging any studies in this vital engineering subject. The U.S. is lagging behind other countries.

The total U.S. sales of fabricated metal goods is in the order of $400 billion. If cost of deburring and surface conditioning is only five percent of the cost of these products, then $2 billion per annum is being spent on labor and materials to mechanically finish the products. That there should be a $2 billion business in the U.S.A. with no formal technological training to back it is clearly a deficiency which needs rectifying. The electro-plating business is not as large in terms of direct labor employed as mechanical edge and surface finishing, yet the technology has grown much further.

In several European countries, and in Japan, the technology of mechanical finishing is growing fast and is being supported by good formal education. In many countries, there are courses in mechanical finishing which are mandatory for the student manufacturing engineer or production engineer. At a number of foreign universities, there are excellent undergraduate courses being offered where the engineer can major in mechanical finishing. There are opportunities for graduate study. In Japan, there are now a number of professors of mechanical finishing. Many research projects are currently underway in Japan and already the results are beginning to emerge with new deburring and finishing processes, computor selection of the most effective processes for given products and new forms of measurement and control. There is government support of some research projects and industry support of many more.

Here in the U.S.A. it seems that a few technical societies, and yet fewer technical publications, are offering some encouragement for increased knowledge in the field of mechanical finishing. The Abrasive Engineering Society, American Electroplaters Society and the Society of Diecasters all encourage papers on the subject and appear to receive these papers well. The American Society for Metals is starting to take interest and the Society of Manufacturing Engineers is more deeply involved. The SME has a Burr, Edge and Surface Conditioning Technology Division which has published a number of books and a video tape. It is encouraging technical research. It supports some research projects, has carried out some market research exercises and develops comparisons of different mechanical finishing techniques.

If the U.S. supply industry is to maintain its lead and if mechanical finishing is to become a mature technology, there is a critical need for education. There is a need to educate industry and in doing so, to receive the proper support of academic institutions. There must be stronger encouragement for graduate work. Electroplaters must surely encourage this. When presented with better and more consistent surface condition; the electroplating department can become more efficient, more economical, and produce a better final product.

## Concusions

During the next few years, the technology of mechanical finishing can progress faster than most other technologies. The first steps are being taken and these show how the technology of mechanical finishing offers means of improving industry productivity and quality of many products. In particular, the tasks of the forming and coating engineers are greatly facilitated. The companies that are employing mechanical finishing engineers and are investing a proper proportion of capital appropriation in finishing equipment, are those which are improving their products and productivity.

The proper development of the technology of mechanical finishing is one of the most important and worthwhile means of improving productivity, product performance, appearance and consistency of quality. Creative and enthusiastic use of this developing technology in U.S. industry is a step toward meeting increased international competition.

Bibliography

Advances In Deburring, SME Book 1978, edited by LaRoux K. Gillespie.

Cost Guide For Automatic Finishing Processes, SME Book 1981, edited by Lawrence Rhoades.

Hignett, J. B., Mechanical Finishing--Is Progress In The U.S.A. Keeping Up With International Competition?, Metal Finishing, March 1981.

Hignett, J. B., Mechanical Finishing--The Future For This New Technology, SME Technical Paper MR81-383.

# M-1

# Energy & Materials Conservation Session M

## Removal of Acids or Bases from Aqueous Solution by Donnan Dialysis

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# Removal of Acids or Bases from Aqueous Solution by Donnan Dialysis

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It is often desirable to neutralize acids or bases in aqueous solution. The conventional approach is to add an appropriate amount of base or acid. Extreme care, however, has to be exercised in systems involving strong acids and strong bases. Introduction of foreign ions into the solution is another problem. In some cases, contamination of the solution by the additional ions cannot be tolerated.

One application is found in the improvement of the new process for making potassium gold cyanide. Potassium gold cyanide is produced by reacting fine gold particles with oxygen in cyanide solution[1]:

$$2\ Au + 1/2\ O_2 + 4\ KCN + H_2O \longrightarrow 2\ KAu(CN)_2 + 2\ KOH.$$

Note that it can be developed as a closed cyanide loop process when the side product KOH is removed. After the main product (potassium gold cyanide) is separated, the solution can then be re-used. Thus no cyanide waste solution is generated and the cyanide ion is contained in the system. If the KOH were neutralized by adding an acid, then the accumulation of the potassium salt would make the recycling impossible. It is therefore desirable to remove the KOH and not to neutralize it.

Another application is in extending the life of plating baths. For example, in a tin-plating bath containing an alkali metal stannate, the would last longer if the potassium hydroxide generated were removed. Similar reasoning is applicable to precious metal plating systems with insoluble anodes. In gold plating with oxygen anodes, the overall reaction is:

$$H_2O + 2\ KAu(CN)_2 \longrightarrow 1/2\ O_2 + 2Au + 2\ HCN + 2KCN.$$

At typical plating conditions, the cyanide ions are hydrolyzed and the HCN formed would evaporate frrom the solution because of its low boiling point. The reaction becomes:

$$3\ H_2O + 2\ KAu(CN)_2 \longrightarrow 1/2\ O_2 + 2\ Au + 4\ HCN(g) + 2KOH$$

When the KOH is removed, the bath composition would remain unchanged and the solution, in principle, would not have to be changed. In other systems, the side product can be an acid instead of a base. For example, in the plating of ruthenium with insoluble anodes, the acid HCl would be the side product if the chloride salt of ruthermium is used to to replenish the bath.

One means of separating acids and bases from solution is Donnan dialysis with an appropriate cationic or anionic membrane. Because the permselective types of membranes have fixed charges incorporated into their structure and are permeable to ions of the opposite charge and not to ions of the same charge, the Donnan[2] equation governs the equilibrium relationship. In a cell with a cationic membrane, the equilibrium equation relating the cation activity in the two cell chambers is

$$( C_{iR}^{Z+} / C_{iL}^{Z+} )^{1/Z} = k ,$$

where $C_i^{Z+}$ is the activity of the $i^{th}$ cation of charge Z; R and L refer to the solutions on opposite sides of the membrane; and k is a constant for all cations in the system. Note that concentration ratios, not concentration differences, are the important factors in determining the equilibrium. For example, if equal volumes of 1.0 M KOH solution and 1.1 M $HNO_3$ acid are initially on each side of the cationic membrane, the equilibrium concentation of potassium ion $3 \times 10^{-9}$ on the feed side and is 1.0 M on the stripping acid side (Appendix I). In effect, the excess hydronium ions pump the potassium ions across the membrane. The complete removal of potassium ions can be accomplished without a large amount of stripping solution.

Donnan dialysis as a separation process has been investigated by Wallace[3] in the stripping and concentration of dilute cations, mainly uranyl ($UO_2^{++}$) ions. Davis et al.[4] worked on similar systems with recycle. Smith[5] studied sodium-calcium exchange for water softening

applications experimentally. In their work on the mass transfer characterization of Donnan dialysis, Lake and Melsheimer[6] reported evidences of mass transfer resistances from the membrane and from both feed and stripping boundary layers. Their studies were performed in a nitrate system with a NAFION* 120 membrane (equivalent weight 1200, 10 mils nominal thickness). The coion (nitrate) leakage transport was found to depend only on temperature and the stripping acid concentration.

In the literature, the main application of Donnan dialysis is in the exchange of ions between two solutions. No paper has mentioned its use as a means of removing acids or bases from solution. Based on the data reported, such an application poses no difficulty. In the present memorandum, the main focus is specifically on removing KOH. The method can be easily generalized to other applications. In this particular case, the membrane is a cationic type and the stripping solution is an acid. The dialysis process works in this manner: the hydronium ions diffuse into the solution and neutralize the hydroxide ions while the potassium ions diffuse out.

One relevant question needing an answer is whether such a process can be implemented so that the rate is sufficiently fast for the proposed process. A promising dialysis arrangement is to incorporate a coil of cationic membrane tubing into the solution from which the KOH is to be removed and to pump the acid through the coil. The necessary stirring is provided by the stirring of the solution and by the pumping of acid on the stripping side. This set-up requires minimal change on the apparatus and yet provides a large surface area. Because the membrane has to be stable in both strong acidic and strong basic media, du Pont's NAFION membrane was selected for the present study.

In the present work, the objectives were to show the feasibility of removing KOH by Donnan dialysis and to determine the rate of such removal by using a coil of NAFION tubing.

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*Trademark of E. I. du Pont de Nemours & Company.

**Experimental**

Figure 1 schematically depicts the apparatus. The membrane tubing, NAFION 810 (1100 equivalent weight, 1/8 inch o.d., 15 mils thick), was kindly supplied by E. I. du Pont de Nemours & Co. The length of tubing submerged was 88 cm and the outer surface area was 88 $cm^2$. The coil of membrane tubing was supported by a 1/4" Teflon rod. With a diameter of 4.5 cm, it has six loops. The stripping solution, 100 to 300 ml of 1-2 molar HCl or $HNO_3$, was circulated through the coil by a peristaltic pump (Cole-Parmer). For the runs at temperatures higher than 22°C, the heat was supplied by a hot plate and the temperature was controlled manually. The KOH solution was stirred by a magnetic bar.

The rate of the KOH removal was determined from the time the hydronium ions took to neutralize 150 ml of 0.17 M KOH solution. This lets the experiment be finished in a reasonable amount of time. A run is over when the pH is less than 7, usually in 30 minutes.

**Results and Discussions**

Table 1 summarizes the results for different conditions. Parameters investigated were the type of acid, the acid concentration, the flow rate of the stripping solution, and the temperature. There is no significant difference between the runs using HCl and $HNO_3$ as stripping solutions. The concentration of the acid and the flow rate of acid solution through the coil also have no substantial influence. This suggests that the rate-limiting step is not due to the mass transfer resistance in the acid solution when the flow rate is higher than 1 ml/sec . It is likely to be the diffusion inside the NAFION membrane.

Temperature is the most important parameter affecting the rate of KOH removal (runs A5, A6 and A7; runs B1 and B2). The flux using HCl solution at 60°C is about twice as fast as that at 22°C. Similar results are obtained for $HNO_3$ solution. The flux increase can be attributed to the temperature dependence of the diffusion coefficient of ions and the membrane swelling characteristic. It is in agreement with the data reported for the diffusion of NaOH through NAFION[7].

There remains the question of whether Donnan dialysis is a practical means of removing KOH. For the small coil of NAFION tubing used in the present study, the diffusion rate of hydronium ions is about 0.1 mole/hr. In the process of making potassium gold cyanide, one mole of KOH is formed for one mole of gold dissolved. The rate is equivalent to 20 grams of gold per hour, the same as the rate of gold dissolution in the laboratory studies.[1] Thus a closed cyanide loop process with a Donnan dialysis set-up can be developed. As for extending the life of plating baths, Donnan dialysis is also adequate. The present coil removes KOH at room temperature with a rate equivalent to 1 ampere, assuming that one mole of KOH is generated for one equivalent of the metal plated.

In summary, the feasibility of removing KOH by Donnan dialysis was demonstrated with HCl and $HNO_3$ as stripping solutions. The diffusion rate of hydronium ions through the NAFION membrane (type 810) is temperature dependent. With the membrane tubing as a coil, the type of acid and the acid concentration do not influence the rate significantly. For an 88 cm long 1/8 inch o.d. tubing, the flow rate also has no influence when it is higher than 1 ml/sec. At $60^{o}$ C, the dialysis rate is about $4 \times 10^{-7}$ mole/sec-$cm^2$.

**References**

1. Law, H. H., to be presented at the International Precious Metals Institute Conference, Newport Beach, CA in June, 1981.

2. Donnan, F. G., *Chem. Rev., 1,* 73(1924).

3. Wallace, R. M., *Ind. Eng. Chem. Process Design Develop., 6,* 423-31(1967).

4. Davis, T. A., J. W. Wu, and B. L. Baker, *AIChE J., 17,* 1006-7(1971).

5. Smith, J. D., O.S.W. Rep. No.506, U.S. Dept. of Interior, Washington, D.C.(1970), quoted from reference (6).

6. Lake, M. A. and Melsheimer, S. S., *AIChE Journal, 24,* 130-37(1978).

7. Berzins, T., presented to the 152nd Electrochemical Society Meeting, Atlanta, Georgia, Oct. 1977.

**Appendix I: Equilibrium Concentration Calculations**

Problem: At time zero, equal volumes of 1.0 M KOH and 1.1 N acid are on each side of a cationic membrane. What is the equilibrium concentration of the cations?

Let HA be the acid with an anion, $A^-$. Subscripts s and f denote respectively the stripping side (acid) and the feed side (KOH initially). From the Donnan equilibrium relationship, the mass balance, and the electroneutrality principle on each side of the membrane, four equations are obtained:

$$[K^+]_f \; / \; [K^+]_s \; = \; [H^+]_f \; / \; [H^+]_s \qquad (1)$$

$$[K^+]_f \; + \; [K^+]_s \; = \; 1.0 \qquad (2)$$

$$[K^+]_f \; + \; [H^+]_f \; = \; [OH^-]_f \; + \; [A^-]_f \qquad (3)$$

$$[K^+]_s \; + \; [H^+]_s \; = \; [OH^-]_s \; + \; [A^-]_s \qquad (4)$$

For an ideal cationic membrane, $[A^-]_f = 0.0$ and $[A^-]_s = 1.1$. With the dissociation constant of water equal to $10^{-14}$, equations (3) and (4) become:

$$[K^+]_f \; + \; [H^+]_f \; = \; 10^{-14} / \; [H^+]_f \qquad (5)$$

$$[K^+]_s \; + \; [H^+]_s \; = \; 10^{-14} / \; [H^+]_s \; + \; 1.1 \quad . \qquad (6)$$

Solving these four non-linear algebric equations (1,2,5,6) exactly is not straightforward, but we can make a likely assumption first and justify it afterward with the answers. By assuming $[H^+]_s >> [H^+]_f$, the calculations are simplified substantially and the answers are as follows:

$$[H^+]_s \; = \; 0.1 \text{ M}$$

$$[H^+]_f \; = \; 3 \times 10^{-8} \text{ M}$$

$$[K^+]_s \; = \; 1.0 \text{ M}$$

$$[K^+]_f \; = \; 3 \times 10^{-9} \text{ M}.$$

The values of $[H^+]_f$ and $[H^+]_s$ validate the assumption and the procedure is correct.

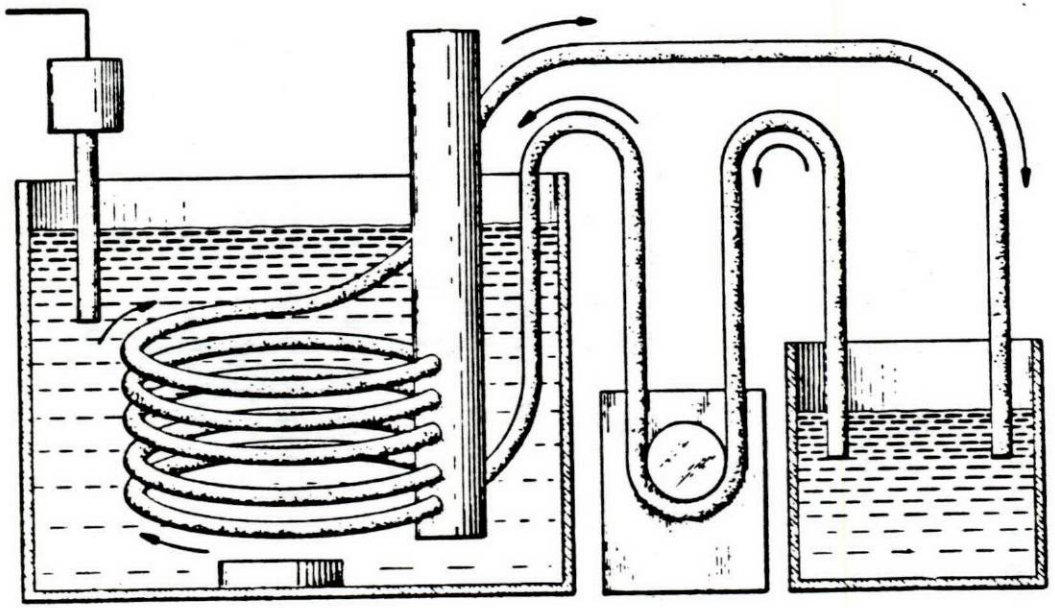


**Fig.1 Apparatus**

Table 1

| Dialysis with NAFION 810 Tubing (1100 eq. wt.) | | | | | |
|---|---|---|---|---|---|
| Acid | Run | Acid | Temp | Flow Rate | $H^+$ Flux |
| | No. | Conc.,M | ,°C | ml/sec | $x10^{-6}$ mole/s-cm$^2$ |
| HCl | A1 | 1.0 | 22 | 4.0 | 0.15 |
| | A2 | 2.0 | 22 | 4.0 | 0.18 |
| | A3 | 2.0 | 22 | 7.0 | 0.18 |
| | A4 | 1.9 | 22 | 1.5 | 0.16 |
| | A5 | 1.0 | 20 | 1.1 | 0.17 |
| | A6 | 1.8 | 40 | 1.8 | 0.31 |
| | A7 | 1.75 | 60 | 1.45 | 0.38 |
| $HNO_3$ | B1 | 2.0 | 22.5 | 1.3 | 0.17 |
| | B2 | 1.9 | 55 | 1.2 | 0.43 |

M-2

# Energy & Materials Conservation Session M

## Energy Savings in Exhaust Ventilation Systems

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# ENERGY SAVINGS IN EXHAUST VENTILATION SYSTEMS

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## Abstract

This paper will discuss two proven methods for significant energy savings in exhaust ventilation systems for electroplating.

One method deals with the return of scrubbed exhaust air utilizing a special return air damper, a return air diffuser system and a continuous monitoring device. The method is based on the continuous monitoring of all variables affecting air quality rather than monitoring actual air quality. The reuse of 85 to 95% of exhaust air is presently being achieved with this method.

The second method deals with energy savings through proper ventilation design, in particular a push/pull system that really works and at minimal cost.

## Energy Savings In Exhaust Ventilation Systems

I would like to talk with you today about two methods presently being employed to conserve energy in exhaust ventilation systems.

The first deals with the reuse of exhausted air from metal finishing and plating tanks.

For years the advantages of recovering plant air exhausted with a fume control system have been obvious, but the idea has only recently been successfully pursued. Some of the previous thinking was that:

1. There have been no Federal or State regulations covering return air.
2. The only known published data on return air systems is in the Ventilation Manual of the American Conference of Governmental Industrial Hygenists. This indicates that back-up scrubbers are recommended as well as continuous monitoring of return air quality. This sort of system is prohibitively expensive and the feasibility of continuous monitoring of return air quality is questionable or at best, impractical.

The concept basically is that it should be just as meaningful to monitor the factors that affect air quality rather than monitor the actual air quality. It follows, that if the quality of the return air is checked initially and found to be within limits, then there is no further need to monitor air quality if the system variables affecting air quality can be continuously monitored.

The return air system, then, consists of:

1. A standard exhaust ventilation system

2. An efficient fume scrubber

3. A system for returning the cleansed air

4. A device to adjust the air flow in or out of the plant and

5. A device to monitor the critical variables.

Let's discuss each of these components individually:

1. A properly designed ventilation system is essential to minimize stray fumes. Our industry normally designs to the exhaust rates as specified in OSHA standards and find them reasonable and effective.

2. A properly designed fume scrubber is the key to the success of a return air system. With most fumes resulting from metal finishing, printed circuit or semi-conductor operations, a wet type fume scrubber provides the best combination of efficiency and economy. The scrubber design must insure that the air being returned is cleaned to some degree below the threshold limit value. A formula for the allowable contaminant level in the return air is presented in the Ventilation Manual of the American Conference of Governmental Industrial Hygenists. The proper use of this formula requires a thorough understanding of the overall return air system.

3. Consideration must be given to proper design and location of the return air distribution system. Factors such as disturbance of exhaust air flow, personnel intensity, potential equipment damage and positive or negative plant air pressures should be considered.

4. It is essential that an air recovery system be able to not only return air, but to exhaust air when necessary. An exhaust stack with adjustable damper must be installed to allow all or partial exhaust of the fumes to atmosphere. During a period of scrubber maintenance or malfunction all fumes will be exhausted to atmosphere. During normal operation a percentage, say 5 to 15%, will be exhausted at all times, depending on the nature of the fumes, the efficiency of the fume scrubber and the location of the return air discharge. This 5-15% of air being continuously exhausted must be replaced with make-up air. The use of make-up air is essential to avoid the possibility of a build-up of contaminants in the plant air.

5. The last system component and the one that makes this whole thing feasible is the continuous system monitor. Fortunately, we are dealing with a minimum number of variables affecting air quality in this system. The critical variables are air flow and the water flow rate to the wet scrubber. Air flow can be affected by fan performance or clogging of the scrubber packing media. Both of these air flow factors can be monitored with a manometer and a pressure switch across the scrubber pack. The water flow rate is easily monitored with a flow switch in the recirculation pump discharge line. The monitor, then, consists simply of a manometer, a pressure switch, a flow switch and an alarm panel. The alarm panel is wired to give both an audible and visual alarm. If desired, it is possible to wire the alarm circuit to the exhaust stack damper. In this manner the fumes would automatically be exhausted to atmosphere upon a malfunction. A source of make-up air during a malfunction period must also be considered, but this need not be heated and an open door or such would suffice.

That about wraps up the air recovery system. Just to quickly summarize, the advantages are:

1. The return of 85 to 95% of exhausted air.

2. The reduction in requirements for heated air make-up with resulting fuel savings. In Michigan this would result in a savings of 75¢ to 85¢ per CFM per heating season.

3. Relief of negative pressure problems in the plant.

4. Improved circulation and ventilation, reducing drafts from windows and doors.

There are also a couple of possible disadvantages:

1. Formal OSHA approval has neither been asked for or received for this system. It was, though, recently reported that the EPA is considering using the concept of monitoring equipment variables as opposed to air quality. There have been no problems with OSHA or local agencies in the plants where return air systems are in operation.

2. If there is a system malfunction and fumes are not quickly diverted to atmosphere, a temporarily undesirable situation is created. This type of failure would only be associated with a recirculation pump failure which is unlikely without some prior warning.

The reuse of exhausted air has some definite limitations. Air return systems are not recommended on fumes containing potentially explosive substances or in situations where there is potential for creation of a toxic chemical by the mixing of two or more non-toxic fumes.

It is worthwhile to examine each situation to determine if a system could be split up to return the air only on a portion and exhaust the balance. In many cases there may be only one or two tanks out of several that require exhaust to atmosphere.

Up until now I've talked about energy saving by returning air. There are other approaches and savings.

One of the biggest savings is simply, do not exhaust more air than absolutely necessary. It is important to do an adequate ventilation job, and meet OSHA standards but costly to over ventilate.

In open surface tank ventilation, hood and duct design is the key factor to a properly engineered ventilation system which conserves energy, may it be heat, water or electricity.

As an example, if your system is over ventilated, this means larger horsepower motors, higher water usage, additional heat loss, extra air make-up and often a drafty working area.

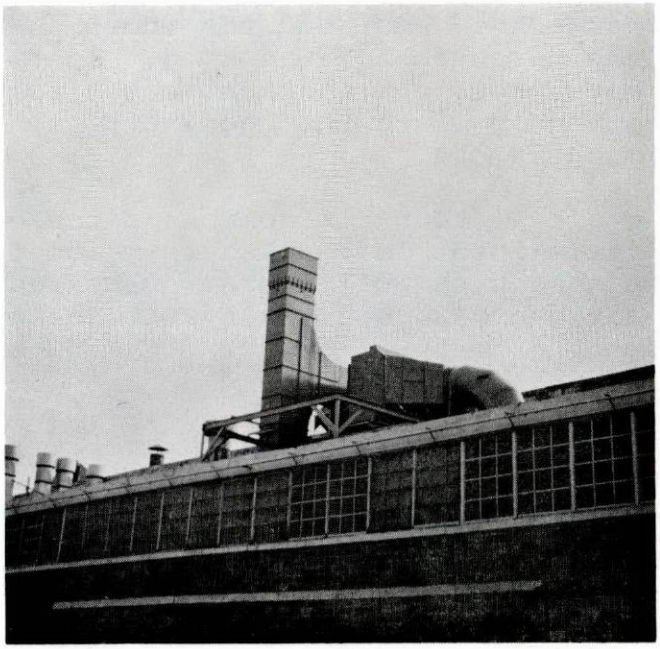
Engineering of the ventilation system starts at the hoods and the design will vary depending upon tank size, type of

fumes, temperature and the distance the fumes must be drawn. An exhaust hood will only draw air about 30". 36" is possible providing no plant negative pressure or cross drafts are present. Over 36" it is nearly impossible and push air should be considered.

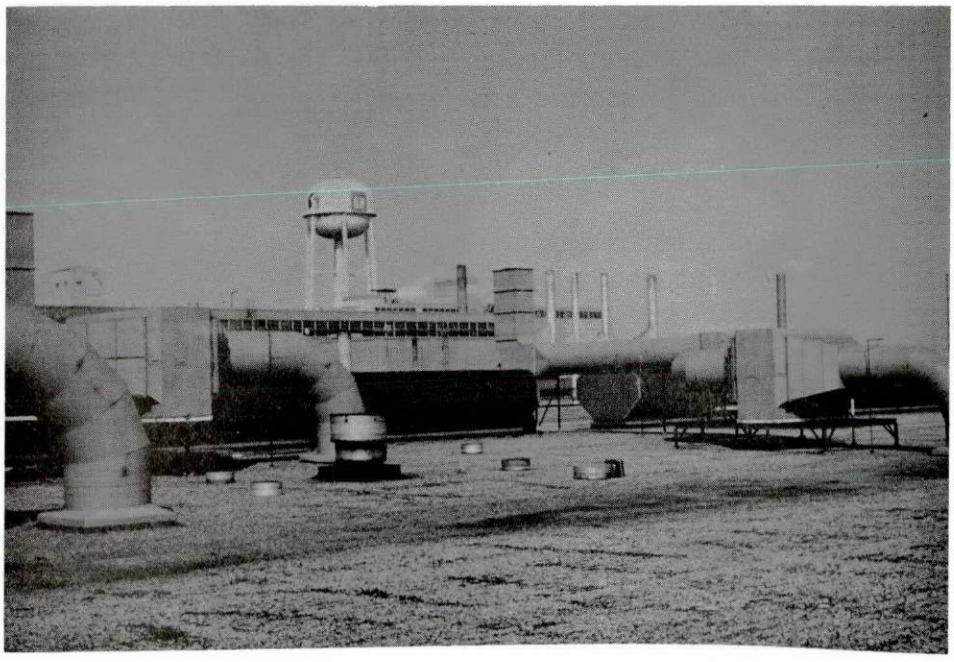
A unique concept is being used on push air that works beautifully. High pressure, low volume push air is provided at around 12 cfm per lineal foot of tank. This results in a small quantity of air forming an air curtain on the side opposite the exhaust hood and send the fumes away from the operator and in the direction of the hood. It's like shooting needles of air across the tank above the solution level. The fumes will not only reach the hood, but the total cfm can be reduced as much as 30%.

Pushing air 4' to 8' is common in these systems, but in some cases it is possible to push from 15' to 30' with a properly designed push-pull system. The reduction of 30% by using push air can be a big savings in energy with little added cost.

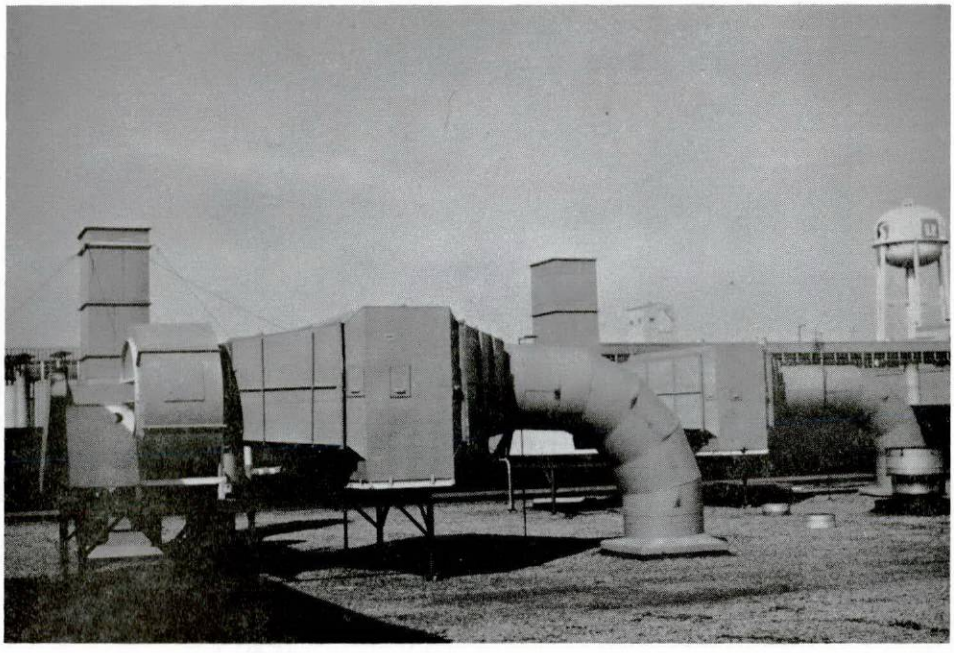
There are many other energy saving factors in a properly engineered ventilation system, such as the use of shields, proper transitions, correct velocities and proper stack design. In these days of high energy costs, the savings resulting from a properly engineered exhaust ventilation system can be significant.



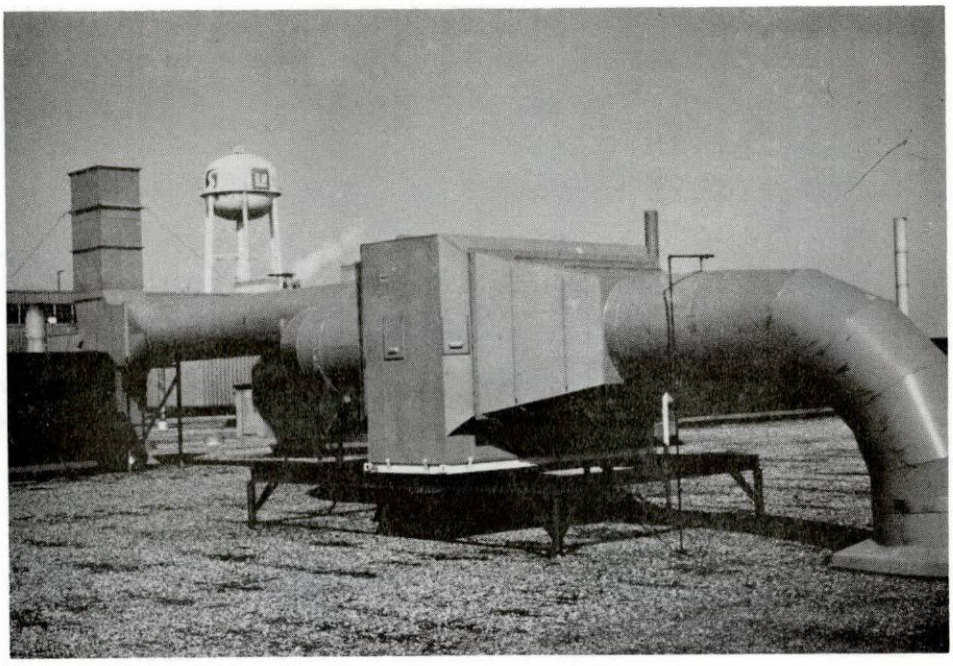
This picture was taken at a major appliance manufacturing plant in Mansfield, Ohio in 1972. The project consisted of four systems, one on a chrome plating line, one on a nickel line, one on a pickel line and one on a cleaner line. The picture shows the roof mounted fume scrubber with stack and return air section.



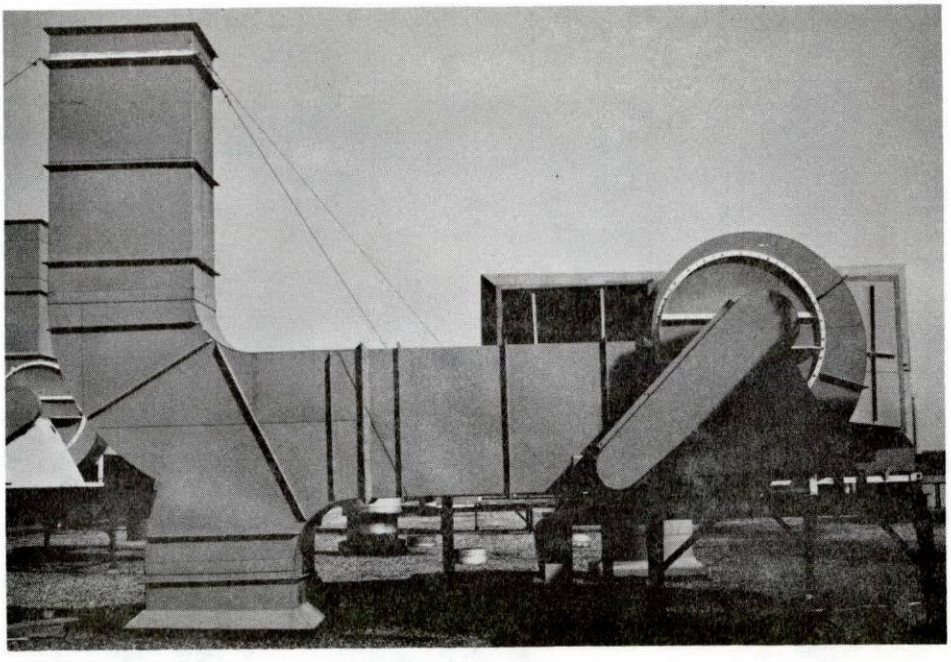
This and the following series show three systems installed in June of 1981 at an automotive plant in Saginaw, Michigan. Two of these systems are set up for return air on caustic cleaners, zinc phosphate and phosphoric acid. The third system was exhausted to atmosphere. Of a total exhaust of 104,000 CFM, 67,000 CFM is being returned for reuse.



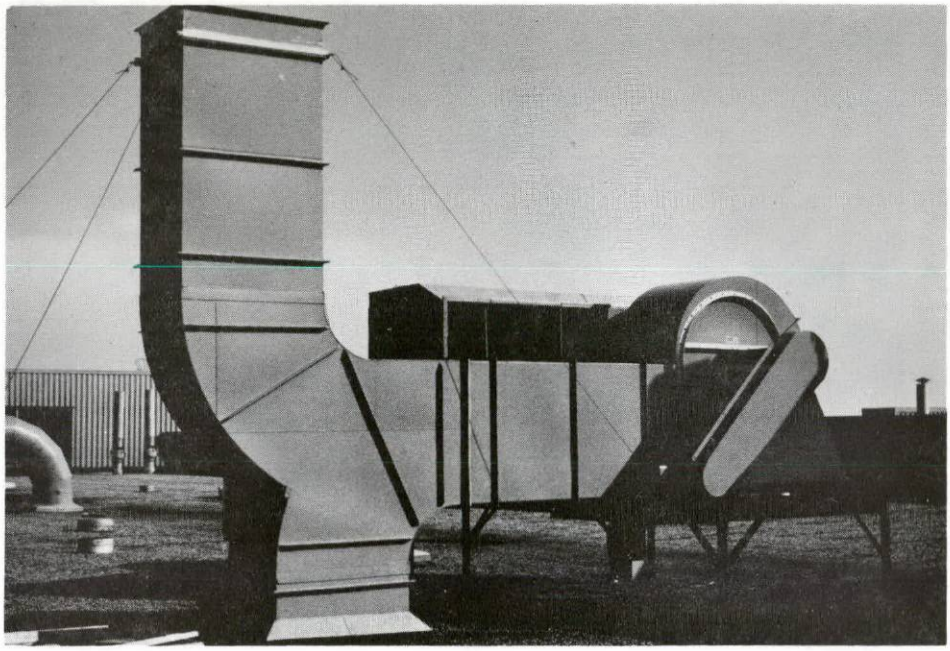
Two of the three systems, note the roof mounted fume scrubbers



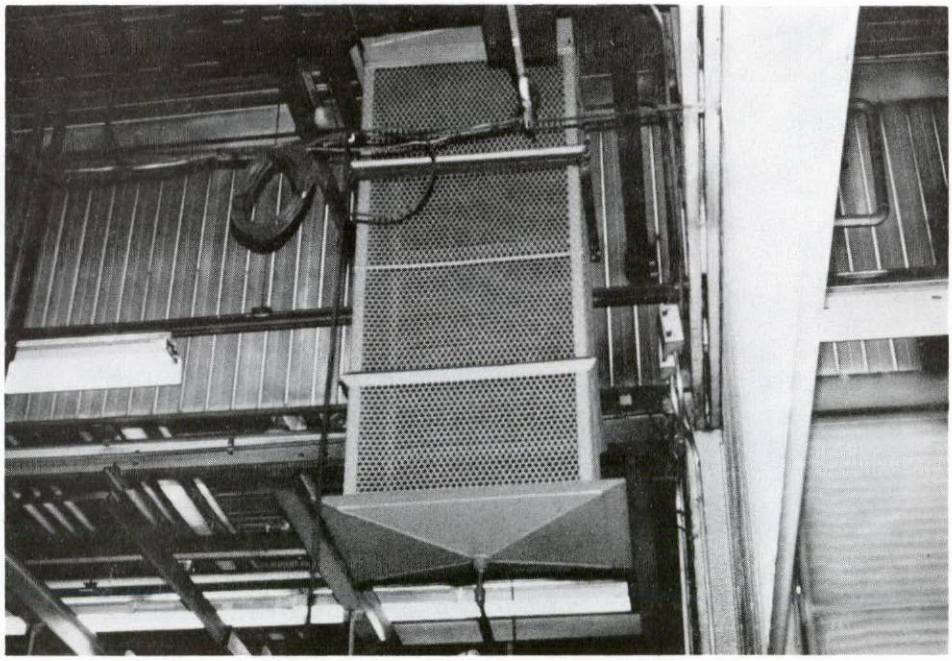
One system, note the long radius elbows for low energy loss



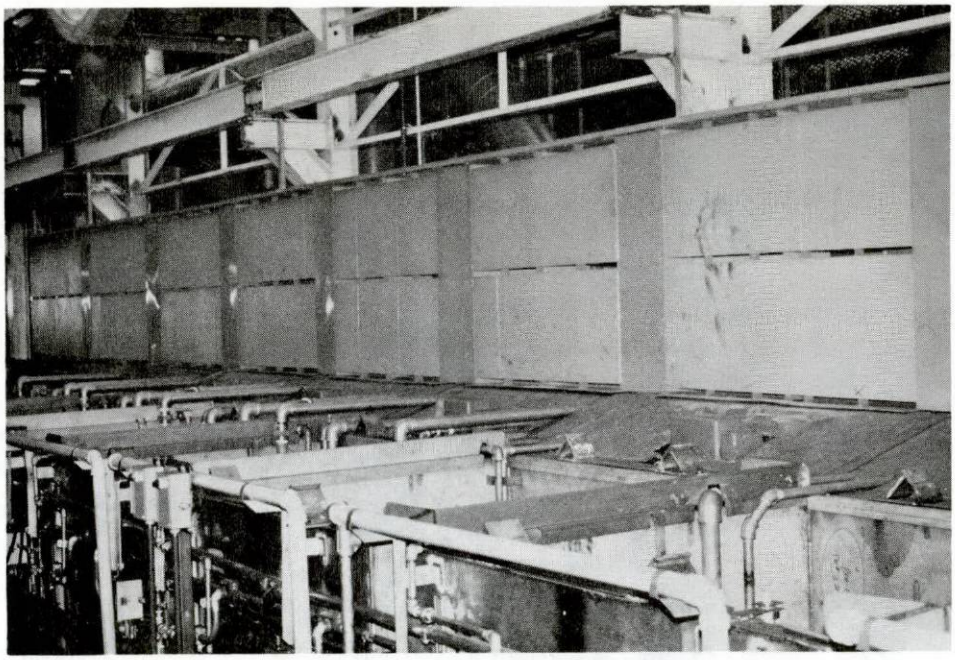
Exhaust fan with stack and return air duct



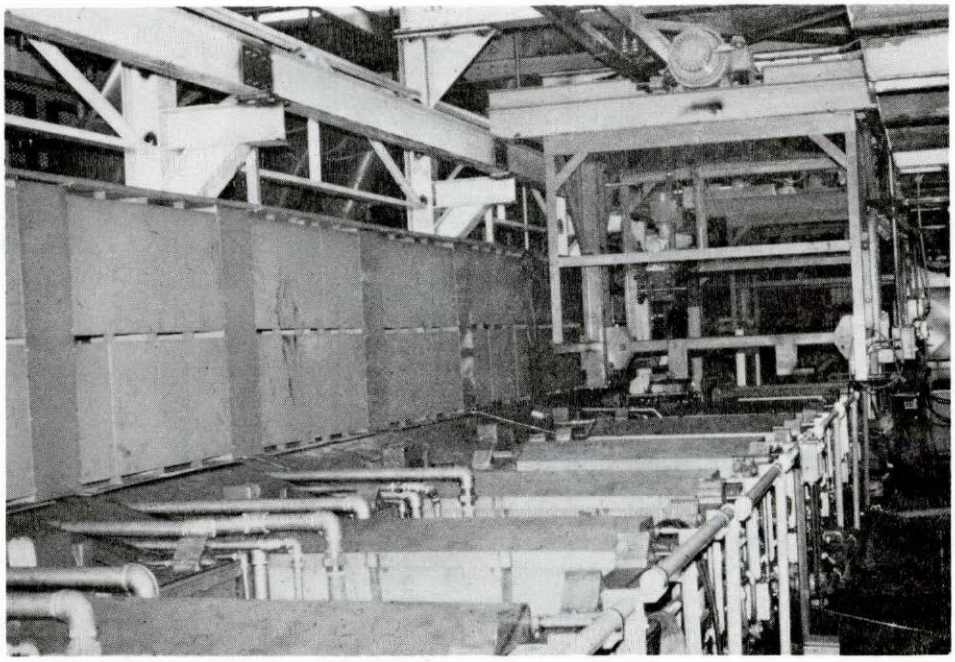
Note adjustable damper at the juncture of stack and return elbows to adjust quantity of return air.



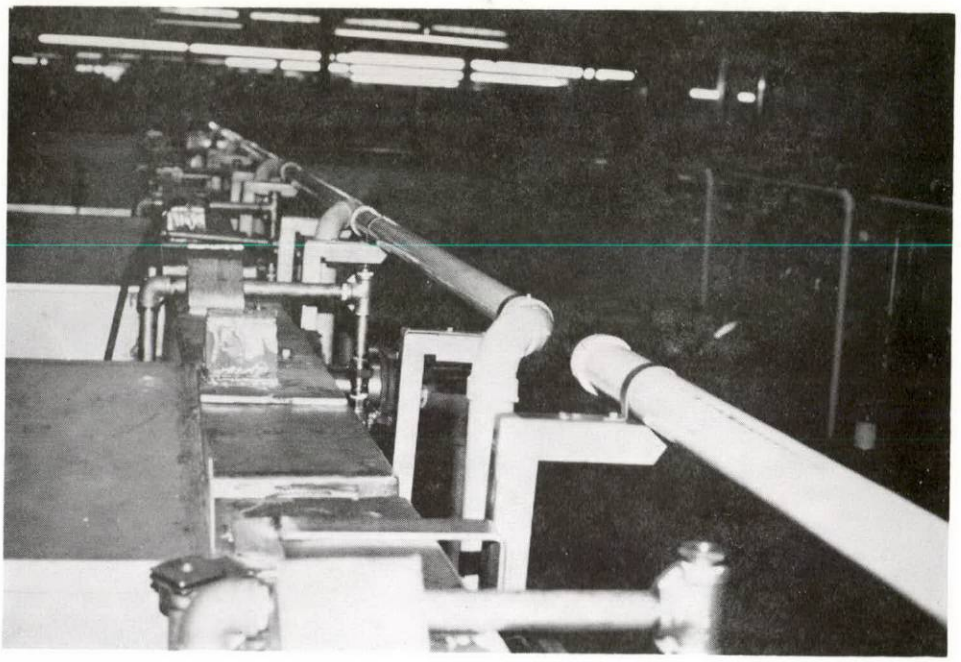
Return air discharge, note perforated walls for effective air distribution and drain pan on bottom for moisture removal



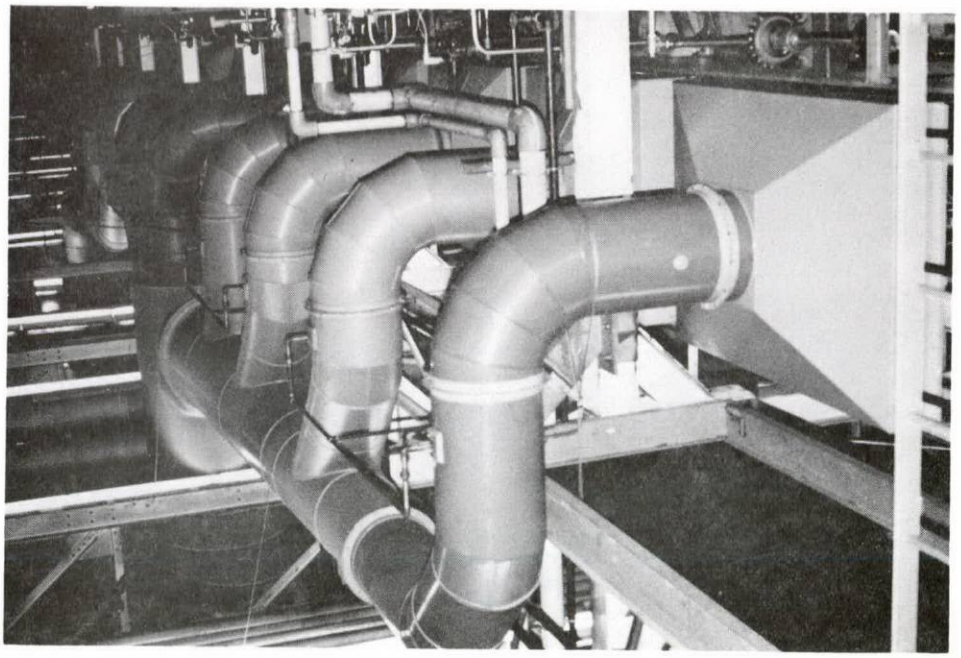
Exhaust hoods, note push pipe, shields between hoods and shields on top of hoods.



Exhaust hoods, note set back on exhaust hood with shields between hood and tank to reduce air loss



Push pipe, note offset from tank due to equipment interference, but the push system is still very effective



Rear of hoods, note long radius elbows and laterals into tapers for low static pressure loss

# M-3

# Energy & Materials Conservation Session M

## Reduced Water Consumption Through Improved Plating Room Design

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Kearny, NJ

# REDUCED WATER CONSUMPTION THROUGH IMPROVED PLATING ROOM DESIGN

(A. V. Siaweleski)

## INTRODUCTION

Western Electric's Environmental Policy Statement includes, together with the need to comply with existing laws governing environmental protection, a policy to conserve, recycle, and reuse materials wherever such practical possibilities exist. The consolidation of several satellite plating facilities into one central finishing plant, to enhance our overall environmental planning, was started in early 1970. Reduction of water usage was made possible during this period through the effective use of monitored controls and plating equipment layout. Further reductions were implemented to meet New Jersey's 1981 mandate to reduce industrial water usage by 25% during an unusually severe drought period. The following is a general overview of our efforts to conserve water usage and the resulting successful reductions.

## CONSOLIDATION

In order to efficiently collect and treat plating wastes, it was evident that the three plating areas shown in Slide #1 should be absorbed and consolidated into a large central facility. The piping of effluents from several sources into a treatment plant was uneconomical and potentially hazardous. The design of a treatment facility in close proximity to the finishing shop was naturally dependent on the location of the consolidated plating plant. We chose to consolidate in two stages.

In the first phase, we moved the operations from Buildings 31 and 32 to Building 170 as an intermediate step to permit: 1. The preparation of a new plating facility in Building 185, and 2. The construction of a waste treatment plant, shown as Building 186.

In the second phase, a newly equipped shop was located on an elevated, acid-proof floor, 560' long x 25' wide, installed and supported on a cluster of 4 piles on 20' centers. Soil conditions at the Kearny Works, because of a high water table, could not accommodate in-ground treatment tanks; therefore, an elevated gravity-fed effluent system was necessary to provide an efficient segregation, collection, and treatment piping system. Consolidation into the new facility made possible a daily reduction of water usage of 100,000 gallons, equating to $15,000 annual savings (based on $.60/m gallons). Slide #2 is an aerial view of the Kearny tract showing the close proximity of the Passaic River. Not shown is the other side of the peninsula bounded by the Hackensack River. The two rivers merge into the Newark Bay.

Slide #3 shows the segregation of our exhaust systems into three categories of which two are scrubbed. Cyanide fumes are not scrubbed, but the design of the units made provisions to include scrubbing chambers if the need

arises. The twelve exhaust units are equipped with two speed fans capable of exhausting up to 303,000 cfm of total fume discharge. Air makeup units consist of six 50,000 cfm units strategically located along the 560' length of the building.

SCRUBBERS

In Slide #4, we illustrate the schematic layout of the plating facility and its relation to the waste treatment plant. Contaminated waters from the rinsing tanks are gravity-fed through segregated piping into their assigned holding tanks. These effluents are then pumped into their related spray systems for fume scrubbing, then gravity-discharged back into their respective holding tanks. As the volume of rinse waters continues to rise in the loop, the excess is overflowed into the treatment tanks.

The acid proof floor is designed to hold and isolate spills from cyanide and acid processes. These spills are confined to curbed areas and are gravity drained to either concentrated chrome or concentrated cyanide holding tanks, which are then eventually bled into corresponding dilute streams for treatment.

Normally, a volume of 2 gpm of water is necessary to scrub 1,000 cfm of exhaust. Under these conditions, we would need a supply 218 x 2 or 436 gpm to perform the job of cleaning our discharged exhaust at an approximate cost of $11,000/year. The recycling of rinse water also reduces the demand on the waste treatment plant, allowing us to operate unmanned during reduced or no production periods in the plating shop.

Initially, the recycling of effluent through the scrubbers presented problems under freezing weather conditions. We experienced damage to the PVC riser and spray piping when the flow of water was reduced or stopped completely during a freeze-up period. It was necessary, therefore, to provide a means of dumping the system when a combination of no-flow and freezing outdoor temperature conditions were detected. These sensing and control procedures have proven to be dependable during the past eight years of operation. In case of failure, we have a paved catch basin under the scrubbers to prevent a contaminant flow into the river. This area is shown in Slide #5. The unit on the extreme right, having to scrub fumes from a critical Nickel-Chrome plating operation, is designed so that if one exhaust fan is inoperable, the other fan can continue to exhaust hazardous fumes from that part of the shop on a reduced, but effective, basis.

RINSE CONTROL

As mentioned earlier in the presentation, the consolidation of our plating shops into one new facility reduced water usage by 100,000 gpd, from a daily use of 350,000 gpd to 250,000 gpd. Most of the savings were the result of employing counter-current rinsing controlled by conductivity cell adjustment of the fresh water supply.

1. Counter-Current Rinsing

Slide #6 depicts a rinse-saving technique used in our automatic Zinc plating of racked parts after Zinc Cyanide plating. Although the concept is generally known in the plating industry, it is not normally implemented -- especially in areas of low water costing rates. We took the opportunity to include counter-current rinsing in all our new operations, including the manual acid cleaning and plating processes. Depending on the requirements, we included two or three counter-current rinsing tanks in all our automatic platers. The manual line rinsing is usually accomplished in two tank arrangements. Introduction of fresh water should be at the bottom of the tank with sparger piping. Air agitation is yet another method to optimize the rinsing effect. Filtered shop air is adequate in most applications. Where more precise rinsing is required, a dedicated compressor can supply clean air for agitation; deionized water would supply a controlled purity level. To maintain a constant water quality a solu-bridge monitoring and water supply system is a necessity. In planning the number of tanks in a system, consider that the first rinse removes 90% of the introduced contaminant; the second rinse removes 90% of the remaining 10%, etc.

2. Conductivity Cell

The control system shown in the schematic is designed to monitor the quality of rinse water constantly exposed to varied concentrations of ionic contaminants. The normally closed solenoid valve is energized when the contaminant level increases beyond the level that is preset on the monitor unit. The water flow continues until the rinse water conductivity falls within the set limits; a signal de-energizes the relay and solenoid within a few seconds. The system's circuitry also includes a thermistor to compensate for temperature.

As with any relatively sophisticated systems, the correct placement of sensing probes and monitor units is important. The probe should be situated away from the influence of a clean water surge. The monitor units should be placed away from any possible drippings and exhaust fumes. Where possible, such as at each of our three automatic machines, the monitor units can be remotely located on a wall or stand for easy operator inspection and adjustment. When located near manual dipping tanks, the monitors should be mounted under cover of plastic bags or other corrosion resistant materials. Following these attainable suggestions, the conductivity cell system should provide an approximate 50% in water savings. The rate of savings depends on the purity of the water supply and the type of ionic contaminant. Our supply averages 100 micromhos/cm conductivity, and our initial settings were at 200-300 micromhos in purity requirements.

When the state of New Jersey mandated a 25% reduction in industrial water usage, it was relatively simple for us to increase the monitor settings to a less critical quality level without compromising plating quality to a damaging level. Our evaluation had shown that in most instances we could adjust our water conductivity levels between 400-500

micromhos with corresponding reductions in water usage. This latest compliance to meet New Jersey's drought emergency resulted in water usage reduction of 34%, from 250,000 gpd to 166,000 gpd, a savings of 84,000 gpd, or $23,000/year.

In many applications the greatest savings in the use of conductivity cell rinse controls are realized by the automatic shutoff of the water supply when the tanks are left unattended.

OTHER RINSING CONSIDERATIONS

The addition of a mist spray to remove plating solution residue as the rack is transported out of the plating tank reduces the contaminant load into the post plating rinse. Spray discharge must be limited to the evaporation and dragout rates to maintain the proper solution level.

Rack design should permit easy shedding of liquids from the processed parts and from the rack itself. Correct part positioning enables good drainage and reduced dragout potential.

We are currently experimenting with back flowing of acid rinse waters into alkaline cleaning rinses to reduce the alkaline dragout into activating acid tanks. This should preserve the pickling action for an extended period.

SHOP FEATURES

The following three Slides, #8, #9, and #10, show portions of our plating shop. Slide #8 depicts the automatic rack platers. The aisle separates the load and unload area from the machine, thereby providing a safe working environment for the operators. The equipment is on the same level as the shops walking and traffic areas, permitting easier solution and equipment maintenance.

Slide #9 presents a view of our two-line programmed barrel facility. Controls are located on the aisle side of the tanks for easy access for adjustment and maintenance.

Slide #10 shows the segregated exhaust ducts colored for identification. Designations are: Gold for cyanide; Orange for acid-alkalis; Red for Chromates. Controls are located between, and to the rear of, the process tanks.

WASTE TREATMENT

The reduction of water usage, coupled with lower production activity on the second shift, enabled us to operate the Waste Treatment plant on a one-shift schedule. Although designed for continuous treatment of effluent produced in the finishing plant, the reduced rate of flow on the second shift can be stored in their surge tanks until treated the following day. Caution must be exercised to avoid accidental, large volume spills during this unattended period. This arrangement eliminates the need for two operators with a resulting savings of $50,000/year.

SUMMARY

Equipment and rack design, counter-current rinsing, conductivity meters, water recycling, and other established methods can significantly conserve water usage. Using existing knowledge with unique specific applications can attain beneficial results in most plating shops. Oftentimes, the relatively low cost of water does not provide the incentive to improve water utilization. But, the eventual necessity to treat waste waters would make it imperative to reduce effluent volumes so that smaller capacity treatment units can be considered.

Slide #11 summarizes the results attained through our conservation efforts. Other than the obvious monetary gains, we feel that we also contributed to the alleviation of water shortages in our State.

M-4

# Energy & Materials Conservation Session M

## A Novel Electrodialysis Recovery Unit

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General Motors Research Labs.
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# A NOVEL ELECTRODIALYSIS RECOVERY UNIT

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## Abstract

A novel electrodialysis recovery unit is described. In a test case nickel salts from a dilute rinse water were recycled directly into a nickel electroplating tank. Experimental performance including recovery rates, control and operational stability, and electrical energy requirements are presented. Versatility as well as limitations of the unit design are noted. The industrial application of this materials recovery unit can eliminate several substantial problems and capital equipment requirements now present with conventional electrodialysis units.

## Introduction

The recovery of materials normally wasted during manufacturing operations is becoming more important year by year. For waste waters, one potentially useful technique for materials recovery is electrodialysis, which is a process using permselective membranes and the passage of an electric current to achieve a useful, selective transfer of materials in solution. A possible application for electrodialysis is suggested in Fig. 1, which is servicing an electroplating process. During many plating operations, a substantial amount of bath solution adheres to plated workpieces as they leave the plating tank. In this manner valuable materials are lost as "drag-out" into the subsequent rinse tank. This contaminated rinse solution can be passed through an electrodialysis system, as shown, where these escaping materials can be recovered and returned to the plating tank.

Problem. Conventional electrodialysis, however, not only requires considerable capital equipment but also introduces several problems. These problems arise because to obtain electrodialysis an additional electric current is required. This separate recovery current necessitates an additional power supply and two electrode reactions, either of which may cause unfavorable phenomena which decrease performance and increase maintenance and operating costs. Electrodes may deteriorate and/or cause solution contamination. Also, unfavorable material deposition or dendrite formation may occur at the electrodes and eventually reduce performance and damage adjacent membranes. Several workers have pointed out these problems (1-6).

Concept. At GMR a parasitic electrodialysis concept has been developed which may avoid the above mentioned problems (Fig. 2). Parasitic electrodialysis entails a simple membrane recovery unit, made without electrodes to function within an operating electroplating tank, thus allowing the solution, electrodes, power supply, and current already present for electroplating to be utilized simultaneously for materials recovery. No

direct electrical connections are necessary. The recovery process thus operates in a parasitic relationship to the electroplating process. Because parasitic electrodialysis does not require a separate recovery current or electrode reactions, two advantages result: (1) several problems and maintenance requirements are eliminated because special end electrodes and end solutions are no longer necessary, and (2) the additional power supply, several pumps, and other auxiliary equipment are also eliminated.

This present study was undertaken to demonstrate whether or not such a recovery concept would indeed work. Secondary goals were to (1) provide quantitative performance data, and (2) determine how the recovery process could be suitably controlled. Although parasitic electrodialysis should be applicable to electrolytic processes in general, this work was limited to a Watt's nickel electroplating system as the test case.

## Experimental

Apparatus. The parasitic electrodialysis membrane unit was constructed as shown in Fig. 3. It consists of a frame with manifolding to allow inflow and outflow of solution through four chambers which were bounded by cationic membranes on one side and anionic membranes on the other side. The plate and frame construction made use of stainless steel nuts and bolts which were coated with an insulating material. Each chamber exposed a 2 x 12 cm cross-section of commercially available permselective membrane. The frame was constructed of 3.2 mm acrylic plastic with 1.1 cm dia. holes drilled in 103 locations as shown. Gaskets were 1.6 mm neoprene. Figure 4 shows the 28 L acrylic plastic electroplating tank which was fabricated with grooves to receive the membrane unit in a manner to block the entire 28.6 x 31.4 cm tank cross-section. The rinse tank system contained 740 mL solution.

Materials and Procedure. A Watt's nickel plating bath was made up as follows:

| | |
|---|---|
| $NiSO_4 \cdot 6\ H_2O$ | 272 g/L |
| $NiCl \cdot 6\ H_2O$ | 44 g/L |
| $H_3BO_3$ | 30 g/L |

Dilute solutions made up from the plating bath and distilled water were used as a synthetic rinse water from which nickel salts were to be recycled into the plating tank. The pH ranges of the plating bath and dilute rinse solutions were 3.2-3.5 and 5.3-6.5, respectively.

The plating bath was maintained by filtration and chemical additions. Nickel electroplating was performed using nickel sheet electrodes and 5A constant current conditions at 49°C. Each experimental run involved placing the parasitic cell in the operating electroplating tank and recirculating fresh rinse solution between the rinse tank and the membrane unit at 6.8 L/h until approximately 40% of the initial nickel content of the rinse water was transferred into the plating tank. The point of completion was approximately indicated by conductivity measurements of the rinse water. After each run, the solution in the rinse tank was analyzed using atomic absorption spectroscopy to determine the exact amount of nickel removed.

Calculations. Quantitative performance of the parasitic electrodialysis unit was calculated as follows:

Rate of Nickel Transfer (g Ni/h)

$$= \frac{c_i v_i - c_f v_f}{t} \qquad (1)$$

Electrical Energy Yield for Nickel Transfer (g Ni/W•h)

$$= \frac{c_i v_i - c_f v_f}{t \; I \; \Delta V} \qquad (2)$$

where

$c_i$ = initial nickel concentration of rinse solution (g/L)

$c_f$ = final nickel concentration of rinse solution (g/L)

$v_i$ = initial volume of rinse solution (L)

$v_f$ = final volume of rinse solution (L)

$t$ = time elapsed during run (h)

$I$ = electroplating current (A)

$\Delta V$ = additional voltage required when the parasitic unit was placed into the electroplating tank

## Results and Discussion

Function. The parasitic electrodialysis unit was successfully demonstrated. Under all conditions investigated, nickel salts were routinely recycled from the rinse water directly into the plating bath. A problem with membrane fouling was initially observed but was readily eliminated. In the earliest work steel nuts and bolts used as part of the membrane unit were inadequately coated with an insulating material. This allowed bipolar action to occur, causing iron dissolution into the nickel bath, which tended to foul the membranes and slow down the recovery action. The problem was remedied by purifying the contaminated plating bath and prevented from recurring by providing a more adequate coating on the nuts and bolts. The fouled membranes were readily restored by simply immersing the membrane unit in 10% hydrochloric acid for a few minutes. There was no evidence of membrane deterioration during this work nor did any other problems surface.

Means of Control. A critical consideration before placing this type of recovery unit in an industrial application is providing a suitable means to maintain control over the recovery process.

One method used in this work to regulate recovery action was by controlling the ratio of membrane cross-section to "open" (plating bath) cross-section. Since the perforated recovery unit frame filled the entire cross-section of the plating tank (see Fig. 4), the ratio of membrane area to open area could be adjusted in this work by merely plugging more or fewer openings in the frame. The effect on performance is shown in Fig. 5. Rate of nickel recovery is seen to be very sensitive to this ratio. As the ratio is increased the rate of nickel transfer also increases. This occurs because a higher ratio of membrane to open area forces a larger percentage of the plating current through the membrane chambers, thus increasing the rate of electrodialysis action. The approximate percentage of the plating current passing through the membranes (computed from $Ni^{++}$ recovery rates) is shown in brackets on the graph. Thus we observe a range of 13 to 25% in this study. Further studies using other ratios and rinse solution concentrations demonstrated an even wider, 1 to 50% range of control. It has been estimated that in general less than 10% of the plating current need be directed through the membrane unit to achieve a sufficient recovery rate, i.e., a recovery rate equal to the material loss rate due to drag-out. Thus, design ratio has been demonstrated to offer a suitable and direct method of control.

A secondary control mechanism is an automatic self-regulating effect which occurs because rate of recovery is directly dependent upon concentration of the rinse solution contained within the membrane unit. Results of one study are shown in Fig. 6. One may note a four-fold increase in recovery rate resulting from a seven-fold increase in rinse water concentration. This suggests the automatic effect would indeed become operative in a practical application -- should a more concentrated rinse water enter the recovery unit, the rate of recovery would increase, as would be desireable and necessary to handle the additional load. Should a less concentrated rinse water enter the unit, a smaller rate of recovery would occur.

Thus control of the parasitic process would seem readily possible in an industrial electroplating installation. The unit could be constructed with a properly selected ratio to provide a recovery rate commensurate with rate of drag-out and desired rinse tank concentration. Then any random fluctuations in drag-out or rinse concentration would activate the self-regulation mechanism to increase or decrease recovery rate as appropriate, thereby tending to maintain the desired rinse concentration and stabilize performance.

Performance. Figure 7 shows performance of the parasitic membrane unit as a function of ratio. As the ratio is increased the rate of nickel recovery increases (as discussed earlier) while electrical energy yield decreases. The amount of nickel recovered per kilowatt-hour decreases because, while the amount of nickel transferred is approximately proportional to current passing through the membrane unit, electrical power

expenditures increase more rapidly, being proportional to the square of that current ($P = I^2R$). This trade-off between rate of recovery and electrical energy yield is typical of electromembrane processes in general (3,4,6).

Figure 8 shows performance of the parasitic membrane unit as a function of rinse water concentration. In this case there is no trade-off. With increasing concentration, rate of recovery and yield per kilowatt-hour both increase together. This trend suggests that best recycle performance would result when maintaining the rinse water at the highest contamination level (of plating bath drag-out) that is consistent with other requirements of the overall plating operation.

Although this recovery unit operates in a parasitic fashion it does not provide "something for nothing" of course. The "cost" of operating this unit in an operating electroplating system shows up as an additional resistive load, meaning that a higher output voltage is required from the electroplating power supply to maintain the same electroplating current. This additional electrical energy requirement from the power supply to obtain materials recovery was unnecessarily large in this work for at least two reasons: (1) excessive separation between membranes, and (2) nonoptimal membrane unit construction.

In this first unit design the membranes were restrained around their peripheral edges only. Therefore, as rinse water was pumped through the unit the pumping pressure caused the membranes to flex, forming an outward bulge which increased the (already large) nominal 6 mm membrane separation to about 10 mm in the central region of each membrane chamber. Because of this the highly resistive rinse solution forms a very long path through which electrical current must pass, resulting in excessive ohmic losses. Better results are expected with an improved design adequate to maintain a membrane separation of 1-2 mm as is typical of many commercial electromembrane units (3).

A second area of possible improvement is suggested by Fig. 9. Shown are experimental determinations of the additional voltage requirements introduced by the presence of the membrane recovery unit in the plating tank. Voltage requirements were increased anywhere from 0.4 to 1.4 volts under the particular conditions noted. The graph also shows similar experimental data for just the empty recovery unit frame, i.e., without membranes or rinse solution. The differences between the extra voltage requirements for the total unit and the empty frame were calculated and also shown in Fig. 9. These values represent additional voltage requirements associated with the membranes plus contained rinse solution. One can observe by comparison that only about half of the additional voltage was productive. The rest of the additional load on the power supply was caused by the insulating frame of the recovery unit. Thus, refinements in unit design to maximize the membrane and open areas (at an appropriate ratio) while minimizing the cross-sectional area of insulating frame would seem to be a profitable area for further development.

## Summary

A novel parasitic electrodialyzer has been successfully demonstrated. While applicable to electrolytic processes in general, this particular recovery unit was made to function within an operating electroplating tank, thus allowing the power supply, electrodes, and current already present for electroplating, to be utilized for materials recovery also. In a test case nickel salts from rinse water were recycled directly to the plating tank. It was found that the rate of recovery could be controlled by the ratio of membrane cross-section to open bath cross-section, and any given ratio can be incorporated in the unit's design. A self-regulating effect (based on a direct relationship between rinse water concentration and recovery rate) then operates to stabilize the recovery process. While long-term pilot studies are still needed, the eventual industrial application of this integrated electroplating/materials recovery system can eliminate several substantial problems and capital equipment requirements now present with conventional electrodialysis units.

## References

1. D. D. Snyder, private communication.

2. R. P. Ouelette, J. A. King, and P. N. Cheremisinoff, Editors, Electrotechnology Vol. I, Wastewater Treatment and Separation Methods, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1978; p. 17.

3. G. S. Solt, Membrane Separation Processes, (P. Meares, editor), Elsevier Scientific Pub. Co., New York, NY, 1976; p. 240.

4. S. Hwang and K. Kammermeyer, Techniques of Chemistry, Vol. VII, Membranes in Separations, John Wiley and Sons, New York, NY, 1976; p. 234-236.

5. S. B. Tuwiner, Diffusion and Membrane Technology, Reinhold Publishing Corp., New York, NY, 1962; p. 240.

6. R. E. Lacy and S. Loeb, Industrial Processing with Membranes, Wiley-Interscience, John Wiley and Sons, New York, NY, 1972; p. 4,28,35,41,97.

Figure Captions

Fig. 1 An electroplating system with materials recycle provided by a conventional electrodialysis unit.

Fig. 2 An electroplating system with materials recycle provided by a parasitic electrodialysis unit. Cationic and anionic membranes are labeled "C" and "A" respectively.

Fig. 3 Parasitic electrodialysis unit.

Fig. 4 Experimental equipment.

Fig. 5 Recovery control by design ratio. Numbers in brackets indicate approximate percentage of electroplating current passing through membranes.

Fig. 6 Recovery control by rinse water concentration.

Fig. 7 Effect of ratio on recovery performance.

Fig. 8 Effect of rinse water concentration on recovery performance.

Fig. 9 Additional voltage requirements introduced by the presence of the parasitic electrodialysis unit.

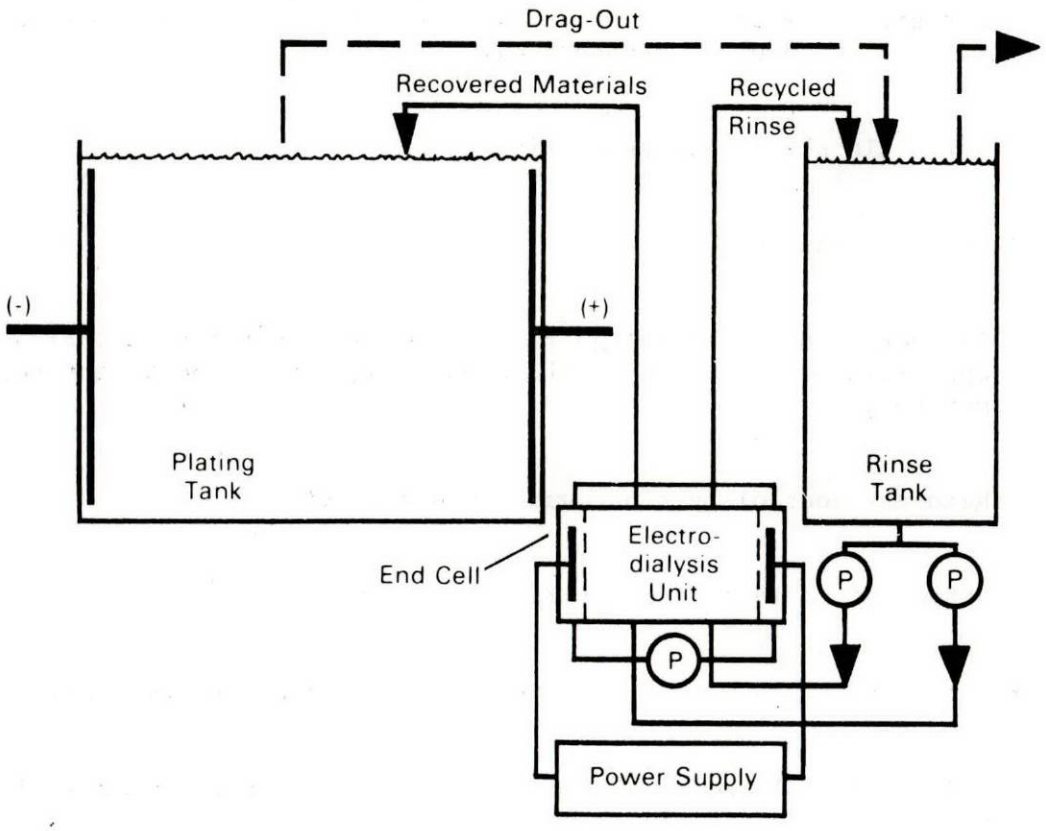



Figure 1. An Electroplating System With Materials Recycle Provided by a Conventional Electrodialysis Unit.

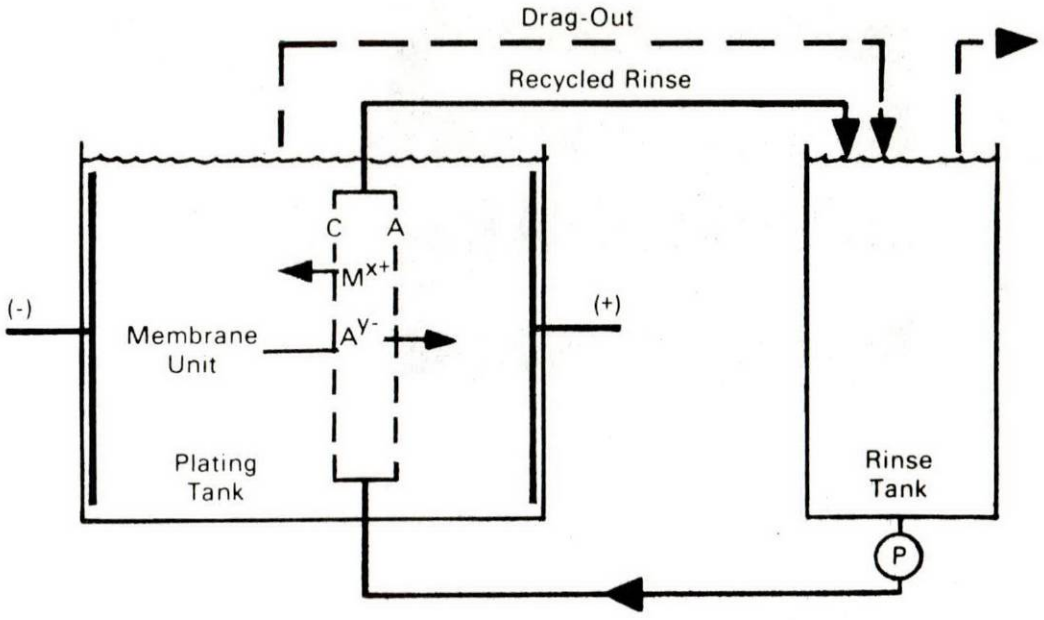



Figure 2. An Electroplating System With Materials Recycle Provided by a Parasitic Electrodialysis Unit. Cationic and Anionic Membranes are Labeled "C" and "A" Respectively.

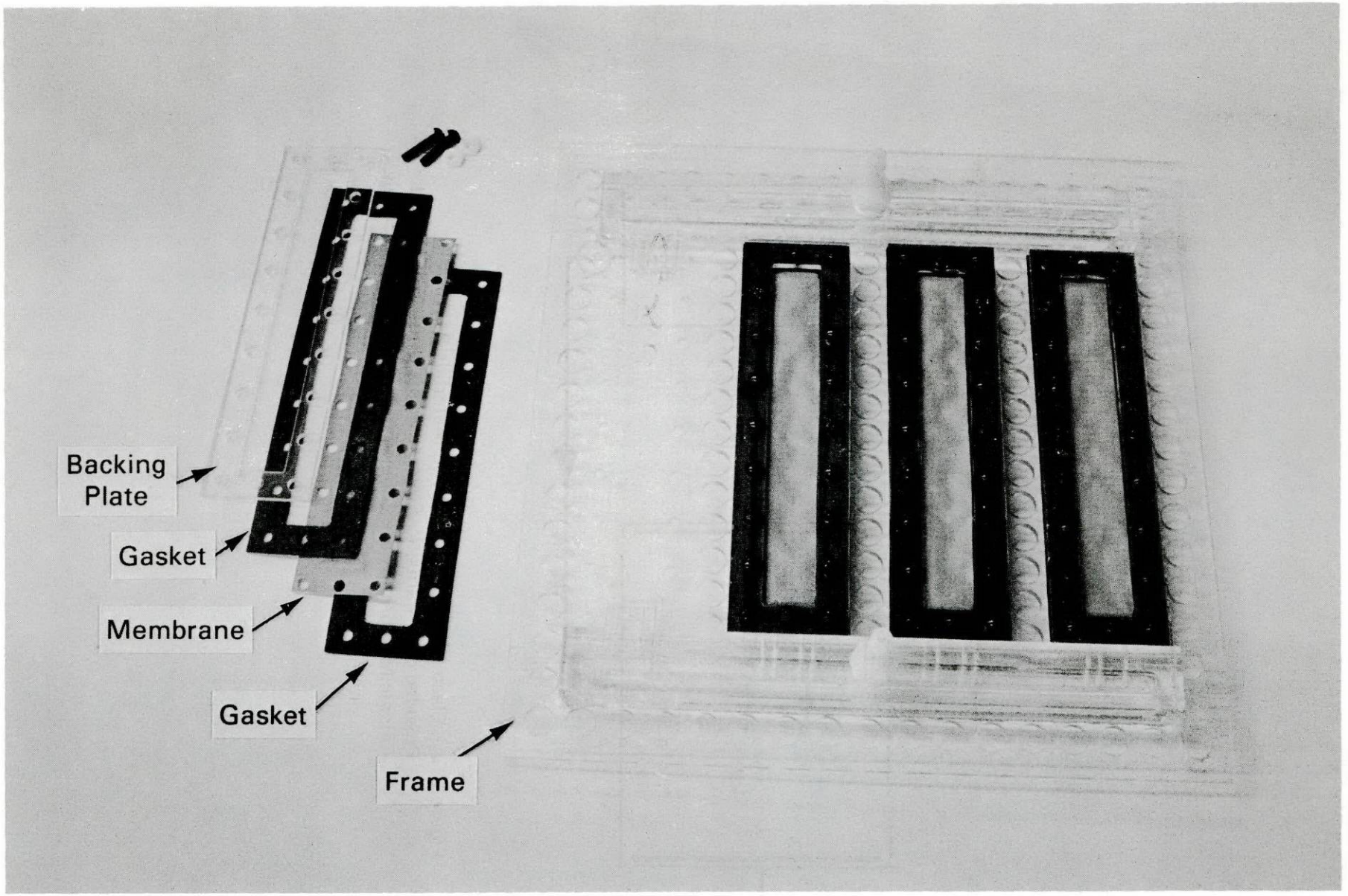



FIGURE 3

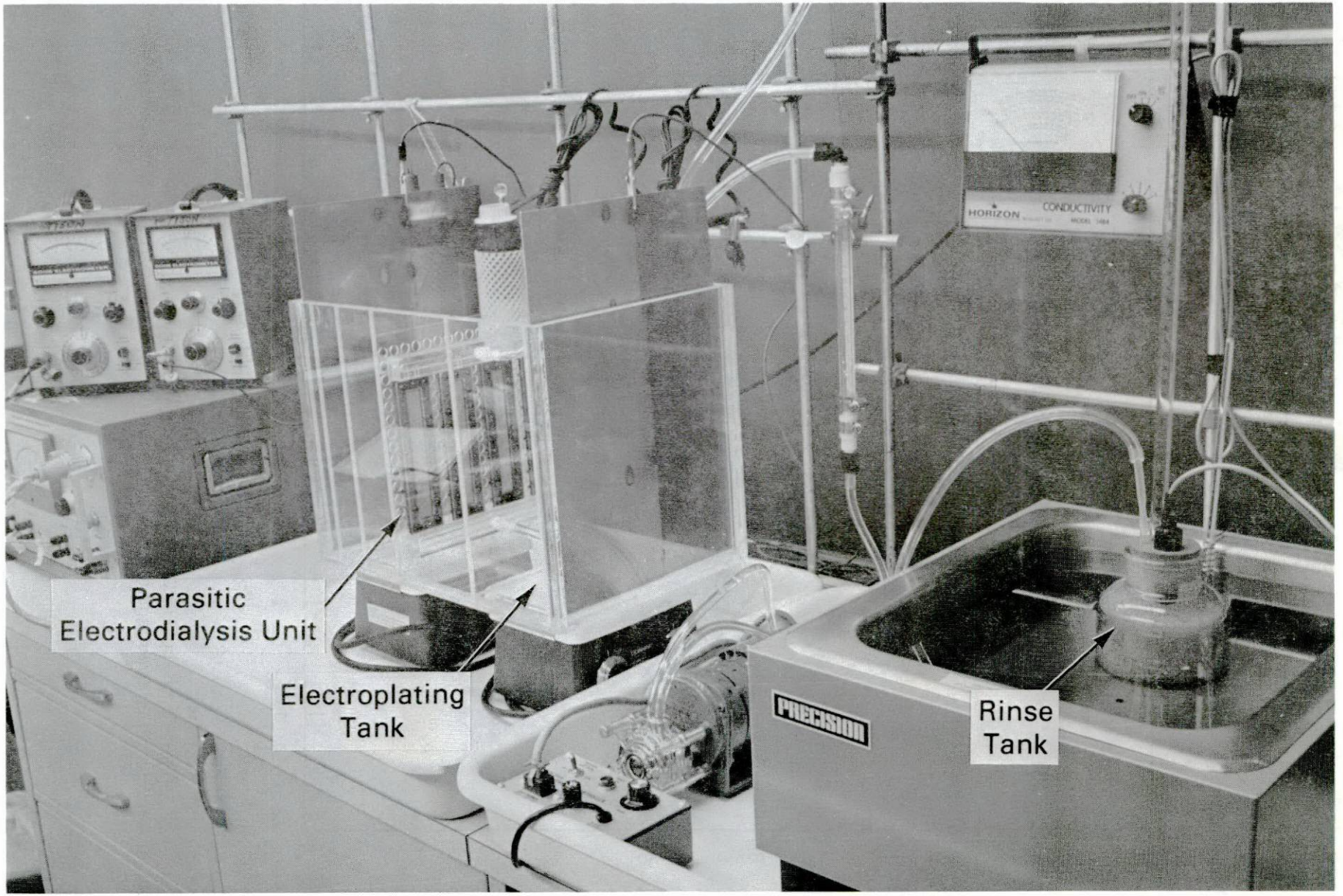

Parasitic
Electrodialysis Unit
Electroplating
Tank
Rinse
Tank
HORIZON
CONDUCTIVITY
PRECISION

FIGURE 4

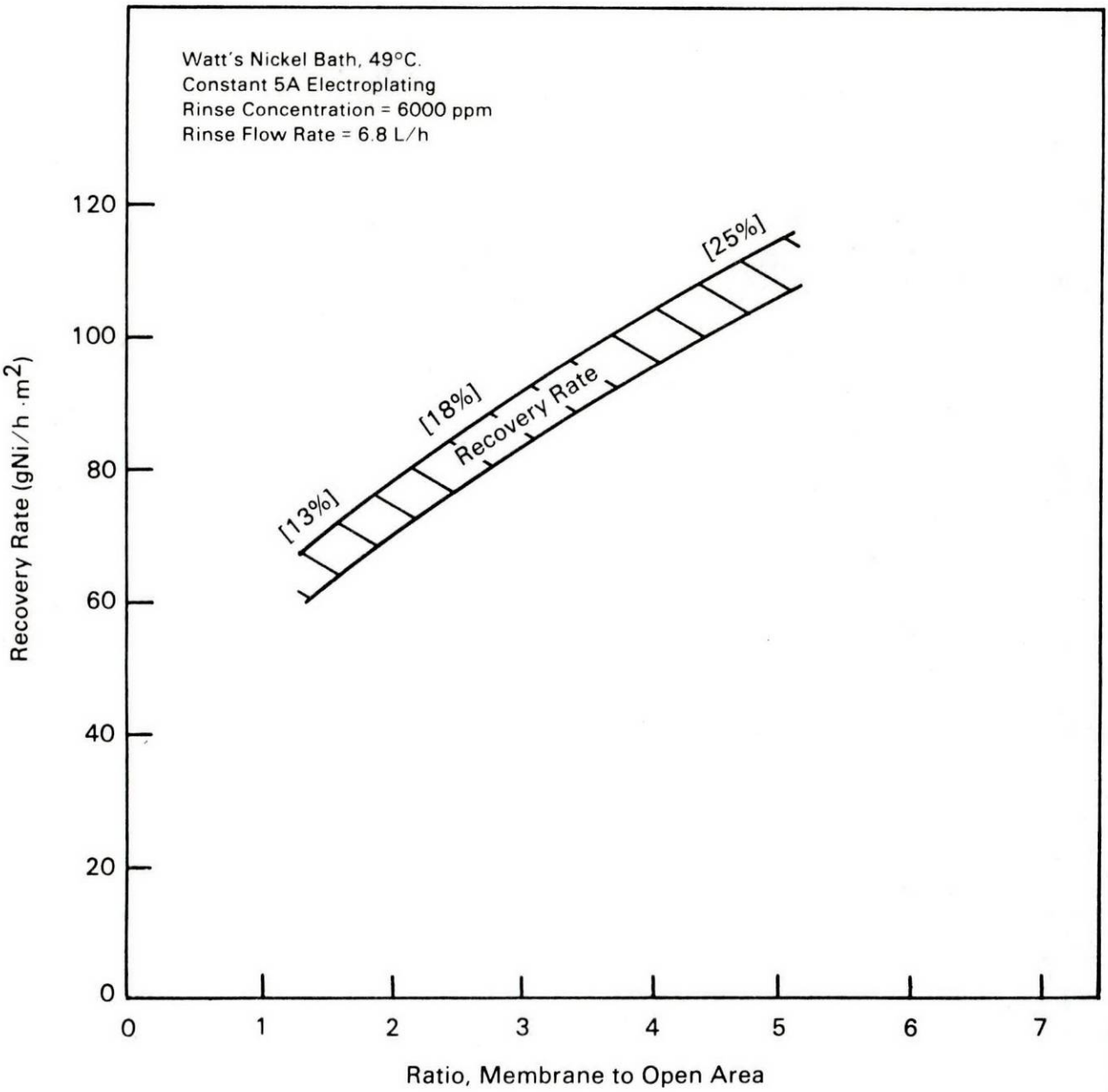



Figure 5. Recovery Control by Design Ratio. Numbers in Brackets Indicate Approximate Percentage of Electroplating Current Passing Through Membranes.

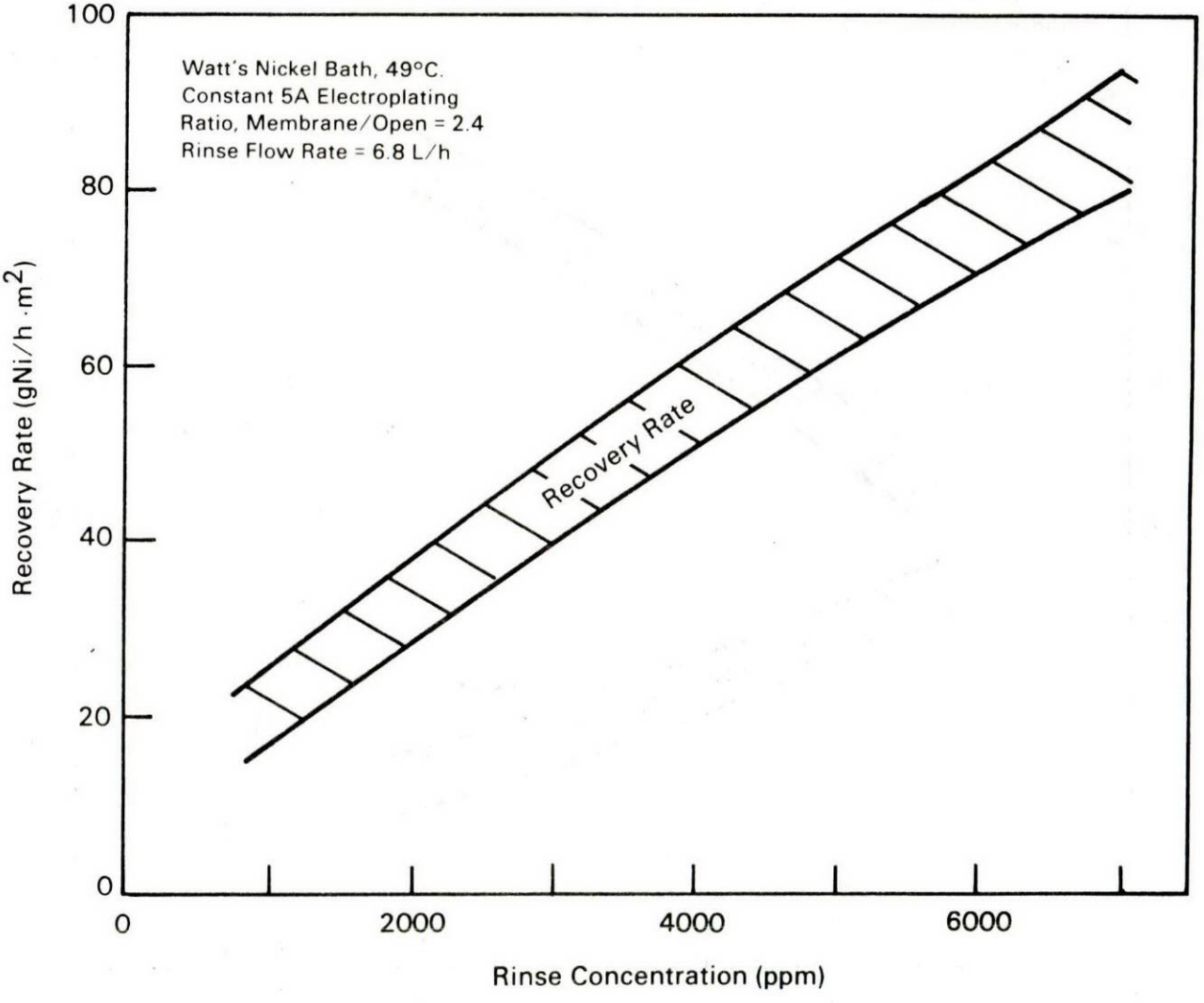



Figure 6. Recovery Control by Rinse Water Concentration.

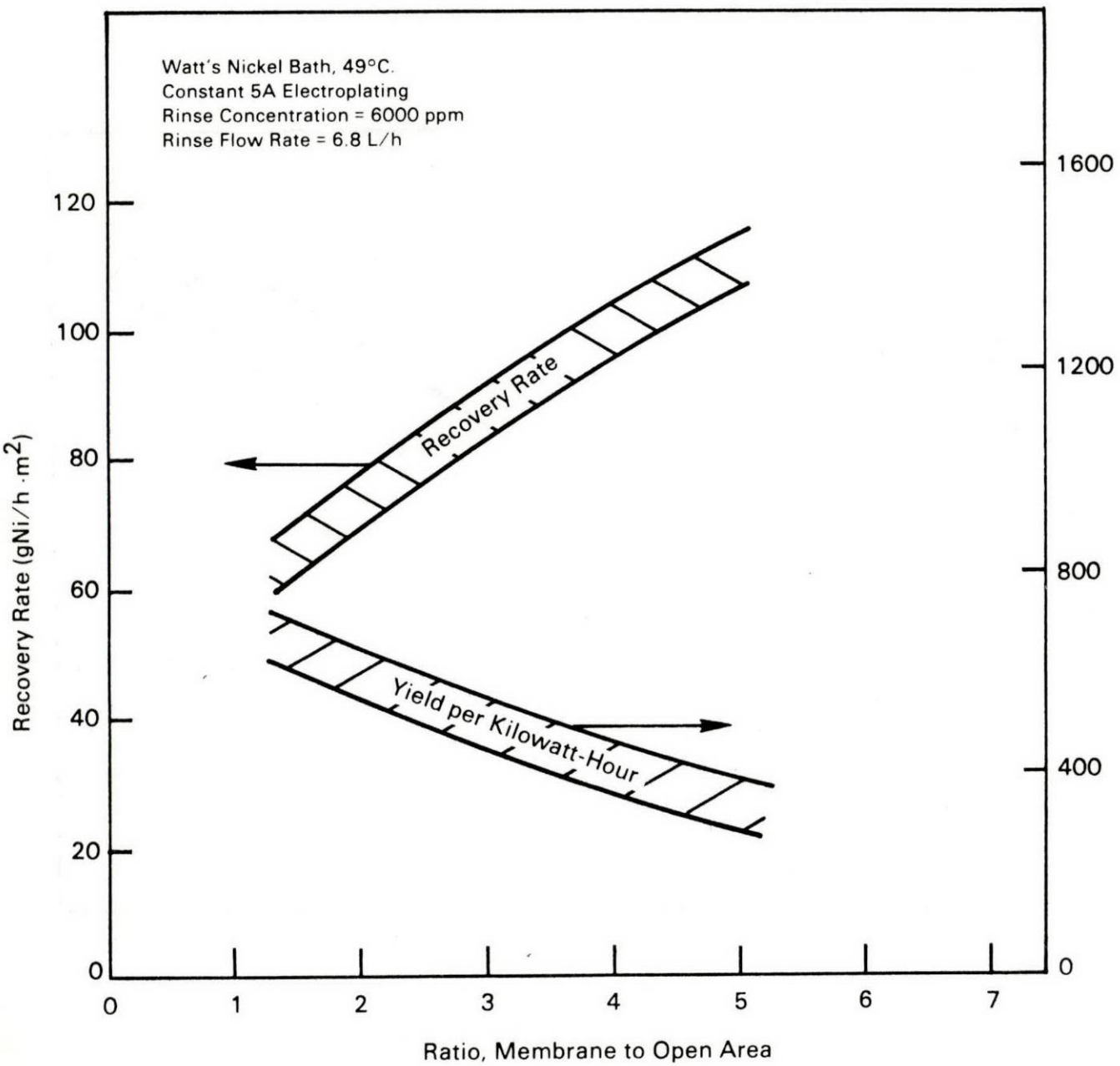



Figure 7. Effect of Ratio on Recovery Performance.

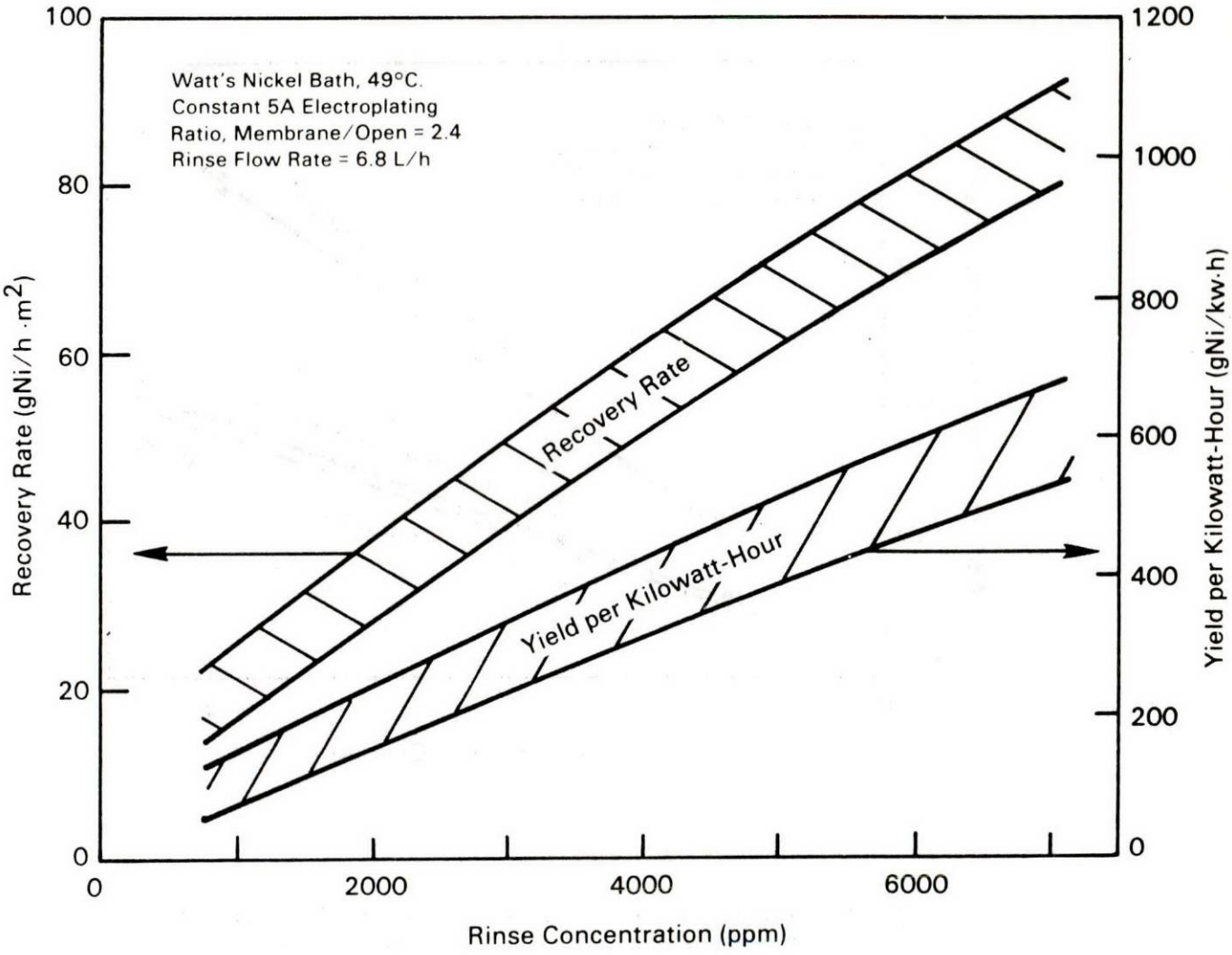



Figure 8. Effect of Rinse Water Concentration on Recovery Performance.

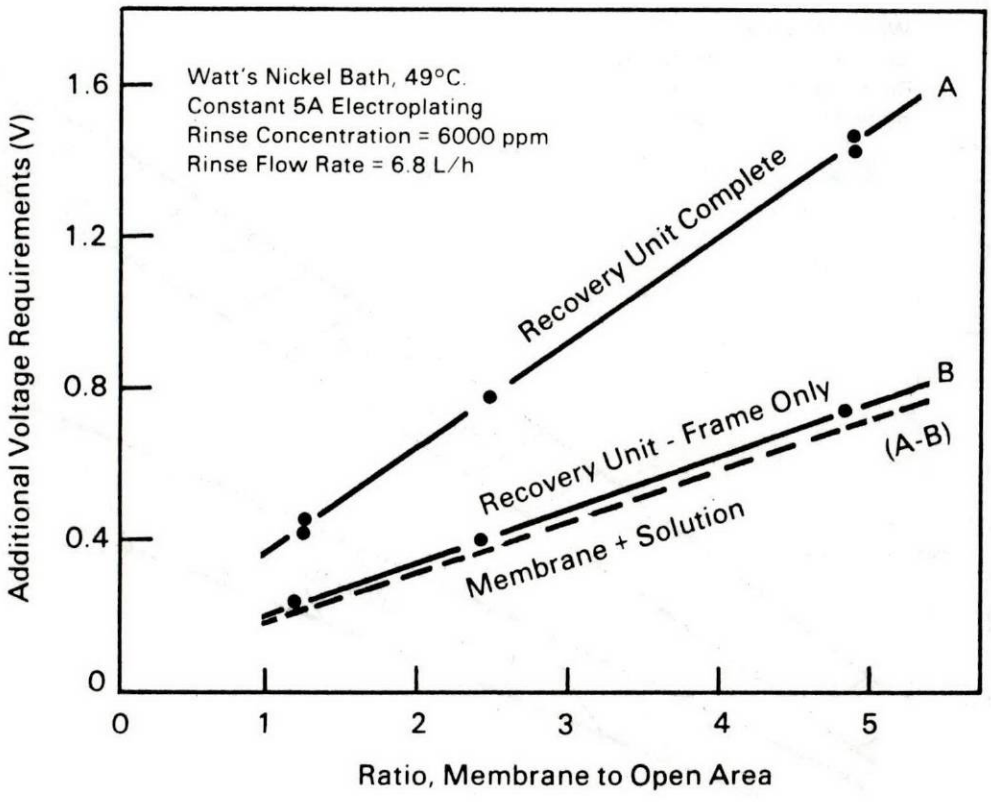



Figure 9. Additional Voltage Requirements Introduced by the Presence of the Parasitic Electrodialysis Unit.

# N-1

# Electroplating For Optics Applications Session N

## Some Thoughts on the Role of Electroplated Coatings in Optics and Some Considerations for Their Production

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# SOME THOUGHTS ON THE ROLE OF ELECTROPLATED COATINGS IN OPTICS AND SOME CONSIDERATIONS FOR THEIR PRODUCTION

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## Abstract

New and exotic applications of optics to directed energy weapons systems, advanced astrophysical, and alternative energy applications to name a few, are forcing reconsideration of the available optical materials and manufacturing processes. Metal and coated metal optics of both conventional and unconventional geometry are of particular importance in these areas due to their unique efficiency and optimal functional properties. The emerging importance of these coated metal optics will be discussed, including the types and characteristics of coatings required, the optical design process and a very short survey of the more common and important applications. Also, a perspective on the optical manufacturing technologies and their implications to the characteristics of the plated coatings is given. Finally, a short survey describing the size of the potential market for coated optics in the next decade will be presented.

## Introduction

With the most recent administration's commitment to increasing the defense budget, a wide variety of industries, including optics, will experience major upheavals in the type, quantity, quality, and mix of products to be manufactured both now and perhaps in the next five to ten years. The principal products for which optical components and systems will be required in this military market include: fire control systems, pointer-trackers, forward looking infrared systems (FLIR), night vision systems, and advanced surveillance devices. In addition to this basic need, research and development in laser weapons systems, inertial confinement fusion (laser fusion), laser isotope separation, and advanced astronomical systems are presenting requirements, geometries and demands that are extremely demanding, if not impossible, utilizing conventional optical technology (grinding and polishing). Both solid and coated metal optical components where the coatings are placed on a wide variety of new and sometimes exotic materials are playing an ever increasing role in the solution to these new needs and requirements. By coated metal optics we mean coatings applied by electrodeposition or electroless plating.

Common materials such as aluminum, copper, brass, gold and electroless nickel are regularly plated onto a wide variety of substrates including beryllium, beryllium copper, aluminum, mild steel and other common metals to manufacture a wide variety of reflective optical components and systems. This paper is directed at providing some view of the need and problems related to coating and subsequent processing of coated metal optics. Included is first, a description of the potential market size for metal and coated metal optics that will likely be required for these

applications. Secondly, the manufacturing processes used to convert the coated metal substrates into optical components will be reviewed followed by a description of some of the applications of these coated metal substrates. Some comparison between conventional optical polishing and precision machining of coated metal optics will be given, as well as some thoughts on the kinds of problems that characteristics of the plating process cause, both to the optical manufacturing and ultimately, the functionality of the completed component.

## Market Size for Metal and Coated Metal Components

The general market category into which metal and coated metal components falls is called the precision optics market. This market is defined by the U.S. Bureau of Census Report[1] as the Optical Instruments and Lenses Industry. The report indicates that the annual growth rate of the optical industry from 1974 to 1977 has been approximately 12% per annum. Projecting this 1977 rate to 1982, the current market size becomes $380 million per year. This figure relates principally to glass, lenses, prisms, mirrors, windows and some special optics. Indicated potential increases in the use of infrared and advanced optical systems by the Defense Department for precision guided munitions, pointer-trackers, fire control and surveillance systems is introducing many new material and functional requirements that are increasing this general market size.

Under a recent U.S. Army Missile Command contract (No. DAAK 40-79-C-0255), a survey of machined optics requirements was carried out for the Army and other DOD applications. By machined optics we mean optical components that are manufactured of materials compatible with a diamond tool in the precision machining process. Table I lists materials that are presently known to be machinable by diamond turning, and commonly used in this market area. The most important materials from the metal and coated metal optics point of view are: aluminum, gold, copper and the electroless nickel. It is the optical characteristics and manufacturability of these materials that is the prime issue in this paper and in the symposium that follows.

Table I. List of materials currently known to be compatible with diamond tools, and hence considered machinable*

| | |
|---|---|
| Aluminum | Electroless Nickel |
| Brass | Alkali Halide (salt) Crystals |
| Copper | Zinc Sulfide |
| Beryllium Copper | Zinc Selenide |
| Gold | Germanium |
| Silver | Many Plastics |
| Lead | Machinable Ceramics |
| Platinum | Potassium Dihydrogen Phosphate (KDP) |
| Cadmium Teluride | |

*Reference. G. M. Sanger, "A Perspective On Precision Machining, Polishing, and Optical Requirements", UCRL #86579, Lawrence Livermore National Laboratory, August 18, 1981.

With respect to the Army Missile Command survey then, data was acquired from a number of government and civilian organizations (see Table II) that was used to compile requirements in this military IR laser optics market. The projected requirement is determined from a period that extended from September 1980 through September 1990 and indicates that some 1.2 million components will be required of various geometries including flats, polygon scanners, spherical components and aspherical components. Table III indicates the geometry, approximate size, number of each type required, projected costs and total costs leading to the given market size. According to this survey, in high production quantities the total market should be approximately $280.64 million. While it is this author's opinion that this survey is extremely conservative, that the list of optics users surveyed is not complete, and that it does not take into account all of the types of optical components required, it is a indicator at least of the general requirement. If the applications of IR and X-ray astronomy, advanced commerical and other military requirements are folded in, this market could conceivably be larger than that indicated, or when all combined, in the order of $900 million. Of these, the greatest majority of flats and polygon scanners will be of metal or coated metal construction, and will comprise approximately 20% of this overall market. If I can be so rash as to assume that the costs for plating will run 15% of this figure, then the annual market during the next decade for plating of these kinds of substrates is approximately 2.7 million a year. While this certainly is not a large number and will probably have no major impact on production capability in the metal plating industry, it is large enough that consideration of the applications and requirements of these kinds of coatings are justified.

Table II. Various components and products that can and have been efficiently fabricated using diamonds and precision machines*

| | |
|---|---|
| Computer memory disc's and drums | Gyro components |
| Recording heads | Precision pump parts |
| Missile components | Bearing bores and races |
| Various precision rolls | Dies for molded lens fab. |
| Photocopier components | Traveling wave tubes |
| Aspheric reflectors | Infrared optical components |
| Precision measuring instruments | Optics of unconventional geometry |
| X-ray telescope objectives | |

*Reference. G. M. Sanger, "A Perspective On Precision Machining, Polishing, and Optical Requirements", UCRL #86579, Lawrence Livermore National Laboratory, August 18, 1981.

Table III. Projected requirement for machined optics including geometry, size and maximum number required between 1980 and 1990.**

| Geometry | Size | Fraction Required | Projected Requirement (Max) |
|---|---|---|---|
| 1. Flats | $\leq$ 2" x 2" | .5501 | 169,000 units |
| 2. Flats | $>$ 2" x 2" | .0391 | 12,000 units |
| 3. Polygon Scanners | $\leq$ 3.5" dia | .3132 | 96,200 units |
| 4. Polygon Scanners | $>$ 3.5" dia | .0976 | 30,000 units |
| 5. Spherics | $\leq$ 5" dia | .6996 | 625,908 units |
| 6. Spherics | $>$ 5" dia | .0335 | 30,000 units |
| 7. Aspherics | $\leq$ 5" dia | .2623 | 234,636 units |
| 8. Aspherics | $>$ 5" dia | .0052 | 4,136 units |
| | | TOTAL | 1,201,880 units |

**Reference. Technical Report RH-CR-81-7, MM&T Precision Machining of Optical Components for U.S. Army Missile Command under Contract DAAK-40-79-C-0255 by Arthur E. Hess and Gordon J. Watt (INTOP Division of Kollmorgen, Wallingford, Conn., 06492).

## Surface Characteristics, Optical Processing and Application

The final product of these optical and coating/plating manufacturing efforts will be an optical surface or component. For an optical component, the most important concern is how the surface interacts with the incident light, i.e., the optical functionality of the manufactured surface. Therefore, when dealing with optical surfaces all aspects of the manufacturing processes must be designed to control those characteristics that result in changes to the optical functionality.

Many properties of the surface and material affect this surface/light interaction. A list of these characteristics is given in Table IV, and while not complete, all must be considered for good basic optical surfaces. In examining this list closely, however, it is found that most of these may be ignored in manufacturing as they concern design and materials rather than processing. That is, once into the manufacturing of an optical component all of these properties may be neglected except where they impact the fabrication process employed, or where the fabrication process, in turn, impacts them. When all these optical factors are properly accounted for, the special problems of plating for optical application reduces itself to one of control of the two principal shape factors and conformance of the actual plated material to the properties of the required material.

While appearing simple, the implications of these three features are far reaching with respect to plating. In material properties, for instance, one must be concerned with both material uniformity and the basic material that is being deposited, as both of these factors affect the spectral reflectance distribution of the resultant optical surface. This implies that careful attention to the physical factors affecting coating material and its uniformity, as well as the chemical behavior of the solutions employed is necessary.

Table IV. Factors that must be considered and, if necessary, specified in the design and manufacture of optical components and surfaces.*

Reflectance
Transmittance } angle of incidence
Absorptance
Spectral response (dispersion)
Index of refraction (homogeneity)
Weight and strength
Resistance to environmental factors
(Temperature, pressure, radiation, humidity, contaminants and corrosives)
Manufacturability
Stress and polarization effects
Scatter and microtopography
Contour
Power level
Geometry
Coatings

*Reference. G. M. Sanger, "A Perspective on Precision Machining, Polishing, and Optical Requirements", UCRL #86579, Lawrence Livermore National Laboratory, August 18, 1981.

The shape factors that must be considered are contour (form) and microtopography (finish). From the coating point of view the coating surface contour and finish are aspects of the same problem, namely shape, and differ only in their affect on optical performance. Also note that plated surfaces for optical applications will be subsequently processed by either precision machining (diamond turning) or conventional grinding and polishing. Such coatings must be mechanically uniform and free of pits, inclusions, bubble, voids, or changes in the physical properties of the materials.

In order to better understand why such careful considerations of the resultant shape and material factors are important, it will be necessary to understand how light interacts with these features and the sensitivity of that interaction. This topic will be covered in detail in another paper during this session, but a short introduction is appropriate here if a good overall prospective on the problem is to be acquired. For these reasons the remainder of this section will concentrate on form and finish for an optical surface. This discussion will be divided into three sections: Contour, Finish and Homogeneity.

## Contour

Optical surface contour, from coated reflecting optics for example, can be specified and qualified with respect to how well the image reproduces the spatial content of the object field (related to resolution). Consider a reflecting optic as a black box linear system (Figure 1) which converts an incident planer or diverging spherical wavefront from any object point into a spherical wavefront converging to its geometrical image point. If we assume that the incident wavefront is perfectly flat or spherical (not always the case when atmospheric effects or other imperfect components are taken into account), then our black box (if perfect) will faithfully reproduce the object differing only in diffraction effects. If our mirror (black box) is not perfectly shaped, the reflected wavefront will not be perfect and forms an image that differs both geometrically and in spatial content from the object.

As in any technology, there are many quality criteria that may be applied, for extraction of tolerances and hence, requirements. Perhaps the most common one in optics is simply the resolution of two object points separated by the diffraction spot size (Rayleigh Criterion)[2]. For the sake of this discussion and brevity, however, consider instead the ability of a mirror/lens to reproduce the spatial content of the object. The most common method is through the Modulation Transfer Function (MTF)[3] whose value at any point measures that surface's ability to image a specific spatial frequency. It relates the image contrast (C) or

$$C = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \qquad I = \text{light intensity}$$

to each spatial frequency the optimal system encounters. All values of

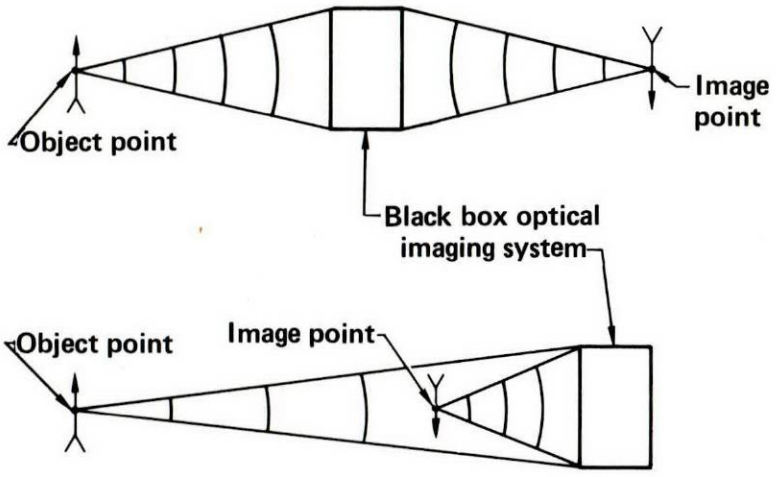



**Figure 1. Possible configurations of a black box, linear imaging system. Imaging relations are identical in both cases with the exception of signs on propagation direction.***

the MTF will be between 0 and 1. A contrast of 1 means perfect duplication and a contrast of zero indicates that it will not be seen in the image. All values in between can be thought of as gray levels in the spatial frequency (i.e. difference between the light and dark in a black-white bar pattern of that spatial frequency). This measure is defined as the modulus of the Optical Transfer Function (OTF) defined by

$$MTF = |OTF| = [(OTF) \cdot (OTF)^*]^{1/2}$$

where

$$OTF(x,y) \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(x,y)P^*(x + a, y + b)\, da\, db$$

a & b = dummy variables  p = pupil function (directly related to part contour)

It is straight forward to see the relationship between the image of a point, the OTF, the MTF and exciting wavefront is shown in Figure 2 where for example (FT = 2 dimensional Fourier Transform)

$$FT\left\{ P(x,y) \right\} = A(\zeta,\eta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(x,y)\, e^{-i2\pi(\zeta x + \eta y)}\, dxdy$$

The MTF and diffraction image of a point object for a perfect-circular mirror is shown in Figure 3. If the mirror contains contour errors due to manufacturing, the exiting wavefront will lead or lag the proper wavefront causing phase errors to appear in the pupil P(x,y). These errors will degrade the image and be noted by drops in the MTF function. As a result, the volume under the MTF drops correspondingly and thus can be a generalized measure of the surface performance. The amount of wavefront lead or lag, expressed in wavelengths of light can be toleranced by the corresponding drop in MTF volume. This lead/lag, if expressed in wavelengths can be directly converted to other physical units of departure from the wavefront (microinches, micrometers, Angstroms) and related to the manufactured mirror surface through a simple factor of two. From this, the contour tolerance or requirement is straight forward, at least for imaging systems. It is important to keep in mind that all values of contour are specified in wavelengths of the light to be used and as such the absolute values change as the wavelength changes. This implies that a visible light optic operating at 0.5 μm wavelength is twice as hard to make λ/4 as an infrared optic working at a 1.0 μm wavelength.

If the deposited coatings are not physically uniform for instance, the subsequent optical finishing operations will process different areas differently. If the material hardness changes for instance, its polishing rate will vary which results in undesired contour changes. These contour changes will adversely effect an optical surface as indicated above. This

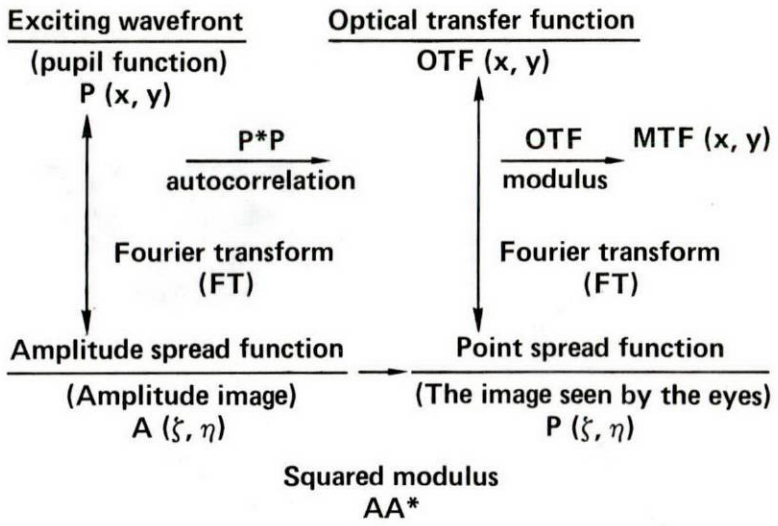



Figure 2. The mathematical relationship between the optical system exit wavefront (described by F#, amplitude distribution, and phase distribution), the image of a point and the MTF.*

*Reference. Same as Table I.

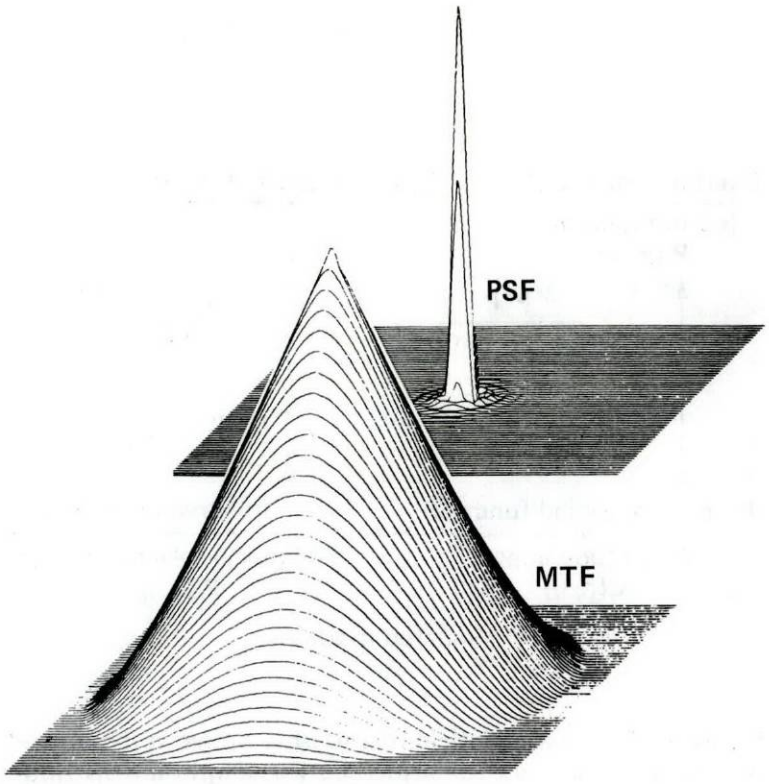



**Figure 3. The diffraction image of a point object [point spread function (PSF)] and MTF for a circular mirror containing no contour errors, i.e., "perfect".**

will also be the case if the chemistry is different from point to point on the surface or if the residual stress level is sufficiently high to warp the substrate. Unfortunately, almost no work has been done to quantify the hardness - polishing rate relationship so tolerances are difficult at best to determine.

Finish

Optical surface finish, roughness, microtopography or microroughness as it is commonly termed is of interest in specification of coated optimal surfaces because of its effect on the reflectance, transmittance and stray light properties of the finished optic. In many applications, crystal structure, bubbles, voids, pits, and inclusions cause unacceptable changes to the optical properties. Therefore, it is important to relate the micro-characteristics (features a few microns across and a few tens of angstroms in height) of coated surfaces to the optical properties and understand when these are or are not important. A complete description of this relationship may be obtained from the work of Church[4] and will be summarized in what follows.

The principal effect of a "rough" surface is scattered light. A schematic of what scattering is and the normally applied geometry is presented in Figure 4. One can think of an optical surface, for the sake of modeling, as a surface consisting of a very large number of sinusoidal diffraction gratings, each a Fourier component of the surface defined by A sin ($2\pi x/d$)) of different amplitude, direction and frequency. Each of these Fourier components with their various spatial wavelengths will scatter light of wavelength $\lambda$ at a specific angle ($\theta_s$) given by

$$\mathrm{Sin}\theta_s = \mathrm{Sin}\theta_i \pm \lambda/d$$

These relationships indicate that the intensity of the scattered light is determined by the vertical amplitude (A) of the roughness and that the angular direction of the scattered radiation is determined by the reciprocal of the spatial wavelength (d) of the roughness or surface features. It can be shown from scalar scattering theory[5] that the relation between the RMS roughness ($\sigma$) and the normal incidence reflectance is

$$\frac{R}{R_o} = \exp\left[\frac{-4\pi\sigma^2}{\lambda}\right] + \frac{2^5\pi^4}{m^2}\left[\frac{\sigma}{\lambda}\right]^2 \cdot \Delta\theta^2$$

where

R = Sum of the scattered light

$R_o$ = Specular reflectance

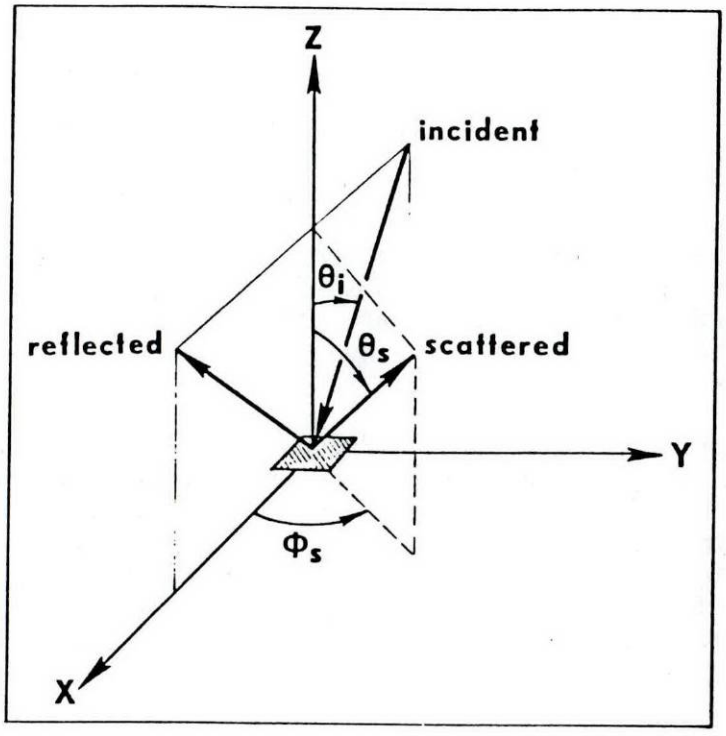



Figure 4. Schematic diagram of a reflective scattering geometry. Indicated are the specularly reflected and scattered radiation from a small collimated beam incident at angle $\theta_i$. (Ref. 4)

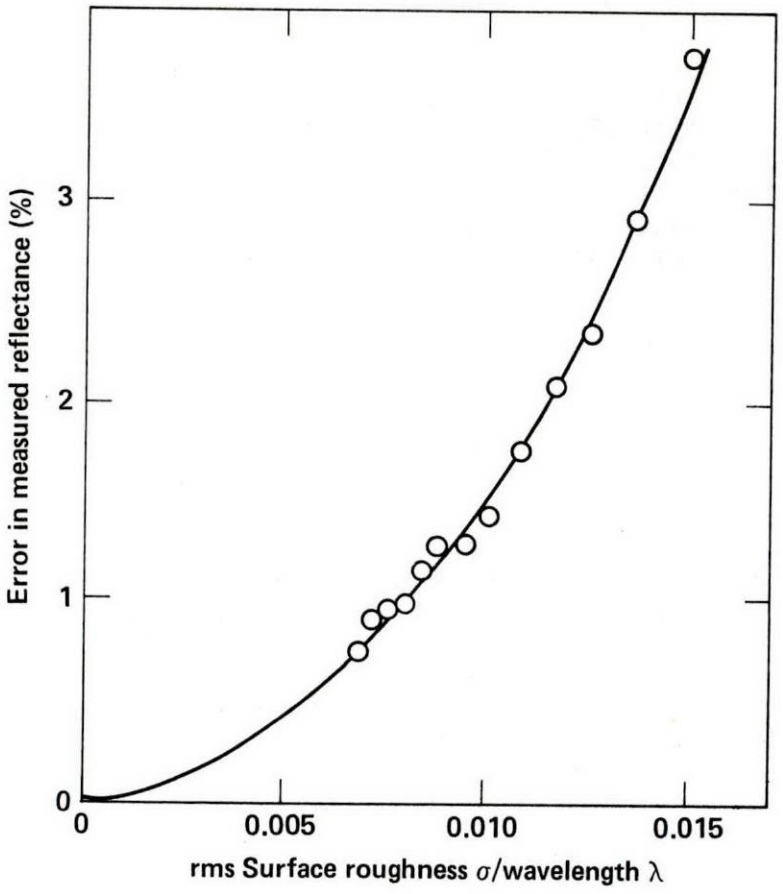
This becomes extremely important in specifying precision optical surfaces when one realizes that over 1% error in measured reflectance will be obtained from surfaces whose roughness $\sigma$ is only $\lambda/100$. In coating terms, this indicates for one thing, the crystal structure should not become apparent during subsequent machining or polishing operations. Also the height and lateral extent should, in general, not exceed 1.23μ" (300 Angstroms) peak to valley or 60A rms as these will cause scatter which correspondingly reduces reflectance. The errors in reflectance as a function of wavelength and rms roughness are shown in Figure 5.

The key factor for an electroplater in all of this is that the surface isn't good enough just because it has a "mirror finish" and one can see himself in it. It is best (though not completely) specified by (primarily for simplicity) by the sum of all scattered light normalized to the specular light reflected from the surface. This is commonly titled Total Integrated Scatter (TIS) and will hopefully be standardized soon through a, to be published, ASTM standard. In some optical applications, scattering at particular angles will be allowable or even desirable while in others, it must be minimized all together. Depending on the situation, surface finish will probably be specified by either wavelengths of rms roughness ($\sigma$) or an allowable TIS within a given surface spatial frequency bandwidth. Through the scattering relations given above and theoretical finish[6] it is possible to convert the optical requirements into feeds and speeds for the machine.

The above is probably the most simplistic view of optical finish and contour specification you will encounter. A variety of other optical aspects must normally be taken into account if correct specification and choice of manufacturing technique are to be accomplished. Such things as coating adhesion, residual strain, angular dependence of scatter, polarization, and damage threshold can all have influence on the requirements applied to a particular surface. Adjustments to and even selection of a process may be significantly altered by these. In some cases, the effects of a manufacturing process are not even understood well enough to know with certainty if the product will be satisfactory. While this is beyond the scope and intent here, the reader should at least be aware of them and the overall complexity of an optical tolerance and requirement problem.

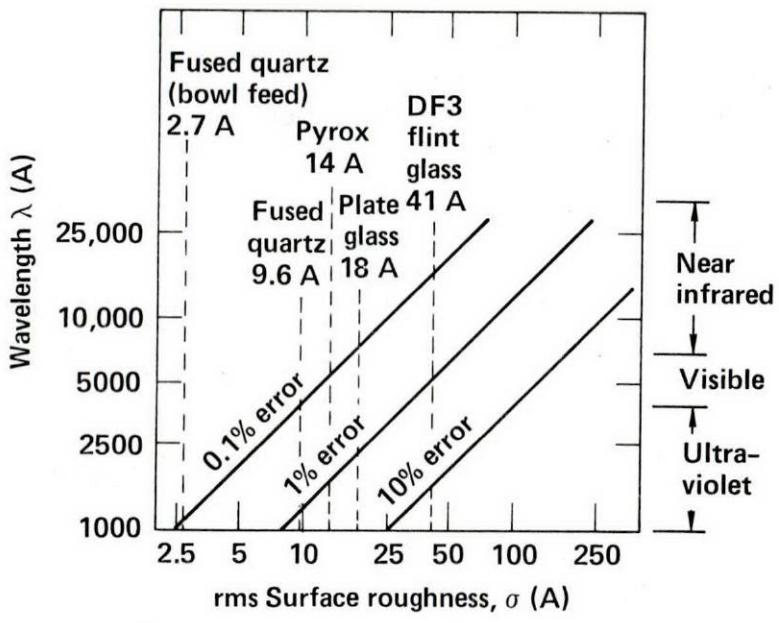
## Homogeneity

Perhaps the easiest way to see the importance of homogeneity in coatings from a material point of view is to note marked differences in the optical properties of metal coatings whose compositions are not greatly dissimilar. The implication, is that small variations in composition across an optical surface will cause corresponding variations in optical properties.




Error made in reflectance measurements when surface roughness is neglected. Circles represent experimental evidence.

Figure 5. The relationship between surface roughness and error in reflectance measurements. (From Bennett and Porteus, JOSA, Vol. 51, Pg 123, 1962).




Error caused by surface roughness in reflectance measurements as a function of wavelength. Dotted lines indicate roughnesses of typical optically polished glass surfaces.

Figure 5 (Cont'd.)

As an example, several 2" diameter x 3/8" thick discs were plated with various nickel coatings to a thickness of 5 mils. These coatings were subsequently ground and polished using conventional optical techniques and placed, one at a time, into a spectrophotometer. Here their reflectance is measured as a function of wavelength of light. The resulting spectral reflectance distribution is a direct consequence of the properties of the material being tested. As can be seen from Figure 6 each of the different platings (bright nickel, sulfamate nickel, tin nickel and electroless nickel) gave similar shaped reflectance curves, but at various levels[7]. While it is true that the variations of material properties across a single coating would be much smaller than those indicated here where the coatings have defined differences and placed down by different processes, changes in material properties would have similar effects. In many optical applications changes in reflectance at a single wavelength of a percent or two are totally unacceptable, and thus, this consideration becomes an important one.

While this author is by no means an expert in plating it seemed evident that a number of factors in the deposition process would affect coating composition. The first and perhaps most important is repeatability. The concentration levels, mixing, temperatures, cleanliness, rates, and types of chemicals and current density used will all affect the ultimate material properties of the coating deposited. Careful attention to consistency from one part run to the next will be important in achieving like material properties and the resultant coatings. Careful attention to such factors as current density and solution mixing concentration as a function of time all seem important to assuring that the plating composition is similar across the entire plated surface.

## Optical Manufacturing Processes Used on Coated Optical Components

Once the coating of an optical component is complete, having taken into account the various factors and technical issues outlined in the previous discussions, it is ready for final optical processing. Here, the coating is converted into a specular optical surface that will reflect light in the manner required. There are two common processes by which this coating can be converted into an optical surface. These are precision machining and conventional optical grinding and polishing. While these processes are quite different the result of their application is the removal of physical irregularities on the coated surface, the generation of specific shape required, and the improvement of finish (reduction of surface roughness) to a level where any resultant scattered radiation is within tolerable limits. The following is a simplistic comparison and description of precision machining and conventional optical polishing. Of particular interest will be how the machine and optical processing works, the types of materials that are processable, relative costs, production speeds, and the ultimate surface qualities achieveable. The following then is a brief attempt to describe and compare the two principal optical processing techniques used on coated surfaces.

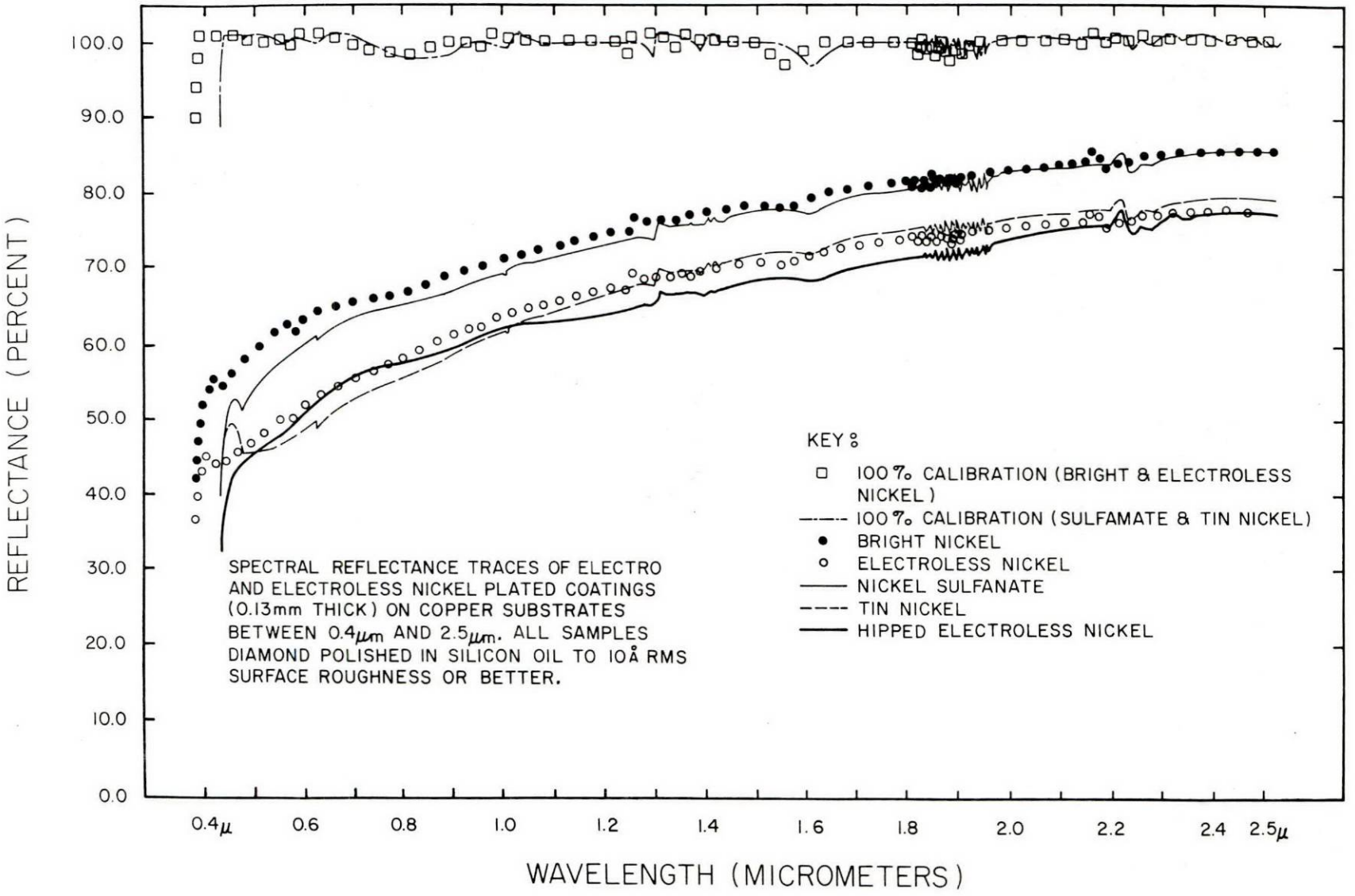

REFLECTANCE (PERCENT)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.4μ
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.5μ
WAVELENGTH (MICROMETERS)
KEY :
100% CALIBRATION (BRIGHT & ELECTROLESS NICKEL)
100% CALIBRATION (SULFAMATE & TIN NICKEL)
BRIGHT NICKEL
ELECTROLESS NICKEL
NICKEL SULFANATE
TIN NICKEL
HIPPED ELECTROLESS NICKEL
SPECTRAL REFLECTANCE TRACES OF ELECTRO AND ELECTROLESS NICKEL PLATED COATINGS (0.13mm THICK) ON COPPER SUBSTRATES BETWEEN 0.4μm AND 2.5μm. ALL SAMPLES DIAMOND POLISHED IN SILICON OIL TO 10Å RMS SURFACE ROUGHNESS OR BETTER.

FIGURE 6

Polishing

The removal of any material by polishing, be it glass or metal, is roughly a process of wear. Here a polishing or grinding lap base is coated with a deformable material (these vary greatly in compliance, viscosity and other material properties depending on the application). This lap is placed against the surface to be worked and continuously fed with a polishing compound, usually a fine, less than 3 μm dia., particle size metal oxide powder. The lap and workpiece are moved with respect to one another in a series of rotating and oscillating motions in a known way. The resultant energy imparted to the surface by the lap through a not-well-understood combination of mechanical abrasion, chemical attack and thermal flow disrupt and remove the material. This process results in surfaces whose finish characteristics are small compared to the wavelength of light being applied and whose shape can be controlled to some extent. This is a removal process where the wear averages itself over the area of the lap being used and has been described by Preston[8] as being proportional to the relative lap velocity, the pressure and the dwell time, or

$$\frac{dH}{dt} = K \times P \times V$$

$$= K \times P \times \frac{ds}{dt}$$

where

V = velocity of lap over the work surface
P = local pressure
K = wear constant (actually not a constant at all, rather a complex combination of physical and chemical properties that will not likely be completely understood or described for many years)
t = dwell time (time which the laps actually spends over some point x, y on the surface)

The advantages of this process with respect to precision machining in general relate to the wide variety of materials that lend themselves to polishing and the relatively high quality finishes normally achieved. Optical polishing has been successfully applied to most all glasses, metals and crystals, as well as most all hard inorganic materials and semiconductors. It is a process that is insensitive to mechanical vibration, acoustic coupling, and in most cases, small variations in temperature. It is evident from the large astronomical telescope objectives in existence that there is no maximum process size (minimum is related to the smallest lap that can be practically made and manipulated). On the other hand the area averaging nature and incomplete understanding of the mechanisms result in a process that has little geometric control, it is both time consuming and beyond a certain level not repeatable. The polishing compounds and carrier fluids interact with the optical material and result in polished surfaces containing

considerable residual contaminant materials as well as mechanical damage (effects spectral reflectance). In addition, the process must be carried out in a particle free environment to achieve the quality finishes. A number of edge effects (roll-off) limit the useful area to something less than the total surface. Finally, and most importantly, polishing is generally limited to simple geometries.

Precision Machining

Precision machining (also termed single point diamond turning or just diamond turning) has become very attractive, and in some cases the perferred method for producing certain classes of optical surfaces. For those not acquainted with this technology, precision machining is here defined as the combination of the very hard and sharp edges obtained from certain crystalline (usually diamond) tools with extremely precise machine tools (either liquid or gas bearing) operating under closely controlled environmental conditions to produce finished or nearly finished optical surfaces. This technology removes some of the difficulties in forming optical surfaces encountered in conventional grinding and polishing, specifically for that family of materials both physically and chemically compatible with diamond tools (see Table I). Because these tools are so hard and sharp no cutting edge contact area is presented to the material. This promotes the cutting process by restricting it to a thin shear plane with a minimum of contract stress or friction[9-11]. This results in a process that minimizes material deformation and hence results in both the specular finish required for optical surfaces and a contour that is exact copy of the tool path.

The origins of precision machining date back to World War II where such organizations as Phillips Research Labs (The Netherlands), Bryant-Simmons (Great Britain), Union Carbide Corp., Lawrence Livermore National Laboratory, Battelle Northwest, and Perkin-Elmer Corp. (USA) began to focus attention and effort on this technology. Studies specifically directed at applying this technology to the production of optical surfaces date back to the late 60's, and is largely due to development of a viable precision air bearing spindle. Optical surfaces that could be considered acceptable for infrared or long wavelength applications appeared in the early 70's. Since that time technological advancements and experience in precision control through such advances as laser distance measuring interferometers and thermal control techniques have contributed to the current status. Today, precision machining enjoys the status of a generally accepted process capable of producing a class of optical components on a routine and often high production basis. As the vast majority of all of the diamond turnable materials can be plated or coated onto other substrates, a large segment of the total number of optical components produced by precision machining have been electro or electroless coated prior to this processing.

The principal advantage of precision machining is that the family of shapes that can be manufactured are limited only to the size of the machine workspace. the machine symmetries (generally rotational), and tool accessibility. It is possible to include the machining of integral precision mounts and references during a set-up to assure extremely accurate references and eliminate the need of several complicating stages in the subsequent alignment processes. In addition the problem of edge effects is markedly reduced or eliminated. Finally, this process is both predictable and repeatable to within the machine accuracy which allows for reliable numerical or computer control. These advantages are obtained at the principal expense of the ultimately achievable contour and finishes achievable (at least today) as is clear from Table V. This table and the previous section on scattering imply a generally inferior optical performance from precision machined surfaces with respect to scatter and finish.

This problem extends even into the infrared wavelengths where this process is commonly used. Here, many systems operate in a regime where the background radiation exceeds the source, in some cases by many orders of magnitude, so that scattering caused from surface roughness can cloud, or in some cases even destroy detection of the signal.

Table V. Best and average finish and contour obtainable from polishing and precision machining*

| | | Finish | Contour |
|---|---|---|---|
| Optical Polishing | Best | ∿ 3A rms | ∿ 50A p to v |
| | Average | 20 to 50A rms | ∿ 250A p to v |
| Precision Machining | Best | ∿10A rms | ∿ 1000A p to v |
| | Average | 100 - 250A rms | ∿ 3000A p to v |

*Reference. G. M. Sanger, "A Perspective on Precision Machining, Polishing, and Optical Requirements", UCRL #86579, Lawrence Livermore National Laboratory, August 18, 1981.

## Optical Processing of Electro and Electroless Coated Components

Successful completion of coated optical components by either precision machining or convential grinding and polishing technologies imposes certain requirements on the material and processes used in the coating stage of manufacturing. In most respects the requirements imposed by the optical processes, either precision machining or optical polishing, will be similar to those described earlier with respect to the actual optical functionality of the completed part. The following is a list of requirements on electrodeposited and electroless coatings that will be subsequently processed by either precision machining or optical polishing.

1. All coatings, either electrodeposited or electroless and requiring subsequent optical processing must be free from nodules, pits, inclusions, small discontinuities in the materials phase, i.e. crystals in a very fine grained material or large variations in grain properties.

   The polishing rate is dependent both on material type and hardness. Should there be small discontinuities in either hardness or material type, polishing laps can gall and subsequently scratch or produce localized depressions immediately surrounding a discontinuous feature that have severe effects on resultant optical performance. In addition such small pieces can be literally pulled out of the coating itself due to the large shear forces applied by the polishing lap and forced to tumble between the optical surface and the polishing lap. This causes large scratches and chips in the optical surface. With respect to precision machining such discontinuous features apply transient loads or transient changes in loads to the tool as it passes over such featuares. These transient changes may force the tool to jump or chip which, of course, would adversely effect the rest of the surface being machined.

2. Electroless and electrodeposited coatings used for optical applications must be homogeneous across the part being plated.

   As previously indicated, the optical polishing process is material dependent. If the properties of the plating vary across the surface then the polishing rate will vary in a like manner. Under these circumstances it is very difficult or perhaps impossible to predict a final shape of a polished optical surface. It is, therefore, necessary that the homogeneity of the material be kept as constant as possible so the wear rate can be considered constant across the optical surface. While it is true that in the optical process there are certain edge effects that effect the wear rate near the edge of a component regardless of the material homogeneity this effect is well known and can be compensated for to an extent. Should there be an edge effect in the coating homogeneity due to plating edge effects, compensation by subsequent polishing would be unlikely.

From the precision machining point of view, homogeneity in the material will not have to be as stringently controlled, but there are two aspects of this process that would dictate a strong preference for coatings with good homogeneity characteristics. First, diamonds being crystallized carbon tend to wear chemically in any material that contains carbon. Therefore, any coating containing carbon will severely wear the diamond and thus destroy the tools capability of producing a specular surface. Secondly, variations in material properties will likely change the machinability characteristics of the coating as a function of position. While one portion of the coating may be considered machinable, another part may not. As such, it will be extremely difficult to produce uniform optical quality surfaces in coatings whose homogeneity and hence machinability varies with position on the surface.

3. Electro and electroless deposited coating would ideally be amphorous or, at least, have extremely fine grained structure.

As has been previously indicated, optical polishing is a material and hardness dependent process. If polishing is carried out on a coating whose crystal structure is large, the wear rate on any one crystal will be dependent on its orientation and its composition. For this reason it is difficult to achieve high quality optical surfaces on any material with large and randomly oriented crystallites[12-15]. The resultant surface wears at different rates and the topography will be stepped either up or down at the various grain boundaries. In a very fine grained coating where the grains are smaller than a wavelength of light the same effect occurs, but will not adversely impact the optical performance and hence is no longer an issue. Coating grain size on the other hand is generally not an issue with respect to precision machining. This is due to the fact that the machinability of the material is generally not grain size dependent. The only grain size issue in precision machining of plated optics would be that the crystallites be strongly enough bonded to one another that the stress field immediately surrounding the cutting edge during machining is not sufficient to pull out large numbers of crystallites as the diamond tool passes.

4. Electro and electroless deposited coating that will be precision machined with diamond tools should contain no carbon.

As indicated, diamond tools carbonize at elevated temperatures in the machining process when carbon is present in the material being machined. Should any of the coatings contain even a few parts per million of carbon the diamond tool edge will wear away with adverse effects to the resultant optical surface.

Considerable care must be taken with carbon in any coating process where the resultant coating is to be precision machined for optical applications.

5. Coatings for optical applications need to be as stress free as possible.

   From an optical point of view a stressed coating can impart polarization and shape change effects to the finished component. In many applications, the polarization must be maintained throughout the optical system. Stress can affect the reflected beam polarization in an unknown way and, therefore, adversely affect performance. Tolerances on optical surfaces are quite small ($\sim$ fractions of a light wavelength) so that small changes in shape will not be tolerable. Small changes in surface shape ($\sim$ 0.1 μm or $\lambda/4$) can change the previously mentioned MTF volume by an order of magnitude and severely alter the faithful duplication of the object by the optical surface or component. Stress in a thick coating need not be very large to significantly affect an optical component at this level.

Applications of Coated Optical Components

It was indicated earlier that anticipated acceleration of Defense Department spending would very likely impact the demand for infrared surveillance, fire control, pointer tracker, and FLIR (forward looking infrared) optical systems required for new and ongoing military applications. A major portion of these optics are metal or coated metal (gold, copper, aluminum, electroless, and silver) optics which due to their durability can be successfully employed in such systems. In addition, the development of advanced laser weapons systems is closely examining electroless nickel plated molybdenum substrates for use in the 2-4 micron region of importance to this program. Finally, a number of grazing incidence X-ray astronomical telescopes have been and are planned as coated optical instruments.

There are several reasons why precision machining has been used for X-ray optics. The very precise rotational accuracies of 15-25 nm is very important for grazing angle of incidence optics, which are also often cylindrical in nature. The accurate absolute positioning and repeatability of diamond machines offers a nearly optimal process for producing the optical surfaces in the coatings and for precisely aligning the individual mirror segments to assure good optical performance. Such an X-ray telescope shown in Figure 7 has been constructed of an electroless nickel plated aluminum forging. The electroless nickel was subsequently precision machined and then polished to assure the high quality optical finishes required for these very short wavelengths. Here the polishing is used primarly to remove the machining marks and improve the X-ray scattering characteristics of the telescope. While the demand for these types of optical components is not excessive the quality requirements on the coating is extreme.

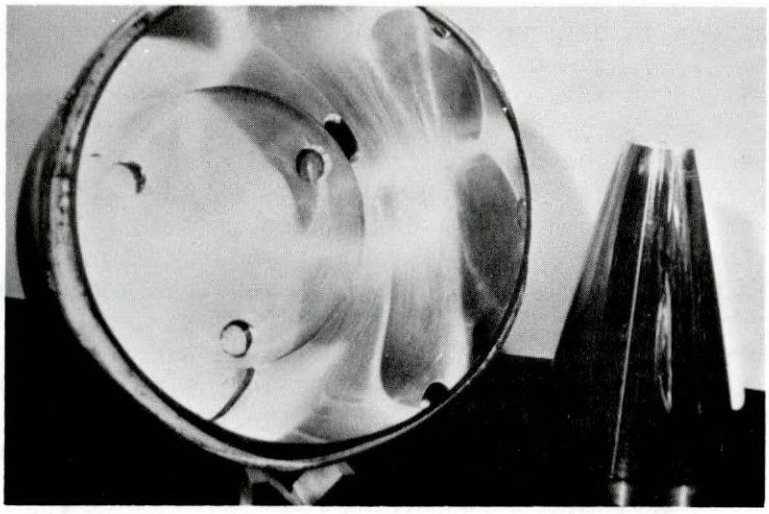


Figure 7. Photograph of ~15'' dia x ray telescope components. Normally made of electroless nickel plated onto aluminum and flown in sounding rockets.

A second application of coated optics, closely related to X-ray telescopes are X-ray microscopes. Such X-ray microscopes are used for imaging X-ray sources by the Department of Energy in fusion research and other high energy physics experiments. Their size is usually 20 to 50 mm I.D. as opposed to the 30 to 70 cm dia. used in typical X-ray telescopes. The requirements here are very similar to the astronomical instruments in that the coatings must be very uniform and free of any pits, inclusions, nodules or voids.

## Waxicon and Axicon Optics

A concave axicon is defined as an optical component with conically shaped surfaces. They have the property of transforming an incoming set of rays parallel to the axis of revolution into a line focus. A convex axicon will transform incoming parallel rays as if they were diverging from a line. Such a axicon differs from a cylindrical lens in that it can be generated by rotating a line about the axis of revolution. Figure 8 is a photographic example of such a linear axicon. These optics are used extensively in the development of unstable resonators for high energy laser fusion and weapon applications. Their construction generally is a molybdenum fabrication coated again with electroless nickel. This electroless nickel is subsequently diamond turned and then polished, any non uniformities or included discontinuities in the coated metal surfaces become sights for light radiation damage at the very high light levels used in these applications. While this technology is a new developing one, it is evidently clear from experiences to date that extremely high quality optical coatings will be required both now and in the future in this general area.

## Mold Masters and Die Masters

A great deal of optical and non-optical components are manufactured by die casting plastics. One process for producing mold masters for aspheric and other plastic optics is to coat mold inserts with a hard precison machinable material that can be diamond turned to high enough quality surfaces for use in mold operations. In this application generally electroless nickel coated stainless steel or other hard metal is employed. The electroless nickel coating can be precision machined relatively easily for use in this application. While it is clear that the durability of such coated mold inserts is not that of a conventional stainless steel insert, in some cases this is the only possible technique for producing the shapes required. Fresnel lenses, for instance, whose radial sawtooth profiles are not polishable by conventional technology are normally molded in large quantities for low cost applications. In such applications, inserts are plated and precision machined without subsequent polishing.

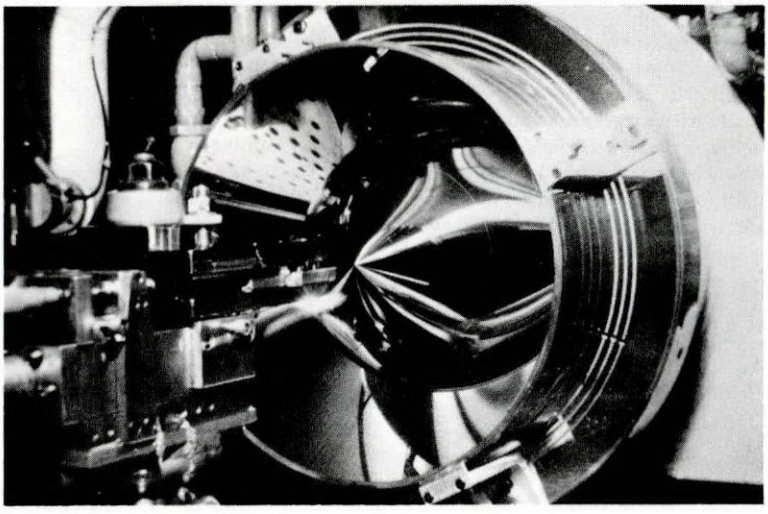


Figure 8. ~10" dia copper axicon on a diamond turning machine. Others made of electroless nickel plated molybdimum.

## Acknowledgement

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract Number W-7405-ENG-48.

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## References


1. U.S. Bureau of Census, International Trade Administration, "Optical Instruments and Lenses Industry", SIC 3832, August 1979.

2. Jenkins, F.A., White, H.E., "Fundamentals of Optics", Published by McGraw-Hill, New York, 1957, Pg. 300.

3. Carlson, F. Paul, "Introduction to Applied Optics for Engineers", Published by Academic Press, New York, 1977, Pg. 47-61.

4. Church, E.L., et al, "Relationship Between Surface Scattering and Microtopographic Features", Optical Engineering, Vol. 18 No. 2, Pg. 125-136, 1979.

5. Bennett, H.E., Porteus, J.O., Journal of the Optical Society of America, Vol. 51, Pg. 123, 1962.

6. Donaldson, R.R., "Nomograms for Theoretical Finish Calculations with Round Nosed Tools", UCRL #76047, Lawrence Livermore National Laboratory, 1974.

7. Sanger, G.M., and Dini, J.W., "A Perspective on Electrodeposited and Electroless Nickel Coatings Used in Optical Applications", Presented in Applications of Electroplating to Optics session of the 69th Annual American Electroplater's Society, San Francisco, June 20-25, 1982.

8. Preston, F.W., "The Theory and Design of Plate Glass Finishing Machines", Journal of the Soc. of Glass Tech., Vol. 9, No. 42, 1927.

9. Burnham, M.J., "The Mechanics of Micromachining", from Advances in Precision Machining of Optics, SPIE Proceedings, Vol. 93, Pg. 38-43, 1976.

10. Merchant, M. Eugene., "Mechanics of the Metal Cutting Process I. Orthogonal Cutting and a Type 2 Chip", Journal of Applied Physics, Vol. 16, No. 5, Pg. 267, May 1945.

11. Merchant, M. Eugene., "Mechanics of the Metal Cutting Process II. Plasticity Conditions in Orthogonal Cutting" Journal of Applied Physics, Vol 16, No. 6, Pg. 318, June 1945.

12. Namba, Y. and Tsuwa, H., "Ultra-Fine Finishing of Sapphire Single Crystal", Annals of the CIRP, Vol. 26, No. 1, 1977.

13. Namba, Y. and Tsuwa, H., "Mechanism and Some Applications of Ultra-Fine Finishing" Annals of the CIRP, Vol. 28, No. 1, 1978.

14. Namba, Y. and Tsuwa, H., "Float Polishing of Mn-Zn Ferrites and Characteristics of Finished Surfaces," Proceedings of the 4th International Conference on Production Engineering, Tokyo, Japan, Pg. 1017, 1980.

15. Namba, Y. and Tsuwa, H., "Surface Properties of Polished Stainless Steel", Annals of the CIRP, Vol. 19, No. 1, 1980.

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# Electroplating For Optics Applications Session N

## Specification And Function Of Metal Optics

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# SPECIFICATION AND FUNCTION OF METAL OPTICS

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## Abstract

This paper is mostly a review of specification of metal optical components, with attention to peculiarities of electroformed and plated parts. Component testing and function are described briefly, and the role of functional testing, where a part is checked in a configuration similar to its end use, is discussed.

## Overview

We will cover four main topics:

Specification: Specifications are directions from designer to fabricator for making a part. These should contain all information needed, have no unnecessary or conflicting instructions, and should be easily understood and unambiguous. Specifications for optical components have some unique features, which we will discuss today.

Function: Function of a part is mainly the designer's concern. He is given or develops a set of system specifications and determines a grouping of components which can satisfy requirements. This is typically a synthesis, where needs and costs are traded based on an analysis of various models. In the analysis, the function of different components is determined based on assumed characteristics. If the system function is unsatisfactory, the model is changed and analyzed again. When and if this process converges to a satisfactory solution, the designer prepares drawings and documents and has his creation built. This procedure may then be repeated. The builder of parts typically sees part specifications but has only incidental knowledge of parts' function.

Component Testing: Component testing is a step-by-step verification of part specifications. Optical parts require tests from a discipline known as optical testing. We will describe, very briefly, the major tests.

Functional Testing: Functional testing consists of exercising a part in a way similar to its end use. The test must be designed by someone who understands the part's function, and special test fixtures might be required. The advantage of functional testing results from substitution of functional testing for testing of some or all component specifications. Economies might be realized due to reduced test costs and acceptance of parts, which, due to compensating errors, are useable but may not satisfy particular individual specifications.

## Specifications

Specifications are a major part of the designer-fabricator interface. Hopefully, they are supplemented by discussion, but they may be the only interface and are the only archival instructions. Specifications for metal optics can be broken into five main groups:

Material: This answers the question, "What do we use to make the part?"

Mechanical: These familiar specifications indicate form and tolerances for all aspects except the optical surface.

Optical Surface: The optical surface is the "reason for being" of the part. Its specification is a bit different from that of general mechanical parts, and there are differences between glass and metal optics as well. This is the topic we'll treat in greatest detail.

Coatings: Optical engineers think of coatings as the reflective layers which are vacuum deposited on vitreous substrates. Such coatings can be put onto electroformed optics, but the topic of interest today is use of plating as a coating substitute.

Environmental: Parts must function and survive under specific conditions. The final coating or plating can be very important in providing longevity.

## Material Specification

Part Material: This is important to the designer for its mechanical, thermal and chemical properties. If the part is to be electroformed, a suitable material must be used. For other metal parts, the material will affect the type and sequence of plating operation. In machined optics, use of certain base materials and the need for given quality levels requires plating operations between machining steps. The designer must account for production requirements in material selection.

Purity: Purity is usually not of concern to the designer unless the part must be chemically resistant.

Heat Treating: Heat treating can be specified to change mechanical properties. Normally this is done to increase abrasion resistance at the expense of stressing the part.

Annealing: Annealing is often specified if additional machining is planned. A stressed part will spring when cut, and this can be very noticeable on an optical part.

## Mechanical Specification

Dimensions: Dimensions are normally given as a nominal and a tolerance range. It is common practice to follow mechanical design conventions.

Locating Surfaces: This is a very important topic. Optical parts require precise aligment in many applications. The designer has three choices. He can hold part tolerances such that simple assembly is possible; he can design tools to locate parts for fastening or potting and require an optical alignment operation; or he can include adjustments for alignment in the instrument. Alignment by assembly is attractive due to reduced labor cost and simplified service procedures; designers choose this approach whenever practical. Alignment by assembly, however, requires precise locating surfaces. The number required, which might include the optical surface, depends on the complexity of the optical surface (sphere versus paraboloid, for example). Locating surfaces are easily achieved in machined optics; electroformed optical parts are more limited. This reduces the number of applications where electroformed parts are useable; an advance in this art would help reduce costs in many instruments.

Fastening Features: Metal optics can have fastening features machined or formed. The designer should avail himself of this opportunity when practical.

Chamfers: Nature abhors a sharp edge. So do assemblers and servicemen.

## Optical Surface Specification

An optical surface sets a metal optical part apart from other metal parts. Here's how an optical surface is specified:

Definition: Optical surfaces are defined by geometrical shapes (sphere, paraboloid, for example) with appropriate parameters (radii, eccentricities, for example) and location of major features (center of curvatures, vertices, foci, for example). The statement may include a procedure for generating the surface, as might be the case with a torus or axicon. The designer can supply tolerances for the parameters or specify deviations as figure error.

Boundaries: Although a geometrical figure is complete, optical surfaces are usually a portion of a figure and require a boundary definition.

Clear Aperture: The clear aperture is an imaginary region on the optical surface and is the portion of the surface actually used. Much looser tolerances and lower quality can often be accepted outside this

region. Clear aperture should always be specified because of potential impact on production techniques and yield.

Figure Error: Figure error is the relatively large-scale departure of the optical surface from its ideal form. Most commonly, errors in shape are treated separately from errors in location. Errors in shape are specified by deviation or slope error or both.

Deviation (Figure 1) is a linear measure of departure of the optical surface from the ideal shape, which is often adjusted, within limits, to a "best fit". Deviation is usually specified for high-quality optics for use in diffraction-limited systems and can be measured in micrometers (microns), wavelengths of light, or the number of interference fringes observed in interferometric testing. It can be expressed as peak-to-peak, peak-to-valley or root-mean-square (RMS) and can be measured on a reflected wavefront or the surface profile. Specifications should be clear on these matters.

Slope error (Figure 1) is the angular departure of the optical surface from its ideal form. It is measured in microradians to milliradians, or equivalent, and is often specified for light collection or illumination optics.

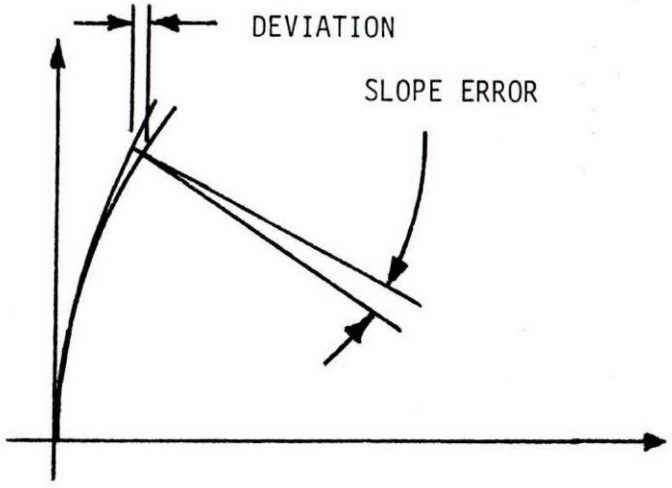



Figure 1: Figure Error

Both deviation and slope error can be specified to insure a smooth surface. As an example, surfaces cut on a two-axis machine can have small deviations but relatively large slope error due to narrow zones.

Surface figure can change as a result of introduction or relief of surface stress due to separation from forms, machining operations or plating. If the change is reproducible, it may be possible to introduce "Kentucky windage" to compensate. Again, keeping clear aperture at a minimum values or oversizing parts might help in maintaining figure.

Surface Quality: Surface quality specifications indicate small-scale deviations of the surface from it's large-scale form. Defects are described as scratches, digs, pits, machine marks or greying.

One class of specification is the cosmetic or scratch-and-dig specification, described in the U.S. Military Specification MIL-O-13830A, "Optical Components for Fire Control Instruments; General Specifications Governing the Manufacture, Assembly, and Inspection of", which we will call, "Mil Spec Thirteen Eight Thirty." This is widely used to specify surface quality for commercial glass optics, because thirteen-eight-thirty is widely known.

The scratch and dig glass optical specification grew out of fabrication. Scratches (Fig. 2) occur mostly in the polishing process and are specified by the apparent width of the scratch in micrometers. Digs (Fig. 2) are pits left from incomplete grinding or are small spots due to mishandling which are round as opposed to long. The dig specification is the average "diameter" of the defect in hundreths of a millimeter.

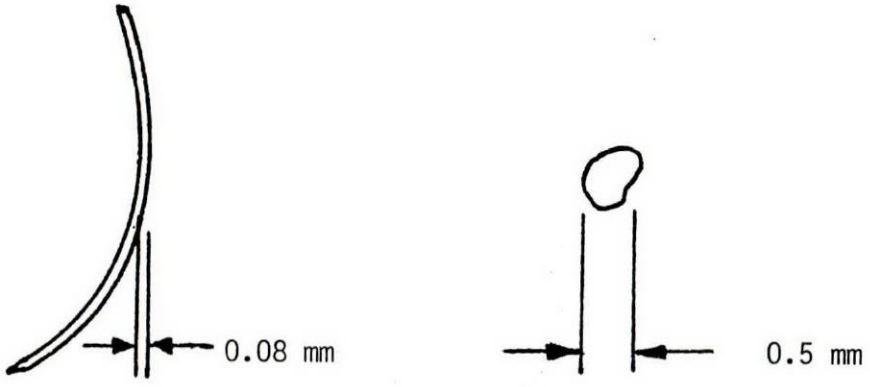



Figure 2: Scratch/Dig of 80/50 per MIL-O-13830A

The scratch/dig specification can be applied to metal optics and often is despite the obvious limitations. Scratches are still scratches and can be used to specify greying; digs are voids or damage marks.

American National Standard PH3.617, published in 1980, has similar coverage to MIL-O-13830A and is intended for use with commercial photographic optics. This standard should gain wide acceptance with time.

A second technique for specifying surface quality is by root-mean-square (R.M.S.) surface roughness (Fig. 3) in the same manner used to specify finish on machine parts. This has advantages over scratch-dig, because the measurement is much less subjective and results can be related to scattering loss. (Elson, Bennett and Bennett, Chapter 7, Volume VIII of Applied Optics and Optical Engineering, Shannon and Wyant, Ed.; Academic Press 1979).

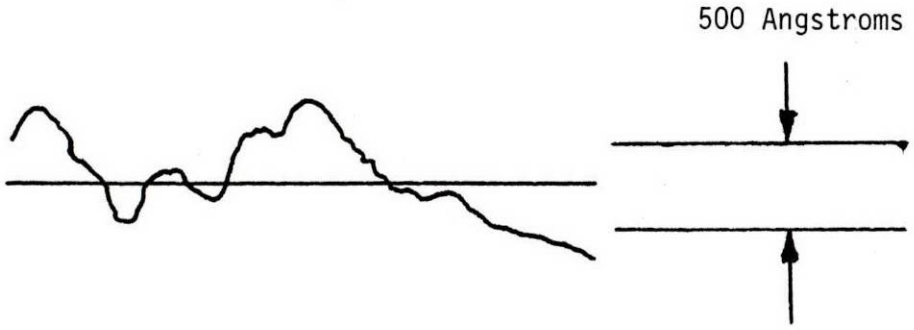



Figure 3: R.M.S. Surface Roughness

Coatings and Plated Surfaces

Optical coatings were originally put down by a chemical process. This was supplanted in the 1930's by evaporation and condensation in vacuum chambers for all front-surface mirrors. When optical engineers think of coatings, vacuum deposition is usually the assumed mechanism, but reflective surfaces can be formed by plating. Specifications are similar in either case.

Coatings can be multiple layers, each of which serves a purpose. Metal is used to form a reflective layer and dielectric materials are used for protective coatings, or to enhance reflection, or both.

Specular Reflectance: Specular reflectance is the ratio of flux reflected, according to the law of reflection, to flux incident. It has some variation with angle, so it is best to specify the angle of incidence for the measurement, typically eight to thirty degrees. Spectral reflectance can vary significantly with wavelength and is typically specified as a minimum value, in percent, at a particular wavelength or over a range of wavelengths.

Scattering: Scattering depends on the small scale irregularities or microstructure of the optical surface and of the coating or plating. It has strong dependence on wavelength. At relatively short wavelengths, the invisible "texture" of the surface due to crystal structure is the main cause of scatter (and of absorption, too). The scatter can be specified as Total Integrated Scatter (T.I.R.), which is a single-number measurement of the diffuse component of reflection (See Elson et. al., p.199). In many cases, scatter is not of interest and is not specified; scattering losses are lumped with absorption losses and covered by a minimum specular reflectance specification.

There can be a noticeable disparity between vacuum coatings and platings with respect to specular reflectivity and scattering. This is due to different texture in the coatings and platings. Platings are often pourous; although the porosity can vary with process parameters and can be changed (improved) by subsequent treatments, such as sintering. These processes are usually considered proprietary, and they can make a substantial difference.

Pinholes and Defects: Coatings and platings have pinholes and defects. These can be specified using scratch-dig numbers per MIL-O-13830A.

Adhesion: The coating is usually tested for its resistance to peeling or flaking by pressing sticky cellulose tape onto the coating and attempting to pull the coating off.

Abrasion Resistance: Coatings are tested for abrasion resistance (hardness) by rubbing with cheesecloth or an abrasive eraser and then inspecting for compliance with a scratch specification.

Tests for adhesion and abrasion resistance are described in various military specifications, notably MIL-M-13508C, MIL-C-14806A and MIL-C-675A.

Environmental Specification:

Environmental specifications indicate conditions under which the part must operate or survive.

Abrasion Resistance: These specifications, which were discussed as coating or plating specifications, are often included as environmental specifications for the part. They relate to ability to withstand cleaning and (mis)handling.

Chemical Resistance: Resistance to deterioration or corrosion in a given environment may be required. Platings with proper heat treatment can excel in this respect.

Survival

The part may be required to withstand a range of humidity, a range of temperature and high radiation flux (either ionizing or non-ionizing but with very high field strengths).

It is in large part the designer's job to insure that the part is specified properly, but the fabricator usually plans for coating processes which permit survival in environmental tests.

Function

The optical part is designed and specified to do a job. This is its function, which might be:

Image Formation: This usually requires good optical figure,

Light Collection: Efficiency is important, which implies high quality coatings of platings,

Illumination: Efficiency and good environmental characteristics are often required,

Beam directing: Precise geometries and low mass are important,

Beam shaping: These optics often have exotic forms.

As mentioned in the introduction, function is the designer's concern. In determining if a part will function properly, the designer considers its

Functional Characteristics:

Functional characteristics are abilities to modify light, usually expressed in quantitative form. You may recognize the terms from the "Optics" chapter of your high-school Physics course!

Deviation of Light Rays: Light rays are reflected according to the law of reflection. This allows the designer to determine image location and abberation. Figure error causes additional deviation and is an unknown or statistical quantity.

Absorption: Absorbed light is lost to the system and results in heating.

Scattering: Scattered light deviates from the law of reflection. It ends up somewhere other than its intended location. The result is termed stray light or glare, and it lowers detection limits or reduces image contrast.

Both absorption and scattering are wavelength dependent and modify the transmission spectrum of the system.

Environmental Changes: Optical system properties change with temperature due to thermal expansion and the system may deform dynamically due to vibration. The designer must account for these changes and specify the system and its components to avoid problems. This often affects material choices and mounting techniques.

Reliability: Reliability is the characteristic of continuing to perform within specification in any allowable environment and at an acceptable failure rate. The specifications most effected are mechanical (particularly locating and fastening) and environmental.

A designer's job involves starting with a specification for the instrument (which states its function in detail), synthesizing a configuration which may do the job, determining the function characteristics of components and the net effects on a system function, and finally specifying the components (which includes determining tolerances). The net result is not unique, but depends on the designer's experience and prejudices. Even if the designer is given a layout, the tolerances he determines for parts will probably differ from those assigned by a different designer. This is due to the statistical nature of part characteristics and judgement used in budgeting errors.

Now that we've talked a bit about optical specifications and their connection to function, we'll discuss methods of testing.

## Optical Testing

One of my professors said "Never specify what you can't measure." The discipline of measuring optical components is optical testing, and it has aspects which differ significantly from other types of test and inspection.

Visual Inspection: The visual inspection identifies the part, checks for cracking or peeling, verifies presence of all features and markings (if required) and checks for compliance with scratch and dig callouts. This is done by visual comparison with standard defects. Not only is this subjective, but some standards are thought to be more favorable than others!

Mechanical Inspection: Standard mechanical inspection techniques can be used to check major dimensions.

Interferometric Testing: Optical surfaces are often steep enough or precise enough that coordinate measuring techniques are not applicable. More commonly, light is reflected from the component and interfered with a known wavefront from a reference surface. If the wavefront from the optic is deformed, parts will be out of phase with corresponding parts of the

reference wavefront producing an interference fringe pattern. Fringes occur as optical path difference changes by a wavelength, corresponding to differences in the test optic and reference surface of 1/2-wavelength. The result is a contour map of the optical surface referred to the reference surface.

This type of testing requires some skill and knowledge in designing the test and interpreting results as well as care in execution, but good equipment is commercially available and automation is both possible and purchasable.

Shadow Tests: These tests comprise the traditional methods of optical testing. A small object is placed in the light beam from a small source of light. The small object is in or near the focal region and casts a shadow on the test optic. The shadow is viewed by putting your eye into the beam and focussing on the optical surface. The test is called a Foucault test if the object is a knife edge, a Wire test if the object is a wire, and a Ronchi test if the object is a grating. Transverse or longitudinal abberation is determined from the shadow positions at various locations of the object.

These tests are still widely used by opticians in figuring glass mirror substrates and can be used for inspecting metal mirrors. The tests require considerable skill for interpretation and, although the test can be automated, packages are not commercially available. These tests have the advantage of greater sensitivity to slope errors of very small spatial extent than does interferometric testing.

Reflectivity Measurements: Specular Reflectivity Measurements are best made on flat samples (witness pieces) using a spectrophotometer and a reflectance test attachment. These are commercially available. Curved surfaces require a custom setup.

Scattering Measurements: Scattering measurements require custom facilities (Elson, Bennett and Bennett p.213).

Functional Testing

There is a corollary to the rule, "Don't specify what you can't measure." This is "Never measure what you specify, unless you have to!" The reason is cost. Testing is a necessity if bad parts are to be kept out of stock, but the cost of doing this must be controlled. The least expensive acceptable alternative should be selected. One alternative to testing for each component specification is testing a part by exercising it in a configuration similar to its end use. This can be termed functional testing which has particular advantages and disadvantages:

"Pass" indicates a useable part: Individual specifications may not be met due to compensating errors.

Lower Inspection Cost: This is one highly desirable result.

Higher sampling rates: Automated testing might be practical.

Tests must be designed: This is a front-end cost. The engineer must insure that parts which meet specifications will pass the test, and that parts which pass the test will function properly.

Fixtures are often required: This is another front-end cost and may result in storage and maintenance costs as well.

Functional testing has proven useful in the author's experience for cost reduction, for insurance against production problems, and in shortening cycle time when defective parts are received. The feasibility of using a functional test should be considered for production situations. Although it uses engineering resources and tooling funds, and even though it's use necessitates good vendor-purchaser relations, the benefits can be significant.

An example of a functional test is shown schematically in Figure 4. It is an enclosed energy test, where the optical part is fixtured and reimages a source onto a detector. Light levels are measured with and without an aperture, and detector readings are ratioed. Other components of the test set up, such as spectral filters, choppers and lock-in amplifiers are not shown. The test will check accuracy of locating surfaces, figure error, and specular reflectance, although compensation can occur.

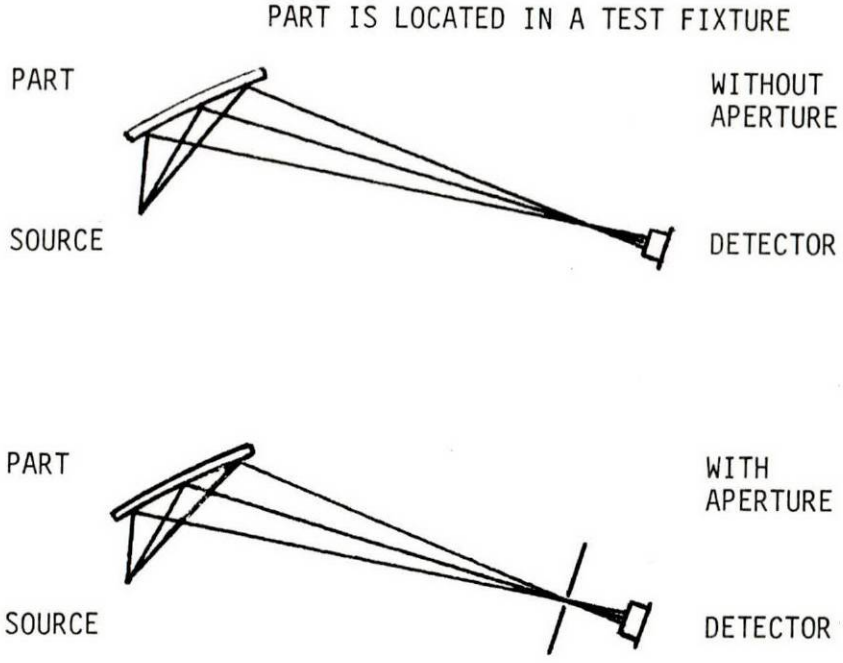



Figure 4: An Enclosed Energy Test

Suggestions for Further Reading:

Modern Optical Engineering by Warren J. Smith, McGraw-Hill 1966 is the best general reference available.

Optical Shop Testing, Edited by Daniel Malacara, Wiley, 1978, is a very detailed reference on general optical testing.

References on electroforming and metal optics include Volume 65 of the Proceedings of the Society of Photo-Optical Instrumentation Engineers (S.P.I.E.) and the Proceedings of the A.E.S. Electroforming Symposium, Atlanta, GA., December 19, 1974.

The series Applied Optics and Optical Engineering, Academic Press, 1965 to present, currently 8 volumes, has detailed articles on various aspects of optical engineering.

Acknowledgements

Greg Sanger put me up to this, and Kathleen Murphy prepared the manuscript. Hewlett-Packard Company donated some of my time.

# N-3

# Electroplating For Optics Applications Session N

## High-Reflectivity Surfaces for Laser Mirrors

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# HIGH REFLECTIVITY SURFACES FOR LASER MIRRORS

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# HIGH REFLECTIVITY SURFACES FOR LASER MIRRORS

by

M. E. Browning and D. B. Pollock

Highest interest in obtaining optimum reflectivity in laser mirrors has been expressed over the last several years in gold, aluminum, and silver surfaces.[1] Classically, silver has the highest reflectivity in the wavelengths in the UV but not in the IR.

One problem that mirror materials, such as silver, aluminum, and gold have in common is that the highest purity coating is usually exceedingly soft and scratches readily. This, of course, limits its efficiency as a high quality mirror coating in most industrial applications. Silver also tarnishes readily since it reacts freely with atmospheric sulfur, oxygen, and other active gaseous species.[2] Aluminum also oxidizes and reacts with caustic materials.

Attempting to electrodeposit hard, highly reflective silver for use in the desired spectral area has not been entirely successful.[3] Optical coatings, applied to minimize thermal absorption while protecting the aluminum

and silver have not been sufficiently successful in the IR region. Multi-layer dielectric coatings for silver have been shown useful in protecting the surface, but effects of operating environments, contamination, humidity and/or thermal cycling pose handling problems.[4]

Gold can be electrodeposited with minor amounts of alloying elements such as nickel, cobalt, indium, antimony, iron, and even arsenic to produce bright finishes over highly polished substrates.[5]

## I. MIRROR SURFACES AND THE TEST PROGRAM

In the current study, electroless nickel was deposited over either molybdenum[2], stainless steel or copper depending on the final application, design and function. To obtain the maximum quality surface, the mirror face was single point diamond turned (SPDT) before final coatings are applied.[6] To examine the reflectance of various types of golds (electrodeposited), $1\frac{1}{2}$ inch diameter test coupons were fabricated from conventionally available 6061-T6 aluminum. The surface was optically polished before electroless nickel was deposited.

After the electroless nickel plating, the coupon was given a final optical polish on the test face and pack-

aged for test gold application. Hardness specimens were also fabricated from 6061-T6 aluminum into ½ inch cubes. One face was to be plated with 0.002 inches of gold for cross-sectional indenting. This method effectively avoids any secondary reacting of substrate material on the accuracy of the measurements. Hardness measurements were made with 25 g. load.

## II. REFLECTANCE FACTORS

Most optical applications which use mirrors are trying to collect signal energy and to condense it. As a consequence the efficiency with which this can be done is of considerable interest. In other applications, signal energy is simple reflected through an optical instrument. Still the reflectance of the mirrors is a property which strongly influences the efficacy of the instrument. Reflectance is commonly considered to be the ratio of the energy leaving a surface to the energy incident as the surface. As such the bulk physical properties of the material which make up a surface and the wavelength of the incident light or radiant energy are properties that need to be considered.

There is another important aspect of reflectance. When light is incident to a surface, the energy flow has some

direction associated with it. Interacting with the surface causes the direction of the energy flow to be changed. Were the surface a plane and a perfect conductor for the wave length of light under consideration then 100% of the incident light would be reflected and it would be travelling in a new direction in accordance with Snell's law. That is to say the angular distribution of the incident energy would not be changed. Such an idealized surface is never realized. For most practical purposes, the differences from a perfect surface can be ignored. However, with the sophistication of instrumentation today, the differences frequently need to be accounted. In addition to the reflectance property the redistribution of the incident energy must be known. A function called the "Bidirectional Reflectance Distribution Function" is used to describe the distribution of the energy which is reflected from a surface. The measurements needed to quantify a BRDF are rather straight forward to make. Instruments and techniques are unsophisticated . Figure 2 schematically illustrates how this is done. In effect, light with a known direction of propagation is reflected from a surface. By appropriate data taking, reduction and analysis, the light going in other directions is measured. Figure 2 is a plot of the data BRDF for the coupons which were used in this study.

It is a plot of the fraction of the incident energy, travelling in a given direction after interacting with the surface. The fraction is normalized for solid angle. The angular direction which it is travelling, $\theta$ , is referenced to the direction which it would be travelling, $\theta_0$ , were the surface ideal. These quantities are labeled on the plot of Figure 3.

There is a large spread in the data. It covers three orders of magnitude. (Each coupon's serial number is listed by its appropriate curve.) All of the coupons underwent the same surface preparation prior to being coated with gold. The thickness of the coatings is, as given in Section VI of this paper, believed to be one of the major contributors to the large spread in the data. The alloying element is also a factor, as discussed later.

It is commonly known that as an electroplated coating is applied thicker, the surface becomes rougher. That is what is shown by the figure, approximately. The coatings are by different processes, and this may contribute to the effect shown. A quantitative proof appears at best, to be difficult. Also shown on the figure is the measurement limit imposed by the experiment hardware.

Conventional reflectance measurements in the test wavelengths (3.5 - 4.0 $\mu$m) were performed.

It is interesting to note that the reflectance of these coupons as shown by Figure 4 reveals very little variation over the 3.5 to 4.0 micrometer wavelength region. The error in the reflectance data reported here due to the surface roughness is less than one part in ten thousand. Much less than other inaccuracies which restrict the reflectance reported to an accuracy of better than one part in a hundred.

## III. DEPOSIT HARDNESS

Mirror surfaces are easily scratched in many operations employed in set up and servicing moderate to high power laser systems. Electro-deposited gold alloys were solicited possessing hardnesses between 180 - 200 DPH. Table I presents the seven test series examined during this study and the hardness determined. One can see that series 10 and 14 have identical average hardness measurements although they are different base alloys and percentage levels.[7]

Additional microprobe examination was performed in series 4 material (nickel added gold) to isolate impurities.

## IV. GOLD TOPOGRAPHY

A microsection of nickel hardened gold, representative of laser mirror material, was studied at 1600X. The deposited gold alloy containing between 0.15 and 0.2% nickel is sufficiently sound (Figure 5) and reflectance measurements, while not the highest, were reproducible from area to area. In other reflectance measurements where values indicated surface imperfections, contamination or other faults, the nickel containing gold was further examined for possible inclusions. Figure 6, taken near an area in question, indicates the material is somewhat inhomogeneous. Electron microprobe analysis detected areas of higher than normal potassium. This may have been in part responsible for significant (8-10%) variations in reflectance in mirror material in this area.

One area of particular concern in examining the nickel-gold mirror material revealed higher than normal amounts of potassium as well as carbon. Figure 7 depicts the roughness discovered in the region just mentioned. Potassium has been previously identified as a potential trouble impurity in deposited cobalt-nickel golds for electronic applications[8]. Figure 8 shows SEM-EDX spectrum of potassium and nickel in nickel-gold electroplate.

## V. DIFFERENCES IN REFLECTIVITY

Differences in reflectance of various gold alloys on laser mirror test coupons were studied with a view toward determining any potential effect of alloying constituent, percentage and major impurities.[9] Table II presents a listing of various alloy golds examined for laser mirror application and their reflectance at various wavelengths of interest to this study. It can be seen from Table II that different hardening (brightening) agents and their respective amounts make a visible difference in reflectivity values taken during this study. Series 12, analyzed to contain small amounts of antimony and iron, gave the highest absolute reflectance values.[10]

In order of descending reflectance, series 17, a sulfite gold containing approximately 0.08 to 0.15% arsenic was very close. The nickel gold, series 4, containing 0.15 to 0.20% Ni ranked third in the reflectance tests. As mentioned earlier, this material was suspect of polymer formation under electron microprobe investigation.[11] Similar occurrences of discrete areas of polymer development ahve been documented in the literature[12, 13]. Additional investigation is in order to determine the full effect of this type of contaminant on long term performance laser system.

## VI. SURFACE PROTECTION

To measure the protective quality of the various gold alloy electrodeposits in this study, the ASTM nitric acid vapor test was used . Since the protective gold mirror coatings must maintain optimum reflectance for several years in use and potential storage in varying unfriendly environments, the test was conducted using a four hour exposure. Series 12, most reflective in initial tests, failed because it was not applied in sufficient thickness (only 3-5μ inches). Because of the very thin deposit, no comment can be made regarding the pore freedom/porosity of this material. Table III presents a summary of reflectance differences comparing initial unexposed measurements to those of specimens exposed to a four hour nitric acid vapor test.[14]

CONCLUSIONS:

Electrodeposited gold, brightened and/or alloyed, with nickel, cobalt, arsenic or antimony appears satisfactory for IR laser mirrors with surfaces that resist minor brushing, rubbing or very light scratching. Under corrosive environments, the gold thickness should be set for 50-70 micro-inches. Above this level reflectance and BRDF values suffer slightly. Hardness requirements for gold alloys of this class should be specified as 180-200 Knoop.

Some occurrences of surface imperfections and reduced reflectivity have been postulated as caused by higher than normal entrapment/inclusion of potassium and carbonaceous polymer. One of seven gold alloys tested revealed between 98.5 and 99% reflectivity in thicknesses less than 20 micro-inches at 3.5 - 4.0 microns. A sulfite gold containing traces of arsenic disclosed reflectivity of 98.3 to 98.8% at 80 to 90 micro-inches in the 3.5 to 4.0 micron region.

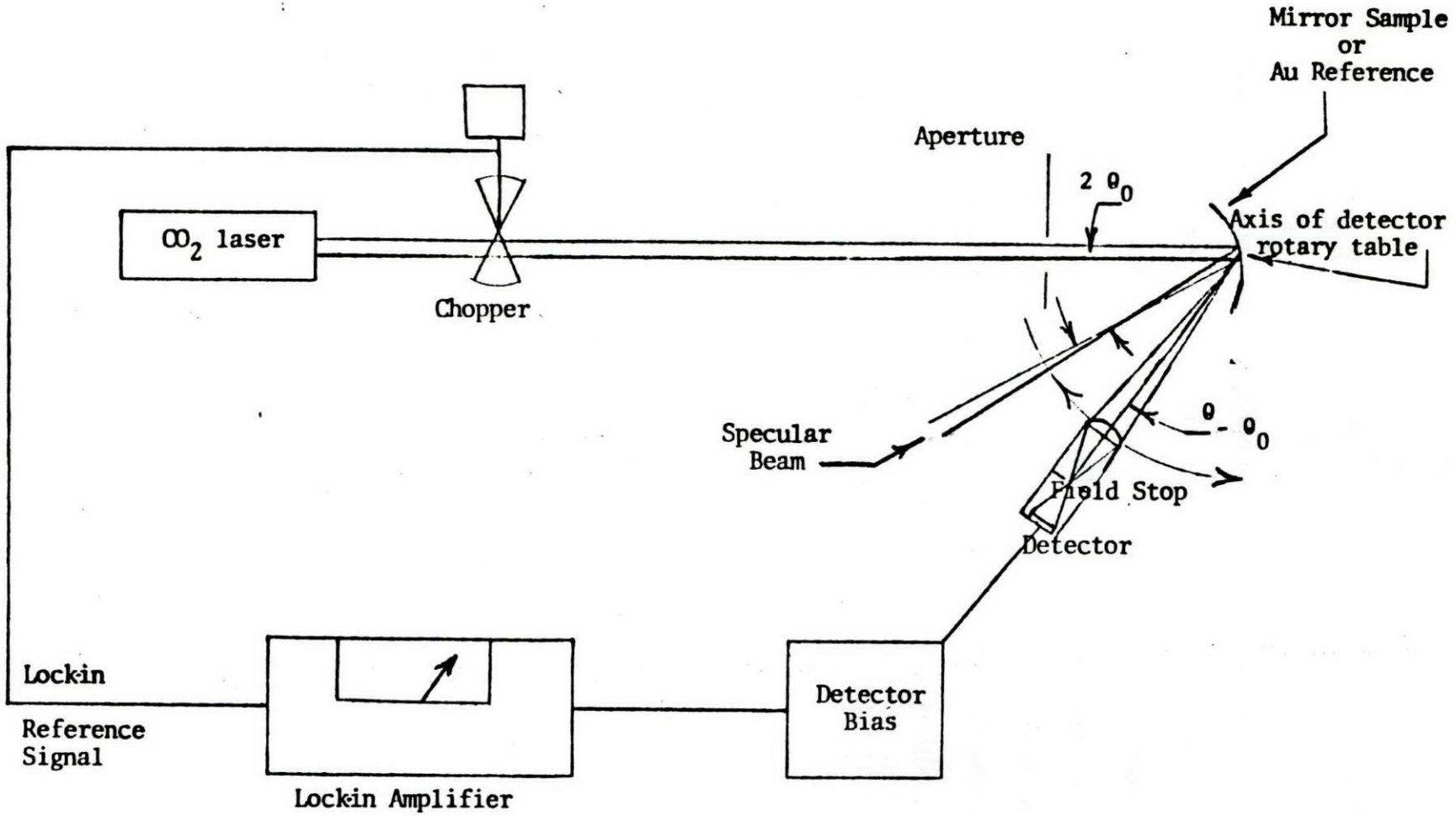



Figure 1. BRDF Measurement Schematic

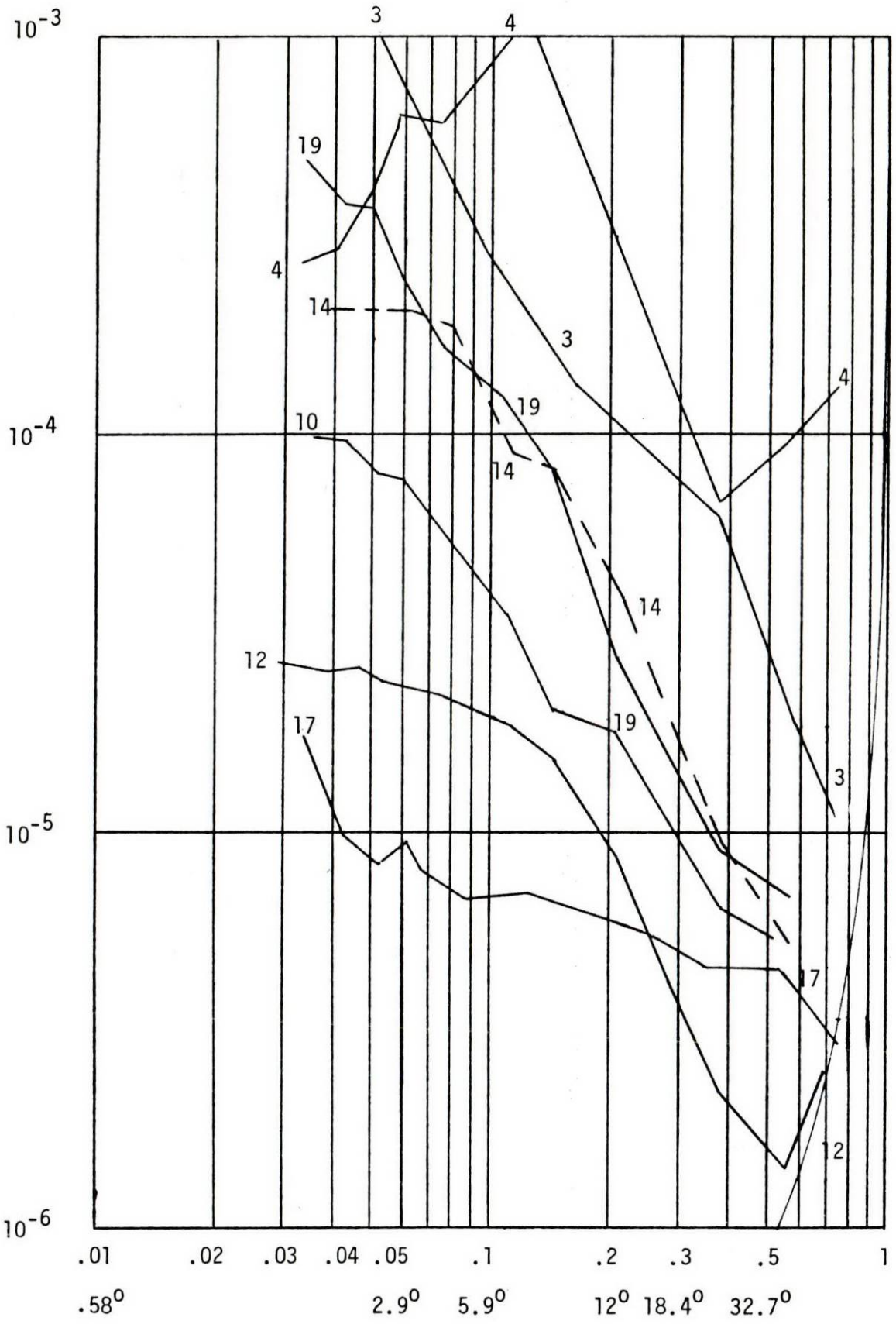



Figure 2. Scatter Profiles of Various Au Coupons

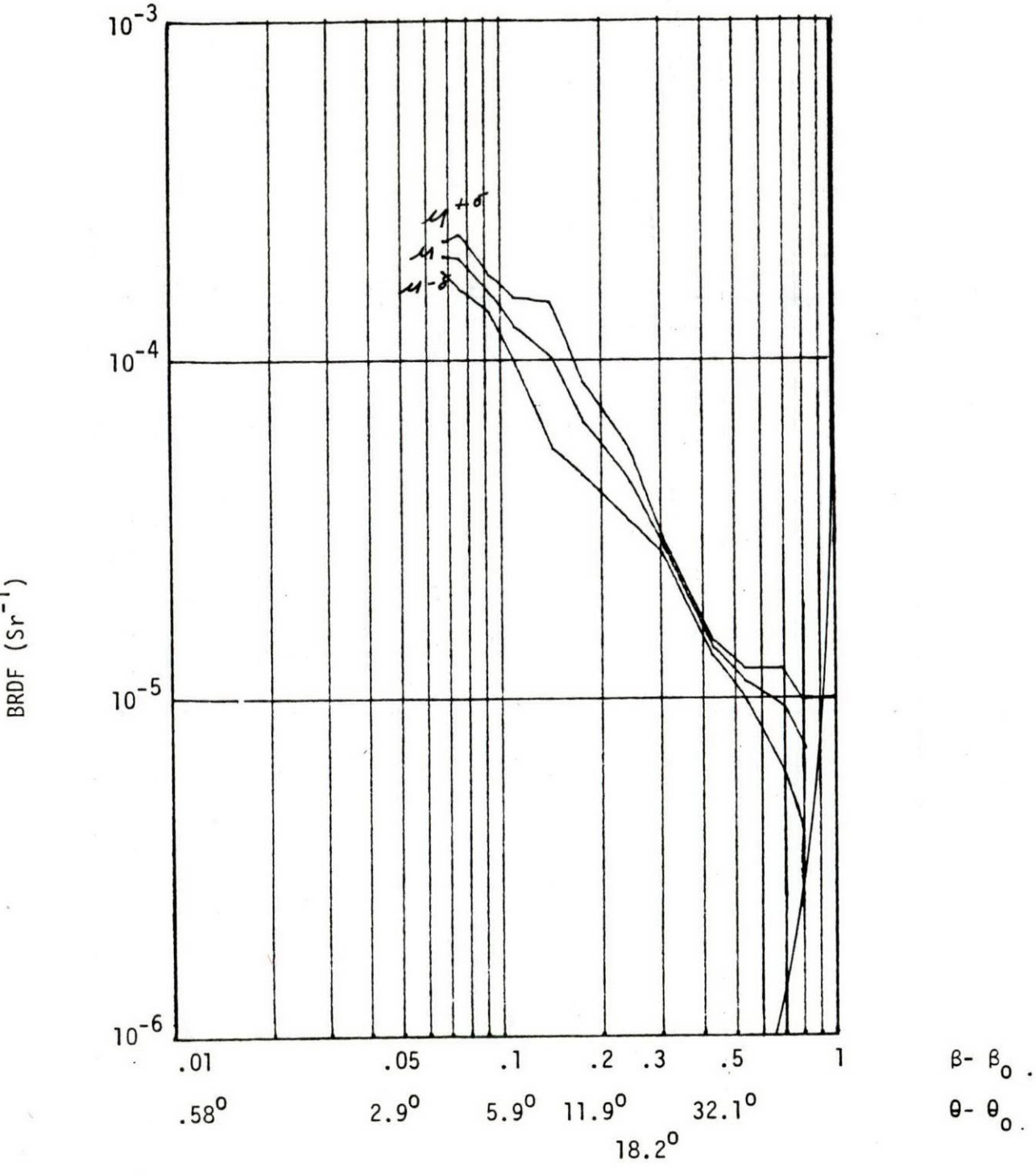



Figure 3: Scatter profiles of Au Coupon #1

#(X)/#6* RATIO SPECULAR REFLECTANCE DATA SUMMARY

| Test Sample #(X) | WAVELENGTH 3.5 μm | 3.6 μm | 3.7 μm | 3.8 μm | 3.9 μm | 4.0 μm |
|---|---|---|---|---|---|---|
| 3 | 0.9724 | 0.9863 | 0.9755 | 0.9766 | 0.9720 | 0.9805 |
| | ±0.0058* | ±0.0144 | ±0.0044 | ±0.0050 | ±0.0042 | ±0.0037 |
| | ±0.0072** | ±0.0178 | ±0.0055 | ±0.0062 | ±0.0052 | ±0.0046 |
| 4 | 0.9869 | 0.9945 | 0.9869 | 0.9883 | 0.9891 | 0.9853 |
| | ±0.0026 | ±0.0133 | ±0.0038 | ±0.0029 | ±0.0030 | ±0.0045 |
| | ±0.0032 | ±0.0165 | ±0.0047 | ±0.0036 | ±0.0037 | ±0.0056 |
| 10 | 0.9739 | 0.9859 | 0.9792 | 0.9745 | 0.9752 | 0.9824 |
| | ±0.0042 | ±0.0136 | ±0.0035 | ±0.0042 | ±0.0030 | ±0.0018 |
| | ±0.0052 | ±0.0169 | ±0.0043 | ±0.0052 | ±0.0037 | ±0.0022 |
| 12 | 0.9958 | 0.9953 | 0.9976 | 0.9988 | 0.9984 | 1.0017 |
| | ±0.0038 | ±0.0023 | ±0.0072 | ±0.0035 | ±0.0030 | ±0.0032 |
| | ±0.0047 | ±0.0028 | ±0.0089 | ±0.0043 | ±0.0037 | ±0.0040 |
| 14 | 0.9726 | 0.9814 | 0.9779 | 0.9781 | 0.9714 | 0.9803 |
| | ±0.0032 | ±0.0094 | ±0.0039 | ±0.0027 | ±0.0031 | ±0.0027 |
| | ±0.0040 | ±0.0117 | ±0.0048 | ±0.0034 | ±0.0038 | ±0.0034 |
| 17 | 0.9939 | 1.0007 | 0.9991 | 0.9987 | 0.9995 | 0.9994 |
| | ±0.0041 | ±0.0046 | ±0.0032 | ±0.0034 | ±0.0033 | ±0.0046 |
| | ±0.0051 | ±0.0057 | ±0.0040 | ±0.0042 | ±0.0041 | ±0.0057 |
| 19 | 0.9825 | 0.9861 | 0.9768 | 0.9812 | 0.9832 | 0.9811 |
| | ±0.0053 | ±0.0125 | ±0.0031 | ±0.0046 | ±0.0035 | ±0.0042 |
| | ±0.0066 | ±0.0155 | ±0.0038 | ±0.0057 | ±0.0043 | ±0.0052 |

*Standard deviation all first ± values.

**Uncertainty of the mean value with 95% confidence all second ± values.

*Gold Specular Reflectance Standard

This is a Standard Reference Material (SRM 2007) Gold on Glass obtained from the National Bureau of Standards. It is designated #6. A reflectance factor of 0.989 is given for this standard in the region of 3-4 micrometers.

FIGURE 4 - GOLD ALLOY**REFLECTANCE TABLE

**( ELECTROPLATED COATINGS )

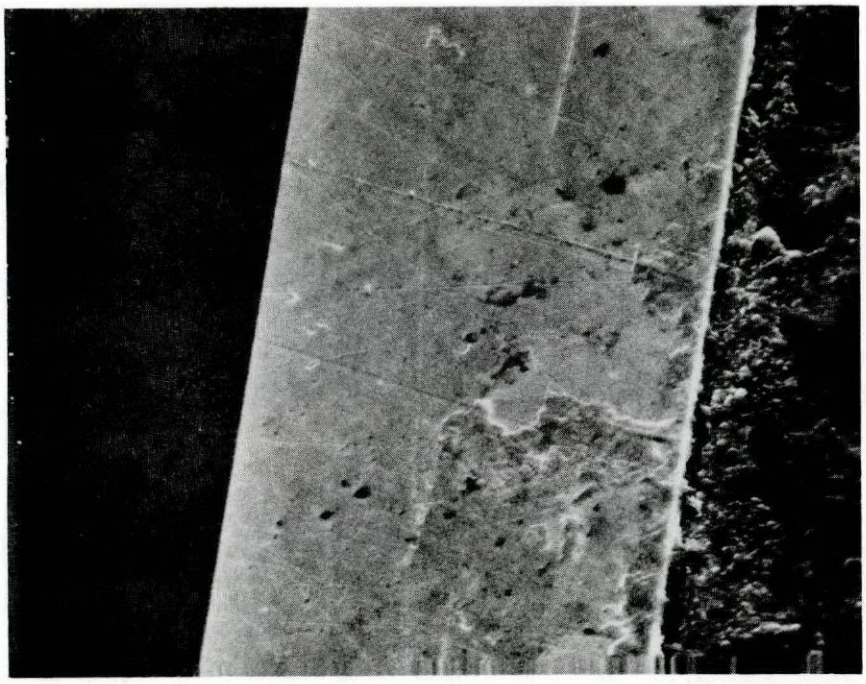


FIGURE 5 - SEM OF NICKEL HARDENED GOLD ELECTROPLATE
1600X

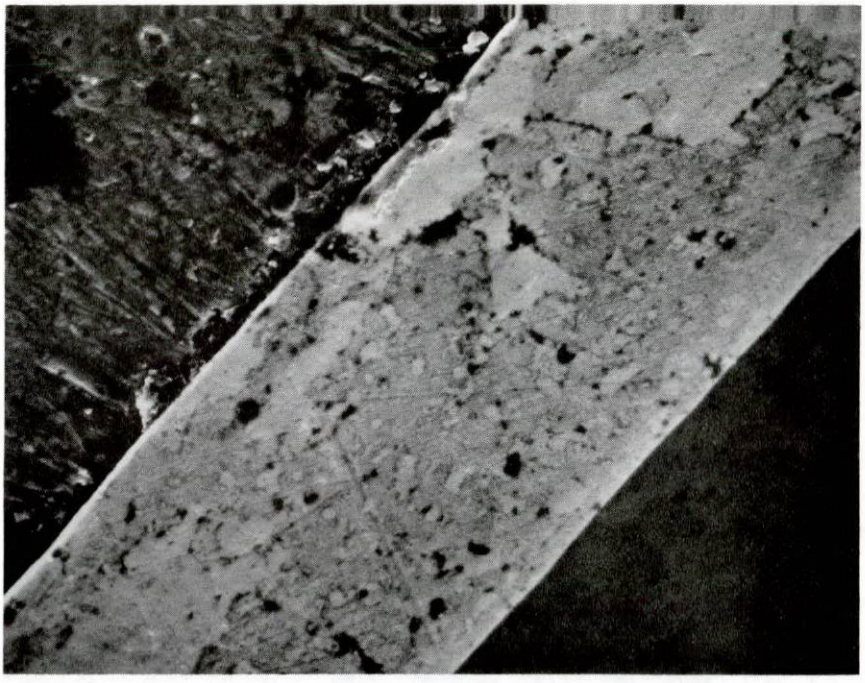


FIGURE 6 - SEM OF NICKEL HARDENED GOLD ELECTROPLATE

NOTE: INHOMOGENEOUS AREAS

1600X

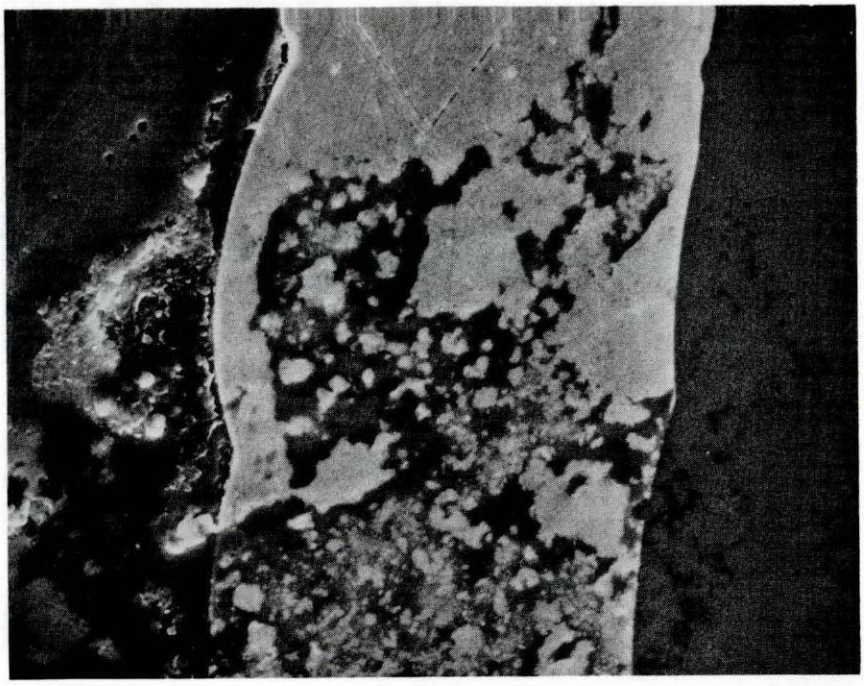


FIGURE 7 - SEM OF NICKEL HARDENED GOLD ELECTROPLATE

NOTE: POTASSIUM & CARBON INCLUSIONS AFFECTED ROUGHNESS

1600X

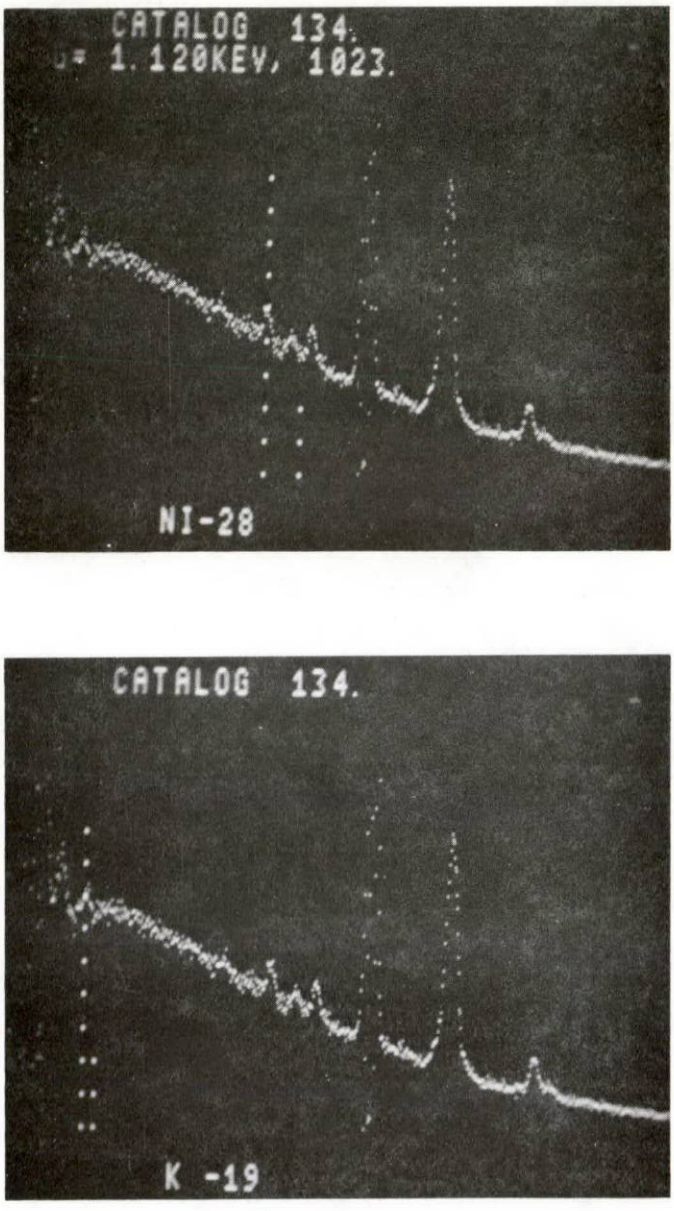



FIGURE 8 - SEM-EDX Spectrum of Nickel-Gold Electrodeposit Illustrating Nickel & Potassium Presence

HIGH REFLECTANCE ALLOY GOLD SYSTEMS

Hardness and alloying constituents

| SERIES NO. | Major brightening/ hardening material | Approx. % | Hardness DPH | Hardness Range |
|---|---|---|---|---|
| 3 | Co | 0.2 - 0.3 | 172 | 155 - 190 |
| 4 | Ni | 0.15- 0.22 | 181 | 160 - 190 |
| 10 | Co | 0.3 - 0.4 | 193 | 170 - 200 |
| 12 | Fe + (x) | 0.13 - 0.25 | 164 | 160 - 185 |
| 14 | Ni | 0.28 -0.55 | 193 | 180 - 200 |
| 17 | Sb/(As) | 0.1 - 0.15 | -- | 170 - 210 |
| 19 | Co | 0.13 - 0.20 | 146 | 130 - 190 |

TABLE I

ABSOLUTE SPECULAR REFLECTANCE BASED ON GOLD #6
SUMMARY DATA

| Test Sample #(X) | | WAVELENGTH 3.5 μm | 3.6 μm | 3.7 μm | 3.8 μm | 3.9 μm | 4.0 μm |
|---|---|---|---|---|---|---|---|
| 3 | Co | 0.962 | 0.973 | 0.965 | 0.966 | 0.961 | 0.970 |
| | (*) | ±0.016 | ±0.027 | ±0.014 | ±0.015 | ±0.014 | ±0.014 |
| 4 | Ni | 0.976 | 0.984 | 0.976 | 0.977 | 0.978 | 0.974 |
| | | ±0.012 | ±0.026 | ±0.014 | ±0.013 | ±0.013 | ±0.015 |
| 10 | Co | 0.963 | 0.975 | 0.968 | 0.964 | 0.964 | 0.972 |
| | | ±0.014 | ±0.026 | ±0.013 | ±0.014 | ±0.013 | ±0.011 |
| 12 | Fe(+) | 0.985 | 0.984 | 0.987 | 0.988 | 0.987 | 0.991 |
| | | ±0.014 | ±0.012 | ±0.018 | ±0.013 | ±0.013 | ±0.013 |
| 14 | Ni | 0.962 | 0.971 | 0.967 | 0.967 | 0.961 | 0.970 |
| | | ±0.013 | ±0.021 | ±0.014 | ±0.012 | ±0.013 | ±0.012 |
| 17 | Sb(+) | 0.983 | 0.990 | 0.988 | 0.988 | 0.988 | 0.988 |
| | | ±0.014 | ±0.015 | ±0.013 | ±0.013 | ±0.013 | ±0.015 |
| 19 | Co | 0.972 | 0.975 | 0.966 | 0.970 | 0.972 | 0.970 |
| | | ±0.016 | ±0.024 | ±0.013 | ±0.015 | ±0.013 | ±0.014 |

(*) Uncertainty of the mean value is 95% confidence, all ± values.

TABLE II

## EFFECT OF NITRIC ACID VAPOR ON GOLD REFLECTANCE

| Test Series* | | WAVELENGTH 2.8μm | 3.5μm | 3.7μm | 3.8μm | 4.0μm |
|---|---|---|---|---|---|---|
| 17 | (Sb)+ | .9501 | .9522 | .9538 | .9548 | .9549 |
| 4 | Ni | .9435 | .9466 | .9483 | .9484 | .9490 |
| 3 | Co | .9390 | .9417 | .9417 | .9423 | .9434 |
| 19 | Co | .9323 | .9373 | .9381 | .9381 | .9393 |
| 14 | Ni | .9301 | .0335 | .9342 | .9348 | .9360 |
| 10 | Co | .9204 | .9273 | .9285 | .9291 | .9296 |
| 12 | (Fe)+ | .8555 | .8570 | .8603 | .8586 | .8594 |

*Placed in descending order according to reflectance measured using a Beckman spectrophotometer with an autocollimating telescope.

TABLE III

## R EFERENCES


1. Hughes Aircraft Co., " Reflective Coatings Reliability Study", Report No. 76-77 ( April, 1976), p. 17-20.

2. P. Binanzer and A. von Krusenstjern, "Verhaltern von Silber-anoden in galvanischen Badern", 8th Congress of the International Union for Electrodeposition & Surface Finishing,(1972),p. 187-92.

3. A. Brenner, Electrodeposition of Alloys, 1963 ( Academic Press ), New York),pp. 614,616,619 & 238.

4. F. O. Bartell et al, "WD-3 Optical Phenomena in IR Materials", December 1976, ( Annapolis, MD )

5. S. E. Craig et al," J. Electrochemical Soc., Electrochem. Technol.", 117, (1970), p. 1450 - 56.

6. F. B. Waldrop et al,"Appl. Optics",14,(8),1975, p. 1783 - 87.

7. J. W. Mellors,"A Comprehensive Treatise on Inorganic & Theoretical Chemistry", Vol XIV, London,(1935),p. 535.

8. J. H. Thomas, III,"J. Electrochem. Soc.",125.(6),(1978),p.898-902.

9. H. H. Shoushanian,"Gold plating bath and process", U. S. Patent No. 3,475,292 (1969).

10. G. S. Vasil'eva in "Theory & Practice of Bright Electroplating" (trans. from Russian), Acad. of Sci. Lithuanian S.S.R., (1965), p.233 -36.

11. Y. Okinaka et al,"J. Electrochem. Soc.", 125,(11),p. 1745 - 50.

12. M. Antler, "Plating",60,(5),(May 1973), p. 468 - 473.

13. W.H. Abbott, Proc. Annual. Holm Conf. Electr. Contacts, 25 th, ( IIT, Chicago), 1979, p.11 - 16.

# N-4

# Electroplating For Optics Applications Session N

## A Perspective on Electrodeposited and Electroless Nickel Coatings Used in Optical Applications

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# A PERSPECTIVE ON ELECTRODEPOSITED AND ELECTROLESS NICKEL COATINGS USED IN OPTICAL APPLICATIONS

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ABSTRACT:

Electrodeposits of copper, gold, silver and electroless nickel coatings are playing an ever more important role in optical technology. Any material that can be adherently coated with these deposits can be finished by conventional polishing or diamond turning techniques, thus greatly expanding design strategies and supporting manufacturing capability for optical surfaces. The importance of good quality coatings, e.g. the absence of surface pits, porosity, nodules, stress and inclusions large enough to damage the diamond tool or adversely effect conventional polishing process are emphasized and information is presented on influence of plating defects on optics. Recent data on the diamond turning and polishing of other electrodeposited coatings including bright nickel, sulfamate nickel and tin-nickel are also included.

## INTRODUCTION

Diamond turning is the use of single-point diamond tools on a precision (microinch accuracy) lathe under very precisely controlled machine and environmental conditions to fabricate components. The technology, which is time and cost effective is new; diamond turning of optics was used in the 1960's but didn't start to gain recognition until the mid 1970's[1]. Both electroplated coatings and electroless nickel coatings offer significant material flexibility for machined optics as well as providing high reflectivity surfaces. Any material that can be adherently coated with these deposits can be finished by diamond turning. A significant advantage of coatings when working with mirrors is that thick deposits can be applied so subsequent optical refabrication entails only a finishing machine cut thereby noticeably reducing fabrication costs.

Since the technology is new, virtually no systemmatic work has been done to determine which coatings are diamond turnable and which are not nor have mechanisms been proposed to explain why one coating is turnable and another is not. Rather, the technology has developed a folklore whereby word of mouth has been used to promulgate supposed facts about various coatings. The purpose of this paper is to attempt to start a systemmatic investigation of various coatings and their capability of

being turned by a diamond tool. The paper is divided in two parts: the first part is a review of the coatings presently used for diamond turning applications while the second part is a presentation of new data on the diamond turning of some deposits of the nickel family, e.g.; electroless nickel, sulfamate nickel, bright nickel and tin-nickel.

## A. Review of Coatings for Diamond Turning

The materials that can be successfully diamond turned are limited in number. Table 1 lists those currently known to be compatible with diamond tools and hence considered machinable. It is interesting to note that all of the metals listed in Table 1 except for beryllium-copper can be deposited from aqueous solutions (brass, copper, gold, silver, lead, platinum and electroless nickel) or non-aqueous solutions (aluminum). This is not to say that all of these coatings have been diamond turned in the deposited condition. Rather, copper[2-7], silver[2-4, 7-9], gold[2,3,7,9] electroless nickel[10-12], and aluminum[13] are the only coatings that have been diamond turned to date; other metals have been in the cast or wrought condition prior to turning.

TABLE 1

Materials which are Machinable by Diamond Turning*

| | |
|---|---|
| Aluminum | Electroless Nickel |
| Brass | Alkali Halide (salt) Crystals |
| Copper | Zinc Sulfide |
| Beryllium Copper | Zinc Selenide |
| Gold | Germanium |
| Silver | Many Plastics |
| Lead | Machinable Ceramics |
| Platinum | Potassium Dihydrogen Phosphate (KDP) |
| Cadmium Telluride | |

*From Reference 14.

The typical thickness of coating provided for diamond turning is around 0.13 mm (0.005 in.). Any thinner plate means that the substrate must be machined with more precision than is really necessary. Also, once the substrate is covered with a coating, setting up the piece for final machining, particularly if it is a complicated shape, may prove quite difficult. An allowance should be made for the uncertainty in knowing precisely where the substrate surface is located. A fact which must be considered is that the electroplated coating will not be evenly distributed over the face of the substrate. Unlike electroless nickel coatings which deposit quite uniformly, electroplated coatings may well be twice as thick or even more in some areas as in others. What the

machinist needs is 0.13 mm minimum thickness. More often the machine shop will ask for 0.25 mm (0.010 in.) minimum plate thickness just to have a comfortable margin of safety. This points up the fact that plating processes chosen for diamond turning applications should normally be capable of consistently delivering relatively thick deposits of good quality.

Coatings for diamond turning should be free of high stresses, surface pits, porosity, nodules, and inclusions large enough to damage the diamond tool or influence resultant optical performance. Copper and silver electroplating defects such as pits deleteriously affect laser damage threshold[15,16]. Occurrence of nodules on the plated surface can be a problem[17]. If the nodules are heavy, they have an area of depressed plate at their bases since current which would have gone to that area was robbed during plating by the nodule. In addition, the crystal regime to which the nodule belonged may be different from the major crystal regime resulting in an occasional nodule being plucked out during machining and leaving a flaw in the surface. Near-threshold laser damage to bare surfaces and coatings of transparent dielectric materials occurs as small, isolated pits which are randomly distributed over the irradiated surface. This damage arises from particulate inclusions, physical defects, or chemical impurities[18]. The presence of submicroscopic cracks and pores can cause local variations in the electric field strengths which can readily account for an apparent lowering of the surface breakdown intensity by a factor of 4 or 5 compared with the bulk. Inclusions, pores and cracks of characteristic dimensions smaller than $10^{-6}$ cm (100A) are not considered harmful for any application other than high energy lasers where damage becomes a key issue. However, any of these larger than 0.1μm (1000A) should be scrupulously avoided[16].

Residual stresses which are inherent in the deposition process can result in distortion[19] or be the cause of poor adherence of subsequently applied dielectric films[20,21]. Some electroless nickel deposits on beryllium induce significant tensile stresses in the composite and for diffraction limited precision optical surfaces, these stresses can produce unacceptable distortions[19]. Even room temperature creep (relief) of silver electroplating stresses can be a problem. For example, a flat brass mirror plated with silver then diamond turned to better than 0.5 fringe deformed 9 fringes within 15 months after machining. Removing the silver by machining eliminated the distortion and essentially restored the original features[9]. One technique used to minimize stress problems in this kind of situation with silver and copper plated parts is to heat at 150C prior to diamond turning. With deposits such as silver, this treatment causes recrystallization and grain growth which could occur even with time at ambient temperature. For example, the grain size of silver deposited in 21.5 $A/m^2$ (∿2 amp. sq. ft.) in a cyanide solution containing carbon disulfide increased from 2.36 to 3.22 x $10^{-6}$ cm during a three month storage period with a corresponding decrease in hardness from 148 to 130 VHN[22].

By judicious choice of operating conditions (e.g., current density, pH, solution composition, and additive content) it is possible to deposit coatings that are in a stress-free state. Figure 1 shows the stress in electroless nickel deposits as a function of phosphorus content for aluminum and brass which have high expansion coefficients[23], and steel, beryllium and titanium, which have low expansion coefficients. Besides showing that the substrate has a very distinct influence on stress, the curves also show that for each metal, a deposit with zero stress can be obtained by controlling the amount of phosphorous in the coating. Of interest is the fact that best results were obtained with electroless nickel coatings containing greater than 7% phosphorous and Figure 1 suggests these deposits would be the ones with the least amount of residual stress. This is but one example showing that if stress is a problem because of thinness of the substrate, etc., deposits can be produced that contain essentially zero stress and this is especially true of coatings that are favored for diamond turning. However, it should be borne in mind that the plating industry has not been challenged to produce stress free deposits so some work is indicated in this area.

As mentioned earlier, the deposits for which there is any appreciable amount of diamond turning experience are copper, silver, gold and electroless nickel. Of the four types of solutions used for depositing copper (sulfate, cyanide, pyrophosphate, and fluoborate) only acid copper sulfate solutions with proprietary additives have been used extensively to provide deposits for diamond turning. Solutions containing high copper-low acid(200 g/l copper sulfate, 50-60 g/l sulfuric acid) and those with low copper-high acid (60-70 g/l copper sufate, 170-180 g/l sulfuric acid), have worked well. Diamond turnable gold deposits have been produced in both acid gold formulations (24 karat) and sulfite solutions while with silver, the standard cyanide solution with proprietary additives has been used. For electroless nickel, the commercially available formulations which contain hypophosphite as the reducing agent are used. Diamond turnable aluminum deposits were produced in a tetrahydrofuran solution[13].

## B. Compatibility of Nickel Sulfamate, Bright Nickel and Tin-Nickel Deposits with Diamond Tools

In an attempt to expand the list of materials which are compatible with diamond tools we investigated some electrodeposited coatings that had not been evaluated before. Electroless nickel coatings were included for control purposes. We chose deposits of the nickel family (nickel sulfamate, bright nickel, and tin-nickel) for two reasons: (1) one of the best coatings for diamond turning is electroless nickel which is another member of the nickel family, and (2) electrodeposited coatings are typically considerably less expensive to produce and this could be an important benefit for some applications. Electrodeposited coatings are produced at lower temperatures than electroless nickel coatings and this could improve chances of applying adherent, machinable coatings on glass. From an X-ray astronomical point of view the optimum situation would be that where the relative secular stability of glass was combined with the easy manufacturability of metal.

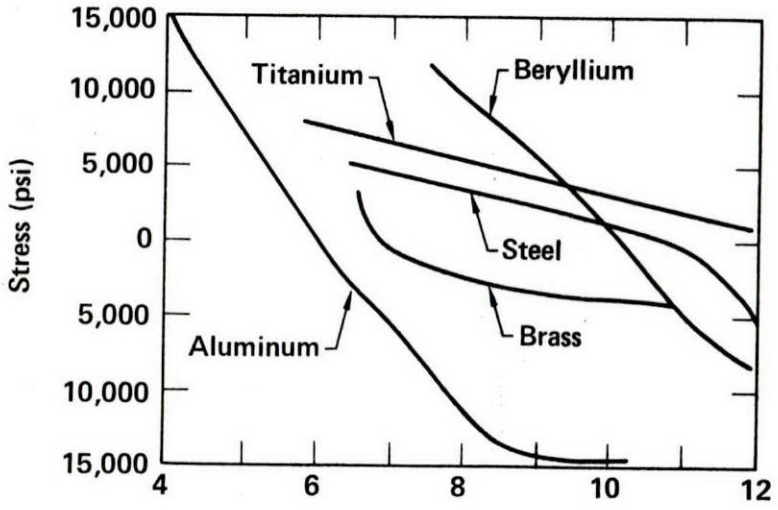



Figure 1. Stress in Electroless Nickel as a function of phosphorous content for metals with a high (aluminum and brass) and low (steel, beryllium, and titanium) expansion coefficient (Reference 23.)

Copper discs, 51 mm (2 in.) in diameter by 10 mm (3/8 in.) thick were used as substrates and plated on only one face. Solution formulations and information on plating conditions are detailed in Appendix I. In all cases, minimum plating thickness was at least 0.13 mm (5.0 mils). The three electrodeposited coatings were evaluated in the as-deposited condition, while the electroless nickel coating was evaluated in both the as-deposited condition and after hot isostatically pressing (HIP) at 590C, 30,000 psi, for 2 hours in an argon atmosphere. The HIP process was, in effect, a high temperature heat treating step and since some of the diamond turning folklore has suggested that heat treating degrades diamond turnability we felt this was a worthy inclusion in the program. Since minute amounts of material impurities have been reported to have a noticeable influence on compatibility with diamond tools, detailed spectrographic and gas analysis were obtained for the coatings which will be discussed later.

Four coated copper discs were used for each of the platings evaluated. Two of the samples were diamond turned to determine machinability and the other two were ground and polished using conventional optical manufacturing techniques to determine their polishing characteristics. Both sets of samples were submitted to a series of optical tests including microsurface topography (roughness, finish) and spectral reflectance distributions to determine some of the optical properties of the finished coatings.

Samples for diamond turning were first rough machined on a Pneumo precision lathe (MSG-326) with a diamond tool by a succession of 6 x $10^{-3}$ mm (0.25 mil) deep cuts in a facing mode until the surface was uniformly machined. This was accomplished at 1000 RPM and a tool feed of 6.35 mm per minute. The tool was a round single crystal diamond with a radius of 0.75 mm.

Once this rough machining was accomplished, the roughing tool was replaced with a 5.08 mm radius single crystal diamond tool and a series of 3-5 ever shallower depths of cut passes were made until the most representative surface was achieved. The typical process included one pass with a depth of 1.27 µm, one pass at a depth of 0.5 µm, one pass at a depth of 0.25 µm, and then two spark out passes. Two samples of each of the coatings were processed in this manner.

Machinability was determined by judging the microsurface character of the machined surfaces and the character and quantity of wear which occurred on the diamond tool edge used for machining.

The remaining two samples were ground and polished by conventional techniques. This included initial grinding with 30 micron RMS particle size aluminum oxide for 4-6 hours on a flat brass lap at approximately 15 cm per second at a pressure of 6.85 grams per square centimeter. The fine grinding was accomplished with 9 micron RMS particle size aluminum oxide under the same set of conditions. These fine ground flat samples were then polished using conventional pitch polishing techniques. Here, a wood

rosin pitch (Gulgolz #82) was used as a lap material. The polishing compound consisted of 3 micron RMS particle size synthetic diamond dust and Dow Corning #200 fluid. Each sample was polished from between 4-6 hours using this lap and slurry at a pressure of approximately 22 grams/cm$^2$. A final polishing was accomplished with exactly the same technique only replacing the 3 micron diamond with 1/2 micron diamond. This final step was carried out at various lengths of time from between 1/2 hour to 3 hours depending on the material being polished. It was clearly evident in this final polishing that electroless nickel control samples required the longest time to polish and the tin-nickel sample the shortest.

## RESULTS

### Precision Machining

Of the four materials evaluated, in addition to as-deposited electroless nickel only the HIPPED electroless and tin-nickel coatings showed promise of diamond machining. This is because they were the only materials other than as-deposited electroless nickel where an optically specular surface was achieved and the tool wear on the diamond was negligibly small when viewed under high magnification (Fig. 2). By contrast, the diamond tools used for machining nickel sulfamate and bright nickel deposits sustained significant damage (Fig. 3). In addition, both of these deposits left a highly grooved finish after machining and this greatly reduces reflectivity while increasing optical scatter. Table II tabulates the results of the microsurface tests, and Figure 4 a-d shows typical surface character for each of the materials tested.

In each of two cases, i.e. the bright nickel and sulfamate nickel where tool damage occurred, it was evident that a new tool edge would generate a specular surface until edge wear degraded the tool shape. All grooves in these materials appeared to bear a 1 to 1 relationship to the worn tool edge, and as such would become increasingly rough as the tool edge damage increased. Examples of these surfaces are shown in Figure 5 and support the one to one relationship notion. It is important to note that if some tool material other than diamond could be made sharp enough to duplicate a diamond edge, these materials may well be machinable and therefore useful as optical materials in the future. Possible candidate materials bearing similar crystal structure to that of diamond are cubic zircona, cubic boron nitride and yittrium aluminum garnate. The point of these discussions is to indicate that perhaps most of the electrodeposited nickel compounds may be machinable by precision techniques and serve as optical materials.

A question to be answered is what is the mechanism that caused tool degradation. It has often been reported in the literature that materials containing carbon are not considered machinable due to the carbonization of the diamond crystal at the high temperatures of machining[14]. Carbides may form at relatively low temperatures with ferrous materials,

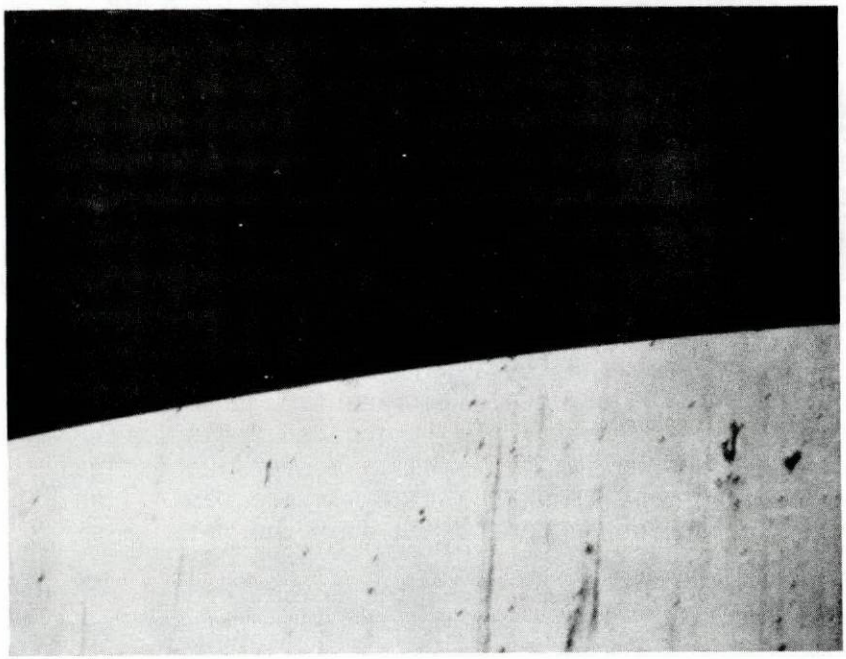
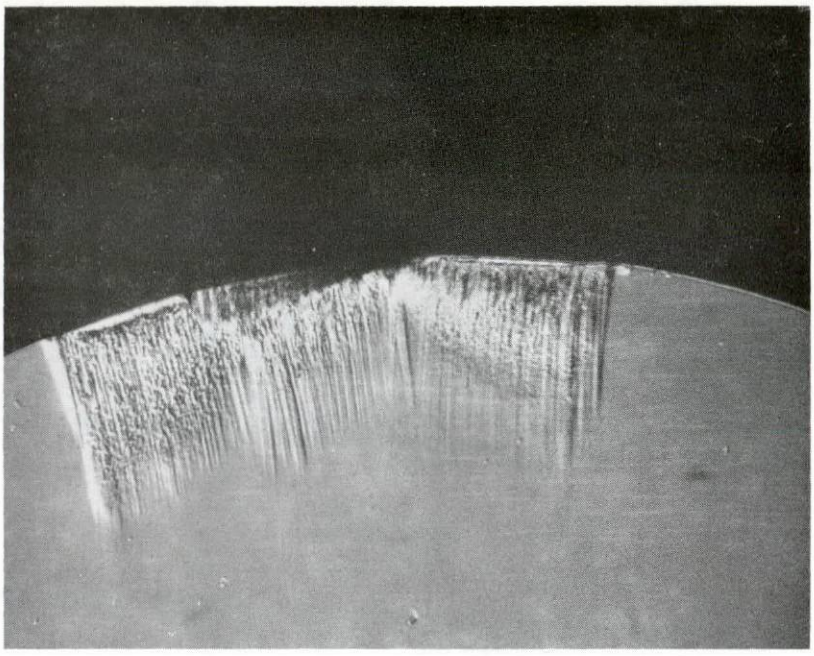
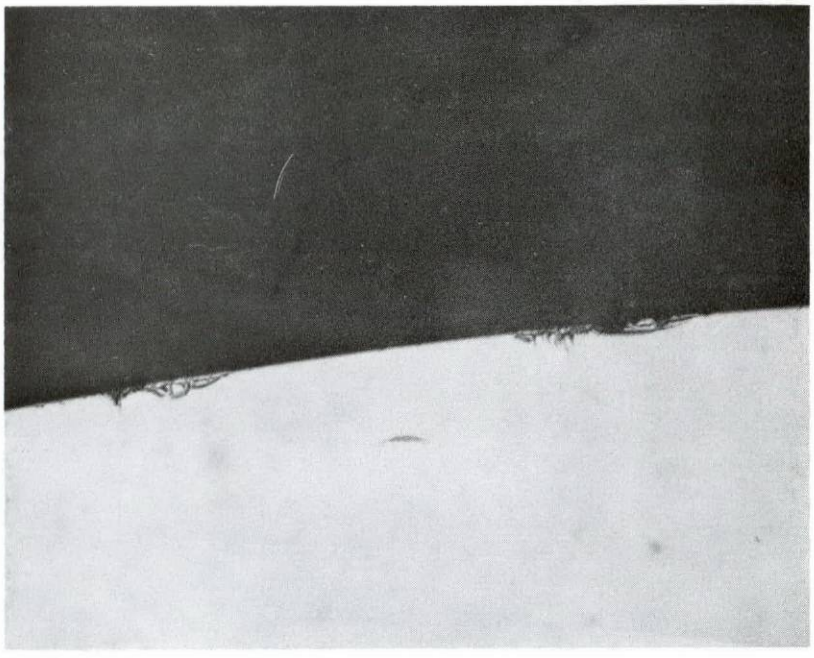


Figure 2. Micrograph (178 X) of the 5mm radius diamond tool after use on tin-nickel (a similar result was obtained when the hipped electroless was machined). Note lack of visible wear or damage

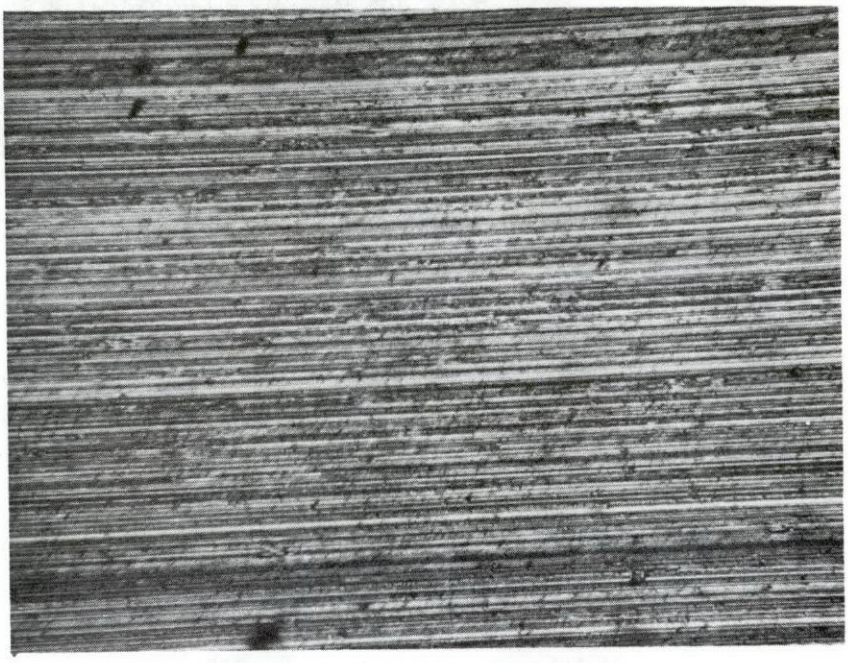


a) Sulfamate nickel (magnification 100 X).

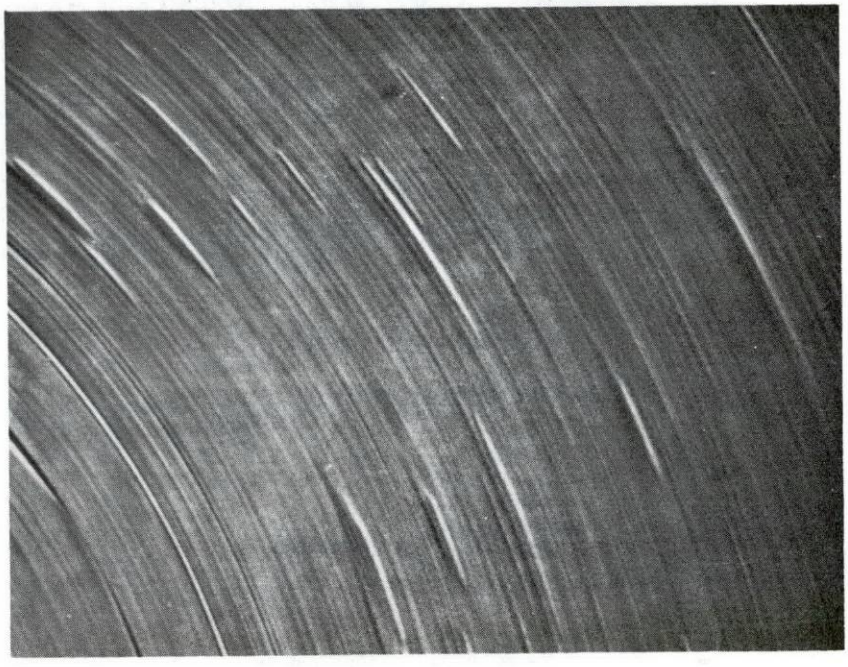


b) Bright nickel (magnification 178 X).

Figure 3. Microphotographs of diamond tools after use in maching sulfamate nickel (above) and bright nickel (below).

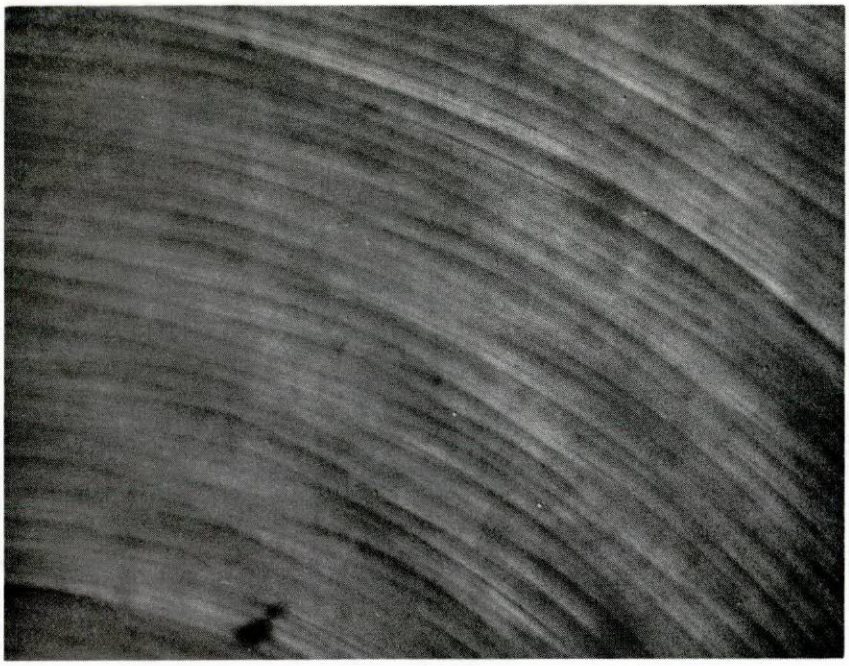


a) Bright nickel (45 $\mu$m/cm image scale).

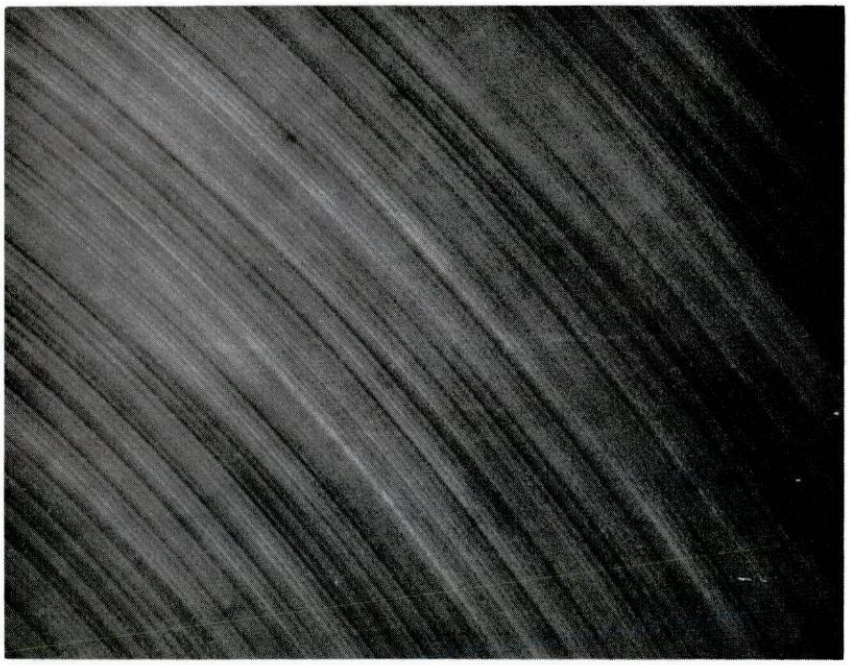


b) Sulfamate nickel (45 $\mu$m/cm image scale).

Figure 4a&b Micrographs of machined bright nickel (above) and nickel sulfamate (below) at 178 X showing rough and damaged surface features.



c) Electroless nickel (178 X)



d) Tin-nickel (178 X)

Figure 4c&d Micrographs of electroless nickel (above) and tin-nickel (below) showing relatively undamaged surfaces.

TABLE II
Relative Microtopographic Properties of Electro and Electroless Deposited Nickel Coatings (all values are averages of like materials)

| Material | RMS Roughness (Angstroms) | Peak to Valley Roughness (Angstroms) | Autocorrelation Length (approx.) (μm) | RMS Slope (A/μm) | Scattered Light/ Incident Light |
|---|---|---|---|---|---|
| 1. Electroless Ni | | | | | |
| Polished | 11.4 | 67 | 22 | 3.8 | .00050 |
| Machined | 64.8 | 327 | 24 | 7.3 | .01685 |
| 2. Brite Nickel | | | | | |
| Polished | 8.1 | 49 | 19 | 2.5 | .00023 |
| Machined | 119.4 | 681 | 22 | 51.0 | .05643 |
| 3. Tin Nickel | | | | | |
| Polished | 7.4 | 40 | 23 | 2.0 | .00022 |
| Machined | 94.3 | 443 | 30 | 9.0 | .03492 |
| 4. Sulfamate Ni | | | | | |
| Polished | 8.3 | 65 | 16 | 3.7 | .00028 |
| Machined | 101.3 | 549 | 42 | 30.0 | .04012 |
| 5. Hot Isotatically Pressed Ni | | | | | |
| Polished | 7.4 | 40 | 20 | 2.7 | .00022 |
| Machined | 119.2 | 685 | 31 | 16.2 | .05191 |

cobalt, nickel, and titanium. Impurity data for the four coatings evaluated in this work are listed in Table III. The carbon content of the bright nickel deposit was quite high (1900 ppm) compared to the other coatings, therefore, one can possibly explain its poor diamond turning performance on this fact. However, the sulfamate nickel deposit had considerably less carbon (30 ppm) than even the electroless nickel (60 ppm) which turned well so something other than carbon content is involved. Since chemical reactions can be catalyzed and/or inhibited by the presence of other non-interacting substances in the presence of heat and stress, perhaps the alloying elements (phosphorus in tin-nickel, and tin in tin-nickel) serve as inhibitors of the carbonization process. It should also be mentioned that both of these systems form eutectics so they melt at lower temperatures than nickel, e.g. the melting point of nickel is 1455C, tin-nickel 1130C and the electroless nickel 880C. Perhaps with the alloy coatings the diamond tool just doesn't get as hot as it does with unalloyed nickel.

Another important result is the observation that the HIPPED electroless nickel deposit diamond turned as well as the as-deposited coating. This is strong evidence that heat treatment (or at least our heating cycle which was 2 hours at 590C) did not degrade the coating from a diamond turning standpoint. As mentioned earlier, there is some folklore which suggests that heat treated electroless nickel deposits do not diamond turn as well as as-deposited coatings and Arnold et al[24] suggested that a coating they encountered as troublesome during diamond turning had been heat treated. Our results suggest that the folklore and the work of Arnold et al[24] should be reconsidered.

Optical Polishing

As with the precision machining tests, all four of the various nickel coatings were investigated with respect to their polishability and the resulting optical properties. Two samples of each material were polished on a best effort basis in an attempt to determine how they compare in absolute and spectral reflectance as well as microroughness. In general, both the polishing and optical characteristics of all four metals were quite similar.

As indicated earlier, it was clearly evident that the electroless nickel required the longest time in final polishing. The records, though sketchy, seem to indicate that the sulfamate nickel has the highest polishing rate (taking ~30 min.) followed, in order, by bright nickel (~1 to 1.25 hr.) and tin-nickel (~1.5 hr.), then electroless nickel (~ 3 hr.). It is generally believed that the polishing rate is inversely proportional to mechanical hardness and, though not well documented, seems to be substantiated by the order of the hardness of the metals coated.

Interestingly enough, while these polishing rates show a pronounced material dependence, the resultant surfaces were surprisingly similar with respect to the optical properties measured. In all cases, the optical

TABLE III

Gas and Impurity Content for Various Coatings*

| Deposit | Lead | Maganese | Silicon | Copper | Iron | Carbon | Hydrogen | Oxygen | Nitrogen |
|---|---|---|---|---|---|---|---|---|---|
| Tin-Nickel | .005 | .008 | .005 | .001 | .015 | .002 | .0002 | .0039 | .0009 |
| Sulfamate Nickel | 0 | .008 | .003 | .002 | .010 | .003 | .0008 | .0055 | .0012 |
| Bright Nickel | 0 | .015 | .008 | .045 | .020 | .190 | .0012 | .0310 | .0075 |
| Electroless Nickel | 0 | .025 | .010 | 0.17 | .015 | .006 | .0012 | .0085 | .0013 |

*All in weight percent. See Appendix I for details on solution compositions and operating conditions.

finish on these polished samples was essentially identical in appearance (Figure 5 a-d) and only slightly different in magnitude. Table II indicates that the RMS roughness ranged only from 8.4 to 11.4 angstroms RMS. Incidentially, roughnesses in this range are all considered as high quality optical surfaces.

The similarity in optical properties does not stop here. While the composition of these coatings is considerably diverse, the spectral reflectance distribution between 0.40μm and 2.5μm wavelengths is nearly identical. While Figure 6 clearly demonstrates this similarity in spectral reflectances, the up to 12% differences indicated in absolute reflectance levels is considerable. Bright nickel and sulfamate nickel both show significantly superior reflectances when compared with electroless nickel. In actuality, all the electrodeposited nickels have a higher reflectance level than electroless so that they may be superior to electroless in certain applications.

The results obtained from the two forms of electroless nickel (as-deposited versus HIPPED) were also quite similar when compared. The polished surfaces were visually indistinguishable with roughnesses differing by only 4 angstroms RMS, the HIPPED being slightly superior. Spectral reflectance curves from the material indicate a maximum reflectance difference of approximately 2.5% with the HIPPED being slightly superior in the visible and ordinary electroless approximately 2% higher from $\lambda$ = 1 μm to 2 μm. These curves were identical everywhere else in the 0.4 μm to 2.5 μm spectral range considered. As with polishing, the diamond machining was found to be indistinguishable. Roughness differed considerably (65A RMS for electroless, 119.2A RMS for HIPPED) but this is believed to be primarily due to variations within the machining process and machine used.

In summary, the fact that the optical properties of these nickel coatings are very similar, and that their deposition conditions allow for coating on a broad variety of substrates, a great deal of versatility in optical component design and manufacture may be achieved.

## SUMMARY

After reviewing the technology on electrodeposited and electroless coatings for diamond turning, some data are presented on the diamond turning of electroless nickel (as-deposited and after hot isostatically pressing) bright nickel, sulfamate nickel and tin-nickel coatings. This work showed that all four coatings could be optically polished but only electroless nickel and tin-nickel could be diamond turned without causing undue degradation of a diamond tool. The hot isostatically pressed electroless nickel deposit which, in effect, was heat treated under pressure, did not cause degradation of the diamond tool and this suggests that heat treating is not a problem with electroless nickel deposits. Some chemical analysis data are presented for the various deposits and speculations made on why some of the coatings were diamond turnable and others were not.



a) Sulfamate nickel (polished) magnification (all four photos 178 X and scale is 45 $\mu$m/cm).



b) Tin-nickel (polished).



c) Polished electroless nickel (178 X and 45 $\mu$m/cm image scale).



d) Polished bright nickel.

Figure 5. Nomarski microphotographs of various nickel plated coatings indicated the high degree of similarity. The principal feature in all cases is the large number of

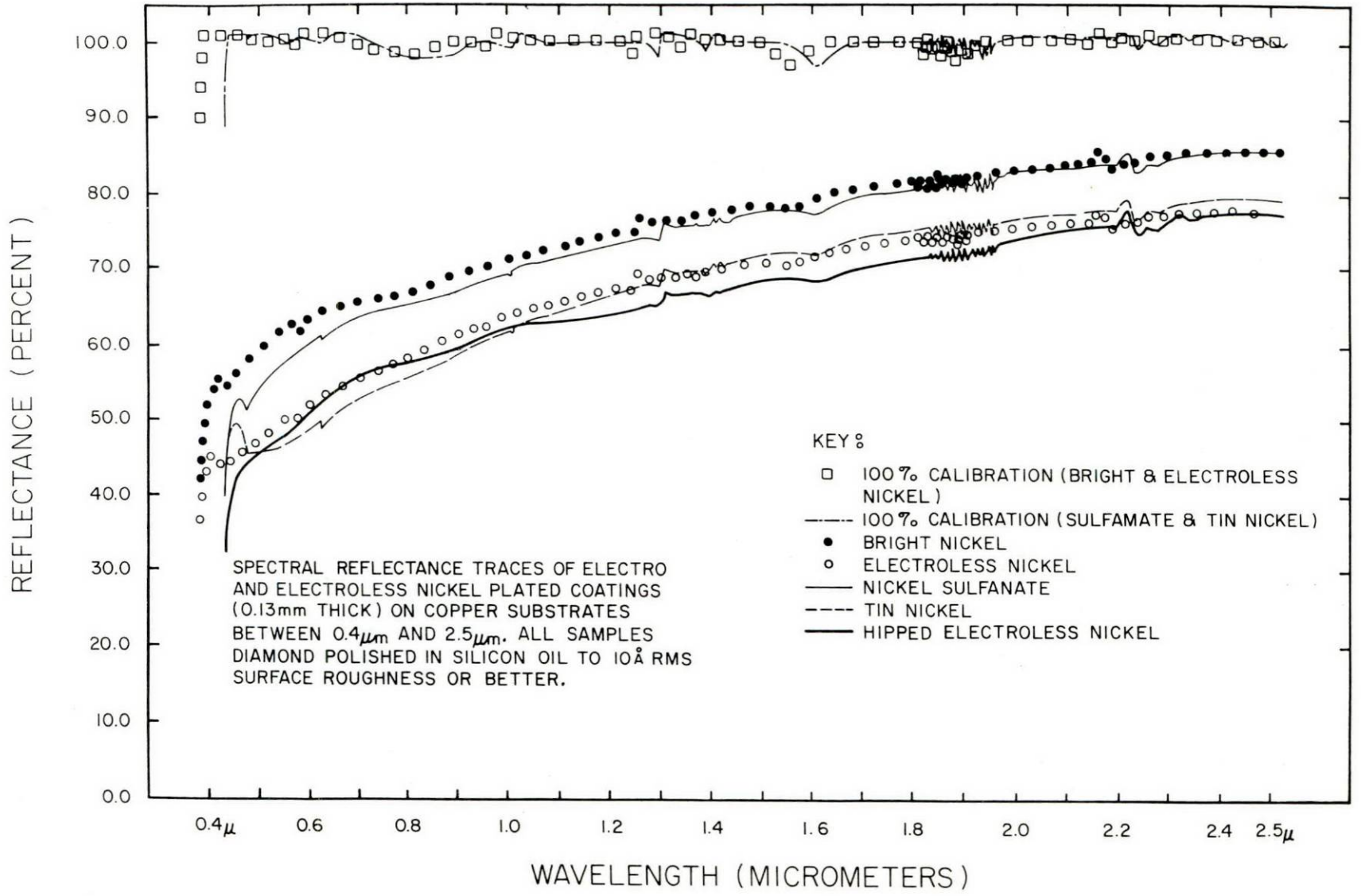

REFLECTANCE (PERCENT)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.4μ
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.5μ
WAVELENGTH (MICROMETERS)
KEY :
100 % CALIBRATION (BRIGHT & ELECTROLESS NICKEL)
100 % CALIBRATION (SULFAMATE & TIN NICKEL)
BRIGHT NICKEL
ELECTROLESS NICKEL
NICKEL SULFANATE
TIN NICKEL
HIPPED ELECTROLESS NICKEL
SPECTRAL REFLECTANCE TRACES OF ELECTRO AND ELECTROLESS NICKEL PLATED COATINGS (0.13mm THICK) ON COPPER SUBSTRATES BETWEEN 0.4μm AND 2.5μm. ALL SAMPLES DIAMOND POLISHED IN SILICON OIL TO 10Å RMS SURFACE ROUGHNESS OR BETTER.

FIGURE 6

In regards to the polishing and optical characteristics of all four metals, they were quite similar with one exception. All polished well but the absolute reflectance was up to 12% higher for bright nickel and sulfamate nickel when compared with the electroless nickel and tin-nickel deposits. This is a significant finding and suggests the former coatings would be more beneficial for certain applications.

ACKNOWLEDGEMENTS:

The authors wish to extend their thanks to Mr. Robert Raether for his patient optical preparation and close observation of the samples. We also gratefully acknowledge the AXAF Project Office of the NASA George C. Marshall Space Flight Center for the encouragement and support of this program.

This work performed under the auspices of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

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REFERENCES:


1. T. T. Saito, Optical Eng. 17 570 (1978).

2. F. B. Waldrop, M. J. Bezik, W. E. Tewes, and R. C. Waldrop, "Electroplating Application to the Fabrication of Optics", Applied Optics, 14 1783 (1975).

3. J. B. Arnold, P. J. Steger and T. T. Saito, "Tool Feed Influence on the Machinability of $CO_2$ Laser Optics", Applied Optics, 14 1777 (1975).

4. T. T. Saito, "1.06 μm Reflectivity Measurements of Metal Optics", Lawrence Livermore National Laboratory, UCID 16815, June 10, 1975.

5. T. T. Saito, D. Milam, P. Baker, and G. Murphy, "1.06 μm 150 psec Laser Damage Study of Diamond Turned, Diamond Turned/Polished and Polished Metal Mirrors", 7th Annual Conf. Laser Induced Damage in Optical Materials, July 29-31, 1975, pp 29-40.

6. H. L. Gerth, R. E. Sladky, M. J. Bezik, and C. A. Washington, "Fabrication of Off-Axis Parbolic Mirrors", Optical Engineering, 17 588 (1978).

7. J. O. Porteus, D. L. Decker, J. L. Jernigan, W. N. Faith, and M. Bass, "Evaluation of Metal Mirrors for High Power Applications by Multithreshold damage Analysis", IEEE Journal of Quantum Electronics, Vol. QE-14, 776 (1978).

8. J. B. Bryan, R. R. Donaldson, E. R. McClure, H. A. Whelan, and R. W. Clouser, "Diamond Turning of Parabolic Mirrors", Lawrence Livermore National Laboratory", UCRL 51213, May 12, 1972.

9. T. T. Saito, "Polishing and Characterizing Diamond Turned Optics", Lawrence Livermore National Laboratory, UCRL 51951, Nov. 3, 1975.

10. J. M. Casstevens and C. E. Daugherty, "Diamond Turning Optical Surfaces on Electroless Nickel", SPIE, Vol. 159, Precision Machining of Optics, 109 (1978).

11. J. B. Arnold, T. O. Morris, R. E. Sladky, and P. J. Steger, "Machinability Studies of Infrared Window Materials and Metals", SPIE, Vol. 93, Advances in Precision Machining of Optics, 96 (1976).

12. J. W. Dini, "Electroless Nickel: An Important Coating for Diamond Turning Applications", Proceedings Electroless Nickel Conference II, Products Finishing Magazine, Cincinnati, OH.

13. T. Daenen, G. Van Dijk, and J. Van de Berg, "Cyclic Reaction Mechanism in the Electrodeposition of Aluminum", Proceedings First International Symposium on Electrodeposition of Aluminum, American Electroplaters' Soc., June 1981.

14. G. M. Sanger, "A Perspective On Precision Machining, Polishing, and Optical Requirements", UCRL 86579, Aug. 18, 1981.

15. T. T. Saito, D. Milam, P. Baker and G. Murphy, "1.06 μm 150 psec Laser Damage of Diamond Turned, Diamond Turned/Polished and Polished Metal Mirrors", 7th Annual Conf. Laser Induced Damage in Optical Materials, July 29-31, 1975, p 29-40.

16. H. Bloemberger, Applied Optics, 12, 661 (1973).

17. H. L. Gerth, R. E. Sladky, M. J. Bezik, and C. A. Washington, Optical Engineering, 17, No. 6, 588 (Nov./Dec. 1978).

18. W. H. Lowdermilk, D. Milam, and F. Rainer, "Damage to Coatings and Surfaces by 1.06 μm Pulses", UCRL-83660, Nov. 28, 1979.

19. R. M. Shemenski, J. G. Beach, and R. E. Maringer, Journ. Electrochemical Soc., 116, 402 (1969).

20. R. A. Hoffman, W. J. Lange, J. G. Gowan and C. J. Miglionico, Optical Engineering, 17, No. 6, 578 (Nov./Dec. 1978).

21. J. R. Buckmelter, T. T. Saito, R. Esposito, L. P. Mott, and R. Strandlund, "Dielectric Coated Diamond Turned Mirrors", Laser Induced Damage in Optical Materials, July 29-31, 1975, p 66-74.

22. N. P. Fedotev, P. M. Vyacheslavov, and V. I. Gribel, Journal of Applied Chemistry (USSR), 37, (6), 1368-1376 (1964).

23. K. Parker and H. Shah, Plating 58 230 (1971).

24. J. B. Arnold, T. O. Morris, R. E. Sladky and P. J. Steger, SPIE Vol. 93, Advances in Precision Machining of Optics, 96 (1976).

## APPENDIX I
## Composition and Operating Conditions for Solutions Used for Coating

| | |
|---|---|
| **Electroless Nickel*** | |
| Nickel | 100 - 105% (7.1 - 7.5 g/l) |
| Hypophosphite | 34 - 38% |
| pH | 4.5 - 4.6 |
| Temperature | 94 - 96C |
| Deposition Rate | 9.0 - 10.0 μm/hour |
| Bath Loading | 484 mm/l |

*Shipley Niculoy 22, Marlboro, MA

| | |
|---|---|
| **Tin Nickel** | |
| Nickel | 74 g/l |
| Nickel Chloride ($NiCl_2.6H_2O$) | 300 g/l |
| Tin | 31 g/l |
| Stannous Chloride ($SnCl_2$) | 49 g/l |
| Ammonium Bifluoride | 56 g/l |
| pH | 2.5 (Adjust with aluminum hydroxide) |
| Current Density | 268 $A/dm^2$ |
| Temperature | 65C |

| | |
|---|---|
| **Sulfamate Nickel** | |
| Nickel | 81 g/l |
| Nickel Sulfamate | 450 g/l |
| Nickel Chloride | <1.0 g/l |
| Boric Acid | 40 g/l |
| Surface Tension | 38 - 40 dyne/cm |
| pH | 3.8 - 4.0 |
| Anodes | Sulfur Depolarized |
| Current Density | 268 $A/m^2$ |
| Temperature | 49C |

| | |
|---|---|
| **Bright Nickel*** | |
| Nickel Sulfate | 300 g/l |
| Nickel Chloride | 60 g/l |
| Boric Acid | 41 g/l |
| pH | |
| Current Density | 268 $A/dm^2$ |
| Temperature | 57 - 66C |
| Y-17 | .25% by vol. |
| A-5 | 4% by vol. |
| SA-1 | 1.2% by vol. |
| B-6 | 0.2% by vol. |

*M&T 724 HiC, M&T Chemicals Inc., Rahway, NJ

O

# Practical Shop-Problem Workshop Session O

(No papers formally presented at this session)

P-1

# Alloy Plating I
# Session P

## Properties and Applications of Electrodeposited Cu-Zn-Sn and Ag-Sn Alloys

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# PROPERTIES AND APPLICATIONS OF ELECTRODEPOSITED Cu-Zn-Sn AND Ag-Sn ALLOYS

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Electrodeposition of alloys is much more challenging than the one of elementary metals. The non-uniformity of current distribution leads not only to a non-uniformity of the thickness of the coating as for elementary metals but also to variations in the composition of the alloy along the profile of the piece to be coated. Therefore the local properties of alloy deposits are influenced by the current distribution. Moreover, the chemistry of electrolytes is more complicated than for elementary metals and the bath is more difficult to control. However, due to a much wider available range of properties than with elementary metals, electrodeposition of alloys is a very attractive field for new developments in the electroplating industries, extending broadly the range of possible applications.

Our successful experience over 30 years in electrodeposition of the ternary gold alloy (Au-Cu-Cd) (ref. 1-3) encouraged us to develop other industrial processes in alloy plating. In this paper we present two more recent developments for Cu-Zn-Sn and Ag-Sn deposition.

## Cu-Zn-Sn

The cast alloy Cu-Zn-Sn (60%, 39.25%, 0.75%) is known under the name "Naval brass" and is used for marine hardware. The electrodeposited Cu-Zn-Sn alloy, with a higher content of tin, has been marketed under the names "Albaloy" and "Spekwite". The composition of the Albaloy is Cu 55-60%, tin 25-28% and zinc 14-18%. The process for its electrodeposition is described in the literature (ref. 4a, 5). Serious difficulties like "changes in color from a clear-bright (resembling nickel) to a cloudy milky appearance, or sometimes yellow or brassy; staining (yellow or brown) from plating bath residue and from contact with bare hands, and variable corrosion behavior with extensive tarnishing in salt spray or humidity tests" have been reported (ref. 5) and therefore this process found only limited applications. After improvements of the process in

stabilizing the bath, we commercialized this alloy under the name "Optalloy".

Optalloy contains approximately 55% of Cu, 20% of Zn and 25% of Sn and has a density of 8,2 g/cm$^3$. It is electrodeposited from an alcaline bath containing copper and zinc cyanide and stannate salt. The process is suitable for both rack and barrel plating; it operates at 0,5 A/dm$^2$ and the deposition rate is approximately 3 µm/h.

Optalloy coatings exhibit a pleasant bright white appearance resembling that of stainless steel. The appearance is not affected by prolonged exposure in industrial atmospheres. In contrast to silver, Optalloy is practically not discoloured by sulfur-containing atmospheres. As expected from the cast alloy, Naval brass, Optalloy is a very good protection against corrosion. Deposit with a thickness as small as 2 to 4 µm passes the internationally accepted salt spray tests (MIL,IEC)*. Measurements of the static potential in 1 M sulfuric acid solution lead to values 500 mV more positive than tin and only 120 mV more negative than gold. Optalloy behaves therefore like a relatively noble metal.

Optalloy has an exceptionally high macro-throwing power. Jacky (ref. 5) reports that brass tubes of an inside diameter of 0,4 mm and a length of 0,9 m could be coated with this alloy. Hence the process is particularly suitable for the plating of highly profiled components with corners, edges, cavities etc. Fig. 1 shows a saw tooth profile of a BNC connector coated with Optalloy. The thickness of the Optalloy layer is very regular along the profile. In order to show it better we plated here 5 µm instead of 2 µm as usual.

One of the main concerns in electrodeposition of alloys as well as in cast alloys is the stability of the existing metallic phases. In reality, and this specially for electrodeposited alloys, the metallic phases can be very different from the thermodynamic equilibrium given by the phase diagrams. The ternary phase diagram of Cu-Zn-Sn (ref. 6) for high copper contents exhibits a region consisting of a monophase of α-mixed cristals. Monophasic deposits in thermodynamical stability are expected with Sn contents up to 15% and Zn contents up to 35% (when both Sn and Zn are present in the α-phase, the solubility of both is lowered). We investigated the structure of an electrodeposited Cu-Zn-Sn alloy by X-ray diffraction. We found that the electrodeposited alloy consisted essentially in one orthorhombic phase with the three following characteristic lengths of the cristal lattice: a = 2.98 Å, b = 3.285 Å

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* MIL : Military specifications
IEC : International Electrotechnical Commission

and c = 2.68 Å. Lattice parameter a was measured with the (200) line, b with the (010) line and c with the (003) line. The fact that we have one dominant phase under conditions where a second phase could be expected to appear in an appreciable amount from the thermodynamic point of view shows that electrodeposited alloys can be very different from the cast alloys and need a separate study of the mechanical and electrical properties.

Optalloy is characterised by a high hardness (600-700 Knoop) and high wear- and scratch-resistance, being comparable to chromium plate in both respects. Thus, for example, coaxial connectors plated with Optalloy permit some ten times the number of insertions possible with a silver-plated part before signs of wear damage occur.

Optalloy is a non-magnetic alloy with a relative permeability of approximately 1. This makes it possible to use it on electrical instruments, the measurements of which would be affected by a magnetic coating, such as nickel.

The resistivity measured with the four points method is 40 μΩcm. This value is typical for alloys and can be compared with the one of a Cu-Ni for example.

Contact resistance measured with the crossed rods method under 100 g load exhibits values ranging from 4 to 8 mΩ. The plated parts have been post-treated as follows: cathodic degrease, dip in 1:1 HCl for 1 minute, water rinse, ethanol rinse, dry. The contact resistance increases after a few days exposure in laboratory atmosphere but drops to its starting value by thermal treatment at 68°C.

With an activated flux, Optalloy fulfilled solder requirements in most applications. In contrast to tin, Optalloy maintains solderability even after long storage. In Fig. 2 we show an application where contact pins coated by Optalloy have been soldered with the wave fluxing method in 60/40 tin-lead.

To sum up, Optalloy can for example replace nickel specially for its much better macro-throwing power, silver for its better tarnish resistance and tin for its much higher hardness and solderability even after long storage. Optalloy is a good coating for protection against corrosion and is mainly used for various parts in electronics, electrical engineering and small precision mechanics. Fig. 3 shows a set of parts for which Optalloy appeared to be a successful coating.

Ag-Sn

Silver-tin alloys are known to possess a greater tarnish resistance than pure silver (ref. 4b). H. Leidheiser Jr. and A.R.P. Ghuman (ref. 7) deposited the intermetallic compound $Ag_3Sn$ from a bath containing a stannate and silver cyanide in low concentration so that silver was presumably deposited under high concentration overpotential. Dendritic growth therefore occured and deposit thicknesses of 15 µm were critical. To circumvent this difficulty they applied the pulse plating technique. We could obtain a deposit of the Ag-Sn alloy with higher silver concentration in the bath so that the silver deposition didn't occur under mass transport controlled conditions, and a dc current could be successfully applied for deposition thicknesses up to a few tens of µm. The composition of our deposited alloy is 90% Ag and 10% Sn. The influence of the hydrodynamic on the composition of the alloy has been studied with a rotating disk system. In the range of 300 to 3000 rpm the hydrodynamic had no significant influence on the content of tin in the alloy. We used a different type of bath than given in ref. 7): tin complexed with pyrophosphate instead of a stannate. A similar bath to ours is described by Reksc, Lagoda and Biedzinski (ref. 8) with the emphasis of a higher wear resistance for Ag-Sn as compared to silver and an increased hardness. The bath operates at room temperature. The range of current density for moderate agitation lies between 0,3 and 1 $A/dm^2$. In this range, the tin content does not vary much with the current density, and the current efficiency is higher than 95%.

The polarization curve for Ag-Sn deposition (Fig. 4) shows a maximum like in a passivation process. Therefore a given current density corresponds to two possible potentials. It has been demonstrated that bright deposits were obtained at potentials lower than the one corresponding to the maximum and dull deposits were obtained at higher ones. Under galvanostatic conditions, due to the non-uniformity of the potential distribution, regions on the cathode can work at the potential leading to bright deposits, but others can work at potentials at which dull deposits occur. Working under potentiostatic conditions at a value located before the maximum of the polarization curve, made it possible to control the brightness of the coating.

The alloy obtained from a bath without organic additives is very bright and exhibits a pleasant colour. Appearance evaluations were made from deposits 5 µm in thickness.

Ag-Sn has been deposited on stainless steel and then detached in order to obtain foils of 1 $dm^2$ and 10 µm in thickness. The foils could be fold without breaking which is a sign of very good ductility. The quality of "extremely ductile" has also been mentioned in ref. 7). As Reksc (ref. 8), we found a hardness of 130 Knoop.

The resistivity of the Ag-Sn alloy has been measured with the four points method on a foil 10 μm thick. We found a value of 30 μΩcm, which is not much higher than the resistivity of an 18 carat gold (20 μΩcm). After different thermal treatments (130°C, 10 h, and 250°C, 5 h), the resistivity remained unchanged.

The contact resistance has been measured on crossed polished brass rods 3 mm in diameter, coated with 2 μm of Ag-Sn. The relationship between resistance and load for the as plated rods is :

| load in g | 10 | 25 | 50 | 100 | 200 |
|---|---|---|---|---|---|
| resistance in mΩ | 7.9 | 5.6 | 3.9 | 2.6 | 1.8 |

An increased tarnish resistance in sulfide environment has been pointed out in both references 7) and 8). We studied this property by two different tests. The first one consisted in a dip in NaS 10% followed by drying in air. The second one is prescribed by the Swiss watch industry norms; it consists essentially in an exposure to a thioacetamide atmosphere. A similar test is described in the ISO norm No. 4538. The humidity was kept constant at 75% by a mixture of a sodium acetate and water (75% and 25%). Both tests evidenced a much better tarnish resistance of the Ag-Sn as compared to pure silver. The prescribed duration of exposure in the second test is 2 days, period after which the pure silver showed advanced tarnishment already but Ag-Sn remained fairly intact. We prolonged the exposure by 4 other days. The results of which are presented in Fig. 5.

The solderability was investigated by the meniscograph method which consists in recording the force applied on a coated plate as a function of time during the wetting process in a solder bath. The plate with a side of 1 cm was immersed up to 5 mm from the bottom. There are two relevant parameters in this test i.e. the wetting time and the wetting force which tends to attract the plate in the solder bath. The results for Ag-Sn were compared with the ones of Ag, both as plated, and showed approximately the same wetting forces and the same wetting times ranging from 1.5 to 1.8 sec. which is considered as good. When taken out of the solder bath, the Ag-Sn surface showed a dewetting trend but the pure silver did not.

We studied the tribological behaviour of the Ag-Sn alloy as compared to the one of pure silver. A steel ball 6 mm in diameter slid on polished disks coated respectively by 2 and 6 μm of Ag-Sn, 2 and 6 μm of pure silver. The applied force on the contact pin-disk was 500 g and the rotating speed was 1 cm/s. The humidity of the experimental atmosphere was 50%. The fric-

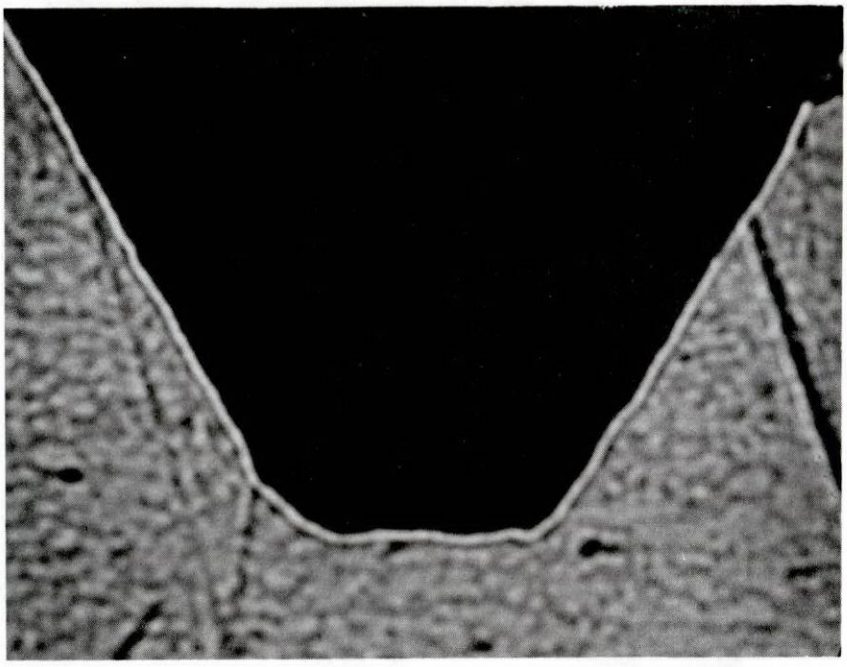
tion coefficient at the beginning of the test was 0.135 for Ag and 0.27 for Ag-Sn. However it took only 128 rotations for the silver disk to have a friction coefficient increased up to 0.3 and 153 for the Ag-Sn disk. Therefore, at the beginning of the friction process, the Ag-Sn shows a better constancy than Ag in its tribological behaviour but beyond a certain friction distance the Ag-Sn layer degrades more rapidly and thus possesses a shorter life duration than silver.

To sum up we can emphasize that the main advantage of the Ag-Sn is to provide a better tarnish resistance as compared to pure silver. This makes the Ag-Sn a good candidate for decorative purposes and for applications where the reflectivity decreases too rapidly. More generally the alloy Ag-Sn can be introduced in technical applications where silver is discarded precisely because of its low tarnish resistance.

References


1) S. Steinemann, W. Flühmann and W. Saxer; Metalloberfläche 29 (4) (1975).
2) W. Saxer, Galvanotechnik 68 (11) (1977).
3) W. Flühmann, W. Saxer, F. Aubert and H.E. Hintermann; Galvanotechnik 65 (8) (1974).
4a) A. Brenner, "Electrodeposition of alloys, Principles and Practice", Vol. I pp. 585-590, Academic Press (1963), New York.
b) id. p. 615.
5) G.F. Jacky, Plating and Surf. Fin. Sept. (1971) pp. 883-87.
6) G. Tamman and M. Hansen; "Ueber das ternäre System Kupfer-Zinn-Zink", Ztschr. anorg. Chem., 138 (1924) 137-161.
7) Henry Leidheiser Jr. and A.R.P. Ghuman; J. Electrochem. Soc. 120 (4) (1973) pp. 484-487.
8) W. Reksc, J. Lagoda and P. Biedzinski; Chemia i Inzynioria Chemiczna 13 (1978) pp. 157-168.

Fig. 1 Part of a saw tooth profile of a BNC connector coated with Optalloy 5 μm in thickness



400 μm

Fig. 2 Contact pins coated with Optalloy, soldered with the wave fluxing method in 60/40 tin-lead.

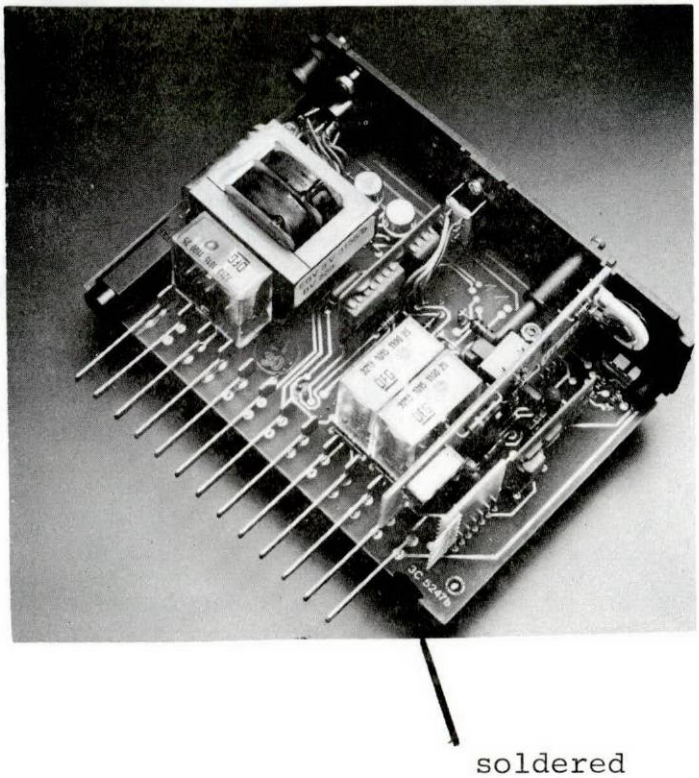


Fig. 3 Set of industrial parts successfully coated by Optalloy.

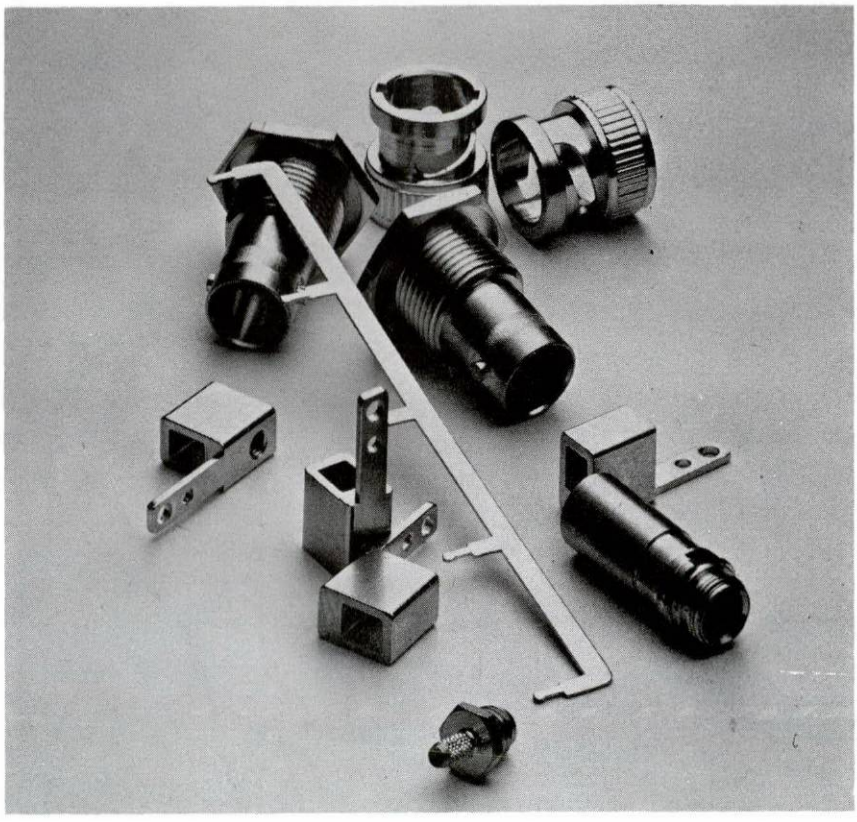


Fig. 4 Polarization curve for the electrodeposition of the Ag-Sn alloy (rotating cylinder, 200 rpm)

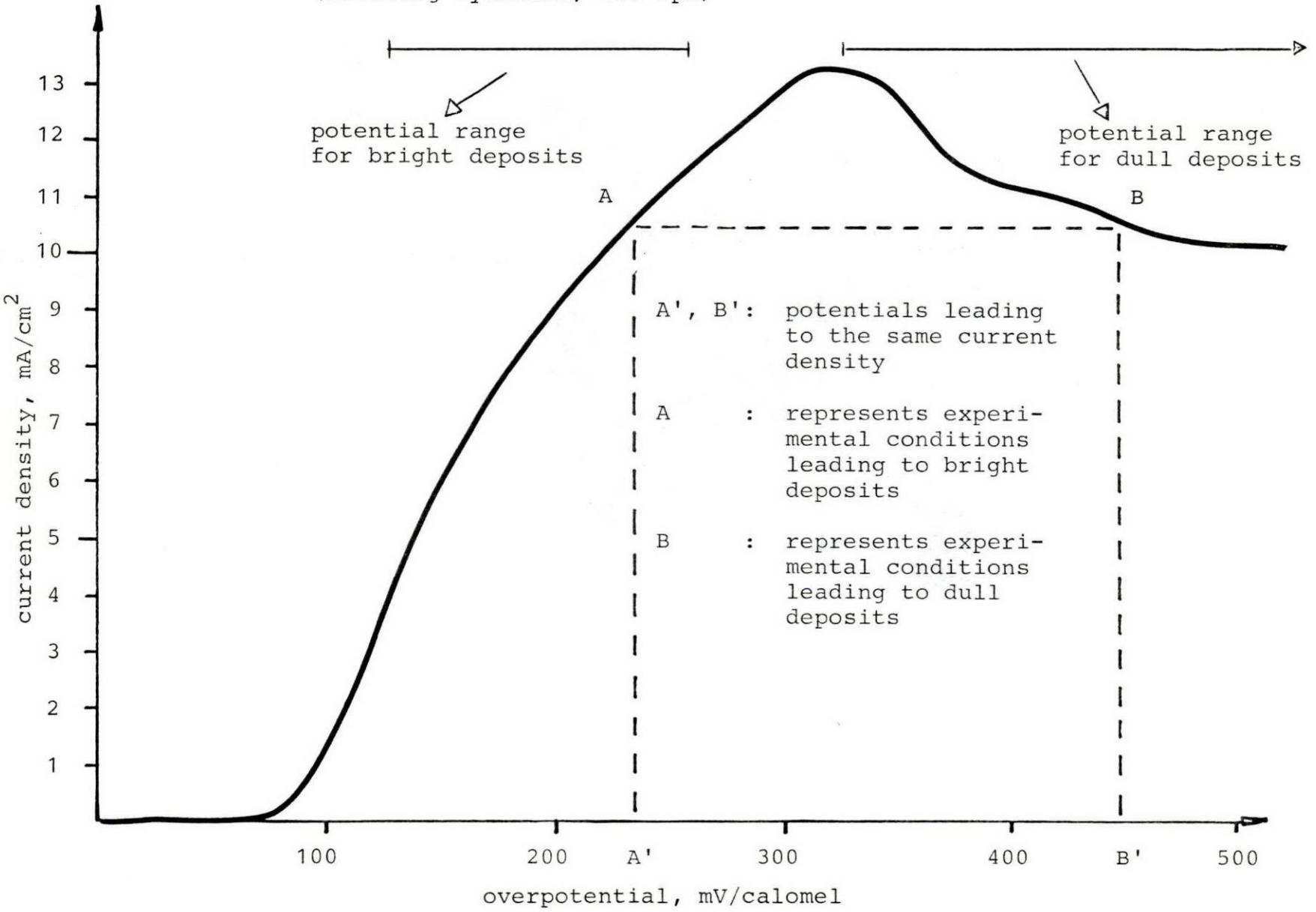
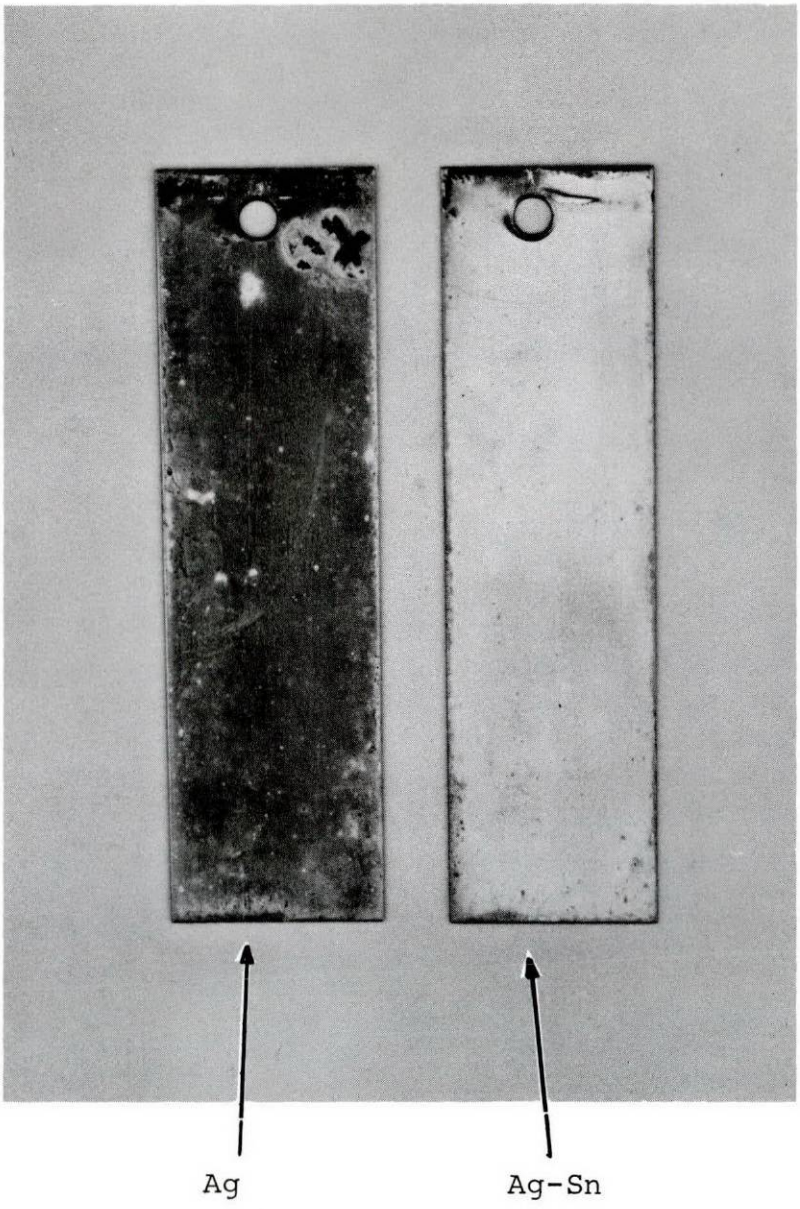


Fig. 5 Ag and Ag-Sn coatings after tarnishing test in thioacetamide.



P-2

# Alloy Plating I
# Session P

## Electrodeposition and Passivation of Bright Zinc-Nickel Alloys

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# ELECTRODEPOSITION AND PASSIVATION OF BRIGHT ZINC-NICKEL ALLOYS

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## Abstract

A new process is described for electroplating decorative zinc-nickel alloy coatings. The operational parameters in depositing bright alloys of 5-20% nickel content are discussed as are the general performance characteristics of the alloy deposits. Based on accelerated test results, the corrosion performance of these alloys is far superior to zinc. Moreover, a novel passivation treatment is shown to provide additional protection. The passivated zinc-nickel alloys exhibit outstanding protection at elevated temperatures.

## Introduction

Zinc alloy plating research has been pursued for many years and it has been reported that plating from various types of electrolytes is possible.[1] However, there have been no reports of successful commercial processes for plating individual articles or components.

In Japan, in the last few years, the steel companies have started production of alloy plated steel sheets for automobile bodies and the high corrosion resistance achieved is drawing widespread attention. High speed strip plating with these zinc alloys is gradually increasing. However, these applications are in the field of nondecorative industrial plating; and alloy technology for general decorative, rust preventative plating has not been introduced.

Due to recent new requirements for corrosion resistance improvements of plated automotive parts, fasteners and paint undercoatings, the development of a decorative, rust preventative alloy plating process was initiated.

## Required Features for Decorative, Protective Coatings

Study of the decorative alloy plating process was carried out with the objective of incorporating the following features:

1. Excellent brightness and appearance.
2. Good covering power.
3. Acceptable physical/mechanical properties.
4. Sound adhesion to substrate.
5. Readily acceptable to passivation.

6. High corrosion resistance.
7. Easy bath control.
8. Economical Operating costs.
9. Suitable for painting after plating.

To develop a process incorporating all these features is a very difficult task, and while all of these characteristics have not been fully attained, significant progress towards these objectives has been achieved.

Bath Composition and Plating Chemistry

The zinc alloy coatings used in the steel mills are from sulfate type electrolytes. However, as a sulfate electrolyte is inferior in throwing power, and does not provide a full bright appearance over a broad current density range, it was judged that a sulfate bath would not be feasible for plating of individual components. For this reason, our experiments were based on chloride baths.

In zinc chloride baths, there are acid and neutral baths as follows:

1. Acid (Chloro-zinc Complex Bath) pH < 4

$$NH_4(ZnCl_3) \longrightarrow ZnCl_3^-$$
$$(NH_4)_2(ZnCl_4) \longrightarrow ZnCl_4^{-2}$$
$$(NH_4)_3(ZnCl_5) \longrightarrow ZnCl_5^{-3}$$

2. Neutral Bath (Amino-Chloride Complex Salt Bath) pH 5-8[2]

$$Zn(NH_3)_4Cl \longrightarrow Zn(NH_3)_4^{+2}$$
$$Zn(NH_4)_2Cl_4 \longrightarrow Zn(NH_4)_2^{+4}$$

In an acid bath, the brightness range is narrow, the nickel-zinc codeposition ratio is unstable and difficult to maintain, and satisfactory results could not be obtained. For this reason, development of a neutral bath seemed a more promising approach.

In a neutral solution, the various components of zinc chloride, nickel chloride, and ammonium chloride were varied and parameters for achieving good brightness over a wide current density range

were developed. Subsequently, it was found that the ranges described in Figure 1 was suitable. These were:

| | |
|---|---|
| $Zn^{++}$ | 30-60 g/l |
| $Ni^{++}$ | 20-40 g/l |
| $NH_4^+$ | 50-120 g/l |

Furthermore, the zinc to nickel ratio should be less than 2.5. The optimum pH range was 5.5-6.0.

When the respective component concentrations and pH were not within the above range, the following unfavorable trends were observed:

Concentration and/or pH too Low

| | | |
|---|---|---|
| $Zn^{++}$ | - | burns easily, poor appearance |
| $Ni^{++}$ | - | poor appearance |
| $NH_4^+$ | - | rough deposits, poor appearance |
| pH | - | poor appearance, burns easily |

Concentration and/or pH too High

| | | |
|---|---|---|
| $Zn^{++}$ | - | poor appearance, corrosion resistance inferior |
| $Ni^{++}$ | - | black deposit, cracks |
| $NH_4^+$ | - | salt precipitation |
| pH | - | unstable solution, ammonia gas evolved |

Brighteners

As a result of studying various addition agents, it was confirmed that some components used in zinc chloride solutions were also effective in specific combinations in the zinc-nickel alloy bath and many materials were evaluated as primary and secondary brighteners.

Primary Brighteners

Polyoxy Ethylene Alkyl Ethers
Polyoxy Ethylene Alkyl Aryl Ethers
Polyoxy Ethylene Propylene Ethers
Polyoxy Ethylene Polyoxy Propylene Ethylene Diamines

Polyoxy Ethylene Alkyl Amines
Polyoxy Ethylene Alkyne Diols

Secondary Brighteners

Aryl Aldehydes
Aryl Ketones
Aryl Olefin Aldehydes
Aryl Olefin Ketones

Auxiliary Addition Agents

Organic Acids
Alcohols

Zinc-Nickel Process Parameters

The alloy deposit from this plating process is typically anomalous type. The cathodic potential and cathodic current density in the alloy plating solution and in the same solution with either zinc or nickel removed were measured with a potentionstat.

The results as shown in Figure 2 indicate that plating starts at 0.86 volts in a solution containing only zinc ions and at 0.6 volts in a solution containing only nickel ions. However, the potential-current curve of a mixed bath, with the exception of the initial stage, closely resembles the curve of a zinc solution and it can be surmised that nickel from this bath does not preferentially deposit. Moreover, it can be deduced that nickel can easily deposit at very low current densities.

Plating conditions that would result in a zinc-nickel alloy deposit having 5-10% nickel content were defined. This alloy composition was selected since passivation of the alloy deposit is difficult above a 12% nickel content. The relationship between the various plating conditions and nickel content is illustrated in Figures 4-8. For these measurements, the bath composition is at the optimum concentrations listed in Table I and the operating conditions are midrange as detailed in Table II.

In Figure 4, the zinc concentration in the solution was kept constant at 50 g/l and the nickel content was varied from 20 to 50 g/l. The desired nickel concentration is in the range of 20 to 35 g/l in order to maintain a nickel content of 5-10% in the deposit.

In Figure 5, the influence of brighteners on the nickel content of the alloy deposit is shown. It is apparent that both primary and secondary brighteners suppress the co-deposition of nickel.

In Figure 6, the affect of solution pH on the nickel content of the deposit is described. In an acid bath of 3.5 pH, nickel content becomes less than 5%. By keeping the pH between 5.4-6.0, the nickel content stabilizes at 5-10% and can be maintained in that range.

Figure 7 shows the results of bath temperature variations. If the bath temperature exceeds 40°C, the nickel content increases, adversely affecting the appearance. Also, when the solution temperature is less than 30°C, the salts in the bath will begin to precipitate and high current density burning develops. Therefore, it is desirable to maintain the bath temperature between 30-38°C.

Figure 8 shows the effect of air agitation of the plating bath on alloy composition. Agitation effects are comparatively small but it does slightly decrease the nickel content of the alloy.

As a result of these studies, standard bath composition and operating conditions for this process were established as detailed in Tables 1 and 2.

The features of the bright zinc-nickel process may be summarized as follows:

| | |
|---|---|
| Appearance and Leveling | Bright appearance, slightly inferior in leveling to zinc chloride processes. |
| Cathodic Current Efficiency | 98-100% |
| Deposit Distribution | Essentially equal to a zinc ammonium chloride bath as shown in Figure 9. |

The features of the deposit with 5-10% nickel may be summarized as follows:

| | |
|---|---|
| Hardness | 150-180 (Hv) |
| Ductility | In the case of thin deposits, equal to nickel. Thicker deposits are less ductile. |
| Internal Stress | Basically equal to a zinc ammonium chloride bath as shown in Figure 10. |
| Heat Resistance | Exceeds passivated zinc deposits by more than 50°C. |
| Wear Resistance | Superior to zinc plating. |
| Paint Adhesion | Very good with passivation or phosphate coating. |
| Corrosion Resistance | In protecting steel, the alloy is significantly more protective than standard zinc coatings. |

## Passivation of Zinc-Nickel Alloy Deposits

### 1) Yellow Passivation

Compared with conventional zinc deposits, formation of passivation films on alloy deposits is difficult and it is generally necessary that they be treated in concentrated chromic acid solutions under severe conditions. If the nickel content is high, it becomes even more difficult to obtain a film and additional processing prior to passivation becomes essential.

### 2) Clear Passivation

Clear or blue bright passivation of the alloy deposit can be obtained by use of a cathodic dichromate based process or by use of a leach type chromate.

## Corrosion and Heat Resistance Characteristics of Passivated Zinc-Nickel Alloy Plating Deposits

A significant feature of the alloy deposits is the outstanding corrosion resistance. Figure 11 shows salt spray test results of passivated zinc and zinc-nickel alloy plated steel panels. The tests were conducted according to Japanese Standard JISZ-2371 which is equivalent to ASTM Standard B-117. In evaluating the appearance of white and red rust, the zinc-nickel alloy plating showed more than 3 times the corrosion resistance of the zinc plate. It features excellent corrosion resistance in low coating thicknesses and red rust also takes a longer time to appear.

The passivated alloy coating shows excellent heat resistance. The normal zinc passivate coating turns brown or decomposes at 100-150°C, but the alloy is resistant to high temperatures of 200-250°C. Passivated zinc and alloy plated panels were placed in an electric oven and heated for 24 hours at constant temperatures of 100, 150, 200, 250°C and corrosion resistance tested by a neutral salt spray test. The results shown in Figure 12 clearly demonstrate the superiority of the passivated alloy deposit.

## Potential Alloy Plating Applications

The excellent performance of zinc-nickel alloy coatings, creates possibilities for applications such as:

Automotive fasteners, machine components, building hardware, and marine parts.

Undercoating for paint.

Parts requiring wear and high temperature resistance.

Alternative coating for nickel deposits.

## Alloy Plating Cost

The cost of the alloy coating, containing 7% nickel, is 40-50% above the cost of a zinc coating of the same thickness. However, the material cost increase can be justified by the improvement in the quality of the plated product or the coating thickness can be reduced which also results in improved productivity.

## Future Developments in Zinc-Nickel Alloy Plating

Future improvements in this new technology will, we believe, be centered on increasing ductility of the alloy deposit, in simplifying the passivation procedures and processes, and in improved control of the more complex bath chemistry.

Bright zinc-nickel alloy plating technology is new and will undoubtedly see even further improvements. This technology is just beginning to find commercial usefulness. Considering the possibilities for substantial improvements in performance by using alloy coatings, a successful future for zinc alloy coatings seems assured.

## References


1. A. Brenner, Electrodeposition of Alloys, Volume II, Academic Press, N.Y., 1963, pp. 194-228

2. K. P. Bellinger, Plating, 56, 1135(October, 1969)

3. A. Shibuya, T. Kurimato, Electrochemical Society Meeting October, 1981, Abstract No. 308

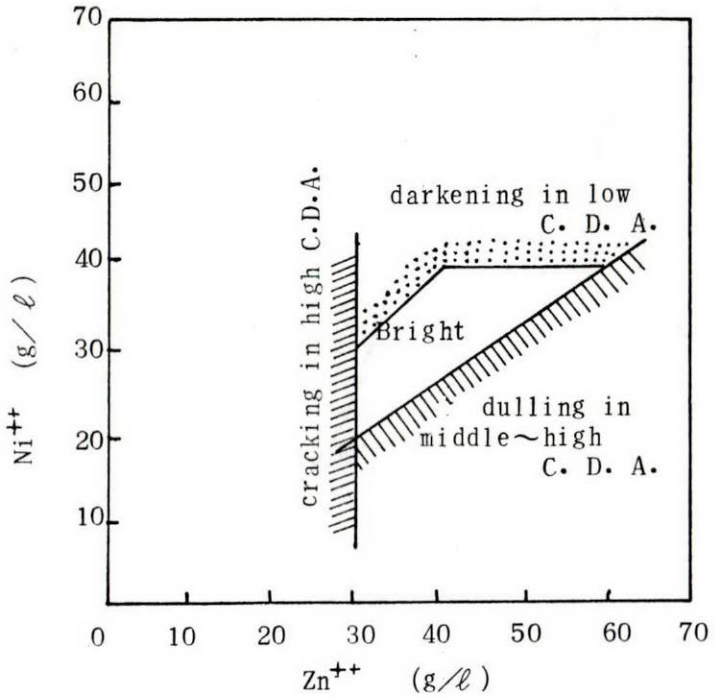



Fig. 1 Proper Zinc and Nickel concentration in the bath.

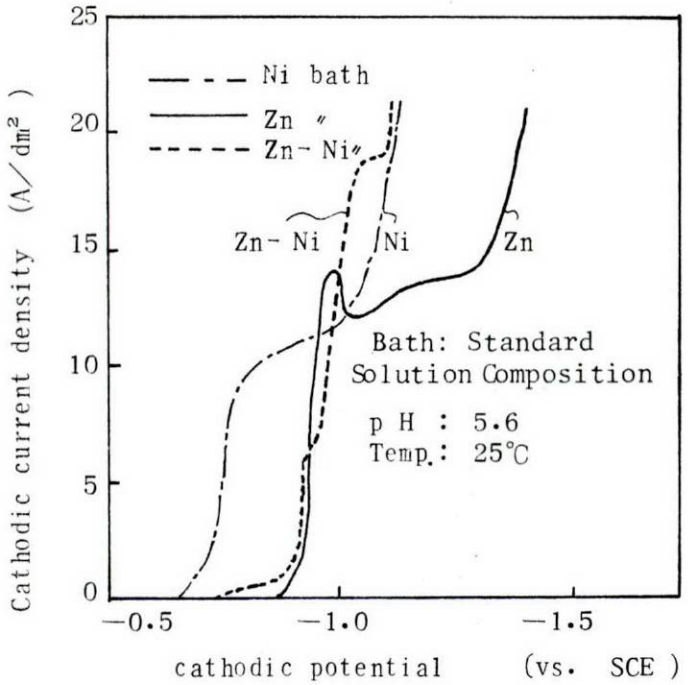



Fig. 2 Cathodic current density vis cathodic potential in each bath.

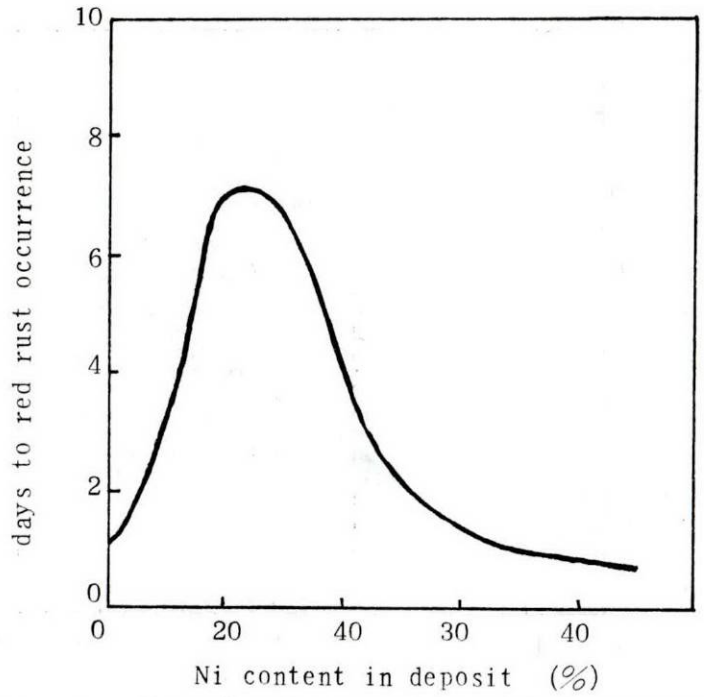



Fig. 3 Relation between the nickel content in the deposit and corrosion resistance by salt spray test.[5]

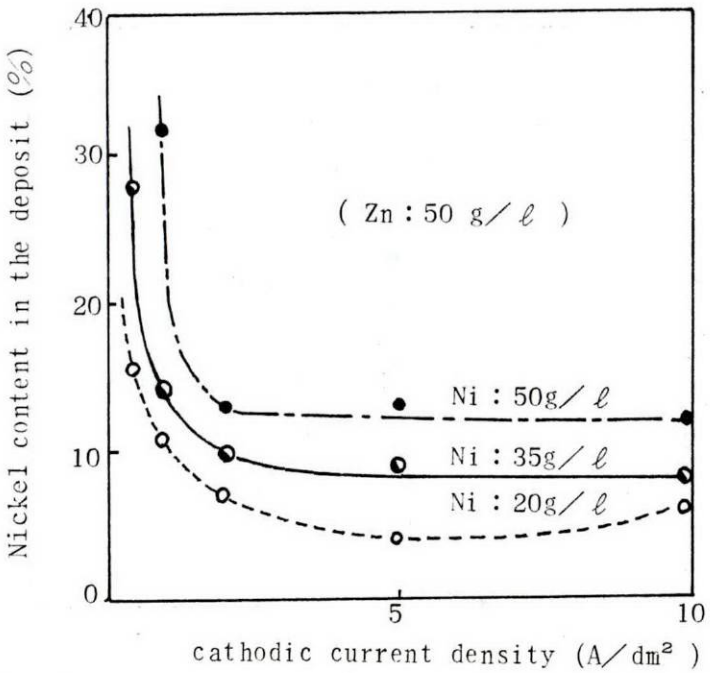



Fig. 4 Relation between Nickel content in the bath and Nickel content in the deposit.

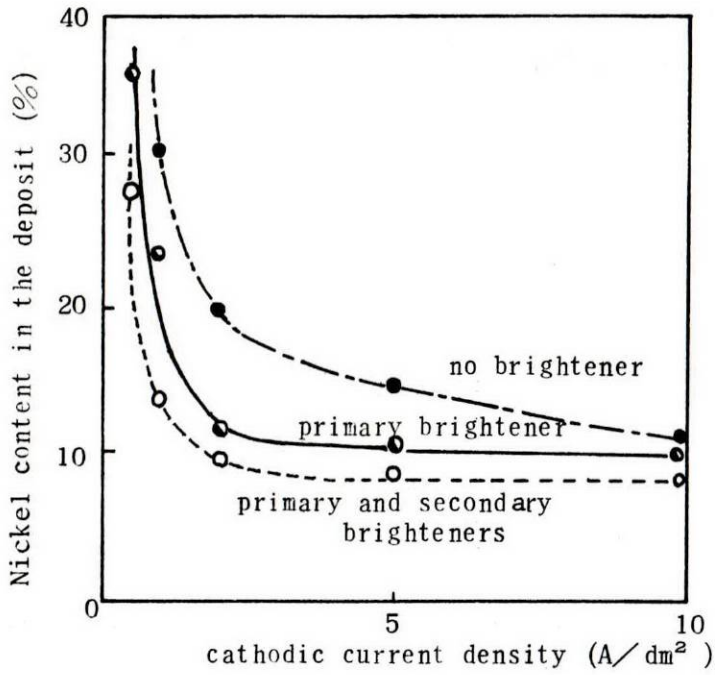



Fig. 5 Effects of brighteners on Nickel content in the deposit.

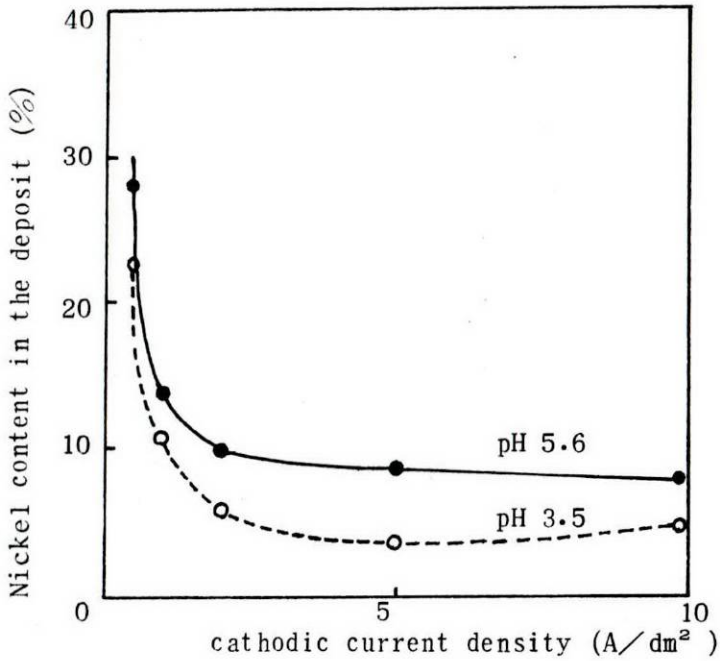



Fig. 6 Relation between pH of the bath and Nickel content in the deposit.

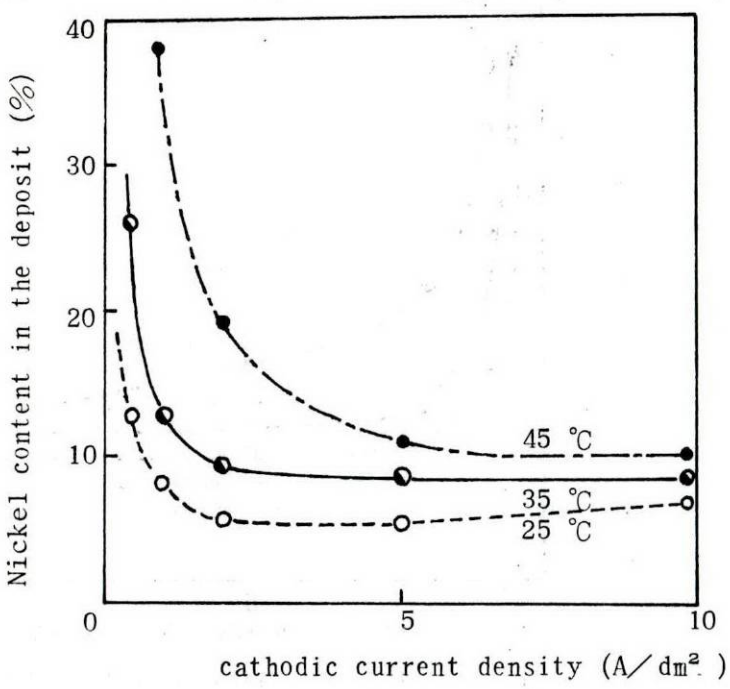



Fig. 7 Relation between bath temperature and Nickel content in the deposit.

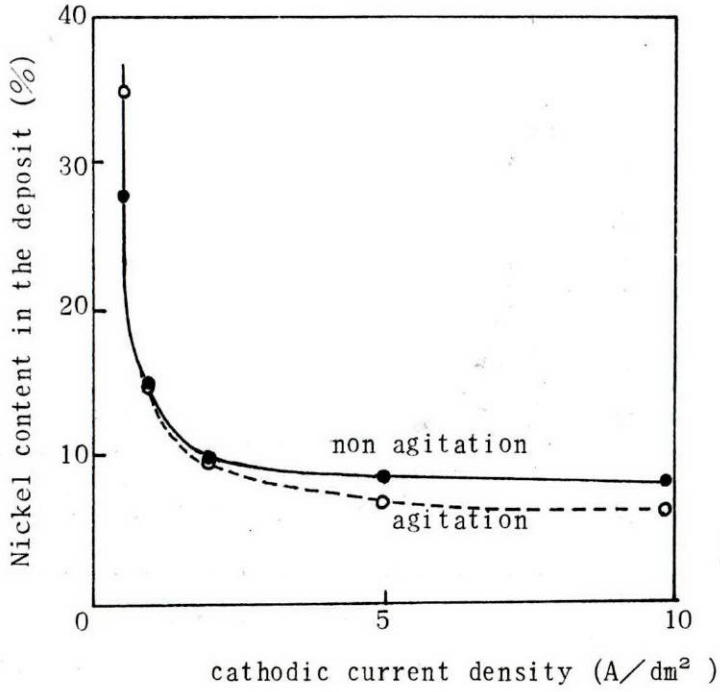



Fig. 8 Effect of agitation on Nickel content in the deposit.

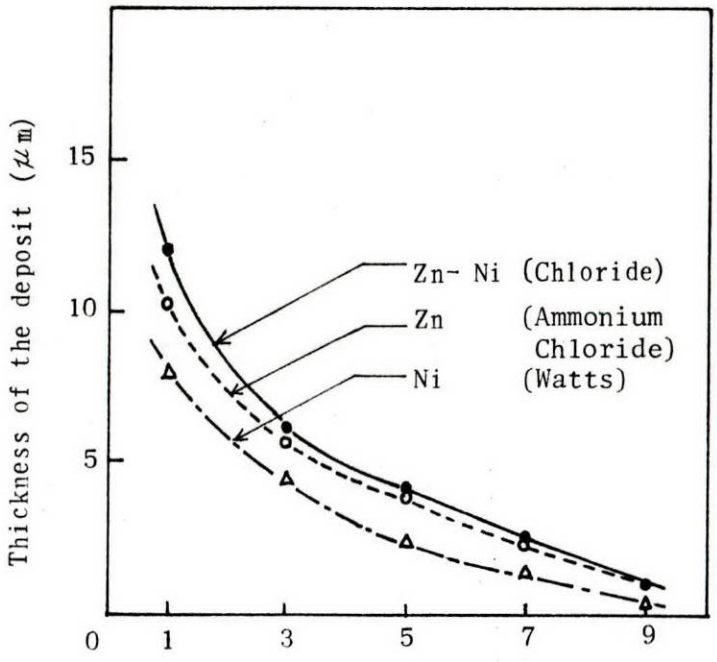



Fig. 9 Thickness distribution on Hull Cell panel plated for 5 minutes at 2 amperes in each solution.

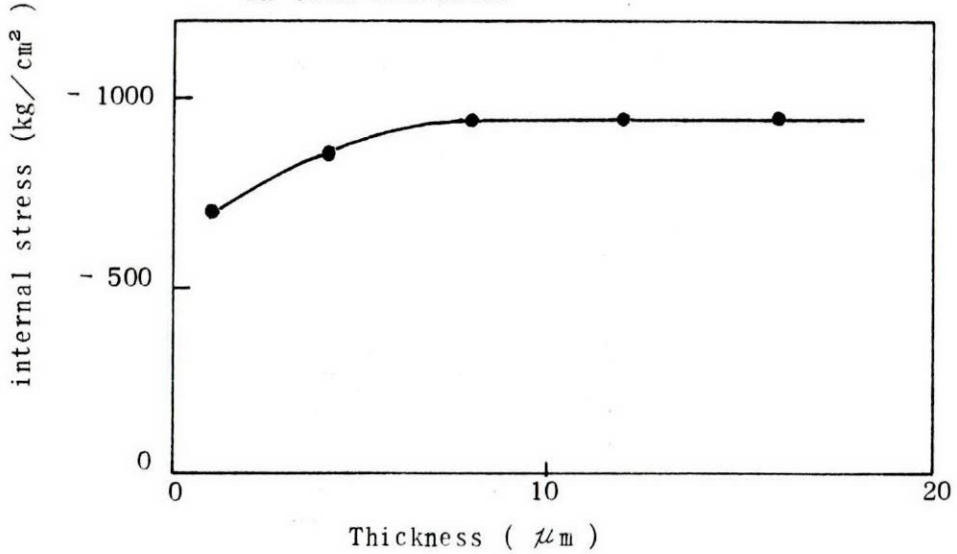



Fig. 10 Internal stress of Zinc-Nickel deposit.

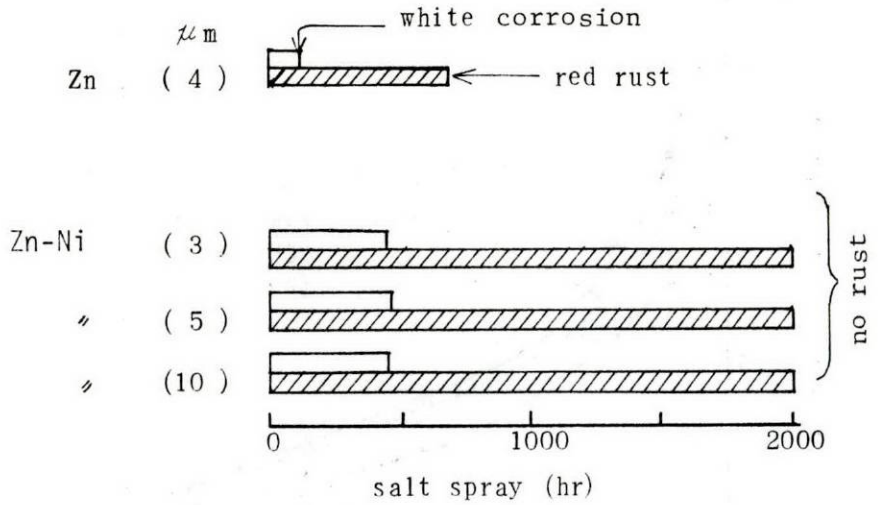



Fig. 11 Corrosion resistance of passivated Zinc-Nickel deposit.

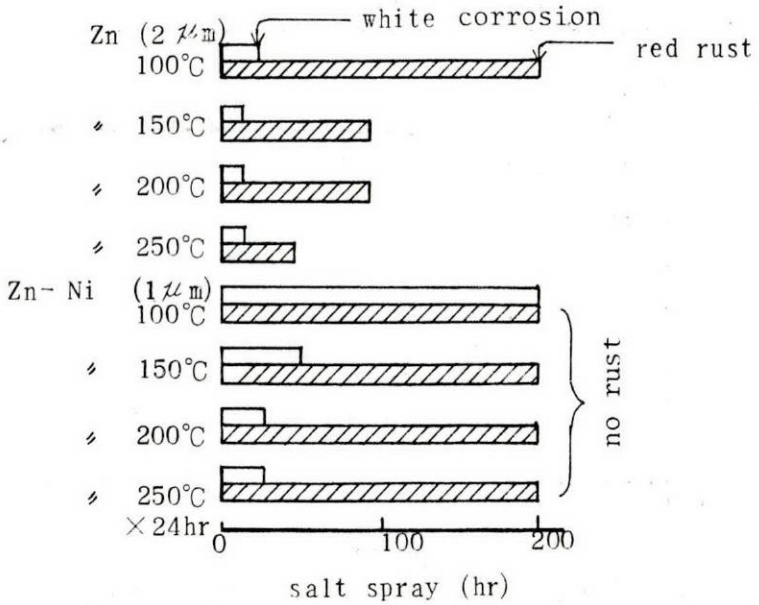



Fig. 12 Heat resistance and corrosion resistance of passivated Zinc-Nickel deposit.

Table- 1 Typical Bath Composition

| Component | | Range | Optimun |
|---|---|---|---|
| $ZnCl_2$ | (g/ℓ) | 80 ~ 120 | 100 |
| $NiCl_2 \cdot 6H_2O$ | ( 〃 ) | 120 ~ 160 | 140 |
| $NH_4Cl$ | ( 〃 ) | 180 ~ 220 | 200 |
| Primary Brightener A | (ml/l) | 30 ~ 60 | 40 |
| Secondary Brightener B | (ml/l) | 1 ~ 3 | 2 |

Table- 2 Operating Conditions

| Item | | Range | Optimum |
|---|---|---|---|
| p H | | 5.5~6.0 | (With $NH_4OH$) |
| Temperature | (℃) | 32 ~ 40 | |
| Cathodic C. D | ($A/dm^2$) | 2 ~ 6 | 3 ~ 4 |
| Anodic C. D | ( 〃 ) | 1 ~ 4 | |
| Agitation | | air agitation | Mild |
| Anode | | Zinc anode | |

P-3

# Alloy Plating I
# Session P

## Tin-Lead Plating Processes: From Bone-Glue to Fluoborate-Free

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# TIN-LEAD PLATING PROCESSES: FROM BONE-GLUE TO FLUOBORATE-FREE

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Tin-Lead electrodeposits were used during World War I to protect sea mines against corrosion. The plated alloy was used even more extensively during and after World War II to provide corrosion protection and lubricating properties on bearings.

With the advent of the electronics era in the 1950's there proved to be a growing need for this alloy coating. Typically 60/40 deposits (60% tin, 40% lead) were used in the emerging printed circuit field as a solderable coating for copper circuits and as an etchant mask during manufacturing. Other applications in the electronic industry included connectors, semiconductors, and IC lead frames.

The solutions used to produce these early deposits were based on the acid fluoborate system:

| | | |
|---|---|---|
| Stannous Tin | 60 g/l | (8.0 oz/gal) |
| Lead | 25 g/l | (3.4 oz/gal) |
| Free Fluoboric Acid | 100 g/l | (13.4 oz/gal) |
| Boric Acid | 25 g/l | (3.4 oz/gal) |

In addition to the above, additives were required to assist in the following functions:

1. Prevent high current density treeing.
2. Improve low current density covering power.
3. Refine grain structure and provide smooth deposits.
4. Improve deposit distribution.

Initially bone-glue or gelatin were used, but chemical instability of these materials quickly led to widespread use of first, solid peptone (a meat protein complex) and later, liquid peptone throughout the 1960's.

In the 1970's, development of stable surfactants and proprietary additives[1,2] in place of peptone led quickly to their prevalent use, especially in printed circuit manufacturing, where the enhanced stability of these additives reduced deposit out-gassing during reflow operations. In addition, the introduction of high throw formulations[3] made it possible to reduce deposit thicknesses on the surface of circuit boards while still achieving adequate thickness of the surfaces of hole walls.

Another drawback of the earlier process was the poor throwing power which presented difficulties when the deposit was used as a final etch-resist. Usually at least 0.001 inch was required on the board surface to ensure a minimum 0.0005 inch on the walls of holes. This minimum thickness was essential when ammonium persulfate or chromic acid was used as the final etchants to insure that the underlying copper was not etched through porosity in the coating. The high thickness of tin lead on the surface aided solderability by sheer bulk of deposit but presented difficulties with the gaps between tracks and pads which were decreasing as designers required higher performances from PC boards.

The following acid fluoborate formula is typical of present solutions:

| | | |
|---|---|---|
| Stannous Tin | 24 g/l | (3.2 oz/gal) |
| Lead | 9 g/l | (1.2 oz/gal) |
| Free Fluoboric Acid | 150 g/l | (20.1 oz/gal) |
| Boric Acid | 20 g/l | (2.7 oz/gal) |

Recent developments[4] include reformulation of this fluoborate model which involves higher concentrations of the basic constituents and the use of specially designed additives to allow much higher current densities and thus, improved productivities.

## HISTORY OF FLUOBORATE FREE BATHS

Although tin lead plating baths based upon fluoboric acids and metal fluoborates have been used successfully for many years, certain problems have always been present.

1. The removal of fluoborate ions from the rinse water is difficult and regulations limiting fluorides in waste waters are often very restrictive. In some areas, boron in the waste water is also prohibited.
2. The solution is very corrosive to plating equipment and harmful to the skin.
3. Anodes baskets can not be used.
4. Insoluble anodes can not be used, even if they are advantageous for certain applications.

Attempts have been made to develop tin-lead plating baths that are free from fluoborates and reference #5 describes a bath based on pyrophosphates. These baths have not been successful since they are subject to rapid parameter and deposit composition variations and are very difficult to control. A pyrophosphate-Rochelle salt process has been described[6] that was claimed to be an improvement over a straight pyrophosphate bath. These baths operated

at a pH of 8.5 - 9 and the temperature was somewhat elevated to about 100°F. Although lead in the effluent could readily be precipitated as the sulfate, it was difficult to remove tin from the effluent and the chelating agents caused additional problems in waste disposal. Other problems with the pyrophosphate based baths were the relative instability of pyrophosphates and their gradual conversion to orthophosphates. These baths have not achieved any real commercial acceptance.

Reference #7 contains an example of a tin-lead bath based upon diammonium citrate and ammonium chloride at a pH of 6. Tin is added in the form of sulphate and lead in the form of acetate. Since ammonium ion and citrates are complexing agents, they also cause problems in waste disposal by complexing the metals and making them difficult to precipitate from the waste water. These baths have not acheived any commercial acceptance.

A tin lead plating bath based upon the metal phenolsulfonates and free pheno sulfonic acid has achieved some acceptance commercially in Japan.[8,9] These commercial baths are said to deposit either semi-bright or bright tin lead deposits. Effluents from these baths contain phenols, which are restricted in the waste water in many communities. The same company also markets a fluoborate free tin-lead bath based upon alkanolsulfonic acids which have achieved limited commercial acceptance in Japan. Although the baths based upon alkanolsulfonic acids are not a problem for waste water treatment, they are the most expensive of all the fluoborate free tin-lead baths proposed so far.[10,11]

A new, recently introduced process[12], contains a non-poisonous organic sulfonic acid that is relatively inexpensive and poses no waste disposal problems. A simple neutralization of the rinse waters preciptates both tin and lead yielding a readily disposable non-hazardous effluent.

## APPLICATIONS OF FLUOBORATE FREE BATHS

### Printed Wiring Boards

The first application for the new fluoborate free solder bath was in the area of printed circuit boards. A uniform matte 60/40 tin-lead deposit was consistently obtained from a plating solution containing the following:

| | |
|---|---|
| Stannous Tin Metal | 18 g/l |
| Lead Metal | 9 g/l |
| Free Acid | 140 ml/l |
| Tin:Lead Ratio | 2:1 for 60/40 Alloy |

It can be seen that the bath chemistry is quite similar to the high throw fluoborate baths now in common use. The operation of these baths is in all ways almost identical to the operation of the fluoborate baths. That is to say

they operate at room temperature require a 1:1 anode to cathode ratio, have a practical current density plating range of 0 - 40 amps per square foot and require small periodic additions of a grain refiner. There are however three areas in which the new fluoborate free bath represents a significant advance over previous technology. These are:

1. Relatively constant alloy composition over a wide current density plating range.
2. The use of titanium anode baskets in place of slab anodes.
3. A readily treatable effluent.

Figure 1 shows that in contrast to deposits from the fluoborate bath containing peptone which show variations in tin concentration ranging from below 30 to as high as 70% as the current density increases from 0 - 40 ASF, deposits from the non-fluoborate bath have a relatively constant 55 - 63% tin concentration. This is of particular significance in light of the large scale plating equipment now being installed at many PCB facilities resulting in wide variations in current density over the surfaces of large panels. If the plater cannot be assured of a constant alloy over the surface of these panels, subsequent fusing problems may well occur.

The use of titanium anode baskets in place of slab anodes will represent a significant cost savings inasmuch as it will no longer be necessary to discard the upper portion of each anode bar. However, there is an even greater advantage to the use of anode baskets and that is the assurance of more uniform distribution of deposit over the surface of the panels due to the fact that the anode configuration in relation to these panels will be constant.

Probably the greatest impetus to the development of a non-fluoborate plating bath was the possibility of obtaining a readily treatable effluent. As we are all well aware in this day and age, the quality of our effluent is often at least as important if not more important than the quality of our product. Both the tin and lead metal contents in the plating bath can be reduced to levels well below 0.5 parts per million by means of a simple neutralization. The results of this neutralization are shown in figure 2.

The tin-lead deposits obtained from this bath can be readily fused by both IR and hot oil methods to yield bright deposits with no signs of dewetting.

## HIGH SPEED REEL TO REEL PLATING

In addition to its use on printed circuit boards the fluoborate free solder bath has been successfully used on continuous reel to reel applications. In one such application a matte continuous stripe was plated onto a strip of phosphor bronze which had been previously copper plated to a thickness of approximately 50 microinches. The operating conditions in the selective

plating cell are shown in Table 1. Of particular significance are the relatively constant alloy composition over the current density range of 100 - 500 ASF and the use of an insoluble platinized titanium anode. The bath chemistry for this new process is such that there appears to be little oxidation of stannous tin to stannate tin even when using an insoluble anode. Experiments run in our laboratory have confirmed this and have shown that fluoborate baths when operated with insoluble anodes tend to produce large amounts of insoluble stannate tin as compared to the non-fluoborate bath which was still clear after many hours of operation.

Figure 3 illustrates the very fine grain deposit which is obtained at 100 ASF. As the current density increases the grain size and the surface roughness also were seen to increase. The deposit also tended to show some darkening with increased current density. Samples from this line were fluxed and fused in hot oil and showed excellent reflow.

In another application in similar equipment a bright 60/40 deposit was obtained on a reel of nickel plated brass connectors. The line is running at an average speed of 20 ft/min. and 150 ASF. In contrast to the first line which was described, soluble 60/40 tin-lead anodes are used in this piece of equipment. I should point out that bright 90/10 tin-lead alloys very similar in appearance to those shown were also obtained in this line by varying the tin and lead concentrations in the plating bath.

## CONCLUSION

In conclusion it is fair to say that tin-lead plating baths have undergone a constant evolution since their introduction in the early 1950's for use on printed circuit boards. It also seems obvious that this evolution will continue as the pressures build for a safer environment and for more sophisticated technology to meet the rapidly changing demands of a technological society.

## REFERENCES


1. Plutin LA Process - Max Schloetter & Co., Geislingen, West Germany
2. SolderGlo 25HJ Process - LeaRonal U.K., Buxton, England
3. B.F. Rothschild & D. Sanders - Plating 1969, 1363
4. U. S. Patent 4,263,106
5. U. S. Patent 3, 039,942
6. U. S. Patent 3,984,291
7. U. S. Patent 4,163,700
8. Ishihara Chemicals Co., Ltd., Tokyo - Unicorn Processes
9. U. S. Patent 3,905,878
10. Dohi and Obata "Electrodeposition of Bright Tin-Lead from Alkanosulfonate Baths" Interfinish 1980
11. U. S. Patent 4, 132,610
12. SolderOn - LeaRonal, Inc.

**TABLE # 1**

OPERATING CONDITIONS FOR STRIPE ON STRIP

| | |
|---|---|
| Length of Cell | 28 inches |
| Feed Rate of Strip | 10 ft/min. |
| Plating Time | 14 sec. |
| Slot width | 0.25 inch |
| Anode | Platinized Titanium |
| Cathode Current Density | 100 - 500 ASF |
| % Tin in Alloy | 63.2 - 69.1 |
| Temperature | 75°F |

TIN-LEAD PLATING BATHS
CURRENT DENSITY VS. TIN/LEAD CONTENT

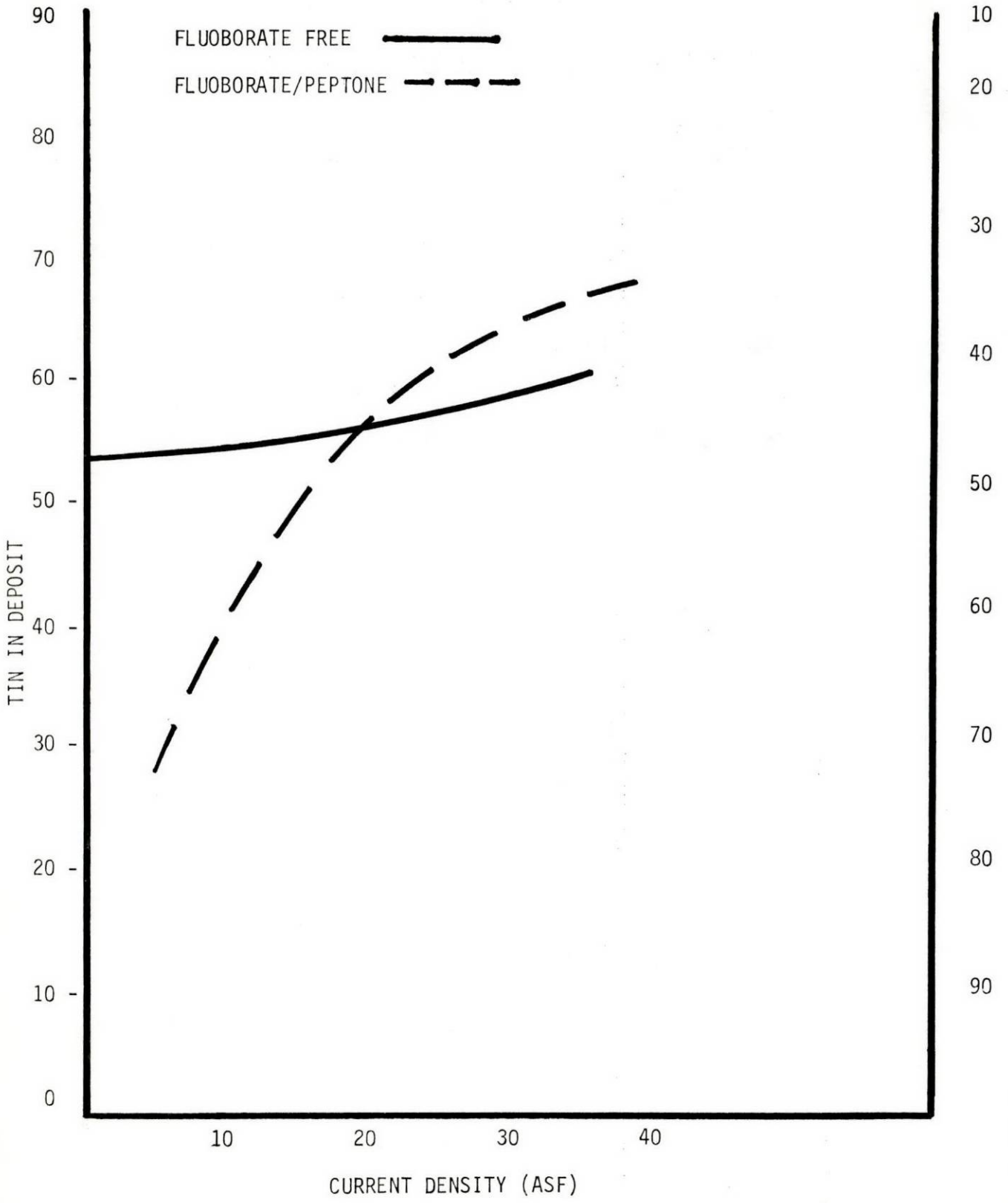



Figure #1

WASTE TREATMENT OF FLUOBORATE FREE TIN LEAD

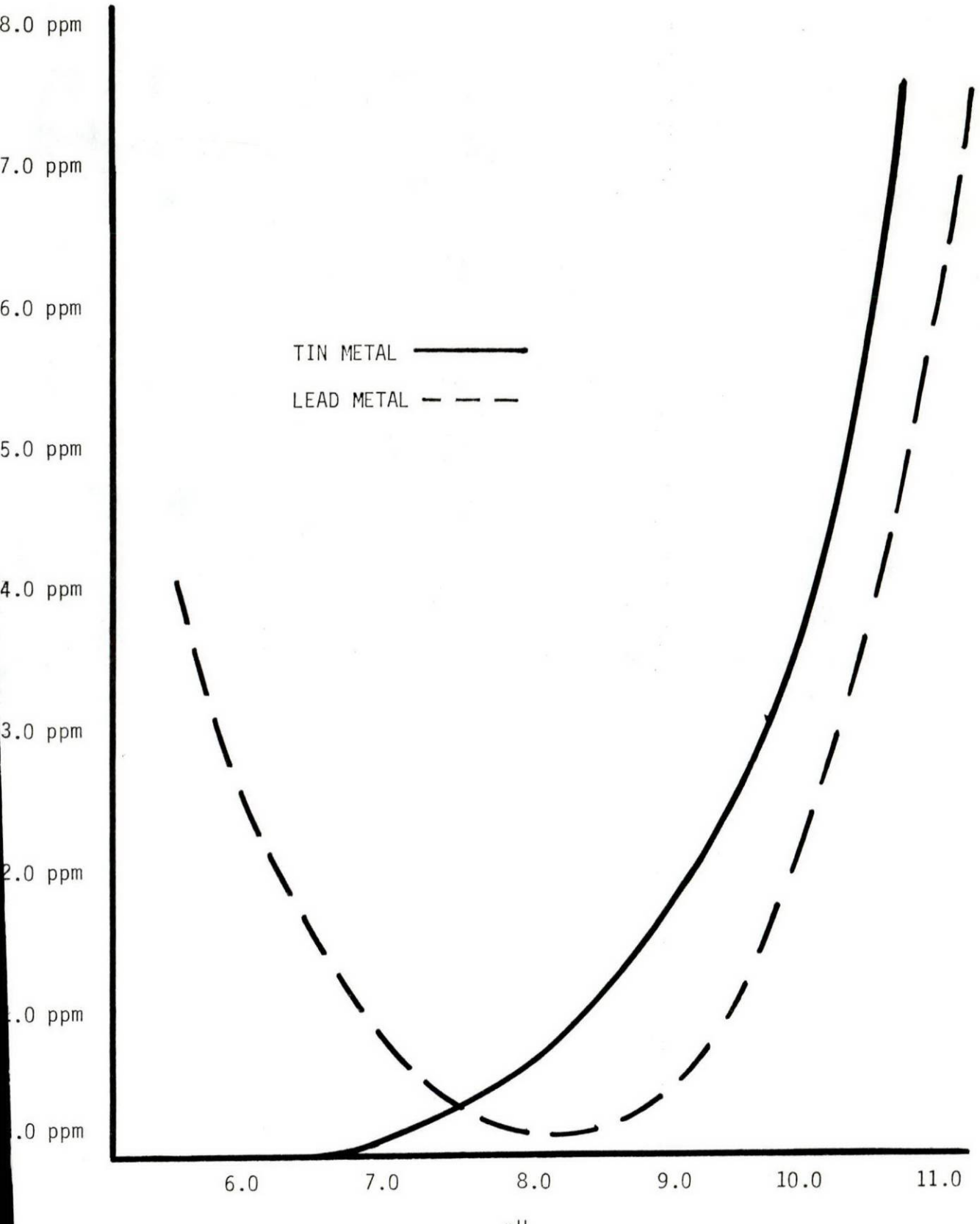
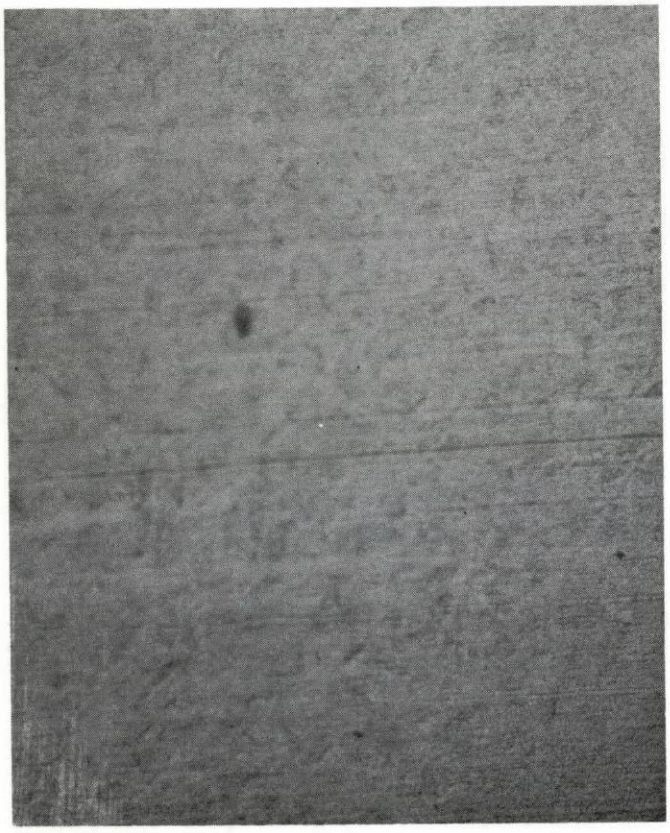
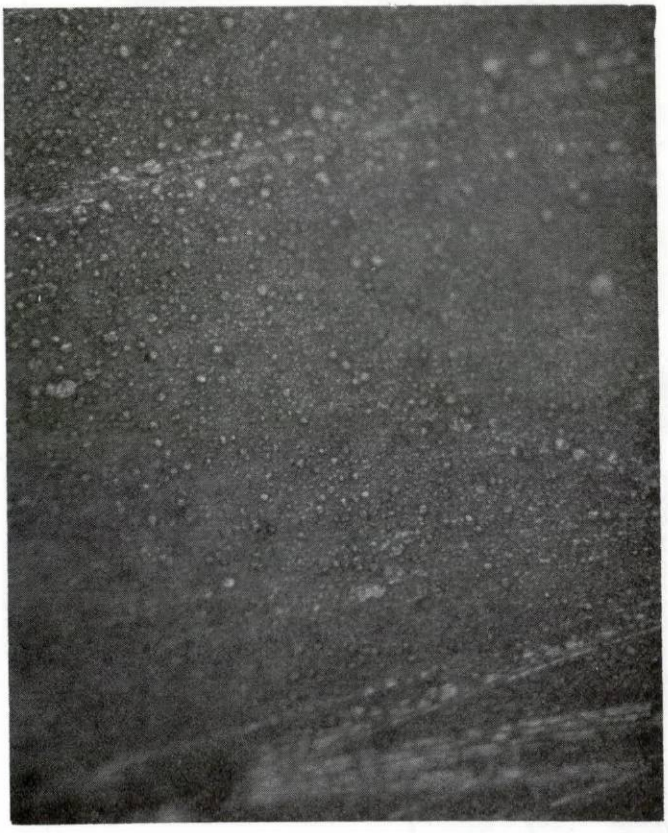



Figure #2



Fluoborate Free Tin-Lead At 100 ASF (400x



Fluoborate Free Tin-Lead At 400 ASF (400x)

FIGURE 3

P-4

# Alloy Plating I
# Session P

## Layered Coatings of Tin Over Zinc by Mechanical Plating

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# LAYERED COATINGS OF TIN OVER ZINC BY MECHANICAL PLATING

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## Introduction

A specialized use of mechanical plating is the possibility of plating dissimilar metals in layers over the basis metal to be coated. The nature of the process is such that this "layering" effect can be achieved with little or no chemical and/or labor penalty. The layers adhere well both to themselves and to the basis metal. The use of chromate on such layered plating can enhance the value of the plating without giving a yellow chromate appearance if tin is chosen as the uppermost layer. This type of plating is being done on a commercial basis every day, using available commercial equipment and chemicals. No standard exists for this plating.

## Production Process

Mechanical plating uses particulate metal for the coating materials. These metal particles vary in size from approximately 3 microns to about 10 microns in diameter, depending on which metal is chosen for coating. In this discussion we confine ourselves to the plating of metallic tin particles over mechanically deposited zinc.

Part preparation normally consists of a caustic descaling and degreasing operation, which is normally done twice in a high production operation with an intermediate rinse. Caustic solutions are held at 150°F. and oil emulsifiers are never used in the preparatory operation. Parts are rinsed twice at ambient temperature after the second caustic treatment, inhibited acidic pickling is next, then a final cold water rinse. Parts are loaded into a plating barrel along with glass beads and water. The plating machine starts rotating, chemicals and zinc are added. At the conclusion of the zinc plating portion of the process, tin powder is added. The barrel rotates to completion of the tin plating, then the machine is unloaded. The parts are separated from the glass media, yellow chromated and dried. The yellow chromate "sinks" through the tin into the zinc, leaving the tin with a faintly tawny appearance.

Thickness of both zinc and tin can be controlled by the quantity of metal added. Coatings as thin as 8 microns (5 microns of zinc, 3 microns of tin) and as thick as 50 microns (42 microns of zinc, 8 microns of tin) have been commercially produced with good results. It is believed coatings

to 80 microns of thickness (72 microns of zinc, 8 microns of tin) are practical; little experience exists. Table 1 on page 3 shows the three coating designations now in use, a graphic profile of the coating and minimum salt spray results. It will be appreciated that the average salt spray results are substantially higher than those listed in the chart.

First Example

A bolt manufacturer supplies a specialized fastener which holds aluminum panels with heavy outdoor exposure in all parts of the North American continent. Traditionally, they have applied mechanical coatings of cadmium approximately 8 microns thick. This coating has proved satisfactory in use. Equivalent thickness of zinc coating has proved unsatisfactory because of the formation of corrosion products and the additional protecting of zinc with yellow chromate is unsatisfactory to the customer. The 08 designation in layered coating was applied to this production and tested on aluminum coupons in comparison with unchromated zinc fasteners commercially produced.

Second Example

A retaining ring has been made of stainless steel PH 15-7 MO and heat-treated to Rockwell C52. The material in the form required is no longer available at commercially feasible prices. To provide an alternative to this stainless steel ring, in atmospheres which were not too acid or too caustic (and for which the non-magnetic and thermal properties of stainless steel are not required), the coating designation 50 was used on parts made of 1075 steel, austempered to C52. Production is commercial and achievable on available equipment and with available materials.

Test Program

Test programs used for these tests were:

1) Salt spray test as per ASTM B117

2) Atmospheric exposure at latitude 27°, longitude 80°, Florida.

3) For the class 50 part only, tide-in-tide-out testing (tide-in-tide-out testing consists of immersing the samples in the Indian River in such a way that they are exposed to the atmosphere at low tide and immersed in the river at high tide).

Florida tests included stress corrosion tests for the retaining rings coated to the class 50 designation. This consisted of loading the parts with bending stresses at or slightly in excess of the yield point of the material (approximately 200,000 lbs. per square inch). Class 50 coating designation was compared to normal stainless steel parts.

TABLE I

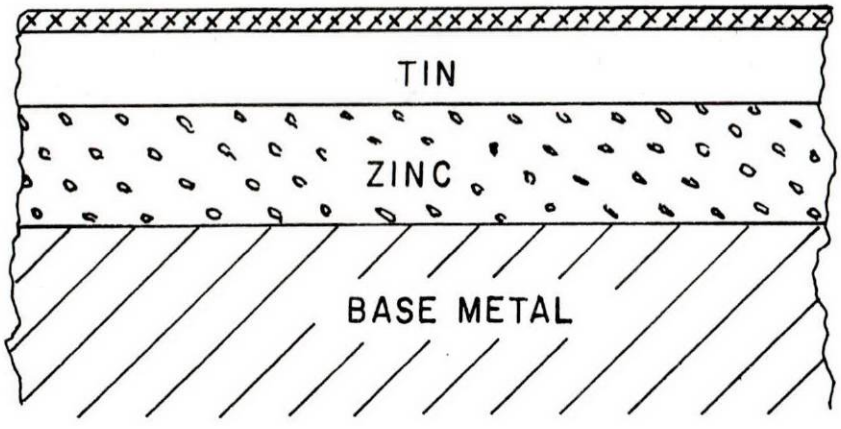
DISCREET LAYER OF MECHANICALLY
PLATED TIN OVER MECHANICALLY PLATED ZINC

IN MICRONS (μ)

| COATING DESIGNATION | ZINC THICKNESS | TIN THICKNESS | Σ THICKNESS |
|---|---|---|---|
| 08 | 5 | 3 | 8 |
| 16 | 8 | 8 | 16 |
| 50 | 42 | 8 | 50 |

COATING LAYERS

YELLOW CHROMATE GOES ON LAST. MUCH
OF IT SINKS IN THROUGH THE TIN INTO THE ZINC




MINIMUM SALT SPRAY RESULTS (IN HRS.)

| COATING DESIGNATION | TO RED RUST | TO WHITE RUST |
|---|---|---|
| 08 | 36 | 36 |
| 16 | 96 | 72 |
| 50 | 300 | 72 |

TEST PER ASTM

## Results

In salt spray all parts lasted the minimum required salt spray hours and on the basis of test results they are deemed suitable alternates for the test parts.

It is hard to pick out a single number in salt spray as being typical of the life of PH 15-7 MO stainless steel after heat-treating, cleaning and passivation, but a typical figure gleaned from many production lots of this material is about 200 hours, with parts occasionally failing in 48 hours and sometimes lasting several hundred hours. A coating yielding a minimum of 300 salt spray hours, while certainly not as good as the best stainless steel results obtained, is a more corrosion-resistant finish in salt spray than most of the stainless steel parts tested. Like comments are made for the class 08 fastener in comparison to cadmium or zinc coating, unchromated.

However, in both the examples given, salt spray is merely an indicator of the reliability with which a given coating has been produced and certainly an unreliable indicator of what may be expected in real life. The Florida tests are far more revealing.

On the threaded fasteners finished with 08 coating, interaction of aluminum with the zinc coating began almost immediately with atmospheric exposure. White corrosion products were significant and deterioration of the aluminum occurred in a few weeks. To the conclusion of this test (in a several month period), no visible interaction occurred on the tin layered plating and the aluminum, though both the aluminum and tin darkened with atmospheric exposure.

The atmospheric exposure of the retaining rings coated with class 50 coating resulted in little change other than a slight darkening during the life of the test. The same was true of the controlled stainless steel samples.

In the tide-in-tide-out test, significant differences occurred. Stress corrosion failures started to occur in the stainless steel group after somewhere between the 20th and 25th tidal exposures (because of the extreme tension, the broken bits of the retaining ring were lost). This is in line with previous experience of such tests on stainless steel. Retaining rings of 1075 steel which were coated class 50 showed no failures in stress corrosion. Both the surviving stainless steel parts and the 1075 steel showed a tendency to darken with exposure. For the life of the test, no stress corrosion failures have occurred on the 1075 steel although experience shows that substantial exposure will induce such failures.

## Discussion

In each of the above cases, the layered mechanical plated tin over the mechanical plated zinc represents a cost-effective solution to an economic

or engineering problem. In the case of the threaded fastener with the 08 coating, for economic reasons this manufacturer desired to terminate the use of cadmium in his plating production. No combination of zinc that could be produced economically in his process were satisfactory to his customer. However, the addition of the layer of tin produces samples which were able to satisfactorily pass every test, to eliminate the use of cadmium in his process without substituting an equally toxic material and fitted into his production economically. A small premium of the plating metal price was the only additional cost.

The layered tin offers an alternative to stainless steel for the retaining ring manufacturer in many ways. 1075 steel heat-treated has better spring properties than the stainless steel and mechanically is a somewhat better part. It seems clear from the tests that 1075 steel coated with this class 50 finish is far more resistant to stress corrosion, at least in a marine application, than is the stainless steel. The cost and availability of the steel part at best will be only a fraction of the cost of the stainless steel part and with the withdrawal of material from the market in the size and shapes needed, the steel ring provides an economic and reasonable alternative for many applications.

## Production Availability

Commercial machinery, chemicals, glass beads, technology and all the components required for this process exist today. They are available in simple, crude, manual processes doing 100 lbs. per hour to highly sophisticated, automatic processes producing a ton an hour. Imaginative use of these processes can resolve many engineering problems which do not start out directly as coating problems.

Q-1

# Statistical Design and Computer Modeling Session Q

## An Introduction to Programmed Experimentation

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# AN INTRODUCTION TO PROGRAMMED EXPERIMENTATION

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## Abstract

The use of programmed experimentation can be of great time-saving advantage in obtaining maximum information in return for a minimum of experimentation, even for those who have little or no understanding of the mathematical basis on which the experimental strategy is based.

Programmed experimentation can be condensed to a simple step-by-step process that can be used to identify the important factors controlling electroplating processes. After the critical factors have been identified, they can be optimized by a simple graphical analysis.

## Introduction

If a plating process has many operational variables that can affect performance, i.e., current density, temperature, pH, agitation, metal concentration, etc., and you have no idea which factors are the most critical to the operation of the process, you start with a screening experiment. What this requires is the running of a series of tests using all of the known variables in combination, as directed by a simple pattern. The results of a relatively small number of tests are then analyzed, and the significant factors are readily identified for further study.

The following is a step-by-step run through of the process used to screen variables in a decorative rhodium plating process. Variables which are found to be non-critical can subsequently be controlled less stringently than those found to be significant to the operation of the process.

## Experimental

First, five variables were identified as potentially critical to the operation of the rhodium plating process, namely, rhodium concentration, acid concentration, temperature, current density, and time.

As with any programmed experiment, only two values for each variable needed to be chosen. These should be somewhat reasonable (often based on experience), and far enough apart so that we will be sure to locate any significant effects caused by the changes in parameter settings, while insuring that any effects noted are, in fact, greater than experimental error. Accordingly, the following high/low settings were chosen for each variable.

| VARIABLE | HIGH (+) | LOW (-) |
|---|---|---|
| Rhodium Metal (X1) | 5 gm/l | 2.5 gm/l |
| Sulfuric Acid (X2) | 50 cc/l | 20 cc/l |
| Temperature (X3) | 130° F | 100° F |
| Current Density X4) | 40 ASF | 10 ASF |
| Time (X5) | 90 sec | 30 sec |

The use of (+) and (-) to designate the high and low set points for each parameter simplifies the substitution of actual operating conditions for the symbols used in the general experimental pattern found in the literature.

For a five-factor screening experiment, Fig. 1 is the pattern which will be found in the literature (1). We will use only the first five columns for actual experiments, while the remaining columns will be used later to mathematically estimate significance factors. You can see that only twelve different tests, or trials, need be run in order to check the effects of five variables.

Tests were run on 500 ml solution samples in 600 ml beakers, using an all-around platinum-clad tantalum gauze anode, and 2" x 1" gold plated brass cathode panels.(*).

In this experiment, the factor measured was current efficiency, and each trial was run only once, with special care taken to insure that all data points were as accurate as possible. Each trial could, of course, be run in duplicate, and the average data points used.

The current efficiencies obtained by weigh-plate-weigh for the twelve trials are shown in Table 1.

TABLE 1. CURRENT EFFICIENCY TEST RESULTS

| TRIAL | EFFICIENCY (mg/amp-min) | TRIAL | EFFICIENCY (mg/amp-min) |
|---|---|---|---|
| 1 | 5.71 | 7 | 1.77 |
| 2 | 8.28 | 8 | 7.05 |
| 3 | 1.71 | 9 | 1.28 |
| 4 | 2.48 | 10 | 7.57 |
| 5 | 8.00 | 11 | 2.14 |
| 6 | 9.33 | 12 | 6.28 |

Once the twelve trials have been run, the balance of the work involves only simple arithmetic manipulation of the data, as follows:

For each vertical column in Fig. 2,

1. Add up the "Y" values opposite the + signs, and enter the value as SUM +.
2. Add up the "Y" values opposite the - signs, and enter the value as SUM -.
3. Add SUM + and SUM - to give the OVERALL SUM, which must be identical for all columns, including the MEAN column.
4. Enter as DIFFERENCE the arithmetic sum of SUM + and SUM -.
5. Divide each DIFFERENCE by the number of +'s in the column to obtain the FACTOR EFFECT. The FACTOR EFFECT can be either + or -, indicating that the current efficiency increases or decreases as the individual parameter is increased from the low (-) to the high (+) setting.

* Bath efficiency will vary with base metal due to $H_2$ overvoltage.

Since this test used five factors, the last six columns in Fig. 2 are used to calculate the "significance factor", which is the minimum FACTOR EFFECT required in any column for the parameter to be considered statistically significant to the process being studied. The calculation of this "significance factor" proceeds as follows:

1. Calculate an EFFECT for each of the last six columns, as was done for the first five columns above.
2. Square each EFFECT.
3. Add the squares of the EFFECTS.
4. Divide by 6.
5. Take the square root.
6. Multiply by 2.45 (t-test for 95% Confidence Level with 6 degrees of freedom, as represented by the six unassigned factor columns.
7. The resulting number is the MINIMUM FACTOR EFFECT, or [MIN].

In this study, two variables (rhodium concentration and acid concentration) were found to have a significant effect on current efficiency, with current density close enough to warrant further study in a factorial study, as described in the next example.

A screening experiment can often be avoided by a judicious choice of variables, based on first-hand experience with the process under study. If, however, a screening experiment is required, it is valuable to pursue a study of the three most significant factors via a two-level factorial study. Since this type of experiment covers only three parameters at two levels each, only $2^3$, or eight, trials are required. However, with fewer tests, it is advisable to run each trial in duplicate. Doing so facilitates the estimation of experimental error.

The basic layout for a two-level factorial in three variables is shown in Table 2.

TABLE 2. TWO-LEVEL FACTORIAL IN 3 VARIABLES

| TRIAL | X1 | X2 | X3 |
|---|---|---|---|
| 1 | - | - | - |
| 2 | + | - | - |
| 3 | - | + | - |
| 4 | + | + | - |
| 5 | - | - | + |
| 6 | + | - | + |
| 7 | - | + | + |
| 8 | + | + | + |

In order to eliminate any bias experimental error, the 16 trials should be run in random order following a random numbers table.

A two-level factorial was performed to determine the significant factors in the Atomic Absorption Spectrophotometric determination of gold in proprietary stripper solutions. The

three factors chosen for study were:

| | (-) | (+) |
|---|---|---|
| X1 Gold Concentration | 10 ppm | 20 ppm |
| X2 Stripper Concentration | 1% | 5% |
| X3 Sodium Cyanide Concentration | 3 oz/gal | 6 oz/gal |

The result (Y) determined was Absorbance, using air/acetylene and nitrous oxide/acetylene flames in separate, but concurrent, studies. Results are shown in Table 3.

TABLE 3. SAMPLE ABSORBANCES

| TRIAL | AIR/ACETYLENE | NITROUS OXIDE/ACETYLENE |
|---|---|---|
| 1 | 0.261/0.264 | 0.044/0.058 |
| 2 | 0.508/0.502 | 0.088/0.098 |
| 3 | 0.269/0.276 | 0.047/0.053 |
| 4 | 0.510/0.506 | 0.090/0.097 |
| 5 | 0.258/0.263 | 0.046/0.052 |
| 6 | 0.491/0.483 | 0.090/0.092 |
| 7 | 0.281/0.278 | 0.052/0.052 |
| 8 | 0.499/0.502 | 0.087/0.093 |

The mathematical treatment of the data is similar to that for the screening experiment, except that the averages of the two results in each trial ($\bar{Y}$) are used. Also, the determination of the MINIMUM EFFECT is slightly different, as follows:

1. Calculate the variance ($S^2$) of each set of trial points, as follows: $S^2=(Y_1-Y_2)^2/2$.
2. To improve the precision of the calculations, calculate a "pooled standard deviation" as follows:

$$S_{pooled}=\sqrt{\frac{S^2}{8}}$$

3. The MINIMUM EFFECT, or $[MIN]$, is calculated as follows:

$[MIN] = S_{pooled} \times 0.5 \times t$, where "t" is the student "t". For 7 degrees of freedom, and a 95% Confidence Level, t=2.36.

The data for these tests are shown in Figs. 3 and 4, which also show additional columns for the calculation of factor interactions.

## Results

The common significant factor in both tests is, as would be expected, gold concentration. The use of a nitrous oxide/acetylene flame is shown to eliminate the cyanide and stripper interferences which are present when an air/acetylene flame is used. Note, also, the gold/cyanide interaction observed with an air/acetylene flame. This effect was noted in an earlier

paper (2).

To make full use of the experimental values, a graphical representation of the data can be made, in order to determine the optimum operating conditions for the process under study. It can be seen by such a representation of the data for an air/acetylene flame (Fig. 5) that, while the introduction of a small amount of either stripper or cyanide into a gold-bearing solution significantly affects the Absorbance, an increase in concentration of either material has no additional affect. This finding has been put to practical use in the analysis of gold cyanide solutions by Atomic Absorption by always adding 1% v/v of prepared stripper (containing 3 oz/gal of cyanide) to gold standards.

## Conclusion

The actual values obtained in the above-cited examples are less important than the demonstration of the simplicity of the procedure described. A great deal of experimental time can be saved by using programmed experimentation. The trial-and-error and the vary-one-parameter-at-a-time approaches are still quite valid. However, it should be noted that, as the number of variables in a process increases, the number of such tests which must be run will quickly become prohibitive, unless the experimenter takes advantage of techniques which allow changing of more than one variable at a time.

The type of variables that can be studied via programmed experimentation is unlimited. Two different tanks can be used in a study, with one assigned as (+) and the other as (-). Even the presence or absence of a factor can be studied, with the absence, or OFF, setting assigned as (-), and the presence, or ON, setting assigned as (+).

Caution is advised if the above procedures are tried out by the reader. The conditions noted should be followed without deviations.

The full scope of programmed experimentation can only be grasped fully by attending a "Strategy of Experimentation" workshop/seminar which is offered by the Applied Technology Division of DuPont & Co., Inc.

## REFERENCES

(1) Plackett, R.L., and J.P. Burman, Biometrika, 33, 305 (1946).

(2) Werbicki, J.J., Jr., "An Atomic Absorption Analytical Technique For Gold Comparable To Fire Assay", Proceedings of the 67th Annual Technical Conference, American Electroplaters' Society, Milwaukee, 1980.

FIG. 1

Twelve-Run Plackett-Burman Design

| TRIAL | MEAN | x 1 | x 2 | x 3 | x 4 | x 5 | x 6 | x 7 | x 8 | x 9 | x 10 | x 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | + | + | + | - | + | + | + | - | - | - | + | - |
| 2 | + | + | - | + | + | + | - | - | - | + | - | + |
| 3 | + | - | + | + | + | - | - | - | + | - | + | + |
| 4 | + | + | + | + | - | - | - | + | - | + | + | - |
| 5 | + | + | + | - | - | - | + | - | + | + | - | + |
| 6 | + | + | - | - | - | + | - | + | + | - | + | + |
| 7 | + | - | - | - | + | - | + | + | - | + | + | + |
| 8 | + | - | - | + | - | + | + | - | + | + | + | - |
| 9 | + | - | + | - | + | + | - | + | + | + | - | - |
| 10 | + | + | - | + | + | - | + | + | + | - | - | - |
| 11 | + | - | + | + | - | + | + | + | - | - | - | + |
| 12 | + | - | - | - | - | - | - | - | - | - | - | - |

## FIG. 2. SCREENING EXPERIMENT - RHODIUM

| TRIAL | MEAN | x 1 | x 2 | x 3 | x 4 | x 5 | x 6 | x 7 | x 8 | x 9 | x 10 | x 11 | Y |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | + | + | + | - | + | + | + | - | - | - | + | - | 5.71 |
| 2 | + | + | - | + | + | + | - | - | - | + | - | + | 8.28 |
| 3 | + | - | + | + | + | - | - | - | + | - | + | + | 1.71 |
| 4 | + | + | + | + | - | - | - | + | - | + | + | - | 2.48 |
| 5 | + | + | + | - | - | - | + | - | + | + | - | + | 8.00 |
| 6 | + | + | - | - | - | + | - | + | + | - | + | + | 9.33 |
| 7 | + | - | - | - | + | - | + | + | - | + | + | + | 1.77 |
| 8 | + | - | - | + | - | + | + | - | + | + | + | - | 7.05 |
| 9 | + | - | + | - | + | + | - | + | + | + | - | - | 1.28 |
| 10 | + | + | - | + | + | - | + | + | + | - | - | - | 7.57 |
| 11 | + | - | + | + | - | + | + | + | - | - | - | + | 2.14 |
| 12 | + | - | - | - | - | - | - | - | - | - | - | - | 6.28 |
| Sum + | 61.60 | 41.37 | 21.32 | 29.23 | 26.32 | 33.79 | 32.24 | 24.57 | 34.94 | 28.86 | 28.05 | 31.23 | |
| Sum - | 0 | 20.23 | 40.28 | 32.37 | 35.28 | 27.81 | 29.36 | 37.03 | 26.66 | 32.74 | 33.55 | 30.37 | |
| Overall Sum | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | 61.60 | |
| Diff | +61.60 | +21.14 | -18.96 | -3.14 | -8.96 | +5.98 | +2.88 | -12.46 | +8.28 | -3.88 | -5.50 | +0.86 | |
| Effect | +5.13 | +3.52 | -3.16 | -0.52 | -1.49 | +1.00 | +0.48 | -2.08 | +1.38 | -0.65 | -0.92 | +0.14 | |

$$S_{fe} = \sqrt{\frac{0.48^2+2.08^2+1.38^2+0.65^2+0.92^2+0.14^2}{6}} = 1.13$$

$$[MIN]_{95} = 1.13 \times 2.45 = \boxed{2.77}$$

FIG. 3. TWO-LEVEL FACTORIAL - AIR/ACETYLENE

| TRIAL | MEAN | X1 | X2 | X1X2 | X3 | X1X3 | X2X3 | X1X2X3 | $\bar{Y}$ | $S^2 \times 10^{-6}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | + | - | - | + | - | + | + | - | 0.2625 | 4.5 |
| 2 | + | + | - | - | - | - | + | + | 0.5050 | 18.0 |
| 3 | + | - | + | - | - | + | - | + | 0.2725 | 24.5 |
| 4 | + | + | + | + | - | - | - | - | 0.5080 | 8.0 |
| 5 | + | - | - | + | + | - | - | + | 0.2605 | 12.5 |
| 6 | + | + | - | - | + | + | - | - | 0.4870 | 32.0 |
| 7 | + | - | + | - | + | - | + | - | 0.2795 | 4.5 |
| 8 | + | + | + | + | + | + | + | + | 0.5005 | 4.5 |
| SUM + | 3.0755 | 2.0005 | 1.5605 | 1.5315 | 1.5275 | 1.5225 | 1.5475 | 1.5385 | | |
| SUM - | 0 | 1.0750 | 1.5150 | 1.5440 | 1.5480 | 1.5530 | 1.5280 | 1.5370 | | |
| OVERALL SUM | 3.0755 | 3.0755 | 3.0755 | 3.0755 | 3.0755 | 3.0755 | 3.0755 | 3.0755 | | |
| DIFF | +3.0755 | +0.9255 | +0.0455 | -0.0125 | -0.0205 | -0.0305 | +0.0195 | +0.0015 | | |
| EFFECT | +0.3844 | [+0.2314] | [+0.0114] | -0.0031 | [-0.0051] | [-0.0076] | [+0.0049] | +0.0004 | | |

$S_{pooled} = 3.68 \times 10^{-3}$

$[MIN] = 0.5 \times t \times S_{pooled}$

At 95% Confidence Level, $[MIN] = \boxed{0.0043}$

FIG. 4. TWO-LEVEL FACTORIAL - NITROUS OXIDE/ACETYLENE

| TRIAL | MEAN | X1 | X2 | X1X2 | X3 | X1X3 | X2X3 | X1X2X3 | $\bar{Y}$ | $S^2 \times 10^{-6}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | + | − | − | + | − | + | + | − | 0.051 | 98 |
| 2 | + | + | − | − | − | − | + | + | 0.093 | 50 |
| 3 | + | − | + | − | − | + | − | + | 0.050 | 18 |
| 4 | + | + | + | + | − | − | − | − | 0.094 | 24.5 |
| 5 | + | − | − | + | + | − | − | + | 0.049 | 18 |
| 6 | + | + | − | − | + | + | − | − | 0.091 | 2 |
| 7 | + | − | + | − | + | − | + | − | 0.052 | 0 |
| 8 | + | + | + | + | + | + | + | + | 0.090 | 18 |
| SUM + | 0.5695 | 0.3675 | 0.2855 | 0.2835 | 0.2820 | 0.2820 | 0.2860 | 0.2820 | | |
| SUM − | 0 | 0.2020 | 0.2840 | 0.2860 | 0.2875 | 0.2875 | 0.2835 | 0.2875 | | |
| OVERALL SUM | 0.5695 | 0.5695 | 0.5695 | 0.5695 | 0.5695 | 0.5695 | 0.5695 | 0.5695 | | |
| DIFF | +0.5695 | +0.1655 | +0.0015 | -0.0025 | -0.0055 | -0.0055 | +0.0025 | -0.0055 | | |
| EFFECT | +0.0712 | +0.0414 | +0.0004 | -0.0006 | -0.0014 | -0.0014 | +0.0006 | -0.0014 | | |

$S_{pooled} = 0.0053$

$[MIN] = 0.5 \times t \times 0.0053$

At 95% Confidence Level, $[MIN] = 0.0062$

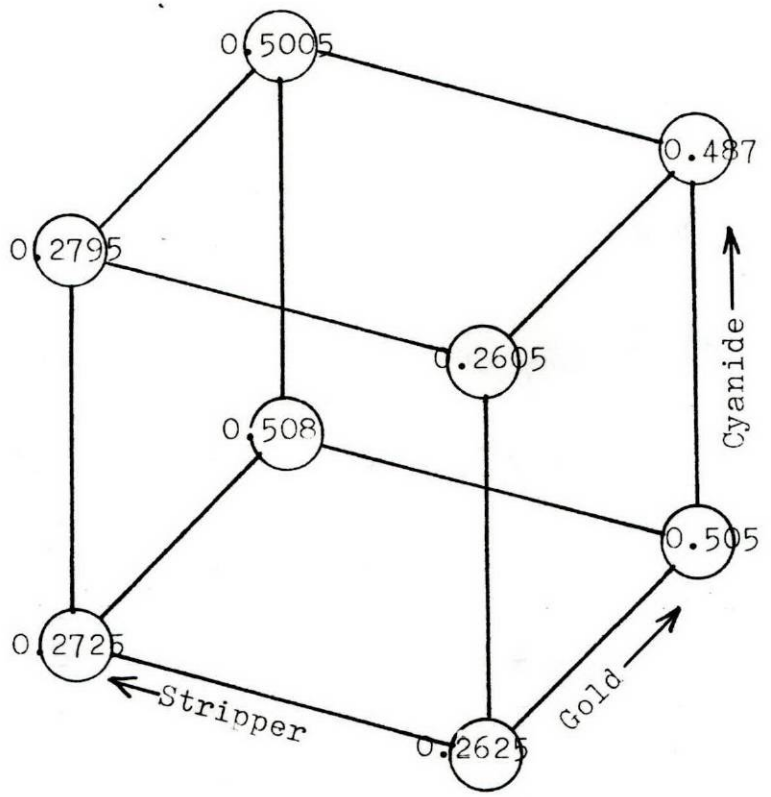



FIG. 5 GRAPHICAL ANALYSIS OF AAS ABSORBANCE USING AN AIR/ACETYLENE FLAME

Q-2

# Statistical Design and Computer Modeling Session Q

## The Simplex Method of Optimization in Problems Related to Metal Finishing

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# THE SIMPLEX METHOD OF OPTIMIZATION IN PROBLEMS RELATED TO METAL FINISHING

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## Abstract

The simplex method is presented as perhaps the easiest technique to use in systematically optimizing properties which are unknown functions of many variable factors. After outlining the method, examples drawn from a search of metal finishing literature are given. These include optimizing the plating parameters in black-chrome deposition, the properties of coating compositions, and the corrosion resistance of alloy compositions. Our work in optimizing additive effectiveness by varying chemical reaction parameters is also discussed.

## Introduction

Often a person involved with technological problems is confronted with having to optimize some product or procedure. Frequently, the properties to be optimized appear to depend in complicated ways upon many variable factors. Our intention is to introduce metal finishers to the idea that there are systematic approaches to determining the combinations of variable values which yield the best properties. In particular, we want to discuss the "simplex method," which we feel is easy to use, does not require mathematical sophistication, involves a minimum number of experiments, and yet is powerful in leading to optimum values of variable factors.

Like other techniques of optimization, the simplex method can be used to optimize desirable properties (which are maximized) or undesirable properties (which are minimized). One does not have to be able to quantitatively measure the property being optimized - the ability to subjectively distinguish between "good" and "bad" results is sufficient.

The simplex method which we are discussing appears in the literature under several different names. When first proposed twenty years ago, the method was called [1] "simplex evolutionary operation", since it was considered to be a variation of the somewhat older technique of evolutionary operation[2]. The method is also known[3] as "self-directing optimization". An often-cited review of the method is the paper by Lowe.[4]

It is easiest to be introduced to the simplex method by following an example which can be graphically visualized. Let us consider maximizing a property which is a function of two variable factors, A and B. In figure 1, an equilateral triangle is constructed connecting points 1, 2, and 3. Each point is a combination of the two variables; the property is measured at each point. The combination giving the lowest measurement (point 1) is discarded, and a new point (4) is set up on the other side of the line joining points 2 and 3 (this setting up of a new point is called a "reflection"). A new triangle has been defined,

but only one new measurement needs to be made (at point 4). As before, the point in the new triangle giving the lowest response (3) is discarded, and the corresponding reflection is performed to set up yet another triangle. This process measuring the property at the new point, discarding the point giving the lowest measurement, and reflection to set up a new triangle is continued until the optimum combination (at point 9, let us say) is reached. One way to recognize the optimum combination is that measurements at all nearby points produce lower values.

An advantage to the simplex method is that it can be easily extended to handle many variable factors. If there are N variables, a regular geometric figure containing N + 1 points can be set up (even though a visual representation cannot be drawn). Such a regular figure is a "simplex".

The two-variable situation is just one particular case of the general simplex method. The variable factors which are believed to influence the property being optimized are chosen. As implied before, N variables leads to the setting up of N + 1 initial experiments. How are the variable values for these initial experiments arrived at? For each variable, a high value and a low value are chosen. These two values must be far enough apart so that significant differences in property measurements are obtained from different experiments. However, if they are too far apart, the rules for determining new experiments often result in impossible conditions (like negative concentrations). So, some experience is helpful in choosing the high and low values.

Table I represents one way to set up the initial experiments. For a given experiment, the variable values in the corresponding row are used. A simple pattern is used to construct the columns of the table. For variable factor number M, the low value of that variable is put into the first M places in the corresponding column. The high value occupies the next place, and the remaining places contain an average of the high and low values. The straight average can be used: (Low (M) + High (M))/2. Sometimes a slightly more complicated average value is used: (M x Low (M) + High (M)) / (M + 1). This formula takes into account the number of occurences of the high and low values in a particular column.

The N + 1 experiments are performed, preferably in random order to minimize errors. As in the two-variable example the combination of variable values giving the "worst" result is rejected, and a new combination is tried. This leaves the final major question - how are the values for the new combination calculated? For a given factor, the values of the retained combinations are averaged (by adding up these values and dividing by N). If R is this average, and $D_5$ is the discarded value, the new factor value is calculated according to [5]: New = (C + 1)R - C x D. C is usually 1 (that is, the average of the retained values is doubled, and the discarded value is subtracted). As in the two-variable example, the new experiment is performed, the worst result in the new simplex is rejected, and a new combination of variable values is calculated, with the process continuing until a suitable optimum is reached.

## Optimization of Coating and Alloy Properties

We made a computer search of the Metals Abstracts and Engineering Index data bases for references to the application of the simplex method

to problems of interest to metal finishers. The rest of this paper will briefly summarize some of these references and some of our own work using the simplex method.

One category of applications is the juggling of component concentrations in order to optimize one or more properties of some formulation. Recently Hesler and Lofstrom described the maximization of hiding power and abrasion resistance, along with the minimization of cost, of a coatings formulation by varying the concentrations of four components (titanium dioxide prime pigment, latex emulsion vehicle, and two extender pigments).[6] By expressing the concentrations as percentages of the variable non-volatile material volume of the formulation, only three components can be independently varied, because the fourth is fixed by the requirement that the percentages add up to 100. The data reported by Hesler and Lofstrom were used to calculate the entries of Table 2, which shows the use of the simplex method on their problem. Actually, maximum abrasion resistance was measured by minimum scrub loss (ASTM method D2486-74 A, proposed revision), so that in Table 2 the measured response is minimized. The first four experiments are set up according to Table I, with the average percentages of all components being equal. The experiment giving the worst response (number 2) is discarded, and percentages for a new experiment are calculated (for each component, by doubling the average of the percentages in experiments 1, 3, and 4 and subtracting the percentage in experiment 2). When the sequence of property measurement, worst point rejection, and new experiment parameters calculation is continued, minimum scrub loss is found at the 22nd experiment, in which the percentages of titanium dioxide, latex emulsion, and the two extender pigments (designated A and B) are respectively 16, 73, 0, and 11.

When the simplex method is applied to the maximization of hiding power (ASTM method D2805-70), starting with the same first four experiments, one finds that the maximum is found at 100% titanium dioxide. It is not surprising that the greatest hiding power is correlated with the highest prime pigment concentration.

As would be expected, alloy compositions can also be treated as formulation problems. Several Russian reports describe the optimization of properties by varying the concentrations of constituent elements. One example is the finding that the maximum corrosion resistance of one particular ternary lead-based alloy is found at 4% antimony, 3.25% strontium, and 92.75% lead.[7] Another example is the maximum hardness of another ternary alloy being found at 25% nickel, 40% chromium, and 35% boron.[8]

## Optimization of Electroplating Additive Effectiveness

In the course of our usual work on screening chemical reaction products for electroplating additives, we found one material which showed promise as a low current density brightener. However, its effectiveness was variable and did not appear to depend in any simple way upon reaction conditions. We decided to apply the simplex method, even though the property being optimized was a matter of subjective judgment of test cell results. We had chosen six reaction parameters to vary, resulting in seven initial experiments (see Table 3). The "slightly more complicated"

method of calculating average values mentioned earlier was used in constructing the initial set of experiments. For example, in the "final pH adjustment" column, the four occurrences of the low value of 1, along with the high value of 3, led us to use an average value of : (4 x 1 + 3)/5 = 7/5 = 1.4. The parameter combination giving the product which appeared to be the least effective brightener was discarded. However, to keep subsequent parameters within reasonable bounds, we found it useful to let C be equal to 1/3 in calculating new factor values (see earlier discussion). The experiments did lead in the direction of a better product; our impressions of the results caused us after the twelfth experiment to start a new simplex sequence with only three variable factors (concentrations of reactants A and B, and reaction time). The four initial experiments were run, and, as it happened, one of these parameter combinations gave a product sufficiently good for our purposes.

Optimization of Optical Selectivity of Black-Chrome Electroplate

Finally, we would like to point out a report of the application of the simplex method (as discussed in this paper) to optimizing a property of an electroplated metal by varying the plating bath parameters. Inal and co-workers studied the optical selectivity (measured by an absorptance/emittance ratio) of solar collectors made by electroplating black chrome on nickel-plated stainless steel.[9] They chose seven variable factors, and calculated average factor values and new parameter combinations in the usual ways (straight average and new values with C = 1; see Table 4). They found that the fifteenth experiment gave the highest selectivity.

We hope that our paper creates interest in the use of systematic experimental design by those who have not tried it before. We think that the simplex method is a good place to start; it is not foolproof and not without certain disadvantages and problems (for example, all variable factors have to be quantifiable). However, for the frequent times when a problem which needs to be solved is complicated by many interacting factors, the simplex method provides guidance with a good chance of finding the best combination of factors. And the range of applications seems wide; the examples cited in this paper show that. Furthermore, after becoming comfortable with the simplex method, one can go on to more sophisticated statistical methods, which can yield a more thorough understanding of the influence of the factors which contribute to products and processes.

References


1. W. Spendley, G.R. Hext, and F.R. Himsworth, Technometrics, 4, 441, (1962).

2. G.E.P. Box and N.R. Draper, "Evolutionary Operation," John Wiley & Sons, Inc., New York, 1969.

3. F.L. Chubb, J.T. Edward, and S.C. Wong, Journal of Organic Chemistry, 45, 2315, (1980).

4. C.W. Lowe, Transactions of the Institution of Chemical Engineers, 42, T334, (1964).

5. J.A. Nelder and R. Mead, Computer Journal, 7, 308, (1965).

6. K.K. Hesler and J.R. Lofstrom, Journal of Coatings Technology, 53, (674), 33 (March, 1981).

7. Z.U. Niyazova, A.V. Vakhobov, M.A. Dasoyan, A.Sh. Murodov, and E.D. Rozenberg, Industrial Laboratory, 42, 778, (1976).

8. V.A. Voznesenskii and V.S. Kalmutskii, Industrial Laboratory, 40, 1043, (1974).

9. O.T. Inal, M. Valayapetre, L.E. Murr, and A.E. Torma, Solar Energy Materials, 4, 333, (1981).

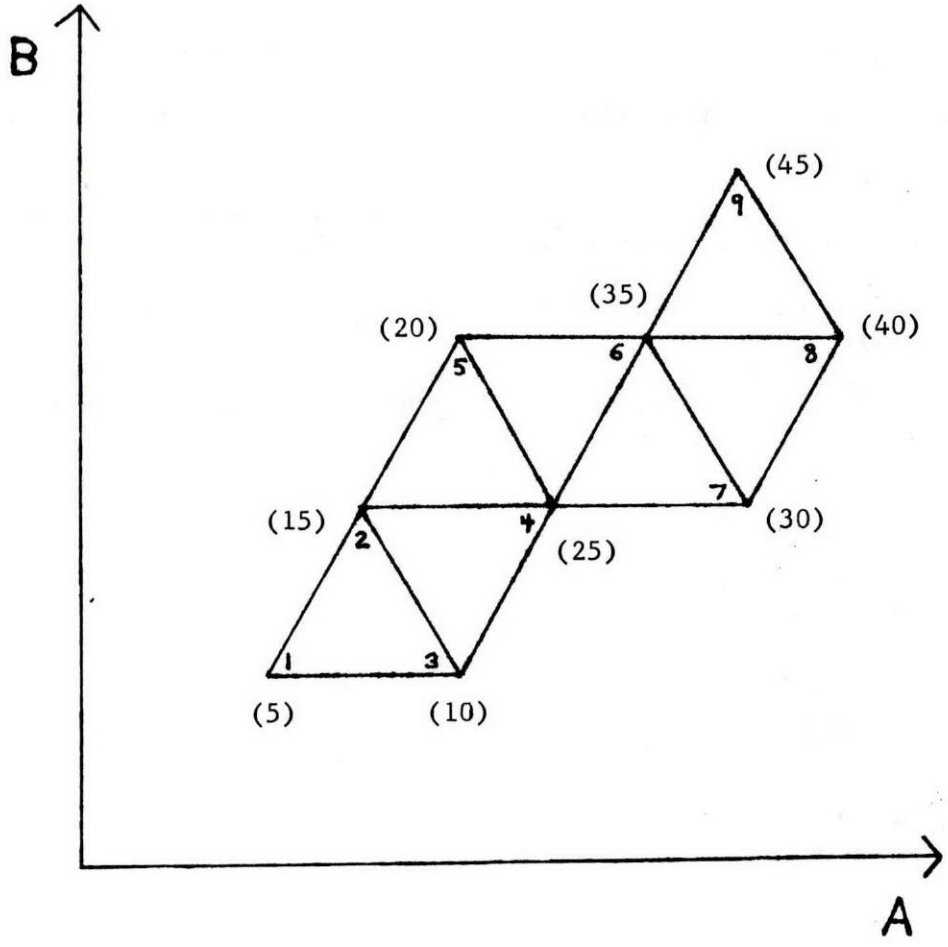



Figure 1. Generalized Example of the Simplex Optimization of Two Variables. (measured responses in parantheses.)

Table 1. Variable Values for Initial Set of Experiments in Simplex Optimization

| Experiment Number | Variable Factors 1 | 2 | 3 ..... | N-1 | N |
|---|---|---|---|---|---|
| 1 | Low(1) | Low(2) | Low(3) ... | Low(N-1) | Low(N) |
| 2 | High(1) | Low(2) | Low(3) ... | Low(N-1) | Low(N) |
| 3 | Ave.(1) | High(2) | Low(3) ... | Low(N-1) | Low(N) |
| 4 | Ave.(1) | Ave.(2) | High(3) ... | Low(N-1) | Low(N) |
| . | | | . | | |
| . | | | . | | |
| . | | | . | | |
| . | | | . | | |
| N | Ave.(1) | Ave.(2) | Ave.(3) ... | High(N-1) | Low(N) |
| N + 1 | Ave.(1) | Ave.(2) | Ave.(3) ... | Ave.(N-1) | High(N) |

Low (M) = Low value for factor M.

High(M) = High value for factor M.

Ave.(M) = Average of high and low values for factor M .

Table 2. Optimization of Abrasion Resistance of Coating Formulations

| Experiment Number | Variable Factors: Titanium Dioxide (%) | Latex Emulsion (%) | Extender Pigment A (%) | Scrub Loss (mg/100 cycles + 30) |
|---|---|---|---|---|
| 1 | 20 | 20 | 20 | 215 |
| 2 | 30 | 20 | 20 | 218 |
| 3 | 25 | 30 | 20 | 130 |
| 4 | 25 | 25 | 30 | 148 |
| 5 | 17 | 30 | 27 | 116 |
| 6 | 24 | 37 | 31 | 77 |
| 7 | 19 | 39 | 22 | 68 |
| 8 | 15 | 41 | 33 | 57 |
| 9 | 22 | 48 | 30 | 44 |
| 10 | 13 | 48 | 26 | 34 |
| 11 | 13 | 50 | 36 | 42 |
| 12 | 16 | 56 | 28 | 28 |
| 13 | 6 | 56 | 29 | 31 |
| 14 | 11 | 56 | 19 | 18 |
| 15 | 9 | 64 | 25 | 25 |
| 16 | 18 | 62 | 18 | 15 |
| 17 | 9 | 65 | 14 | 9 |
| 18 | 15 | 59 | 9 | 14 |
| 19 | 17 | 67 | 8 | 6 |
| 20 | 10 | 66 | 2 | 8 |
| 21 | 8 | 73 | 7 | 7 |
| 22 | 16 | 73 | 0 | 3 |
| 23 | 17 | 76 | 7 | 12 |

Data calculated from reference 6.

Table 3. Experiment Sequence for the Optimization of Electroplating Additive Effectiveness of Chemical Reaction Product

| Experiment Number | Variable Factors: Reactant A (g/l) | Reactant B (g/l) | Sodium Hydroxide (g/l) | Final pH Adjustment | Reaction Time (min.) | Reaction Temp. (°C.) | Least Effective |
|---|---|---|---|---|---|---|---|
| 1 | 30 | 1 | 0.1 | 1 | 15 | 22 | |
| 2 | 150 | 1 | 0.1 | 1 | 15 | 22 | |
| 3 | 90 | 20 | 0.1 | 1 | 15 | 22 | #3 in Initial Experiment Set |
| 4 | 90 | 7.3 | 2.5 | 1 | 15 | 22 | |
| 5 | 90 | 7.3 | 0.7 | 3 | 15 | 22 | |
| 6 | 90 | 7.3 | 0.7 | 1.4 | 60 | 22 | |
| 7 | 90 | 7.3 | 0.7 | 1.4 | 23 | 100 | |
| 8 | 90 | 0.3 | 1.0 | 1.6 | 27 | 39 | #5 |
| 9 | 90 | 2.9 | 0.9 | 0.6 | 29 | 43 | #7 |
| 10 | 90 | 2.0 | 1.0 | 1.0 | 28 | 5 | #2 |
| 11 | 57 | 4.3 | 1.3 | 1.2 | 34 | 27 | #8 |
| 12 | 69 | 5.4 | 1.1 | 0.9 | 31 | 18 | |

Table 4. Optimization of Optical Selectivity of Black-Chrome Electroplated Solar Collectors

| Experiment Number | Variable Factors: Electrode Spacing(cm) | Time (min) | Current Density($A/dm^2$) | Temp. ($^oC.$) | Chromium Trioxide(g/l) | Addition Agent (vol%) | Anode/Cathode Area Ratio | Optical Selectivity |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.27 | 3 | 32.4 | 10 | 300 | 24 | 2 | 6.37 |
| 2 | 3.81 | 3 | 32.4 | 10 | 300 | 24 | 2 | 6.44 |
| 3 | 2.54 | 5 | 32.4 | 10 | 300 | 24 | 2 | 4.70 |
| 4 | 2.54 | 4 | 43.2 | 10 | 300 | 24 | 2 | 5.28 |
| 5 | 2.54 | 4 | 37.8 | 20 | 300 | 24 | 2 | 5.77 |
| 6 | 2.54 | 4 | 37.8 | 15 | 340 | 24 | 2 | 4.03 |
| 7 | 2.54 | 4 | 37.8 | 15 | 320 | 27 | 2 | 6.08 |
| 8 | 2.54 | 4 | 37.8 | 15 | 320 | 25.5 | 3 | 5.40 |
| 9 | 2.54 | 3.7 | 34.7 | 10.7 | 271 | 25.3 | 2.3 | 6.56 |
| 10 | 2.54 | 2.3 | 40.8 | 15.9 | 303 | 25.7 | 2.4 | 6.98 |
| 11 | 2.54 | 2.9 | 29.3 | 17.6 | 304 | 26.1 | 2.5 | 6.75 |
| 12 | 2.54 | 2.6 | 32.2 | 13.4 | 280 | 24.8 | 1.3 | 7.13 |
| 13 | 2.54 | 2.1 | 30.7 | 16.5 | 294 | 26.5 | 2.1 | 7.15 |
| 14 | 2.54 | 1.6 | 28.6 | 11.9 | 266 | 23.4 | 2.2 | 7.17 |
| 15 | 4.17 | 2.2 | 32.9 | 17.4 | 277 | 26.2 | 2.2 | 9.80 |
| 16 | 1.73 | 2.0 | 33.1 | 19.5 | 270 | 26.9 | 2.3 | 9.78 |

Data from reference 9.

Q-3

# Statistical Design and Computer Modeling Session Q

## Statistical Investigation of the Effects of Citrate Gold Plating Process Variables on Throwing Power

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# STATISTICAL INVESTIGATION OF THE EFFECTS OF CITRATE GOLD PLATING PROCESS VARIABLES ON THROWING POWER*

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## Abstract

A Box-Behnken statistical design has been used to study the effects of four plating process variables (gold concentration, temperature, current density, and pH) on throwing power. The experimental results were fitted by the method of least squares with a polynomial in four variables, and all the linear coefficients were statistically significant. Gold concentration and current density were the dominant variables and had negative coefficients; that is, an increase in these variables resulted in a decrease in throwing power. There was also a large statistical interaction between gold concentration and current density, and a significant quadratic effect was noted for current density. The least squares fit was highly statistically significant and accounted for 92% of the total variation in throwing power.

## Introduction

In an earlier paper[1] we utilized the methodology of statistical experimental design to gain a better understanding of the influence of various plating variables on efficiency, throwing power, and appearance using a cyanide-citrate gold plating solution. That paper reported on work done with a Plackett-Burman design and a $2^3$ factorial analysis. Plackett-Burman designs can be viewed as building limited response surface models because they estimate only the constant and linear terms. Similarly, the $2^3$ design supports limited response surface models comprised of main effects and interactions.

The present work is a continuation of the earlier work. Here, because we wanted to investigate the response surface for throwing power in more detail, a Box-Behnken[2] statistical design was used. For this investigation we studied the effects of four plating process variables: gold concentration, temperature, current density, and pH.

*Work supported by U.S. Department of Energy, DOE, under Contract DE-AC04-76DP00789.

## Experimental Details

A Box-Behnken statistical design describes a response surface by a full quadratic polynomial. Since we were interested in four variables, the design we chose required 27 tests. The experimental layout and test conditions are given in Tables I and II for the four variables. The lower and upper ends of the ranges are the same as those in our earlier work; here, however, a mid-point was included for each variable as required by the Box-Behnken design.

Throwing power, which is the ability of a solution to plate uniformly regardless of cathode configuration, was measured with a Haring cell 6.3 cm wide, 12.7 cm deep, and 24 cm long. In this cell, two cathodes are arranged at different distances from a central anode. Throwing power (TP) is calculated from the equation

$$TP(\%) = \frac{P-M}{P-1} \times 100 \ ,$$

where P is the distribution ratio for the primary current (5/1 for this work) and M is the distribution ratio of the metal (the weight of the metal deposited on the near cathode divided by the weight of the metal deposited on the far cathode).

One-liter solutions were made for each test condition. Where more than one test was run for each condition, the amount of gold plated out during the test was replaced before the next. Plating time at 11, 32, and 65 $A/m^2$ (1, 3, and 6 asf) was 43, 14.5, and 7.5 minutes, respectively. The anode material was expanded platinum-coated titanium screen. The solution was heated to temperature prior to placement in the Haring cell, and an immersion heater maintained the temperature. The cell was placed on a magnetic stirrer and the solution was agitated mildly to maintain the temperature uniformly throughout the box. The throwing power results are shown in Table III.

## Statistical Analysis of Throwing Power

Model and Least Squares Fit--Throwing power response data were fitted with a full quadratic polynomial model in four variables, and two cubic terms were added to improve the fit. Although the Box-Behnken experimental design is nearly orthogonal, independent variables were standardized by subtracting the mean and dividing by the standard deviation.[5] This procedure avoids any problems due to the slightly unequal current density spacing and the fact that unequal replications were run. Standardization also permits a direct comparison of coefficients in the prediction equation because the variables have the same scaling.

Standardized variables were as follows:

| Variable | Standardization |
|---|---|
| $X_i$ | = (Independent Variable - Mean)/Standard Deviation |

TABLE I. BOX-BEHNKEN DESIGN FOR FOUR VARIABLES

| Trial No. | $X_1$ | $X_2$ | $X_3$ | $X_4$ | |
|---|---|---|---|---|---|
| 1 | +1 | +1 | 0 | 0 | |
| 2 | +1 | -1 | 0 | 0 | |
| 3 | -1 | +1 | 0 | 0 | |
| 4 | -1 | -1 | 0 | 0 | |
| 5 | 0 | 0 | +1 | +1 | Block 1 |
| 6 | 0 | 0 | +1 | -1 | |
| 7 | 0 | 0 | -1 | +1 | |
| 8 | 0 | 0 | -1 | -1 | |
| 9 | 0 | 0 | 0 | 0 | |
| 10 | +1 | 0 | 0 | +1 | |
| 11 | +1 | 0 | 0 | -1 | |
| 12 | -1 | 0 | 0 | +1 | |
| 13 | -1 | 0 | 0 | -1 | |
| 14 | 0 | +1 | +1 | 0 | Block 2 |
| 15 | 0 | +1 | -1 | 0 | |
| 16 | 0 | -1 | +1 | 0 | |
| 17 | 0 | -1 | -1 | 0 | |
| 18 | 0 | 0 | 0 | 0 | |
| 19 | +1 | 0 | +1 | 0 | |
| 20 | +1 | 0 | -1 | 0 | |
| 21 | -1 | 0 | +1 | 0 | |
| 22 | -1 | 0 | -1 | 0 | |
| 23 | 0 | +1 | 0 | +1 | Block 3 |
| 24 | 0 | +1 | 0 | -1 | |
| 25 | 0 | -1 | 0 | +1 | |
| 26 | 0 | -1 | 0 | -1 | |
| 27 | 0 | 0 | 0 | 0 | |

TABLE II. GOLD PLATING VARIABLES

| | Variable | Lower limit (-) | Upper limit (+) | Recommended conditions[3] (0) |
|---|---|---|---|---|
| $X_1$, | Potassium gold cyanide (g/l) | 6 | 36 | 21 |
| $X_2$, | Temperature (°C) | 50 | 70 | 60 |
| $X_3$, | Current density ($A/m^2$) | 11 | 65 | 32 |
| $X_4$, | pH | 3.8 | 6.8 | 5.3 |

TABLE III

BOX-BEHNKEN GOLD PLATING EXPERIMENTAL LAYOUT[a] AND RESULTS

| Trial No. | Gold Concen. (g/l) | Temperature (°C) | Current Density ($A/m^2$) | pH | Throwing Power (%) |
|---|---|---|---|---|---|
| 1 | 36 | 70 | 32 | 5.3 | 65.9, 67.1, 71.4 |
| 2 | 36 | 50 | 32 | 5.3 | 56.8, 61.1 |
| 3 | 6 | 70 | 32 | 5.3 | 96.2, 92.3 |
| 4 | 6 | 50 | 32 | 5.3 | 82.0 |
| 5 | 21 | 60 | 65 | 6.8 | 76.8, 82.4, 82.9 |
| 6 | 21 | 60 | 65 | 3.8 | 79.2, 71.0 |
| 7 | 21 | 60 | 11 | 6.8 | 91.0, 85.4 |
| 8 | 21 | 60 | 11 | 3.8 | 92.8, 93.3, 94.7 |
| 9 | 21 | 60 | 32 | 5.3 | 68.9, 67.9 |
| 10 | 36 | 60 | 32 | 6.8 | 66.1 |
| 11 | 36 | 60 | 32 | 3.8 | 55.9 |
| 12 | 6 | 60 | 32 | 6.8 | 81.4, 80.6 |
| 13 | 6 | 60 | 32 | 3.8 | 73.2 |
| 14 | 21 | 70 | 65 | 5.3 | 56.0, 60.5 |
| 15 | 21 | 70 | 11 | 5.3 | 84.4, 87.7 |
| 16 | 21 | 50 | 65 | 5.3 | 81.2, 82.7 |
| 17 | 21 | 50 | 11 | 5.3 | 78.3, 87.0, 84.3 |
| 18 | 21 | 60 | 32 | 5.3 | 69.5, 69.4, 66.3 |
| 19 | 36 | 60 | 65 | 5.3 | 46.8, 50.8, 49.3 |
| 20 | 36 | 60 | 11 | 5.3 | 83.6, 80.4, 81.8 |
| 21 | 6 | 60 | 65 | 5.3 | 94.6, 98.2, 96.3, 97.0 |
| 22 | 6 | 60 | 11 | 5.3 | 84.0, 84.4, 79.7 |
| 23 | 21 | 70 | 32 | 6.8 | 75.2 |
| 24 | 21 | 70 | 32 | 3.8 | 74.4, 71.8 |
| 25 | 21 | 50 | 32 | 6.8 | 72.0 |
| 26 | 21 | 50 | 32 | 3.8 | 55.2, 59.2 |
| 27 | 21 | 60 | 32 | 5.3 | 65.9, 68.4 |

[a]Ammonium Citrate (75 g/l) and Ammonium Sulfate (75 g/l) concentration were kept constant during all experiments.

$X_1$ = (Gold Concentration - 21.00)/10.13

$X_2$ = (Temperature - 60.17)/6.35

$X_3$ = (Current Density - 35.31)/20.45

$X_4$ = (pH - 5.27)/0.91

The model equation was

$$TP = \beta_0+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_4X_4+\beta_5X_1^2+\beta_6X_2^2+\beta_7X_3^2+\beta_8X_4^2$$

$$+\beta_9X_1X_2+\beta_{10}X_1X_3+\beta_{11}X_1X_4+\beta_{12}X_2X_3+\beta_{13}X_2X_4+\beta_{14}X_3X_4+\beta_{15}X_3^2X_2+\beta_{16}X_3^2X_4$$

The coefficients (betas) in the model equation were estimated by the method of least squares, with results given in Table IV. The least squares coefficients can be tested to determine whether they are signficantly different from zero. Significance tests are based upon Student's - t distribution, and the calculated value of t is given in Table IV. The significance level is also shown, a low value (<0.01) meaning a highly significant coefficient.

The standard deviation s, given in Table IV, is the standard deviation after the standardization transformation. Since $X_1,\ldots,X_4$ were standardized, they have a standard deviation of exactly one. The remaining terms in the model were formed from the linear terms by making the appropriate transformation; for example, the variable $X_1^2$ equals $X_1$ times $X_1$. Consequently, the remaining variables do not have a standard deviation of exactly one. This was compensated by multiplying the least square estimate ($\hat{\beta}$) by the standard deviation to obtain an adjusted coefficient. The adjusted coefficients then have equal scaling and can be compared directly. The adjusted coefficients are used for determining important effects, but the unadjusted coefficients are used for prediction in the model equation.

Examination of the adjusted coefficients shows that those involving gold concentration ($X_1$) and current density ($X_3$) have large coefficients, including quadratic and interaction terms. Temperature ($X_2$) and pH ($X_4$) have smaller coefficients, although temperature has some interaction effects.

TABLE IV
THROWING POWER LEAST SQUARES ESTIMATES AND SIGNIFICANCE TESTS

| Variable | Standard Deviation, s | Coefficient, $\hat{\beta}$ | Adjusted Coefficient, $s\hat{\beta}$ | Rank of Abs. Value | Coefficient Std. Error, $s_{\hat{\beta}}$ | $t = \beta/s_{\hat{\beta}}$ | Significance Level |
|---|---|---|---|---|---|---|---|
| Gold Concen. ($X_1$) | 1.000 | -7.429 | -7.429 | 1 | 0.585 | -12.70 | <.001 |
| Temperature ($X_2$) | 1.000 | 3.622 | 3.622 | 6 | 0.812 | 4.46 | <.001 |
| Current Dens. ($X_3$) | 1.000 | -6.435 | -6.435 | 2 | 0.644 | -9.99 | <.001 |
| pH ($X_4$) | 1.000 | 3.085 | 3.085 | 7 | 0.850 | 3.63 | .001 |
| $X_1^2$ | 1.100 | 0.530 | 0.583 | 15 | 0.585 | 0.91 | .370 |
| $X_2^2$ | 1.223 | 0.596 | 0.729 | 13 | 0.525 | 1.14 | .263 |
| $X_3^2$ | 0.908 | 6.680 | 6.065 | 3 | 0.754 | 8.86 | <.001 |
| $X_4^2$ | 1.316 | 1.096 | 1.431 | 11 | 0.491 | 2.23 | .031 |
| $X_1X_2$ | 0.870 | -0.698 | -0.607 | 14 | 0.675 | -1.03 | .307 |
| $X_1X_3$ | 0.951 | -5.968 | -5.676 | 4 | 0.604 | -9.88 | <.001 |
| $X_1X_4$ | 0.725 | 0.630 | 0.457 | 16 | 0.810 | 0.78 | .441 |
| $X_2X_3$ | 0.832 | -2.251 | -1.873 | 10 | 0.743 | -3.03 | .004 |
| $X_2X_4$ | 0.838 | -1.062 | -0.890 | 12 | 0.697 | -1.52 | .135 |
| $X_3X_4$ | 0.921 | 2.113 | 1.946 | 9 | 0.691 | 3.06 | .004 |
| $X_3^2X_2$ | 1.099 | -3.710 | -4.077 | 5 | 0.731 | -5.08 | <.001 |
| $X_3^2X_4$ | 1.240 | -1.980 | -2.455 | 8 | 0.710 | -2.79 | .008 |

Constant $\hat{\beta}_0 = 66.853$
Std. Error of $\hat{\beta}_0 = 1.669$

The linear coefficients $\hat{\beta}_1$ to $\hat{\beta}_4$ give the predicted change in throwing power when the independent variable is changed by one standard deviation. The summary below gives the results for the linear effects.

| Variable | Standard Deviation[a] | Least Squares Coefficient |
|---|---|---|
| Gold Concentration ($X_1$) | 10.13 | -7.4 |
| Temperature ($X_2$) | 6.35 | 3.6 |
| Current Density ($X_3$) | 20.45 | -6.4 |
| pH ($X_4$) | 0.91 | 3.1 |

[a]The standard deviation of the independent variables before any transformations were made.

Since the linear terms are also associated with quadratic and interaction terms, they cannot be interpreted directly. Consider, for example, the effect of pH, shown in Figure 1. The curves were obtained by solving the throwing power prediction equation for different values of pH and current density, with gold concentration and temperature held fixed at their mean values. A one-standard-deviation increase in pH of 0.91 results in a 3.1% increase in throwing power because the linear coefficient for pH is plus 3.1. In Figure 1 the mean curve averaged over the current density levels shows the increase in throwing power with increase in pH. The curve is not linear, however, because of the quadratic term for pH. Figure 1 also shows a pH by current density interaction caused by a decrease in throwing power with increase in pH at the low level of current density (11 $A/m^2$).

Temperature ($X_2$) also has a positive linear coefficient, whereas gold concentration ($X_1$) and current density ($X_3$) have negative linear coefficients, that is, an increase in the levels of these factors resulted in a decrease in throwing power.

By far the largest effects on throwing power were those due to gold concentration and current density. These had the highest absolute linear terms and a high interaction between them. Furthermore, the second degree term for current density ($X_3^2$) was highly significant. These effects are shown graphically in Figures 2-4, where the least squares prediction equation was solved for values of current density and gold concentration at temperatures of 50°, 60°, and 70°C, respectively. These curves show the large quadratic effect of current density on throwing power.

There is also a minimum throwing power, which depends upon the gold concentration. Additionally, this minimum shifts toward a higher current density when the temperature is increased (compare the three figures). However, at a temperature of 70°C there is no longer a distinct minimum and

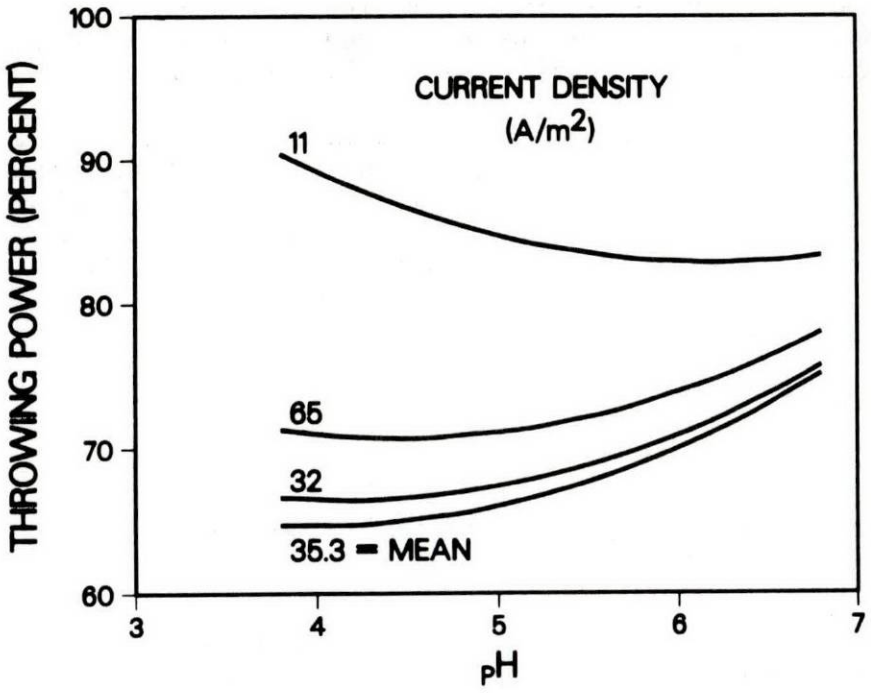



Figure 1. Effect of pH on Throwing Power

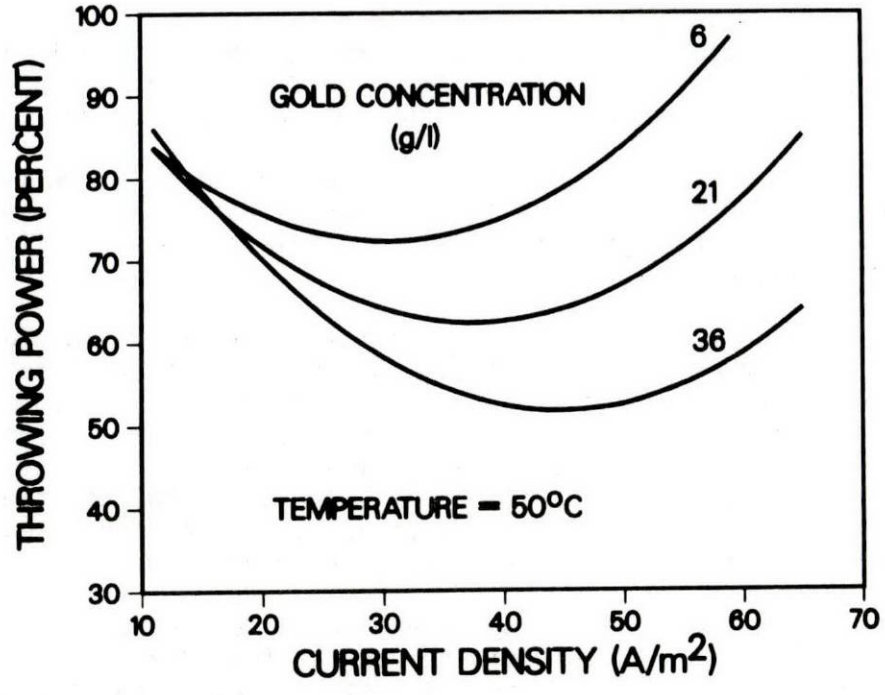



Figure 2. Effects of Current Density and Gold Concentration on Throwing Power at 50°C

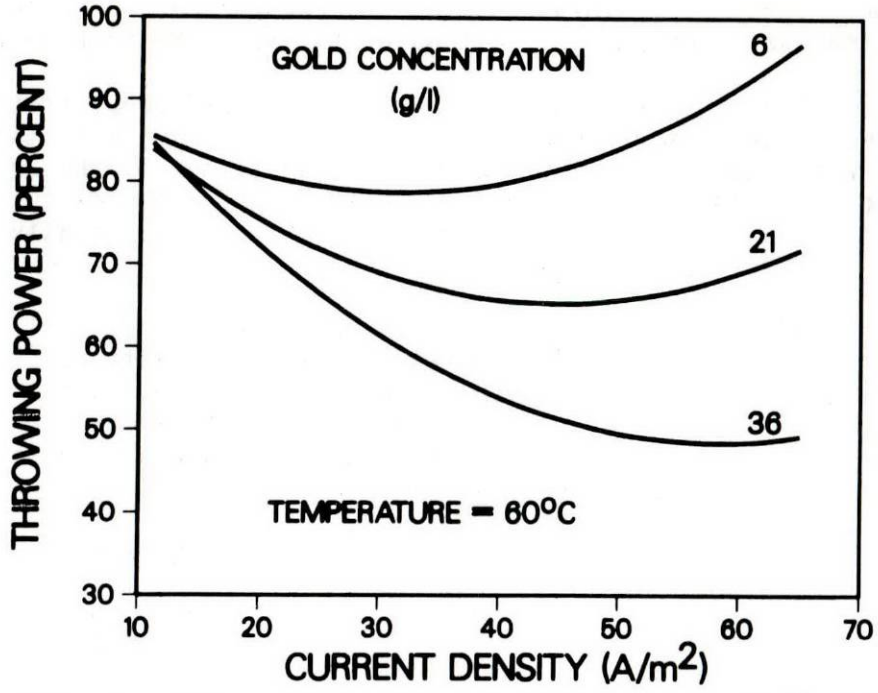



Figure 3. Effects of Current Density and Gold Concentration on Throwing Power at 60°C

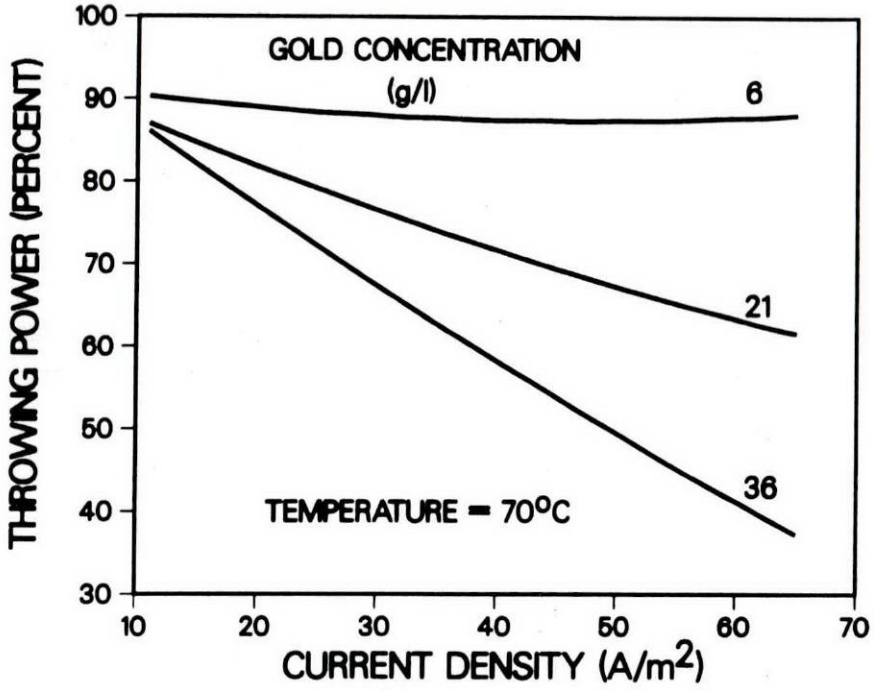



Figure 4. Effects of Current Density and Gold Concentration on Throwing Power at 70°C

the curvature disappears. This behavior occurs because of the 3rd-order term $X_3^2X_2$ that was added to the full quadratic model to improve the fit.

Figures 2-4 also show the negative effect of gold concentration ($X_1$) on throwing power, but this effect must be interpreted along with the interaction with current density ($X_3$). The interaction is due to the absence of an effect of gold concentration at the low level of current density, but the gold concentration effect increases and is at its highest negative effect at the highest level of current density.

Another coefficient in the least squares equation that is large is the term for $X_2X_3$, the temperature by current density interaction. This interaction is shown graphically in Figure 5 where it is noted that the temperature behavior at the high current density level is different from that of the other currents. Trials 14 and 16 were at high current density and the same levels of gold and pH. The results were:

| Trial | Temperature (°C) | Throwing Power (%) |
|---|---|---|
| 14 | 70 | 56.0, 60.5 |
| 16 | 50 | 81.2, 82.7 |

The least squares fit at high current density reflects these experimental results.

Goodness of Least Squares Fit--In a least squares regression analysis, the total variation in the response variable (in this case throwing power) is partitioned into a portion accounted for in fitting the regression model and the "left-overs" or residual.[6] Because repeated runs were made on most experimental trials, the residual can be further partitioned into what is called pure error and the difference, which is used to investigate lack of fit. Pure error is defined as random experimental error in the throwing power response when runs are made at the same levels of the independent variables. The standard deviation for pure error is 2.6%, indicating good repeatability in the experiment. The partitioning is tabulated below in what is called an analysis of variance (ANOVA) table.

| Source | Degrees of Freedom | Sum of Squares | Mean Square | Sq. Rt. of Mean Square |
|---|---|---|---|---|
| Regression | 16 | 9141.1 | 571.32 | |
| Residual | 41 | 764.18 | 18.638 | |
| Pure Error | 33 | 221.97 | 6.726 | 2.594 |
| Lack of Fit | 8 | 542.21 | 67.776 | |
| Total about Grand Mean | 57 | 9905.28 | | |

Statistical significance tests based upon the F-distribution can be made from the mean squares in the ANOVA table. A test for significance of the regression is

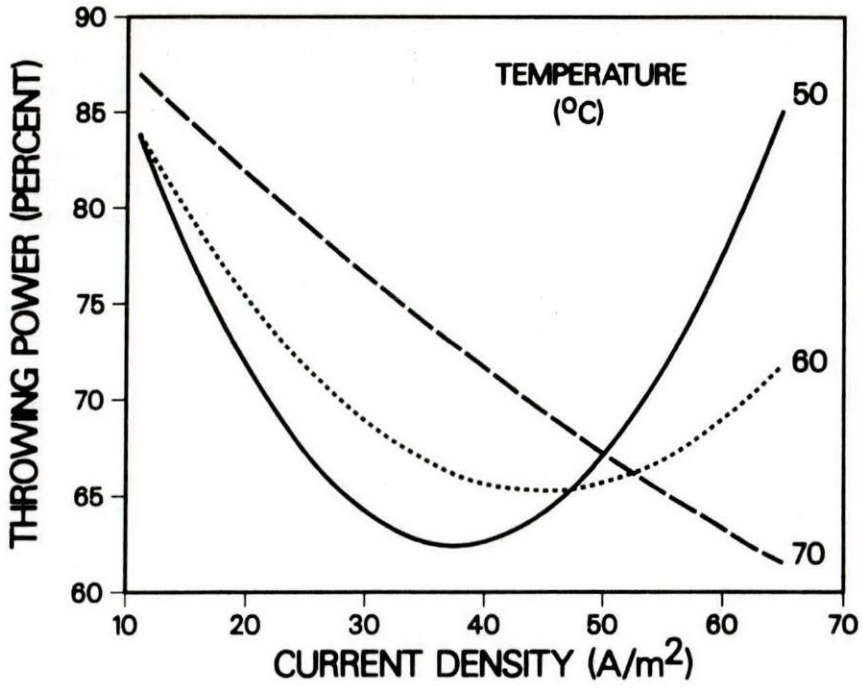



Figure 5. Interation Effect of Current Density and Temperature on Throwing Power

$$F_{16,41} = \frac{\text{Mean Square}_{\text{Regression}}}{\text{Mean Square}_{\text{Residual}}} = \frac{571.32}{18.638} = 30.65$$

This was compared with the tabulated value of the F-distribution with 16 and 41 degrees of freedom and found to be highly statistically significant ($<<$ 0.1% significance level). Hence the independent variables in the model explain a significant portion of the experimental variation in throwing power. A measure of the proportion of the sum of squares explained, relative to the total sum of squares variation about the mean throwing power, denoted by $R^2$, is

$$R^2 = \frac{9141.1}{9905.28} \times 100 = 92.3\% \quad .$$

Thus the regression equation explains 92.3% of the total throwing power variation. (Note: Before the two third-degree terms were added, $R^2$ was 85.9%). The remaining 7.7% is both pure error and lack of fit of the model to the data.

The lack-of-fit test is

$$F_{8,33} = \frac{\text{Mean Square}_{\text{Lack of Fit}}}{\text{Mean Square}_{\text{Pure Error}}} = \frac{67.776}{6.726} = 10.1,$$

which is highly statistically significant, indicating significant lack of fit of the model to the throwing power response data. This F-ratio, although statistically significant, is not nearly as high as the regression F-ratio (the higher the F-ratio the higher the statistical significance).

The significant lack of fit means there is significant throwing power variation unaccounted for by the regression or random experimental error. This can be caused by an inadequate model, observed responses that are outliers, or a response surface that is not smooth and continuous. The latter reason may be the case if there are competing reactions taking place in the plating experiment.

An indication of the areas of lack of fit can be gained by examining the difference between the predicted and experimental throwing power response, the residuals of Table V. When the residuals are large and of the same sign for all runs at that trial, the prediction equation misses the experimental data. The trials with the largest residuals are 3 and 4. These trials were at the low gold concentration level of 6 g/l so the fit appears poorer in this region. Another statistical technique can be used to determined which trials have the greatest influence on the fit. Trials 10, 23, and 25, which did not have repeated runs, were high leverage points. Large experimental errors in these runs could heavily influence the fit.

Another explanation is that the model itself is inadequate and some other model, perhaps one having many third order terms, would be better. However, the Box-Behnken statistical design was generated for a second-order model, and linear dependence conditions arise when higher order terms are added. Some third-order terms were estimable, however, and the two third-order terms added did improve the fit.

In conclusion, while the lack-of-fit test is statistically significant, the model does not appear grossly inadequate. It does explain 92% of the variation in thowing power.

Prediction and Prediction Error--One approach in regression analysis is to eliminate variables from the model that are not statistically significant; prediction is based on the remaining ones. However, this approach results in a small loss in $R^2$. Rather than take this loss, it is better that all variables be kept and prediction be based upon the full regression model. With a computer the extra effort of more regression variables is of no consequence.

Table V also shows the 90% two-sided confidence limits for the "true" mean throwing power response. The confidence limit does not account for the bias due to lack of fit, so the confidence band may miss the actual true mean due to bias. The band is for the mean response, so individual throwing power responses may be outside the confidence band. Also notice that the confidence band is narrower at the center (Trials 9, 18, 27) than at the extremes of the design space.

TABLE V
PREDICTED THROWING POWER AND CONFIDENCE LIMITS

| Trial No. | Throwing Power (%) Observed | Predicted | Difference | 90% Confidence Limits Lower | Upper |
|---|---|---|---|---|---|
| 1 | 65.9 | 65.567 | 0.333 | 61.912 | 69.223 |
| 1 | 67.1 | 65.567 | 1.533 | 61.912 | 69.223 |
| 1 | 71.4 | 65.567 | 5.833 | 61.912 | 69.223 |
| 2 | 56.8 | 56.770 | 0.030 | 52.644 | 60.895 |
| 2 | 61.1 | 56.770 | 4.330 | 52.644 | 60.895 |
| 3 | 96.2 | 87.854 | 8.346 | 83.683 | 92.024 |
| 3 | 92.3 | 87.854 | 4.446 | 83.683 | 92.024 |
| 4 | 82.0 | 72.545 | 9.455 | 67.629 | 77.462 |
| 5 | 76.8 | 78.241 | -1.441 | 74.472 | 82.009 |
| 5 | 82.4 | 78.241 | 4.159 | 74.472 | 82.009 |
| 5 | 82.9 | 78.241 | 4.659 | 74.472 | 82.009 |
| 6 | 79.2 | 71.411 | 7.789 | 67.080 | 75.742 |
| 6 | 71.0 | 71.411 | -0.411 | 67.080 | 75.742 |
| 7 | 91.0 | 83.313 | 7.687 | 78.985 | 87.641 |
| 7 | 85.4 | 83.313 | 2.087 | 78.985 | 87.641 |
| 8 | 92.8 | 90.342 | 2.458 | 86.575 | 94.109 |
| 8 | 93.3 | 90.342 | 2.958 | 86.575 | 94.109 |
| 8 | 94.7 | 90.342 | 4.358 | 86.575 | 94.109 |
| 9 | 68.9 | 68.043 | 0.857 | 65.297 | 70.789 |
| 9 | 67.9 | 68.043 | -0.143 | 65.297 | 70.789 |

TABLE V (continued)
PREDICTED THROWING POWER AND CONFIDENCE LIMITS

| Trial No. | Throwing Power (%) Observed | Predicted | Difference | 90% Confidence Limits Lower | Upper |
|---|---|---|---|---|---|
| 10 | 66.1 | 68.790 | -2.690 | 63.510 | 74.069 |
| 11 | 55.9 | 56.546 | -0.646 | 51.588 | 61.504 |
| 12 | 81.4 | 84.747 | -3.347 | 80.436 | 89.059 |
| 12 | 80.6 | 84.747 | -4.147 | 80.436 | 89.059 |
| 13 | 73.2 | 78.651 | -5.451 | 73.600 | 83.701 |
| 14 | 56.0 | 61.477 | -5.477 | 57.050 | 65.903 |
| 14 | 60.5 | 61.477 | -0.977 | 57.050 | 65.903 |
| 15 | 84.4 | 86.894 | -2.494 | 82.512 | 91.275 |
| 15 | 87.7 | 86.894 | 0.806 | 82.512 | 91.275 |
| 16 | 81.2 | 85.177 | -3.977 | 80.750 | 89.603 |
| 16 | 82.7 | 85.177 | -2.477 | 80.750 | 89.603 |
| 17 | 78.3 | 83.762 | -5.462 | 79.968 | 87.557 |
| 17 | 87.0 | 83.762 | 3.238 | 79.968 | 87.557 |
| 17 | 84.3 | 83.762 | 0.538 | 79.968 | 87.557 |
| 18 | 69.5 | 68.043 | 1.457 | 65.297 | 70.789 |
| 18 | 69.4 | 68.043 | 1.357 | 65.297 | 70.789 |
| 18 | 66.3 | 68.043 | -1.743 | 65.297 | 70.789 |

TABLE V (continued)
PREDICTED THROWING POWER AND CONFIDENCE LIMITS

| Trial No. | Throwing Power (%) Observed | Predicted | Difference | 90% Confidence Limits Lower | Upper |
|---|---|---|---|---|---|
| 19 | 46.8 | 49.237 | -2.437 | 45.689 | 52.787 |
| 19 | 50.8 | 49.237 | 1.563 | 45.689 | 52.787 |
| 19 | 49.3 | 49.237 | 0.063 | 45.689 | 52.787 |
| 20 | 83.6 | 84.570 | -0.970 | 81.334 | 87.806 |
| 20 | 80.4 | 84.570 | -4.170 | 81.334 | 87.806 |
| 20 | 81.8 | 84.570 | -2.770 | 81.334 | 87.806 |
| 21 | 94.6 | 96.784 | -2.184 | 93.570 | 99.999 |
| 21 | 98.2 | 96.784 | 1.416 | 93.570 | 99.999 |
| 21 | 96.3 | 96.784 | -0.484 | 93.570 | 99.999 |
| 21 | 97.0 | 96.784 | 0.216 | 93.570 | 99.999 |
| 22 | 84.0 | 85.455 | -1.455 | 82.150 | 88.760 |
| 22 | 84.4 | 85.455 | -1.055 | 82.150 | 88.760 |
| 22 | 79.7 | 85.455 | -5.755 | 82.150 | 88.760 |
| 23 | 75.2 | 80.353 | -5.153 | 75.140 | 85.566 |
| 24 | 74.4 | 76.698 | -2.298 | 72.353 | 81.044 |
| 24 | 71.8 | 76.698 | -4.898 | 72.353 | 81.044 |
| 25 | 72.0 | 73.815 | -1.815 | 68.447 | 79.183 |
| 26 | 55.2 | 59.130 | -3.930 | 54.705 | 63.554 |
| 26 | 59.2 | 59.130 | 0.070 | 54.705 | 63.554 |
| 27 | 65.9 | 68.043 | -2.143 | 65.297 | 70.789 |
| 27 | 68.4 | 68.043 | 0.357 | 65.297 | 70.789 |

Summary

1. A least squares fit to the throwing power data is highly statistically significant, accounting for 92% of the total variation.

2. Linear coefficients in the least squares model give the predicted change in throwing power for a one standard deviation change in the independent variable. The results are as follows:

| Variable | Standard Deviation | Least Squares Coefficient |
|---|---|---|
| Gold Concentration ($X_1$) | 10.13 | -7.4 |
| Temperature ($X_2$) | 6.35 | 3.6 |
| Current Density ($X_3$) | 20.45 | -6.4 |
| pH ($X_4$) | 0.91 | 3.1 |

All of these are statistically significant. Gold concentration and current density have negative coefficients, indicating that an increase in these variables is associated with a decrease in throwing power.

3. There is a large quadratic effect for current density, and a large interaction effect between current density and gold concentration. Moreover, interaction is caused by no effect of gold concentration at the low current density but a high negative effect at the highest current density.

4. Gold concentration and current density were the dominant variables in the experiment. The effects of these two variables tended to be altered somewhat by temperature, the next most important variable. The least important variable was pH.

5. There is a statistically significant lack of fit of the model to the data in some areas of the experimental design space. This should not preclude careful use of the prediction equation.

6. Good repeatability in throwing power response was observed under repetition of the same experimental conditions, giving a standard deviation for random error of 2.6%.

## Acknowledgments

We would like to thank D. A. Zehnder (Materials Development) for his valuable assistance in the collection of plating data, and R. Tucker (Publications) for technical editing.

## REFERENCES

1. J. W. Dini and H. R. Johnson, "Use of Strategy of Experimentation in Gold Plating Studies," Plating and Surface Finishing, 68, 52, February 1981.

2. G. E. P. Box and D. W. Behnken, "Some New Three-Level Designs for the Study of Quantitative Variables," Technometrics, Vol. 2, No. 4, November 1960, pp. 455-475.

3. D. L. Rehrig, Plating, 62, 43(1974).

4. H. E. Haring and W. Blum, Trans. Electrochemical Soc., 44, 313(1923).

5. R. D. Snee, "Some Aspects of Nonorthogonal Data Analysis," Journal of Quality Technology, Vol. 5, No. 2, April 1973, pp. 67-79.

6. N. R. Draper and H. Smith, Applied Regression Analysis, John Wiley & Sons, Inc., New York, N.Y. 1970.

Q-4

# Statistical Design and Computer Modeling Session Q

## Computer Modeling of Current Flow in Electroplating Cells: Part 2—Polarization

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# COMPUTER MODELING OF CURRENT FLOW IN ELECTROPLATING CELLS. II. POLARIZATION

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## Abstract

The modeling of current density distributions at the cathodes of electrolytic test cells has been extended to include the effects of polarization. Linear and Tafel polarization in the Haring-Blum cell are shown to contribute to throwing power. The computational method of finite differences has been modified so that linear and Tafel polarization can also be handled in the Hull cell. Potential maps of the Hull cell showing the changes due to polarization are included.

## Introduction

At the Sur/Fin '81 conference in Boston, the first paper in this series was presented. There the basic features of the finite difference computational method were outlined. It was shown that the fundamental governing equation (the Laplace equation) leads to the result that the electrostatic potential at any point in an electrolytic cell can be expressed as an average of the potentials at nearby points. Potentials near the cathode are used to calculate primary cathode current density distributions. Results of applying the method to the Hull, Casey-Asher and Tena cells were given. Very good agreement with exact analytical solutions of the Laplace equation can be achieved.

Rarely in the real world, however, is the primary current density distribution the one which is obtained. Secondary effects often change the distribution substantially. One of the most common effects is that of polarization, which arises because application of an external voltage to a cell creates a non-equilibrium situation. Since metal-electron transfers are not instantaneous, it is often found that a greater external potential than expected must be applied in order to produce a given cell current. This happens because the potential at an electrode surface differs from the applied potential by an amount known as the "overvoltage" or "overpotential". Electrochemical theorists have derived relationships between overpotentials and current densities at electrode surfaces.[1] In this paper, two such relationships (Linear and Tafel) are examined in two well-known electrolytic test cells (Haring-Blum and Hull cells).

## Linear Polarization in the Haring-Blum Cell

This cell has been used for decades to measure throwing power. It is a rectangular box, pictured in Figure 1, with the ends occupied by cathodes and an anode placed between them. One cathode is farther from the anode than the other. Each electrode is large enough to fully occupy

the cross-sectional area inside the cell, so that the current density at each electrode face is uniform. Let us work out an example; let the cross-sectional area be (for ease of calculation) 0.1 square foot. A cell 3.8 inches wide filled to a depth of 3.8 inches has such a cross-sectional area. Let the cell be 12 inches long with the anode and near cathode 2 inches apart. Let a potential of +2 volts be applied to the anode, with the cathodes held at 0 volts. Let the electrolyte have a resistance between the anode and near cathode of 1 ohm. Then the primary current density at the near cathode is 2 volts/1 ohm/0.1 square foot = 20 amperes/square foot. At the far cathode the primary current density is less by a factor of 5 (4 amperes/square foot).

It seems reasonable, for a first guess at a current density - overpotential relationship, that the overpotential is a linear function of the current density. That is,

$$N = BI$$

where N is the overpotential, I is the current density, and B is a numerical constant. If N and I are expressed in volts and amperes/square foot, B then has units of ohms-square feet. The overpotential is added to the imposed cathode potential, and subtracted from the imposed anode potential (having the overpotential be the same mag nitude at the anode and the cathode is a good approximation, particularly when the anode is made of the same metal as that being deposited, but is rarely precisely true). The net effect is that the current density is lowered at both cathodes; the change is greater at the near cathode. If no other secondary effects enter in,more metal is deposited at the far cathode than would be expected from the primary current density, and a positive throwing power is observed. The effects of various values of B in the Haring-Blum cell are summarized in Table 1.

Linear Polarization in the Hull Cell

The Hull cell is pictured in Figure 2 with a "coarse" grid of 39 points inside the cell and on the boundaries. As outlined in the previous paper, the values of the electrostatic potential at the points 1, 3, and 4 are used to calculate the current density at point 2. Polarization complicates the situation, however, by causing points on the cathode (and anode) to have non-constant values of potential. These values are the sums of the imposed potential and overpotentials. The current density at point 2, for example, is a function not only of the potential differences between points 1 and 2, 3 and 2, and 4 and 2; but also of the particular overpotential at point 2. Fortunately, in the case of linear polarization, after the proper rearrangements, the problem remains that of solving many simultaneous linear equations. A reasonably efficient algorithm to do this was developed for the previous paper.

In Table 2, the effects of various values of B in the Hull cell are summarized. The calculations were based on a cell having a grid of 741 points. In this table, the external potential applied to the electrodes is kept at a constant value. As in the case of the Haring-Blum cell, the total cell current drops as B increases. Over the left-hand three inches of the cathode (the left edge being the high current density end), the current density at every point also drops. However, at 3.2 inches from the left edge, the current density slowly rises, and then starts to fall. At the right edge, the current density continuously rises. Thus there is a "current shift" from the high current density region to the lower current density region.

This current density shift is more apparent in Table 3. Here, for each value of B, the external applied voltage is raised to maintain a constant total cell current of 2 amperes. In general, current is shifted away from the left-hand 1.6 inches. And again, positive throwing power is observed.

Figure 3 is a contour map of the potential distribution in a Hull cell without polarization. The anode is set at +2 volts, the cathode at 0 volts, and the separation between equipotential lines is 0.1 volt. Figure 4 is the same situation, except that linear polarization (the B = 0.02 case) has been incorporated while maintaining the same applied external potential. Now the effective anode potential is less than 1.5 volts, while the effective cathode potential ranges from more than 0.1 volt to more than 0.7 volt. The equipotential lines are farther apart, and less curved, than in the unpolarized case.

Tafel Polarization in the Haring-Blum Cell

A natural question is whether linear polarization describes the real world. It happens that linear polarization is a limiting case of the Butler-Volmer equation, and, assuming that the Butler-Volmer holds for a particular situation, linear behavior is valid only for small overpotentials (less than 0.01 volt in the case of one-electron transfer processes). In Table 1, for all values of B greater than zero, none of the overpotentials is sufficiently small. For overpotentials greater than 0.1 volt, a different limiting case of the Butler-Volmer equation can be derived:

$$N = A + B \ln I.$$

Here the overpotential depends upon the logarithm of the current density. Now B has volts for units. A is the contribution from the "equilibrium exchange current density" (see reference 1). Table 4 summarizes the effects of various values of B in the previously described Haring-Blum cell if A is made zero, which is the case if the exchange current density is 1 ampere/square foot. As B becomes larger, the currents and throwing power become increasingly less sensitive to changes in B. It can be shown that, if the exchange current density is less than 1, the same B and total current density I correspond to a larger overpotential (compared to the overpotential calculated when A is zero).

## Tafel Polarization in the Hull Cell

Accomodating Tafel polarization in the Hull cell introduces a substantial jump in computational difficulty. Points on each electrode surface and in the next row inside the cell (parallel to the electrode surface) are now related by non-linear equations. The potentials at all the points cannot be calculated directly, and turning to an iterative method is required.

One of the best techniques for solving many simultaneous non-linear equations is the Newton-Raphson method.[3] In general, it involves setting up a system of linear equations, which, when solved, produces a set of corrections to be applied to an initial estimate of all the potentials. The set of corrections usually has to be generated several times and successively applied to the potentials, but, with a reasonable initial estimate, the corrections rapidly become very small. In this work, no more than six iterations (calculations of the corrections to the potentials) was ever needed.

Similar to Table 4, Table 5 summarizes the effects of various values of B in the Hull cell. (When A is made zero). Compared to linear polarization, at the same total cell current, the shift of current density to the low current density region is not as great. However, compared to the unpolarized case, the shift is still large.

Figure 5 is a contour map (similar to the two other maps) showing Tafel polarization (B = 0.2 case). As in the linear polarization map, the effective cathode potential (applied potential plus overpotential) at the high current end is more than 0.7 volt. The fewer equipotential lines ( compared to the linear map) can be associated with a smaller total cell current.

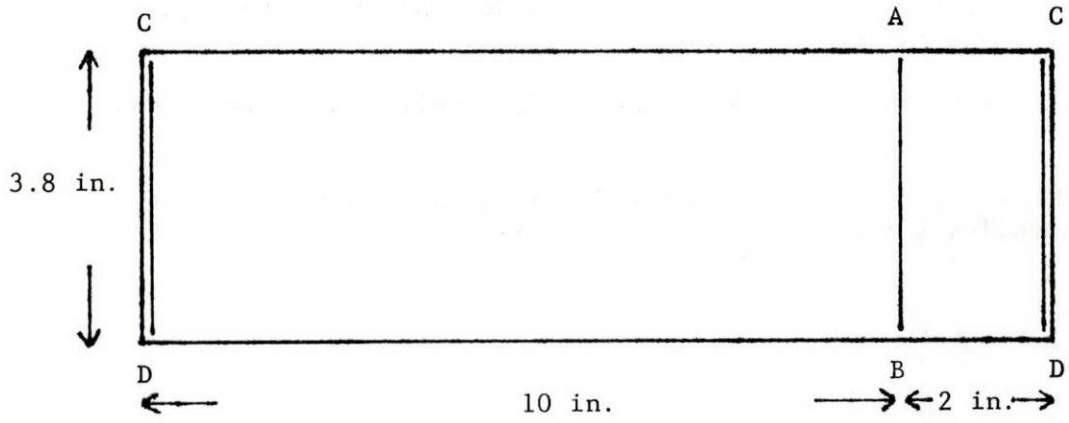
In this paper, the Hull cell results in particular demonstrate that the complicating factor of polarization can be taken into account in the computer modeling of current and potential distribution. At least in the linear and Tafel cases, the kinds of current shift and throwing power which are often observed can be associated with polarization. Further explorations of the computer modeling of electrochemical complexities are anticipated.

References:

1. J. O'M. Bockris and A.K.N. Reddy, "Modern Electrochemistry," Plenum Press, New York, 1973.

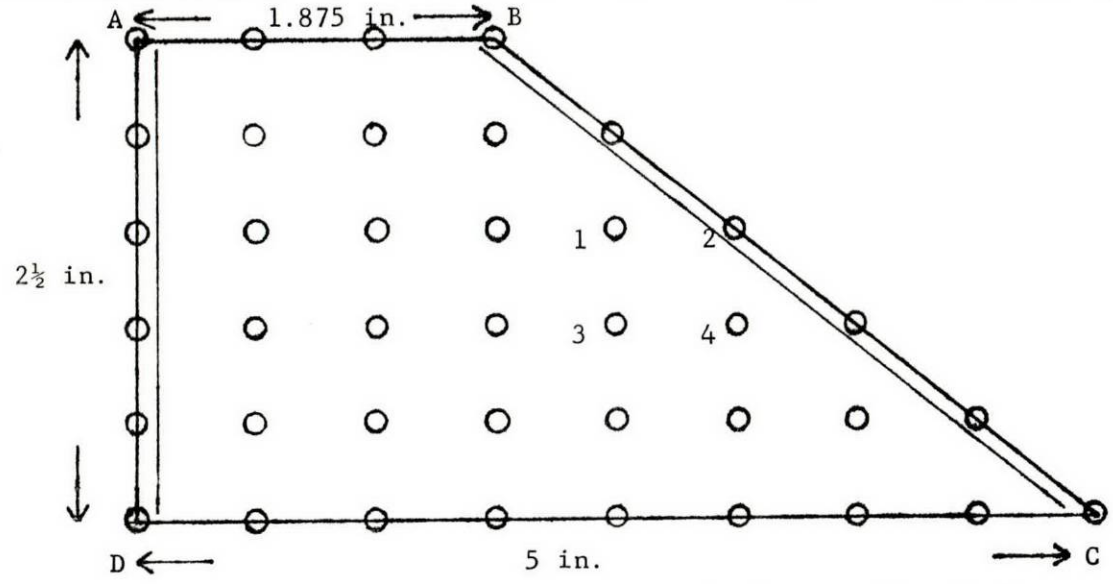
2. F.A. Lowenheim, "Electroplating," McGraw-Hill, Inc., New York, 1978.

3. J.H. Ferziger, "Numerical Methods for Engineering Application," John Wiley & Sons, Inc., New York, 1981.




A-B = anode (set to +2 volts)
C-D = cathode (set to 0 volts)

Figure 1. A Haring-Blum Cell




A-D = anode (set to +2 volts)
B-C = cathode (set to 0 volts)

Figure 2. Hull Cell with Grid of 39 Points

Table 1

EFFECTS OF LINEAR POLARIZATION IN THE HARING-BLUM CELL

| B (ohms-sq.ft.) | Total Cell Current (amps) | Current Density, Near Cathode (amps/sq.ft.) | Current Density, Far Cathode (amps/sq.ft.) | Throwing Power (percent) |
|---|---|---|---|---|
| 0 | 2.40 | 20 | 4 | 0 |
| 0.01 | 2.05 | 16.7 | 3.8 | 9.1 |
| 0.02 | 1.80 | 14.3 | 3.7 | 16.7 |
| 0.03 | 1.61 | 12.5 | 3.6 | 23.1 |
| 0.04 | 1.46 | 11.1 | 3.4 | 28.6 |
| 0.05 | 1.33 | 10.0 | 3.3 | 33.3 |
| 0.06 | 1.23 | 9.1 | 3.2 | 37.5 |
| 0.07 | 1.15 | 8.3 | 3.1 | 41.2 |
| 0.08 | 1.07 | 7.7 | 3.0 | 44.4 |
| 0.09 | 1.01 | 7.1 | 2.9 | 47.4 |
| 0.10 | 0.95 | 6.7 | 2.9 | 50.0 |

Throwing power calculated by the Field formula[2]

Table 2

EFFECTS OF LINEAR POLARIZATION IN THE HULL CELL
(CONSTANT APPLIED EXTERNAL POTENTIAL)

| B (ohms-sq.ft.) | Total Cell Current (amps) | Current Density (amps/sq.ft.) for Various Distances along Cathode from HCD End | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 in. | 0.800 in. | 1.601 in. | 2.401 in. | 3.202 in. | 4.002 in. |
| 0 | 2 | 189.2 | 60.5 | 36.9 | 21.0 | 8.4 | 0.1 |
| 0.002 | 1.81 | 124.3 | 55.6 | 35.0 | 21.0 | 9.8 | 0.8 |
| 0.004 | 1.65 | 95.7 | 50.4 | 32.9 | 20.6 | 10.6 | 1.8 |
| 0.006 | 1.52 | 78.4 | 45.6 | 30.8 | 20.1 | 11.2 | 2.7 |
| 0.008 | 1.41 | 66.6 | 41.5 | 28.9 | 19.5 | 11.5 | 3.5 |
| 0.010 | 1.32 | 57.9 | 38.0 | 27.1 | 18.8 | 11.6 | 4.2 |
| 0.012 | 1.23 | 51.3 | 35.0 | 25.6 | 18.1 | 11.7 | 4.8 |
| 0.014 | 1.16 | 46.0 | 32.4 | 24.1 | 17.5 | 11.6 | 5.3 |
| 0.016 | 1.10 | 41.7 | 30.1 | 22.8 | 16.9 | 11.5 | 5.6 |
| 0.018 | 1.04 | 38.1 | 28.2 | 21.7 | 16.3 | 11.4 | 5.9 |
| 0.020 | 0.99 | 35.1 | 26.4 | 20.6 | 15.7 | 11.3 | 6.2 |

HCD = High Current Density

Table 3

EFFECTS OF LINEAR POLARIZATION IN THE HULL CELL
(CONSTANT TOTAL CELL CURRENT)

Current Density (amps/sq.ft.)
For Various Distances Along Cathode From HCD End

| B (ohms-sq.ft.) | 0 in. | 0.800 in. | 1.601 in. | 2.401 in. | 3.202 in. | 4.002 in. |
|---|---|---|---|---|---|---|
| 0 | 189.2 | 60.5 | 36.9 | 21.0 | 8.4 | 0.1 |
| 0.002 | 137.2 | 61.4 | 38.6 | 23.2 | 10.8 | 0.9 |
| 0.004 | 115.7 | 60.9 | 39.8 | 25.0 | 12.8 | 2.2 |
| 0.006 | 103.0 | 59.9 | 40.5 | 26.4 | 14.7 | 3.6 |
| 0.008 | 94.4 | 58.8 | 41.0 | 27.6 | 16.3 | 5.0 |
| 0.010 | 88.0 | 57.7 | 41.2 | 28.6 | 17.7 | 6.4 |
| 0.012 | 83.0 | 56.6 | 41.4 | 29.4 | 18.9 | 7.8 |
| 0.014 | 79.0 | 55.7 | 41.5 | 30.1 | 20.0 | 9.0 |
| 0.016 | 75.7 | 54.8 | 41.5 | 30.6 | 21.0 | 10.3 |
| 0.018 | 72.9 | 54.0 | 41.5 | 31.1 | 21.9 | 11.4 |
| 0.020 | 70.6 | 53.2 | 41.4 | 31.6 | 22.7 | 12.4 |

Total Current = 2 amps
HCD = High Current Density

TABLE 4

EFFECTS OF TAFEL POLARIZATION IN THE HARING-BLUM CELL

| B (volts) | Total Cell Current (amps) | Current Density, Near Cathode (amps/sq.ft.) | Current Density, Far Cathode (amps/sq.ft.) | Throwing Power (per cent) |
|---|---|---|---|---|
| 0 | 2.40 | 20 | 4 | 0 |
| 0.1 | 1.81 | 14.6 | 3.5 | 11.4 |
| 0.2 | 1.37 | 10.6 | 3.1 | 24.7 |
| 0.3 | 1.05 | 7.7 | 2.8 | 38.3 |
| 0.4 | 0.84 | 5.9 | 2.5 | 50.3 |
| 0.5 | 0.70 | 4.6 | 2.3 | 59.9 |
| 0.6 | 0.60 | 3.8 | 2.2 | 67.3 |
| 0.7 | 0.53 | 3.3 | 2.0 | 72.8 |
| 0.8 | 0.48 | 2.9 | 1.9 | 77.1 |
| 0.9 | 0.45 | 2.63 | 1.83 | 80.3 |
| 1.0 | 0.42 | 2.41 | 1.75 | 82.9 |
| 10.0 | 0.22 | 1.10 | 1.08 | 98.9 |

Throwing power calculated by the Field formula[2]

Table 5

EFFECTS OF TAFEL POLARIZATION IN THE HULL CELL
(CONSTANT APPLIED EXTERNAL POTENTIAL)

Current Density (amps/sq.ft.)
For Various Distances Along Cathode From HCD End

| B (Volts) | Total Cell Current (amps) | 0 in. | 0.800 in. | 1.601 in. | 2.401 in. | 3.202 in. | 4.002 in. |
|---|---|---|---|---|---|---|---|
| 0 | 2 | 189.2 | 60.5 | 36.9 | 21.0 | 8.4 | 0.1 |
| 0.02 | 1.85 | 166.7 | 55.6 | 34.0 | 19.6 | 8.6 | 1.9 |
| 0.04 | 1.71 | 145.6 | 50.9 | 31.3 | 18.4 | 8.9 | 2.9 |
| 0.06 | 1.57 | 126.1 | 46.5 | 28.9 | 17.3 | 9.1 | 3.5 |
| 0.08 | 1.44 | 108.3 | 42.2 | 26.5 | 16.3 | 9.1 | 4.1 |
| 0.10 | 1.31 | 92.2 | 38.2 | 24.4 | 15.4 | 9.1 | 4.5 |
| 0.12 | 1.20 | 77.9 | 34.5 | 22.4 | 14.5 | 9.0 | 4.8 |
| 0.14 | 1.09 | 65.4 | 31.0 | 20.5 | 13.7 | 8.9 | 5.0 |
| 0.16 | 0.99 | 54.7 | 27.8 | 18.8 | 12.9 | 8.7 | 5.2 |
| 0.18 | 0.89 | 45.7 | 24.8 | 17.2 | 12.1 | 8.5 | 5.3 |
| 0.20 | 0.81 | 38.1 | 22.1 | 15.7 | 11.4 | 8.2 | 5.4 |

HCD = High Current Density

# HULL CELL - NO POLARIZATION

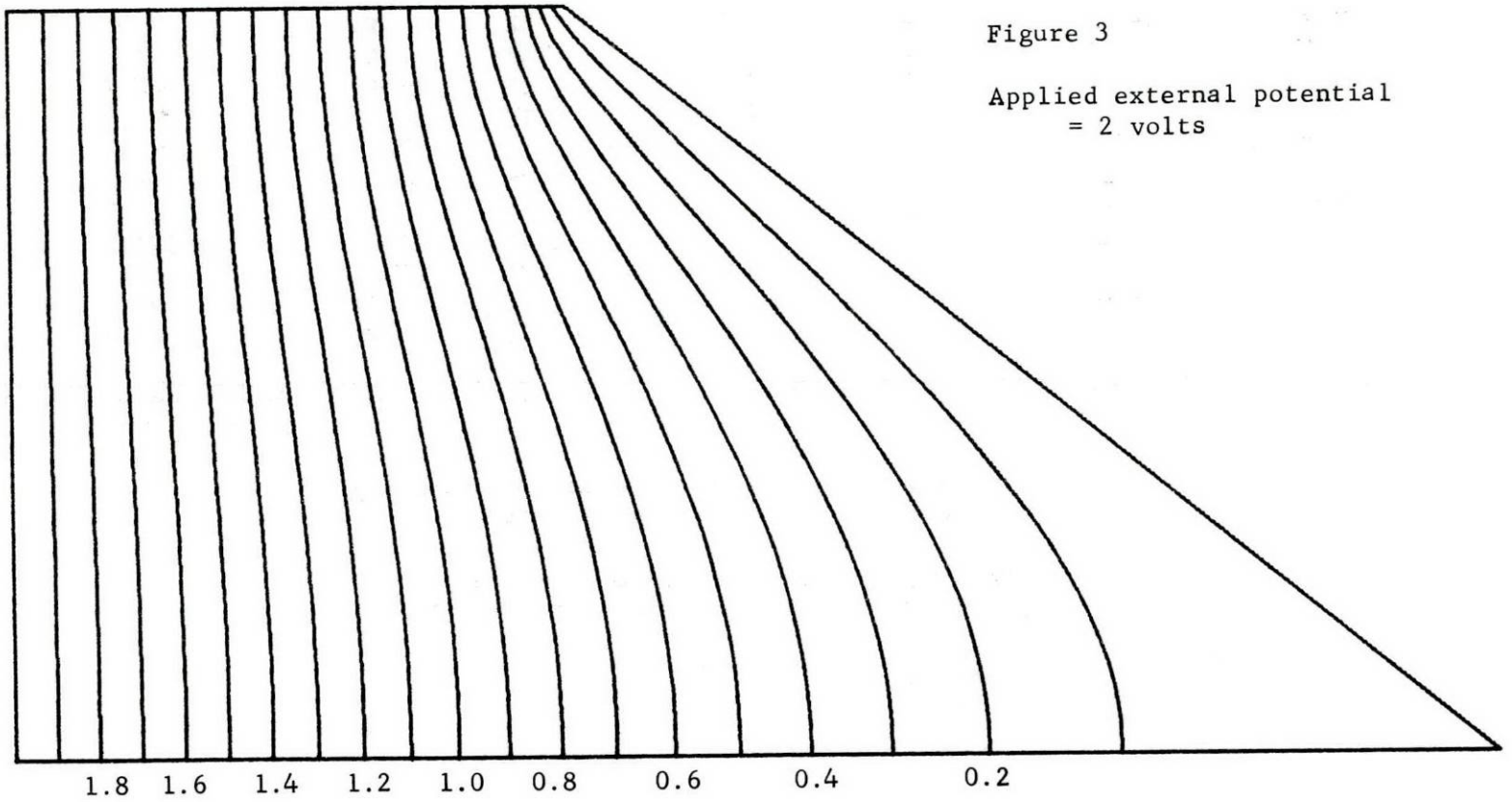



Figure 3

Applied external potential
= 2 volts

# HULL CELL - LINEAR POLARIZATION

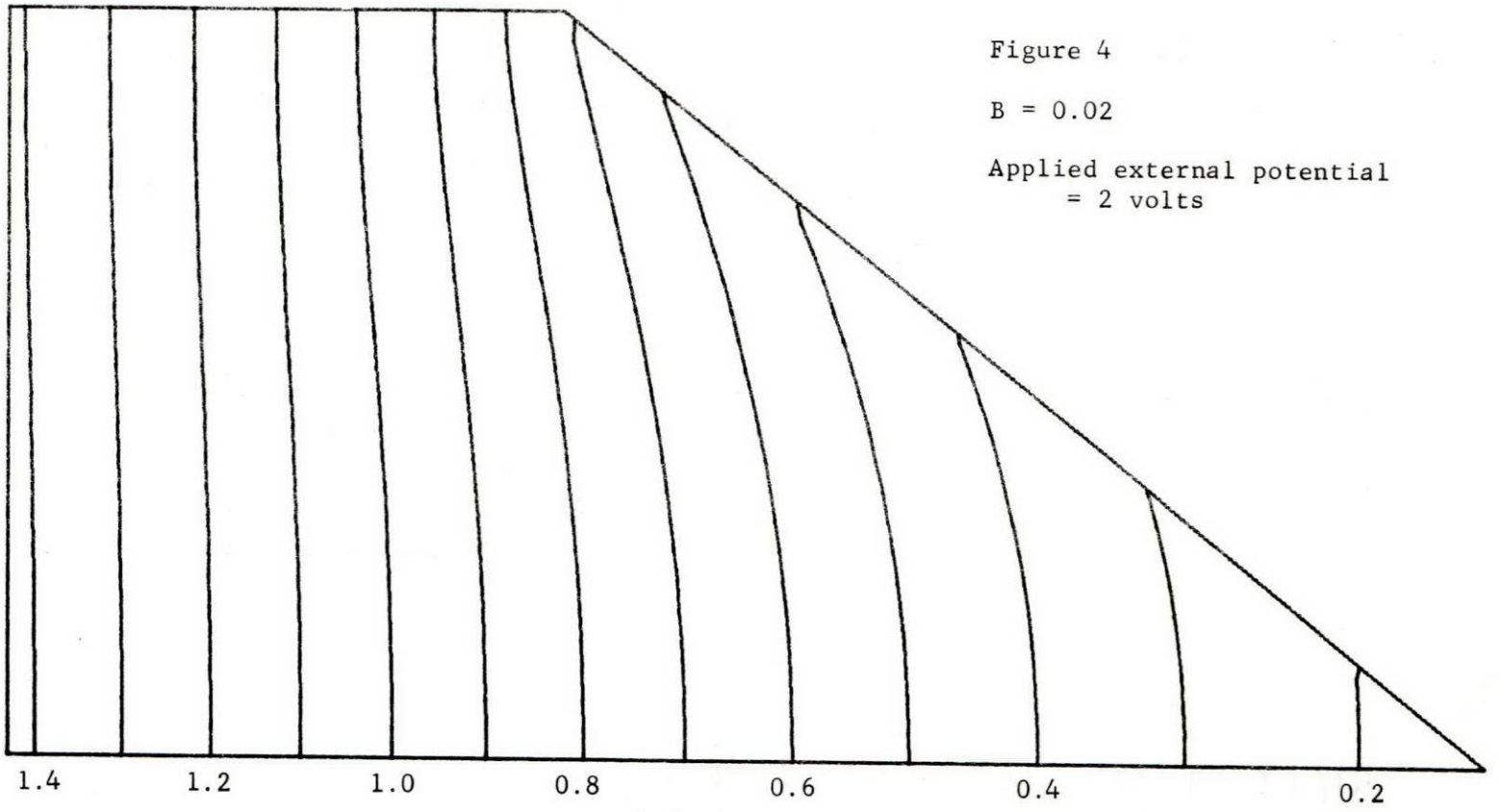



Figure 4

B = 0.02

Applied external potential
= 2 volts

# HULL CELL - TAFEL POLARIZATION

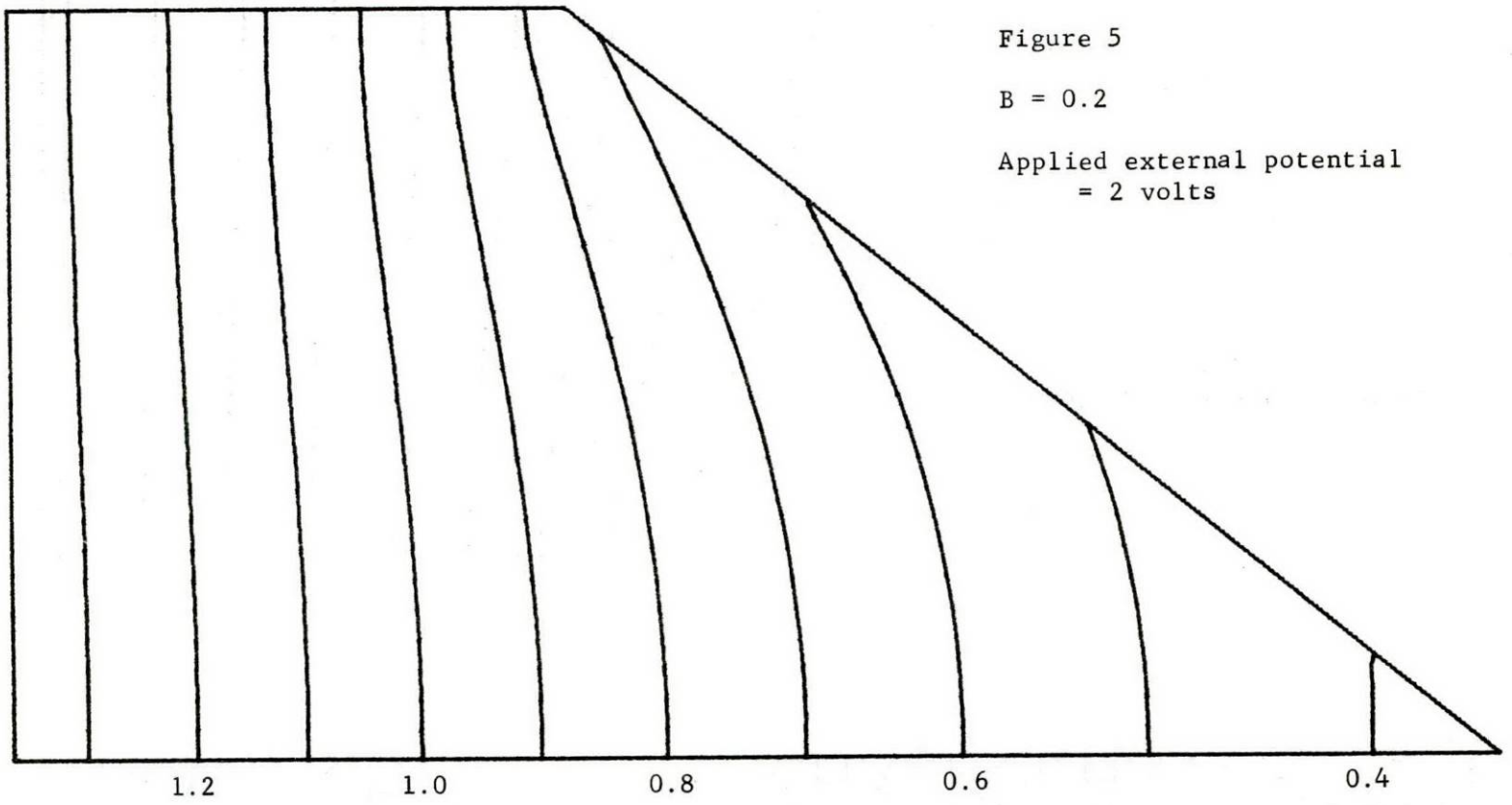



Figure 5

B = 0.2

Applied external potential
= 2 volts

# R-1

# Electroless I
# Session R

## Nitric Acid Test Correlated With 5% Neutral Salt Spray. Is the Nitric Acid Test a Valid Indicator of Corrosion Resistance for Engineering Electroless Nickel/Phosphorus Systems?

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Waterbury, CT

# NITRIC ACID TEST CORRELATED WITH 5% NEUTRAL SALT SPRAY. IS THE NITRIC ACID TEST A VALID INDICATOR OF CORROSION RESISTANCE FOR ENGINEERING ELECTROLESS NICKEL/PHOSPHOROUS SYSTEMS?

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## ABSTRACT

An evaluation of corrosion resistance in 5% Neutral Salt Spray testing compared with "blackening" in the nitric acid test for engineering electroless nickels was conducted. The scope of this paper is to determine if the nitric acid test is a valid criterion for corrosion resistance for engineering electroless nickel coatings. The parameters covered are:

1. Various substrates - steel and brass.
2. Effect of pH.
3. Various combinations of metallic and non-metallic stabilizers.
4. Plating rate.
5. Phosphorous content.
6. Temperature of bath.
7. Surface condition of plate and substrate prior to plate.
8. The ratio of nickel to reducers.

## BACKGROUND

The nitric acid test has been considered a good indicator for corrosion resistance. It is used primarily because it is a fast check to determine uniformity and porosity of the deposit. The nitric test included the immersion of an electroless nickel plated part in concentrated reagent grade nitric acid. A 0.0001 inch deposit of electroless nickel should withstand a 30 second immersion at room temperature (70-75$^{o}$F.) without discoloring the electroless nickel coating. After each specimen is tested, the solution must be discarded and fresh solution used.

In direct comparison to the nitric test, the specimens were 5% Neutral Salt Spray tested. This was in accordance with B-117 ASTM "Standard Method of Salt Spray (FOG) Testing". Failure was defined as the first sign of substrate corrosion, as opposed to the percent corrosion method.

The variables considered were substrate, pH, stabilizer, rate, and phosphorous content.

## METHODOLOGY

The substrates evaluated were cold rolled steel panels and brass Hull cell panels. A total of 8 variables were examined on each of the substrates.

The variables studied on both steel and brass substrates included pH (a low range approximately 4.4 to 4.5 and a high range 6.0 to 7.5), various bath stabilizers (a metallic variety compared to a non-metallic), rate (0.3 to 0.9 mil/hour), phosphorous content (a low range of approximately 7% by weight to a high range of greater than 12% by weight), surface condition of the substrate, and finally, the ratio of nickel to reducer (7 gm.:20 gm., respectively). All plating was conducted with newly made-up baths. None of the electroless nickel baths had a metal turnover (regeneration) greater than 1.

The pretreatment cycle for the steel panels was as follows:

| | | Conc. | Temp. | Time |
|---|---|---|---|---|
| 1. | Proprietary Soak Clean | 10 oz./gal. | 180°F. | 2 min. |
| 2. | Cold Water Rinse | | | |
| *3. | Proprietary Electroclean (P/R) 10"/10" cycle | 2 lbs./gal. | 180°F. | 2 min. |
| 4. | Cold Water Rinse | | | |
| 5. | Proprietary Acid Pickle | 4 oz./gal. | R.T. | 1 min. |
| 6. | Cold Water Rinse | | | |
| 7. | Electroless Nickel Plate | | | |

*In Step 3 above, P/R refers to periodic reverse in the electrocleaner.

Pretreatment cycle for the brass Hull cell panels was as follows:

| | | Conc. | Temp. | Time |
|---|---|---|---|---|
| 1. | Proprietary Soak Clean | 8 oz./gal. | 160°F. | 2 min. |
| 2. | Cold Water Rinse | | | |
| 3. | Proprietary Electroclean | 6 oz./gal. | 140°F. | 2 min. |
| 4. | Cold Water Rinse | | | |
| 5. | Proprietary Acid Pickle | 4 oz./gal. | R.T. | 1 min. |
| 6. | Cold Water Rinse | | | |

7. Electroless Nickel Plate

For ease of identification, the baths tested were separated into five (5) categories. These baths are listed below in the table labeled TEST SOLUTIONS. Baths A through E are listed by the stabilizer used, the pH range, phosphorous content, temperature, and rate of deposition.

TEST SOLUTIONS

| Bath | Stabilizer | pH | P content | Temperature | Rate |
|---|---|---|---|---|---|
| A | Metallic | 4.8-5.0 | 9% ± 1 | 185°F. ± 5 | .9 mil/hr. ± .1 |
| B | Metallic | 4.8-5.0 | 9% ± 1 | 185°F. ± 5 | .7 mil/hr. ± .1 |
| C | Metallic | 6.0-7.5 | 7% ± 1 | 145°F. ± 5 | .4-.5 mil/hr. |
| D | Non-metallic | 4.4-4.5 | 12% ± 1 | 185°F. ± 5 | .3 ± .1 |
| E | Metallic | 4.8-5.0 | 7% ± 1 | 185°F. ± 5 | .5 ± .1 |

A series of both steel and brass panels were processed through the above baths, the results of which are tabulated in Tables 1 and 2 in the Appendix.

As can be seen in the graph on the following page, deposits containing a relatively high concentration of phosphorous may demonstrate poor 5% Neutral Salt Spray results, but relatively good nitric acid results depending on the effect of other variables, such as the generic stabilizer and rate.

The graph is a summary of Tables 1 and 2. The blue line on the graph depicts the steel specimens plated in baths A and B. Both A and B have metallic stabilizers, a relatively high concentration of phosphorous and a rate of 0.6 mil/hr. or greater.

The dotted line in the graph represents bath D. Both the steel and brass specimens in bath D exceeded 30 second immersion in nitric and 500 hours 5% Neutral Salt Spray. Bath D is of the non-metallic stabilizer type, has a high concentration of phosphorous, and deposition rate is slow (0.3 mil/hr.).

The short black line in Table 3 represents steel specimens plated in bath E. Bath E's characteristics are as follows: metallic stabilizer, moderate rate, and low phosphorous content.

Finally, the next significant line in the graph is the red line. This line represents steel specimens plated in bath C. Bath C utilized a metallic stabilizer, high pH, a moderate rate, and one variable that is a constant in other baths. The variable we are discussing is the concen-

tration of reducer. The ratio of nickel to reducer in this test bath was 7 gm.:25 gm. The reducer runs slightly higher to drive the reaction at the lower temperature.

## SEM SUBSTRATE AND COATING INTERPRETATION

In the following illustrations, the surface morphology of some of the deposits was examined.

Figures 1 and 2 are SEM's of the brass and steel Hull cell test panels. These micrographs were taken at a magnification of 4000X and a 45° tilt. The brass panel is smooth and void-free as compared to the steel panel. The horizontal lines running through the brass panel are brush marks.

Figure 3 is also an SEM, but of coating D taken at a magnification of 10,000X and a 45° tilt. The surface of this coating is relatively smooth and pore-free.

Figure 4 is an SEM of coating C. It is also a 10,000X magnification and a 45° tilt picture. This surface is very porous and rough in comparison to Figure 3.

Figure 5 is an SEM of coating E at 10,000X, 45° tilt. The surface of this deposit does not appear to be as rough as that of coating C, but is not nearly as smooth as coating D.




Figure 1. Brass Hull cell panel after pretreatment, prior to plate. 4000X.




Figure 2. Steel panel after pretreatment, prior to plate. 4000X.



Figure 3. Steel test panel coated in bath D. 10,000X magnification, 45° tilt.

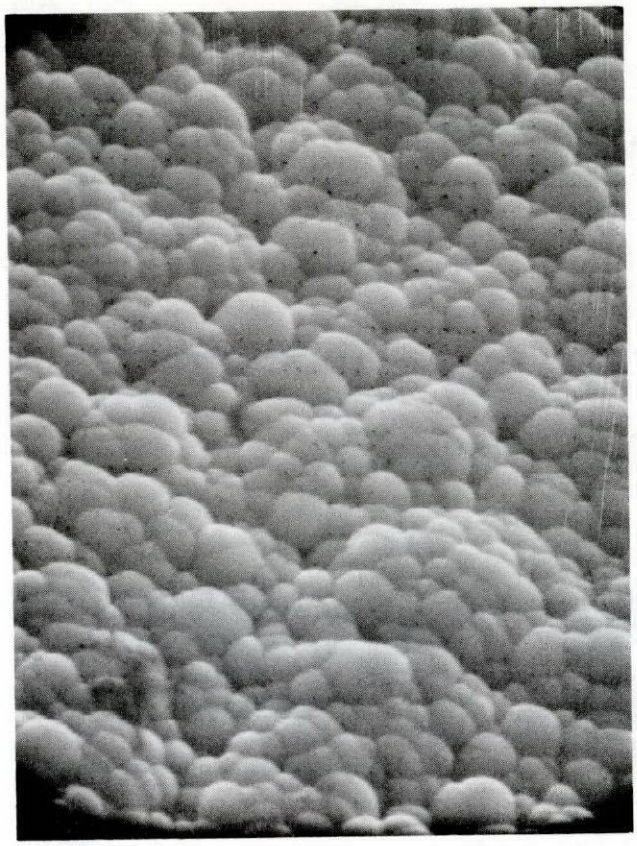


Figure 4. Steel panel coated in bath C. 10,000X magnification, 45° tilt.

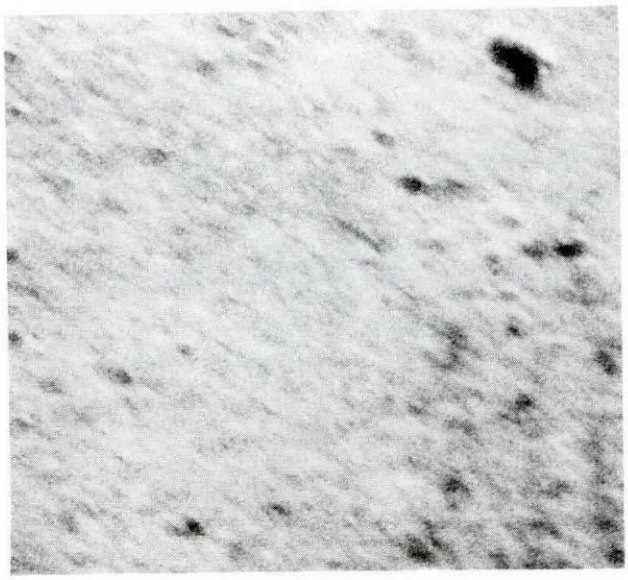


Figure 5. Steel panel coated in bath E. 10,000 magnification, 45° tilt.

DOT MAP INTERPRETATION

In the next set of illustrations, we will be looking at a DOT MAP of phosphorous in coatings C (Figure 6A) and D (Figure 7A). The DOT MAP pictures were done by using Robinson Backscatter Imaging in conjunction with a SEM (scanning electron microscope). The DOT MAP pictures indicating the phosphorous correlate to the cross-section pictures above them. Figures 6 and 6A are SEM's of the exact same location in the cross-section of coating C. This also holds true for Figures 7 and 7A.

Figure 6 is a cross-section of coating C at 4,000X; the deposit appears to be cracked in the center indicating a stressed deposit. Areas 1 and 2 in this figure correlate directly to Figure 6A. Area 1 (closest to the surface) shows the phosphorous to be less concentrated than Area 2. The non-uniformity of phosphorous in the deposit in conjunction with the cracks would probably lend itself to poor resistance in both the nitric test and 5% Neutral Salt Spray, this data requires further investigation.

In Figure 7, we are viewing a cross-section of coating D. This picture shows no indication of cracking. Figure 7A is the DOT MAP of phosphorous in D, unlike coating C the phosphorous in D is uniform throughout the coating. There appears to be much more phosphorous in this deposit than there is in coating C. This type of coating probably would lend itself to much better resistance in both the nitric and 5% Neutral Salt Spray; again, this data requires further investigation.

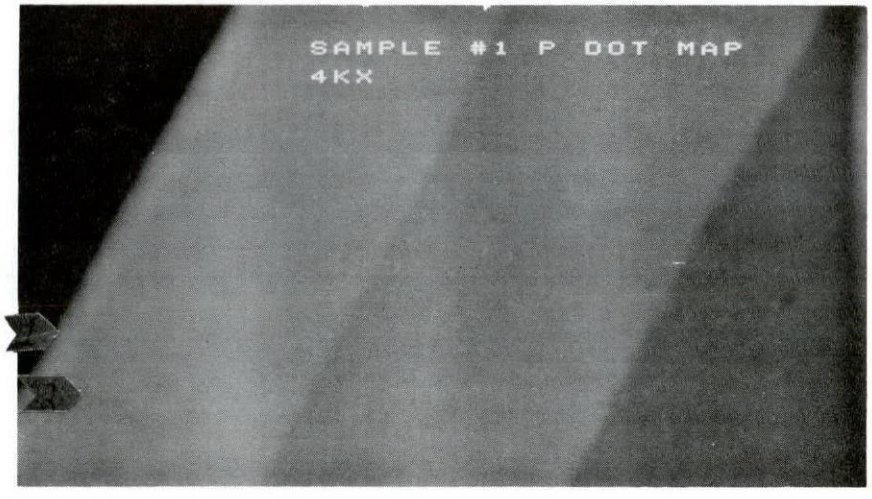



Figure 6

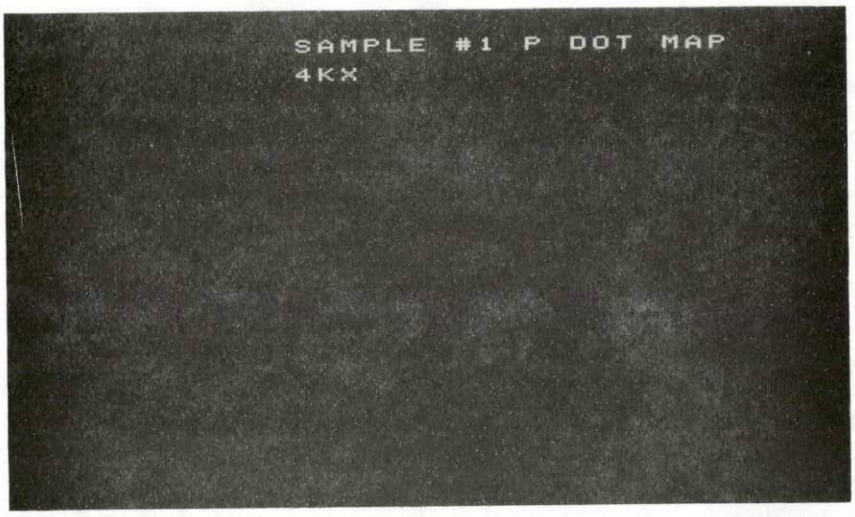



Figure 6A

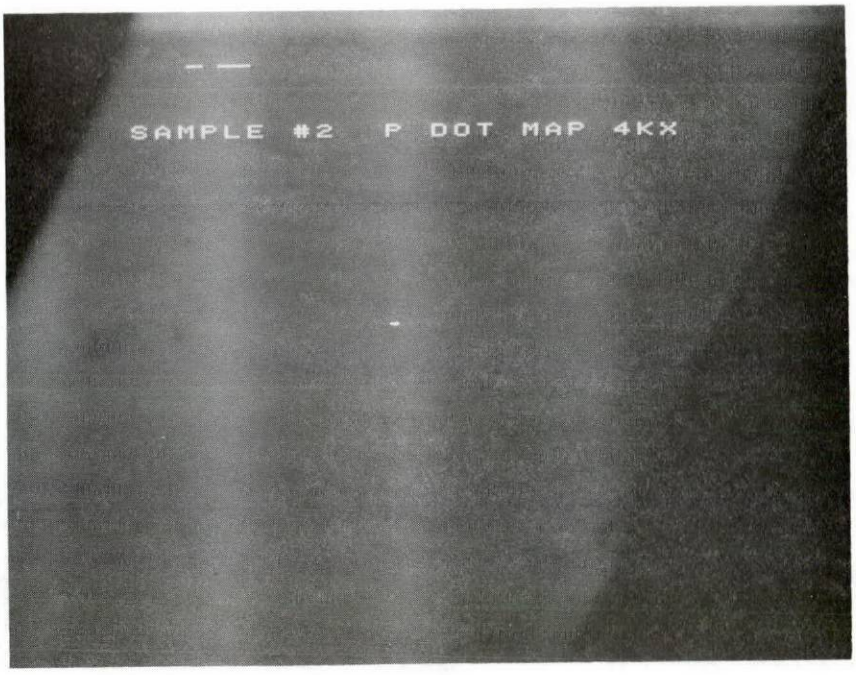



Figure 7

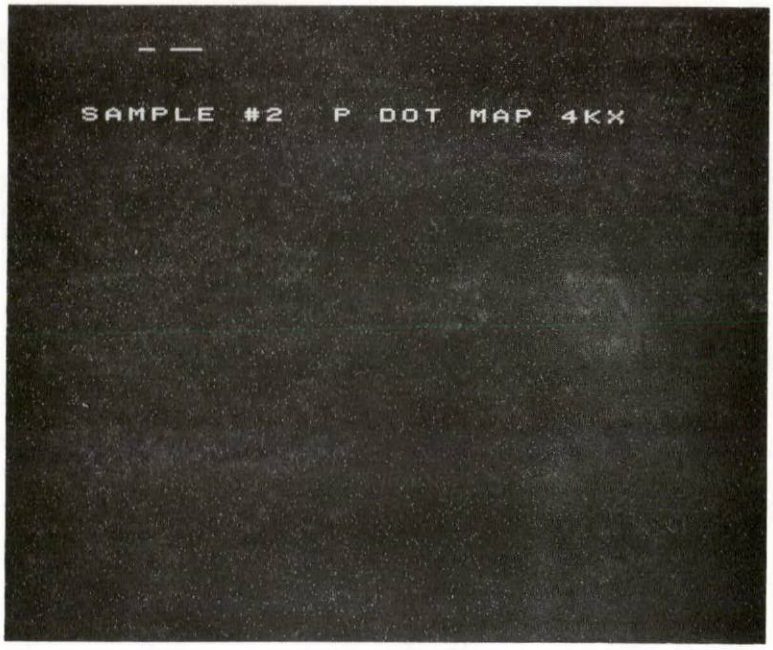



Figure 7A

## CONCLUSIONS

Based on the data which was generated for this paper, nitric acid resistance cannot - in all cases - also assure maximum corrosion resistance. This was demonstrated by specimens from solutions A and B on the graph; those specimens passed the nitric acid immersion test, but would have been considered very marginal in traditional corrosion testing.

Other test specimens performed dismally in nitric, but produced almost identical results to specimens A and B.

Still another test specimen passed both nitric and 5% Neutral Salt Spray with flying colors.

The intent here is to point out that more than one test criterion is necessary to reasonably assure field corrosion performance; also, a number of quality control tools are available to determine precisely the quality of the substrate, the quality (and physical characteristics) of the electroless nickel coating, the phosphorous content, and the uniformity of phosphorous dispersion.

Each application will dictate the type of performance required and the degree of sophistication of the equipment to monitor the substrate and coating quality.

Also, there were a number of variables not studied here which must be introduced and studied for future presentations.

TABLE 1

STEEL

| Bath Type Steel | Hours 5% Neutral Salt Spray | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 24 | 48 | 72 | 96 | 120 | 144 | 168 | 192 | 216 | 240 | 264 | 288 | 500 |
| A | X | X | X | X | X | | | | | | | | |
| B | X | X | X | X | X | | | | | | | | |
| C | X | | | | | | | | | | | | |
| D | X | X | X | X | X | X | X | X | X | X | X | X | X |
| E | X | X | X | X | | | | | | | | | |

| | Nitric Test/Seconds/Steel | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| A | X | X | X | X | X | X | X | X | X | X | X | X |
| B | X | X | X | X | X | X | X | X | X | X | X | X |
| C | X | X | X | X | | | | | | | | |
| D | X | X | X | X | X | X | X | X | X | X | X | X |
| E | X | X | | | | | | | | | | |

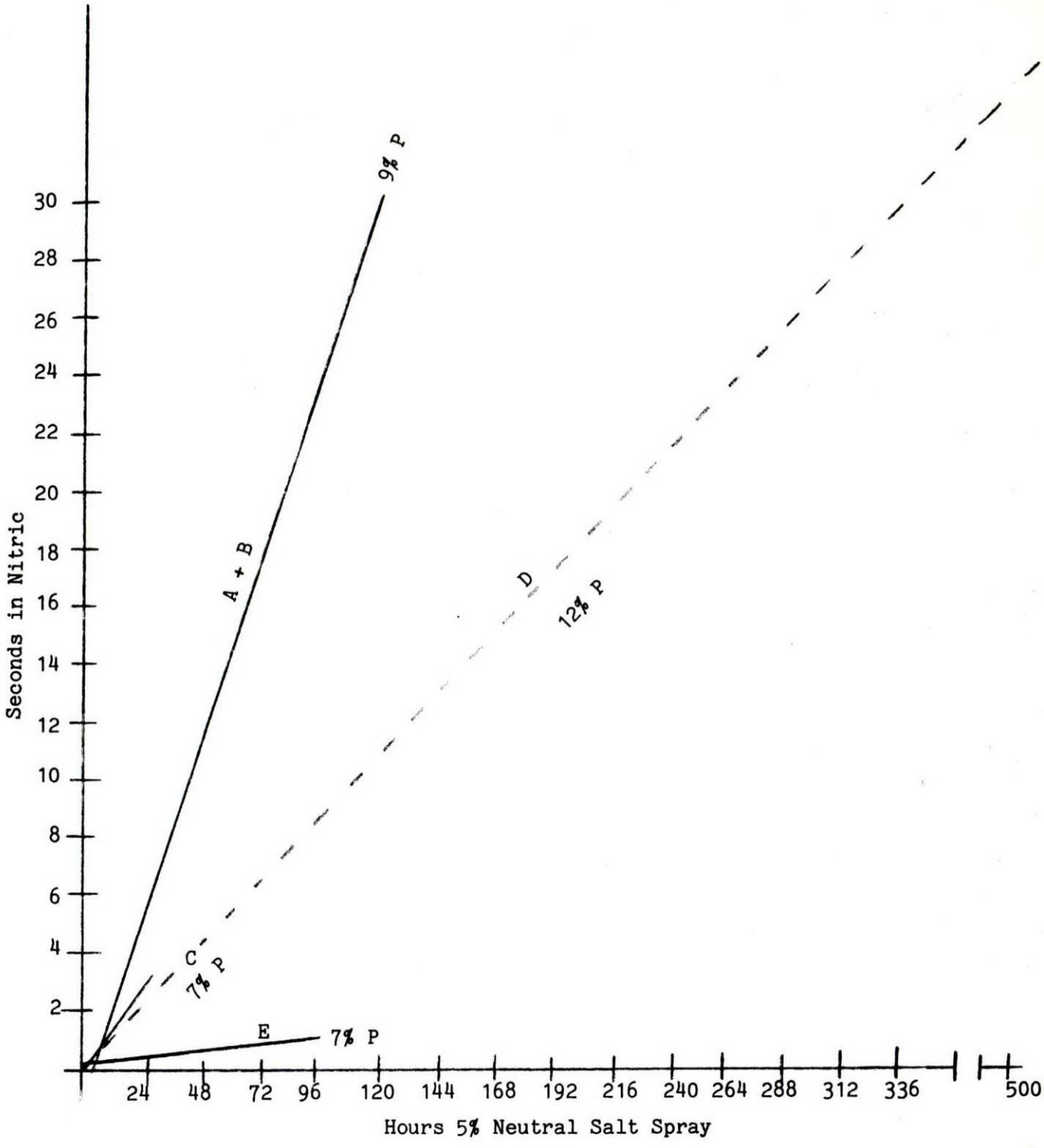
TABLE 2

BRASS

| Bath Type Brass | Hours 5% Neutral Salt Spray | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 24 | 48 | 72 | 96 | 120 | 144 | 168 | 192 | 216 | 240 | 264 | 288 | 500 |
| A | X | X | X | X | X | X | X | X | X | X | X | X | X |
| B | X | X | X | X | X | X | X | X | X | X | X | X | X |
| C | X | X | X | X | X | X | X | X | X | X | X | X | X |
| D | X | X | X | X | X | X | X | X | X | X | X | X | X |
| E | X | X | X | X | X | X | X | X | X | X | X | X | X |

Nitric Test/Seconds/Brass

| | 0 | 1 | 2 | 3 | 4 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | X | X | X | X | X | X | X | X | X | X | X | X |
| B | X | X | X | X | X | X | X | X | X | X | X | X |
| C | X | X | X | X | | | | | | | | |
| D | X | X | X | X | X | X | X | X | X | X | X | X |
| E | X | X | X | X | X | X | | | | | | |




GRAPH

SUMMATION OF TABLES 1 AND 2. GRAPH SHOWS OUTCOME OF STEEL SPECIMENS. SEE IN NITRIC VS. HOURS N.S.S.

R-2

# Electroless I
# Session R

## A Comparison of Analytical Methods for Percent Phosphorus Determination in Electroless Nickel Plate

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# A COMPARISON OF ANALYTICAL METHODS FOR PERCENT PHOSPHOROUS DETERMINATION IN ELECTROLESS NICKEL PLATE

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Operated by Union Carbide Corporation, Nuclear Division
for the U.S. Department of Energy
under Contract W-7405 eng 26

## Abstract

Electroless nickel plate characteristics are substantially influenced by percent phosphorous concentrations. Available ASTM analytical methods are designed for phosphorous concentrations of less than one percent compared to the 4.0 to 20.0% concentrations common in electroless nickel plate. A variety of analytical adaptations are applied through the industry resulting in poor data continuity. This paper presents a statistical comparison of five analytical methods and recommends accurate and precise procedures for use in percent phosphorous determinations in electroless nickel plate.

## Introduction

The physical characteristics of electroless nickel (EN) coatings make them suitable for the production of laser mirror surfaces. The plated surface, after machining using a diamond-tip tool, provides a highly reflective surface suitable for laser equipment.[1] A number of plate characteristics are critical to this application process. Among other properties these include: stress, thermal expansion and conductivity, hardness, ductility, tensile strength, and elasticity. All of these properties vary to some extent with the concentration of phosphorous in the EN plate. It is essential, then, to control the phosphorous concentration for maintaining plate properties within acceptable limits. In order to define and control phosphorous concentration levels in EN plate, it is necessary to have an accurate and precise method for analysis that will, with 95% confidence, determine percent phosphorous concentrations to within ± 0.5% of the true value. This provides the degree of control necessary for accurate plate property measurements.

A survey of the wide variety of methods used in the industry to determine percent phosphorous in EN plate indicated that there were variances in comparative test results between methods. A more extensive survey of industry and literature resulted in the selection for further evaluation of five analytical techniques currently in use or techniques that appear to

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have good potential for meeting precision requirements. This report presents the results of the evaluation of these five selected analytical methods for percent phosphorous determination and makes recommendations for the use of common methods to provide accurate and precise results in the field.

## Discussion

Electroless nickel (EN) plate is described in literature as an amorphous alloy of nickel and phosphorous.[2] Recent publications describe EN plate as having the structure of an amorphous solid with its atoms in disorder "like those of a liquid".[3] Phase diagrams of EN material indicate that nickel phosphides are present in the nickel metal matrix primarily as $Ni_2P$, $Ni_3P$, and $Ni_5P_2$.[3] The presence of a variety of nickel phosphides in unknown proportions prevents the theoretical calculation of percent phosphorous in EN plate which results in the need for accurate and precise analytical techniques to determine phosphorous concentration levels.

The need for reliable plate physical property data coupled with the confusing array of field test methods presently in use has lead to the evaluation of several analytical procedures for the determination of percent phosphorous in EN plate. Selection of the five analytical methods was based upon their potential for meeting the following set of criteria:

1. The test procedure must be applicable to percent phosphorous concentrations of 3.0 to 20.0%.

2. The test procedure should utilize accepted analytical methods, primarily ASTM based procedures.

3. The test procedure should have the potential for determining percent phosphorous within ± 0.5% of the true value at a 95% confidence level.

4. Test procedures, involving the conversion of phosphides to phosphates, must provide for complete oxidation to the phosphate state to prevent low side bias in the test. (Most test procedures require phosphate conversion which changes phosphorous from a -4 oxidation number in $Ni_2P$ to +5 in $PO_4^{\equiv}$.)

5. The test procedure should be practical and appropriate for use in most industrial and development laboratory facilities.

A number of sources for candidate test procedures were surveyed using the above criteria as a basis for selection. A review of ASTM test procedures was also conducted. Most of the ASTM test procedures were rejected because they were designed to measure phosphorous concentration in materials containing less than 1% phosphorous. Development groups, independent labs, proprietary bath chemical manufacturers, and reference materials were also surveyed. Of the five tests, three test methods, adapted from ASTM and analytical texts were found to be representative of activity in the field and were selected for evaluation.

I ASTM-E39 (75) Gravimetric Method.

This ASTM method was selected in its entirety for use as a test procedure based upon its indicated ability to measure phosphorous concentrations above 1%. ASTM-E39 provides for the determination of up to 99.9% nickel using the dimethylglyoxime gravimetric method.[4] The nickel concentration is subtracted from 100% to determine the percent phosphorous. Accuracy is dependent upon the proportion of trace elements in the plate. Although this approach to percent phosphorous determination is indirect, it was selected because of its repeatability of analytical results.

II Development Colorimetric Method.

This second test method was obtained from one of the leading plating consultants who was instrumental in the earlier development of EN plating. This method uses a colorimetric analysis technique based upon ASTM standard Practice E60 for low phosphorous concentrations.[4] This procedure has been used in the preparation of a significant number of published articles on electroless nickel.

III Independent Colorimetric Method.

The third procedure selected for evaluation was obtained from an independent commercial analytical laboratory that performs work for suppliers of electroless nickel plating chemicals among others. This colorimetric procedure was derived from ASTM-E156 (68)[4] and an analytical text.[5]

The final two test procedures evaluated were recommended by the Analytical Chemistry Department at the Oak Ridge Gaseous Diffusion Plant. They represent alternative test procedures to colorimetric based methods and provide more direct phosphorous concentration determination techniques than test method I.

IV UCC-ND Alkalimetric Method.

This method was designed by the Analytical Chemistry Department to meet the criteria established as evalutation guidelines and is based upon alkalimetric wet chemistry techniques. The procedure was derived from ASTM-E350 (81)[4] and an analytical chemistry text.[6] This method is outlined in Appendix A.

V UCC-ND Inductively Coupled Plasma (ICP) Method.

This fifth method was recommended by the Analytical Chemistry Department as an instrumental technique independent from the chemistries associated with the first four test methods being evaluated. The ICP method uses a high temperature flame to produce emitted light energy. Measurement of the emitted light allows identification and proportioning of elements present in the sample. This method does not meet the criterion of being appropriate to most industrial labs

because of the cost and availability of the instrument, but does have the advantage of not requiring changes in the oxidation state of phosphorous. The procedure was derived from published technical articles[7,8] and is outlined in Appendix B.

Procedure

The framework for evaluation of the five test methods was based upon direct data comparisons using a common sample solution for all tests. Application of statistical principles to the data from each test procedure provided the precision comparisons. Two solutions were used in the evaluation. The first was the common sample solution which was prepared by dissolving EN plate in a 50 vol % nitric acid solution and diluting to one liter. The solution was stirred before each individual test aliquote was removed. The second solution was used as a secondary check to establish the accuracy potentials of test methods IV and V due to their lack of previous field use. The second solution was prepared by dissolving nickel metal and potassium phosphate in the weight ratio of 90 wt % nickel to 10 wt % phosphorous. This solution would not be chemically representative of plate or of nickel phosphides but would provide a means of accurately measuring phosphates in solution. No National Bureau of Standards samples containing nickel phosphides were available resulting in the use of the second solution as an internal standard.

The Oak Ridge Gaseous Diffusion Plant Statistics Group designed the statistical test program. Individual data sheets were prepared for each test procedure. An example is given in Figure 1.

Figure 1

RAW DATA SHEET DESIGN

| Day | Date | Analyst | Sample | Data Columns | | | % P |
|---|---|---|---|---|---|---|---|
| 1 | | | 1 | | | | |
| | | | 2 | | | | |
| 2 | | | 1 | | | | |
| | | | 2 | | | | |
| 3 | | | 1 | | | | |
| | | | 2 | | | | |
| 4 | | | 1 | | | | |
| | | | 2 | | | | |
| 5 | | | 1 | | | | |
| | | | 2 | | | | |
| 6 | | | 1 | | | | |
| | | | 2 | | | | |
| 7 | | | 1 | | | | |
| | | | 2 | | | | |
| 8 | | | 1 | | | | |
| | | | 2 | | | | |
| 9 | | | 1 | | | | |
| | | | 2 | | | | |
| 10 | | | 1 | | | | |
| | | | 2 | | | | |

Ten days of testing were prepared for each procedure. Two separate and distinct test samples were scheduled each day. A total of twenty data points for each procedure was scheduled. The ten separate days of testing for each method allowed for reflection of normal technician, equipment, and environmental day-to-day variances in the data. Procedures were carefully defined, but no special supervision or instruction was made available to the experienced technicians doing the work to allow for normal worker variances. The percent phosphorous concentration in each sample was calculated by the statistics group and computer plots representing individual and composite test method results were provided.

## Conclusions

All values on the raw data sheets were obtained according to the program schedule except for two days in the ICP (Method V), due to scheduling problems, resulted in compressing four tests into each day. The data sheets are summarized in Table I. It should be noted that the data for day number six in the Independent Lab Colorimetric test (Method III) was disregarded due to colorimeter instrument problems that occurred. Analysis of the data summary in Table I indicates the concentration of phosphorous in the sample to be approximately 12.1%. All of the methods evaluated demonstrated the capability of determining percent phosphorous accurately through the accumulation of a large number of readings. The primary difference among the methods is the precision capabilities of individual tests.

Table I

DATA SUMMARY COMPARISON OF FIVE TEST PROCEDURES

| | I<br>ASTM-E39<br>Gravimetric | II<br>Development<br>Colorimetric | III<br>Independent Lab<br>Colorimetric | IV<br>UCC-ND<br>Alkalimetric | V<br>UCC-ND<br>ICP |
|---|---|---|---|---|---|
| N | 20 | 20 | 18* | 20 | 20 |
| $\bar{X}$ % P | 12.15 | 11.8 | 12.0 | 12.22 | 12.10 |
| Low % P | 12.00 | 9.5 | 10.6 | 11.95 | 12.08 |
| High % P | 12.37 | 13.1 | 12.9 | 12.56 | 12.13 |
| Range | 0.37 | 3.6 | 2.3 | 0.61 | 0.05 |
| $\alpha$ | 0.138% | 0.824% | 0.613% | 0.188% | 0.015% |
| $2\alpha$(95%) | 0.276% | 1.65% | 1.23% | 0.376% | 0.030% |

*Day 6 data not included.

Both the UCC-ND Alkalimetric (IV) and the UCC-ND ICP (V) procedures, having no previous field evaluation experience, were tested to verify their capability for accuracy in the determination of percent phosphorous. The solution containing dissolved nickel metal and potassium phosphate in the weight ratio of 90 wt % nickel to 10 wt % phosphorous was tested ten times using the UCC-ND Alkalimetric Method (IV). Test data indicated the average percent phosphorous in the standard solution was 10.1% ± 0.04% with a 95% confidence. A second check with the UCC-ND Alkalimetric Method (IV) was performed using a National Bureau of Standards cast iron standard No. 7G with a certified phosphorous value of 0.79%. The test result was 0.78% phosphorous. The standard solution was also tested using the UCC-ND ICP (V) procedure. Results indicated that the standard solution had a 10.0% phosphorous concentration. The above results agree well with the experimental data in establishing the accuracy of all five procedures within their individual precision limits.

The range and standard deviation values on all of the five methods are indicators of the precision capabilities of the procedures. The two colorimetric procedures (Methods II and III) are shown to be significantly less precise than the other methods. Any individual reading obtained for percent phosphorous using the Development Calorimetric Method (II) would be expressed with 95% confidence as that value ± 1.65%. The same percent phosphorous value using the Independent Lab Colorimetric Method (III) would be expressed with 95% confidence as that value ± 1.23%.

The UCC-ND Alkalimetric (IV) and ASTM-E39 Gravimetric (I) procedures are shown to be significantly more precise than either of the two colorimetric methods. Sample size, precision in obtaining readings in terms of significant figures, and the geometric position of sample tubes in the colorimeter are some of the factors influencing comparative precision of the methods. At a 95% confidence level any individual reading from the ASTM-E39 Gravimetric Method (I) would be expressed as that value ± 0.28%. Likewise, the same individual reading using the UCC-ND Alkalimetric Method (IV) would be expressed with 95% confidence as that value ± 0.38% phosphorous. Both the ASTM-E39 Gravimetric Method (I) and the UCC-ND Alkalimetric Method (IV) provide the level of precision required to establish percent phosphorous values to within ± 0.5% of the true concentration.

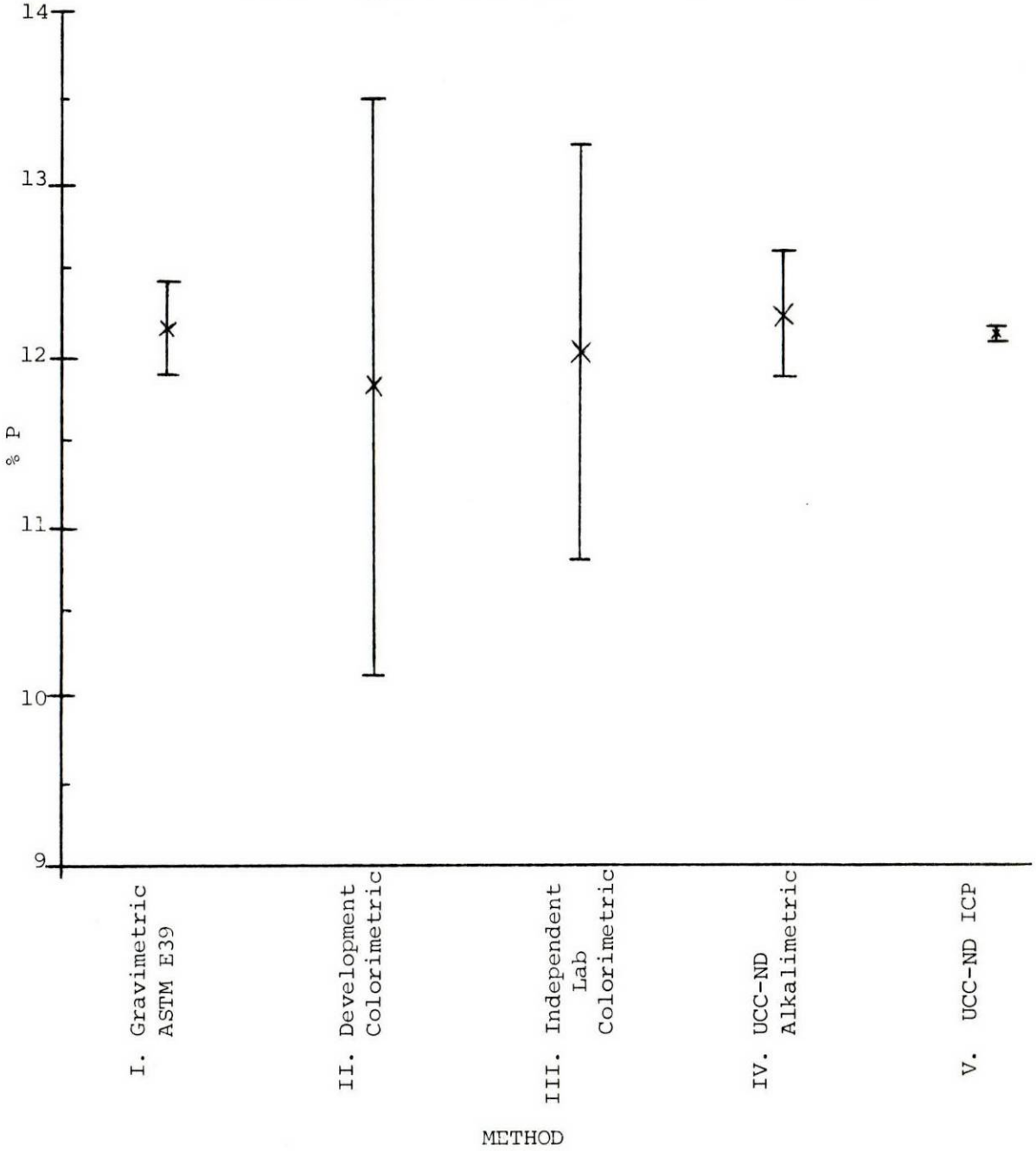
The UCC-ND ICP Method (V) produced an even greater degree of precision as indicated by the small range of data and the very small standard deviation value. Any individual reading obtained using the ICP Method would be expressed as that value ± 0.03% with 95% confidence. The ICP Method is shown as the superior test method; however, the major drawback in its use results from the expense of the equipment involved and its availability in most laboratories.

A plot comparing average values and 95% confidence standard deviation values for all five procedures is shown in Figure 2. The plot shows the comparative precision capabilities of the five test procedures. The UCC-ND Alkalimetric (IV) and ASTM-E39 Gravimetric (I) test procedures meet all criteria for acceptance as acceptable methods for determination of percent

phosphorous concentrations. These methods are precise enough for most applications; however, they are more time consuming to perform than the other three. The least recommended methods of the five are the two colorimetric methods due to their low degree of precision.

Figure 2

COMPARISON OF 95% CONFIDENCE LIMITS ON THE TRUE MEAN FOR ONE INDIVIDUAL MEASUREMENT (n = 1)



References


1. Casstevens, J. M., and Daugherty, C. E.; SPIE, Vol 159, "Precision Machining of Optics," 109 (1978).

2. ASTM Publication No. 265, "Symposium on Electroless Nickel Plating," ASTM, Philadelphia, Pennsylvania, (1959).

3. Gawrilov, G. G.; "Chemical (Electroless) Nickel Plating," Portcullis Press LTD; Surrey, England (1979).

4. ASTM Annual Book of Standards, Part 12, ASTM, Philadelphia, Pennsylvania. (1981).

5. Boltz, D. F.; "Colorimetric Determination of Nonmetals," Interscience Publishers, Inc., New York, New York (1958).

6. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., Hoffman, J. I.; "Applied Inorganic Analysis," pp. 706-708, John Wiley & Sons, Inc., New York, New York (1953).

7. Fassel, V. A.; Anal. Chem., 51,1290A (1979).

8. Floyd, M. A., Fassel, V. A., Winge, R. K., Katzenberger, J. M., and D'Silva, A. P.; Anal. Chem., 52,431 (1980).

Appendix A

UCC-ND ALKALIMETRIC METHOD (IV)

Analysis of Phosphorous in Electroless Nickel Plate

The principal steps in the analysis of phosphorous (3% to 20%) in electroless nickel plate, as developed by the Inorganic Analysis group of the Analytical Chemistry Department, Oak Ridge Gaseous Diffusion Plant, Union Carbide Corporation, Nuclear Division, is as follows:

1. Weigh approximately 0.1 to 0.3 g of the sample to the nearest 0.1 mg into a 400 ml beaker.

2. Add 20 ml of distilled water, 10 ml of concentrated nitric acid, and 20 ml of perchloric acid and fume to near dryness.

3. Cool and dilute to about 100 ml with distilled water.

4. With constant stirring, add in order 25 ml concentrated nitric acid, 40 ml of 23 vol % ammonium hydroxide, (4 parts concentrated $NH_4OH$ to six parts distilled $H_2O$) and 100 ml of 3 wt % ammonium molybdate.

5. Continue stirring intermittently for 30 min, adding filter pulp toward the end.

6. Let settle for at least 2 hr and filter the precipitate through Whatman No. 42 filter paper.

7. Rinse the beaker with 1 wt % potassium nitrate and filter.

8. Wash the precipitate on the filter paper with 1% potassium nitrate until the filtrate is free of acid (about 10 times).

9. Transfer the precipitate along with the filter paper to the original beaker rinsing with distilled water and dilute to about 150 ml.

10. Add 0.5N NaOH until all the yellow color has disappeared plus a small excess.

11. Titrate the excess NaOH with 0.5 N HCl to a phenolphthalein end point.

Calculation:

$$\%P = \frac{[(\text{ml of NaOH} \times \text{N of NaOH}) - (\text{ml HCl} \times \text{N HCL})] \times .031/23 \times 100}{\text{wt of sample (g)}}$$

Appendix B

UCC-ND ICP METHOD (V)

ICP Analysis of Phosphorous in Electroless Nickel Plate

The experimental facilities and operating conditions utilized in this work are summarized in Table I and a block diagram of the analytical system is illustrated in Figure 1 of this appendix. The programmable scanning monochromator used in this work is based on a similar scanning monochromator system described by Floyd, et al.[1]

Reagents

Reference solutions of P and Ni were prepared by the incremental addition of commercial stock solutions (Fisher Scientific Company) to an appropriate blank solution of deionized water. A complete set of reference solutions was prepared that provided multielement calibrations throughout specified analytical ranges. Each reference solution was confined to only one concentration level of the analyte elements (Ni and P) so that any cross contamination due to impurities in the stock solutions was insignificant.

Analytical Calibrations

Analytical calibration curves were generated by measuring the net relative intensities of the 231.6 nm Ni and 253.6 nm P analysis lines emitted when synthetic reference solutions were run under the conditions defined in Table I. The analytical calibration curves, plotted on a log I vs log C coordinates, can be observed directly on the video terminal upon completion of the calibration routine, thus, providing the operator with an immediate visual check of the shape of the curve and the fit of the data points.

Figure 1

BLOCK DIAGRAM OF THE COMPUTER CONTROLLED SCANNING MONOCHROMATOR SYSTEM

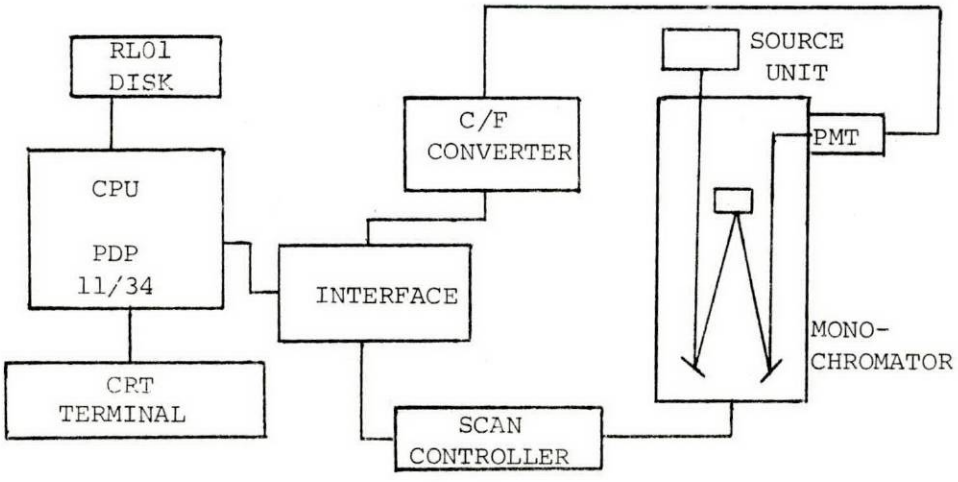


Table I

EXPERIMENTAL FACILITIES AND OPERATING CONDITIONS

| | |
|---|---|
| Monochromator | McPherson Model 2051, 1 m focal length. 1800 g/mm holographic grating, "range of optimum efficiency" 200-700 nm. Entrance and exit slit widths were 10 um. |
| Plasma | |
| RF generator | Plasma-Therm Type HFP 2500D, 27.12 MHz. |
| Incident Power | 2000 W. |
| Reflected power | 5 W. |
| Plasma air flow | 18 l/min. |
| Aux plasma flow rate | 1 l/min used only for starting plasma, otherwise this flow is turned off for normal operation. |
| Vertical observation zone | Zone height of 4 mm centered at 15 mm above the load coil. |
| Nebulizer | Ultrasonic nebulizer with desolvation as described by Olson, et al. Operated at 1.4 MHz. |
| Aerosol carrier air flow rate | 1 l/min. |
| Sample uptake rate | 3 ml/min. |
| Data Acquisition System | |
| Scan controller | McPherson Model 786-A |
| A/D converter | Analog Technology Corp. Model 151 current to frequency converter. |
| Computer | Digital Equipment Corp. PDP 11/34 minicomputer with 128K memory and dual drive RL01 hard disk. |
| Interface | Designed and constructed by Ames Laboratory, Iowa State University. |
| Intergration period | 3.0 sec/data point. |

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# Electroless I
# Session R

## Wear Mechanisms of Chemically Reduced Nickel Phosphorus Alloys

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# Wear Mechanisms of Chemically Reduced Nickel Phosphorus Alloys

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Electroless Nickel Deposits have been used in wear service for over 35 years. Typical service conditions include pump housings, ball valves, print rollers, hydraulic cylinders, electronics parts, connectors, memory discs, artillary parts, and many other applications.

Electroless Nickel provides these applications with a means of protecting the base material (substrate) with a thin, hard amorphous nickel. The qualities of corrosion resistance, uniformity, lubricity, hardness, and low stress all come together to provide an excellent bearing and wear surface for a wide number of applications.

This paper covers the wear mechanism, and mechanical testing of wear for the evaluation of the electroless nickel deposit.

Wear is a general term to describe the mechanical loss of material on a surface. There are many types of wear and nearly 200 specific wear tests, making for a complex evaluation of many applications. We have divided wear into four categories which can be combined to define most wear situations.

## FRETTING WEAR

This type of wear is produced when the surface is mechanically deformed causing material to be fractured and removed. A recent application which required electroless nickel to eliminate fretting was the Diesel Valve Spring Retainers on locomotive engines. As the springs and valve stems moved the retainer clips, made of hardened RC 35 steel exhibited fretting, causing movement and wear debris on the valve stem. To eliminate this fretting .0003 inches of electroless nickel was applied with a 375 (F) 1 hr bake for hydrogen embrittlement release. The retainers now show no sign of fretting wear at overhaul.

Fretting wear generally occurs when there is small movement at high loads. This type of wear can be simulated by ball and block, and pin and notch blocks with loads in excess of 1000 lbs. with oscillatory motion.

The development of a standard test method for testing of fretting wear of electroless nickel has not been proposed nor are there any reference of individuals testing for fretting wear of the deposit. This area requires further study and will be the subject of further investigation by us.

## ADHESION WEAR

This type of wear is the most common in metal to metal wear situations. Adhesive wear is produced when microwelds cause the material interface to join and the adhesive failure of the coating or wearing material occurs below the weld. The structure of the alloy and morphology of the deposit is important in determining the degree of adhesion failure and the wear performance of the coating.

Adhesion wear is produced on cams journals and high load surfaces of similar materials. In these applications any lubrication failure will generally cause immediate catistrophic failure of the bearing surface. For many years electroless nickel has been providing the lubricity and hardness at the interface to significantly reduce the adhesion wear and improve the service of the plated article.

Adhesion wear can be evaluated by using ring and block type test LFW1 and run lubricated or dry. Analysis of the friction and wear scar with weight loss correlation can be used to describe the dynamics of the matting surfaces.

There are several ways to describe adhesion wear; weight loss of ring and block, wear scar lengths and depths, volume of wear debris, relative to coefficient of friction, hardness, and heat-treatment. Other factors which play an important factor are the type of lubricant used, load, surface finish, speed, and acceleration at start.

## WEAR MODEL

To describe the wear taking place at the interface of ring and block wear test the following formulas are commonly used:

### Volume Ring Loss

$$Vr = W \times \pi \times [r(i)^2 - r(f)^2]$$

W = width of ring
r(i) = radius ring initial
r(f) = radius ring final

### Volume Block Loss

$$Vb = W \times [(r(i))^2 \cos^{-1} r(f)/r(i) - r(f) \times [2r(f) \times (r(i) - r(f)) - (r(i) - r(f))^2]^{1/2}]$$

$$Ls = 2[(r(i))^2 - (r(f))^2]^{1/2}$$

W = width of scar
r(i) = radius ring initial
r(f) = radius ring final
Ls = Scar length

Note: The above calculations are made in radian measurement and require radius measurement before and after test runs.

Many studies have been performed on electroless nickel deposits
r adhesive wear using these formulas or variations of them. Measure-
nts are generally taken on the scar length rather than the change
radii due to the accuracy of the measurement.

The correlation of weight loss, density measurements and
ar dimension make the assumption that the scar is uniform and that
ar debris does not build on the trailing edge.

In most experiments profilometer analysis have been run at
gular intervals. This data can then be used to compute the exact
lume of material lost and produce a much more accurate evaluation. (1)

This wear testing of electroless nickel on a continuous basis
ing the LFW-1 Design by the NBS (National Bureau of Standards) shows
at a 5% P 890 (HK 500) electroless nickel (HAC formulation) wears
a rate of 0.07 x 10^-4 mm3/m while a chrome deposit with a hardness
(HK 500) wear at 0.18 x 10^-4 mm3/m. Note: These units take into
fect the linear wear for the duration of the test. These tests
re run dry and revealed a coefficient of friction of 0.77 for the
ectroless nickel against electroless nickel and hardchrome
ainst hardchrome was 1.02. (2)

Other LFW-1 tests confirm that the minimum wear and lowest
efficient of friction is obtained with coatings which have a hardness
890 (HV100). With lubricated plated blocks 890 (HV100) 540C/1 hr.
ar is about 2 mg/5000 cycles while ring wear is 0.7 mg. With
bricated plated blocks 890 (HV100) 400C/1 hr. with a hardness of
60 (HV100) the ring wear is negligible with wear debris building up
the block. In these tests electroless nickel is running against steel
th final a coefficient of friction for as-plated and heat-treated 0.12. (3)

When precipitation is continued to recrystalize the wear on
e ring will increase to 5 to 10 mg/25000 cycles and the block will
ill collect debris with minimal wear.

Constraints which are important in these evaluations are the
eed of the ring, the loading force on the block, the type of lubricant,
mperature of the test, surface condition, and the starting conditions.

## ABRASION WEAR

This type of wear is produced when solids are cut from the
face. Abrasion wear is produced when paper, textiles, debris,
pass over the wearing surface and cut into the substrate,
oving material.

Electroless nickel has been applied to print rollers, copier
d mechanisms, textile equipment and many other similar applications
significantly reduce the abrasive wear and extend the service of the
ted article.

Abrasive wear can be evaluated by abrasive wheels that run over a wear critical surface. This test can be useful in evaluating the general abrasion performance of materials.

A recent Round Robin with ASTM B 08.08 has produced a test method which has reasonable laboratory correlation. Using a Taber Abrader with CS10 wheels and redressing the wheels after each 1000 cycles for 50 cycles and analyzing for weight loss produced reasonable data between three labs while the fourth was low. (see Appendix)

The reason for these variations especially on the as-plated deposit wear has been discussed by those working on the project. It has been assumed that the lower humidity in the laboratory in Tucson and the subseqent increase in static charge on the wheel produced the variation. It is presumed that the vacuum was unable to remove wear debris on the wheels producing a bearing and making the appearance of less abrasive wea

Typical abrasive wear values for electroless nickel range from between 2.5 mg/1000 cycles to 30 mg/1000 cycles. Hardness, and deposit morphology are important in the abrasion wear mechanism with a 5% P, 920 (HV100), 400 C/1 hr. deposit wearing at 9 mg/1000 cycles and as plated 5% P wearing at 18 mg/1000 cycles. Obtaining very low abrasion wear values less than 4 mg/1000 cycles are accomplished by heat-treatments in excess of 650 (C) for one hour.

## EROSION WEAR

This type of wear is the most complex of the four. It involves the movement of liquids, solids, and gasses near or on the surface producing micro failure and abrasion eventually causing macro amounts of material to be removed.

In order to describe the erosion phenomenon, we will break this subject down into the different mechanical phases.

### SINGLE PHASE

This is the type of erosion where a liquid or gas is directed toward a surface, the eroding material being free of all other phases. A liquid flow in an elbow or pipe which is solid and gas free or a gas flow in an elbow or pipe void of solid and liquid would be a single phase wear system. In actual service, this type of wear phase may be impossible to obtain.

### MULTI PHASE LIQUID-GAS

This type of wear can be tested by degassing and filtering a neutral solution of dionized water and directing through a venturi and across a surface under test. This venturi device provides the means of converting kinetic head into static pressure, causing the vapor pressure to be equal to the static pressure causing cavitation. This test represents a means of modeling the general flow regimes of a hydraulic system Constraints which control this model include flow rate, temperature, head pressure, and venturi dynamics. (4)

The mechanism of wear for this test is produced by the formation of cavitation bubble ahead of the specimen and their subsequent decay and micro implosion causing removal of the electroless nickel deposit. Since the surface of an electroless nickel deposit is protected by by an oxide film, cavitation is far more critical in corrosion services.

Results from the venturi testing shows that regions along the erosion specimen receive various degrees of wear based on vortex and static pressure drop across the surface. Microscopic examination of the specimen can be used to evaluate the location and depth of the erosion wear.

MULTI PHASE SOLID-LIQUID-GAS

This type erosion wear is more complex and the development of a standard test does not seem likely. Constraints like solid particle size and structure, velocity and impingement angle, and corrosive nature of the liquid all control the total erosion process.

The venturi device used to test liquid gas systems can also be used to test for solid-liquid-gas wear. A sand of 200 um to 300 um diameter is slurred at 20 gm/min into the flow which is directed towards the specimen. Wear is then evaluated by microscopical examination for location and depth of wear for given velocity and impingement angle.

## SUMMARY

Electroless nickel deposits will continue to find new wear applications. The development of standard test methods for plated coatings, and expecially electroless nickel will be require the industry to classify the main types of wear. The abrasion wear test method is being studied in ASTM and will most likely be adopted. Other specific wear tests will need to be investigated and inter-laboratory studies will be required before valid comparisons between electroless nickel deposits can be made.

Wear testing is a good means of classifying wear performance between electroless nickel and other coatings under test. Actual wear performance is dependent on many factors. A laboratory model in some instances is not able to predict the true wear found in a specific application. A periodic inspection of the wearing surface is always recommended along with documentation of case histories to provide the most reliable means of identifying wear performance.

## FOOTNOTES

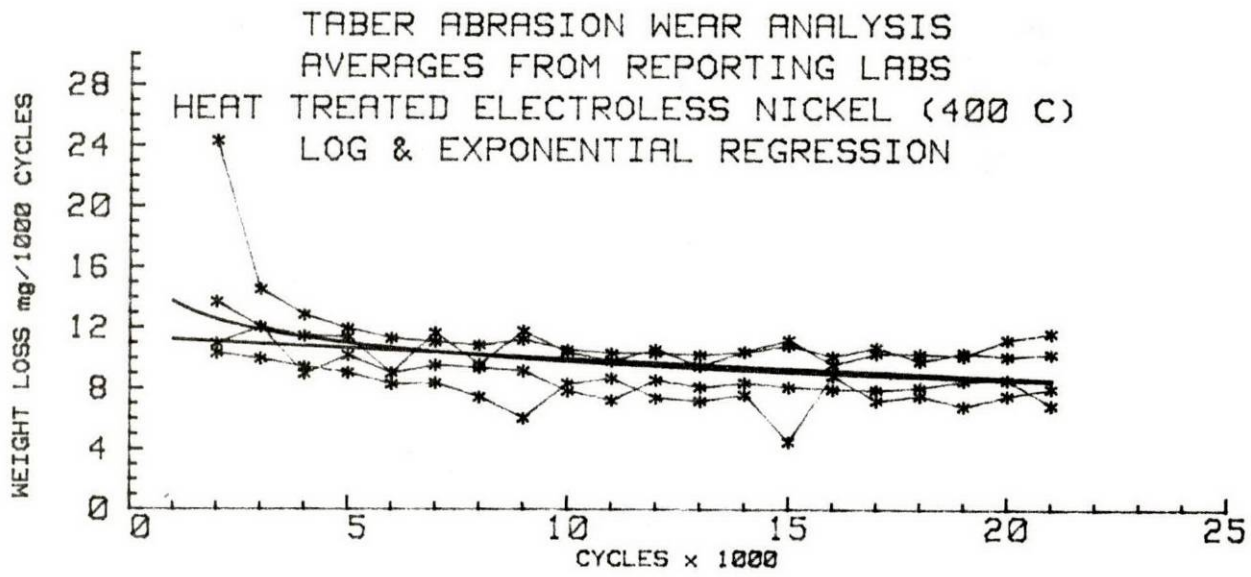

(1) Tucker, R.C. and Miller, A.E., Low Stress Abrasion and Adhesion West Testing, ASTM STP 615 pp 76-89

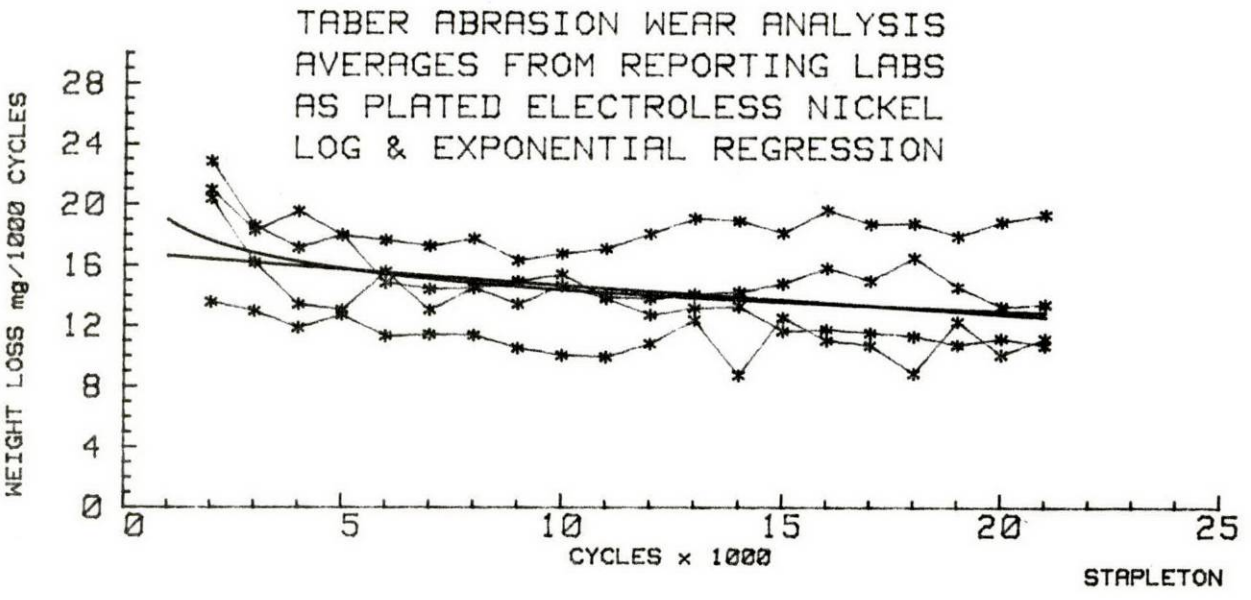
(2) Ruff, A.W., Lashmore, D.S., Dry Sliding Wear Studies of NiP and Cr coatings on 02 Tool Steel, G2 Wear Symposium, Phoenix, AZ December 9, 1981

(3) Parker, K., Hardness and Wear Resistance Test of Electroless Nickel Deposits, AES Technical Conference, Chicago, IL June 18, 1974

(4) Boetcher, H.N, Transactions, ASME Volume 59, 1936 pp 355-360


## APPENDIX



# APPENDIX

## ABRASION WEAR TEST METHOD

ABRASION WEAR - The abrasion wear resistance of the deposit can be determined by the use of a TABER WEAR ABRADER. The results are reported in mg/1000 revolutions weight loss with typical values between 18 and 25 for as plated and as low as 2 for heat-treated electroless nickel deposits.

## APPARATUS:

1 TABER ABRASION WEAR TESTING UNIT - Unit must be capable of loading with 1000 gm load and operate with a vacuum.

2 ABRASION WHEELS - Use CS-10 (Resilient Rubber) wheels from TABER. To reface the CS-10 wheels use S-11 discs.

3 TEST SPECIMENS - Test Specimens shall be made from 20 gage CR steel 4 in. X 4 in. (100mm X 100mm X 1.3mm) with a 1/4 in. (6.35mm) diameter hole in the center.

4 ANALYTICAL BALANCE - Scale 0 to 150 gm (+/- 0.1 mg)

## PROCEDURE:

1 Plate the specimen with 0.001 in. (25 um) of electroless nickel.

2 Heat-treat the specimen with the article requiring abrasion wear. The time and temperature of the heat-treatment are important factors controlling the wear quality of the deposit.

3 Dress the CS-10 Wheels on the deposit under a 1000 gm load for 1000 cycles to remove any surface roughness and grain dimples.

4 Brush the specimen lightly and wipe with dry soft cloth. Wash in ultrasonic for 5 minutes using Freon TF or MEK. Dry and weigh the specimen and record the weight loss.

5 Dress the wheel for 50 cycles with a S-11 disc prior to each 1000 wear test cycles.

6 Abrade the specimen for 1000 cycles using a CS-10 wheel with a 1000 gm load.

7 Repeat steps 4, 5, and 6 for 21000 cycles.

R-4

# Electroless I
# Session R

## Particle-Enhanced Electroless Coatings for High-Temperature Environments

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# PARTICLE ENHANCED ELECTROLESS COATINGS FOR HIGH TEMPERATURE ENVIRONMENTS

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## Introduction

The concept of producing particle enhanced electroless coatings was demonstrated in the early to mid-70's and commercialized during the latter part of the 70's (1, 2, 3, 4). Using discrete hard particles, current commercial applications rely on the nickel phosphorus matrix with silicon carbide particles and to a lesser extent, synthetic diamond particles (5). These coatings find use in environments requiring a surface to have both abrasion and corrosion resistance. Specific uses include plastic injection molding tooling, foundry patterns, and textile equipment components (5, 6, 7, 8). Many potential industrial applications exist which could utilize their corrosion resistance, cost-effectiveness, and non-line-of-sight feature of electroless deposition, if the coating could be modified to operate at elevated temperature. We, therefore, sought to explore and characterize particle enhanced electroless coatings which might have potential for performing in hostile high temperature environments. This presentation describes preliminary efforts undertaken at EC Technologies.

## Technical Program

Three matrixes were selected for this study: a nickel-9% phosphorus which would be produced using a standard sodium hypophosphite reduction, a nickel-5% boron using diethylamine borane reduction, and a cobalt-2% boron using dimethylamine borane reduction. The nickel-phosphorus alloy, suitably modified, should be useful for long term service at operating temperatures up to 1000 F (538 C). The boron bearing species should have useful properties up to 1500 F (816 C).

Two to six micron size particles of aluminum oxide, calcium fluoride, chromium oxide, silicon carbide and boron carbide were chosen for incorporation into the coating matrixes. The latter two species were to serve as base lines for reference. Alumina is a hard, inert particle which would have extreme stability at intended operating temperatures of these coating systems. Calcium fluoride is an inert, soft particle having a low coefficient of sliding friction, and was intended to act as a high temperature lubricant in these systems. Chromium oxide is a particle known to have a low coefficient of sliding friction, and thus was included in the study. Chromium oxide has also been known to decompose and interact with the coating surface and therefore might also prove to be an effective means of modifying the surface oxide scale of these coatings at elevated temperature.

AISI 304 stainless steel substrate was selected to avoid potential phase changes which would occur using a conventional mild steel during the elevated

temperature testing program. Table I details the combinations of materials tested. In general, a nickel strike method was used to activate the stainless steel prior to coating. Deposition parameters were adjusted to produce approximately a 0.002 in. (50 um) thick coating. Particle loading in the process solution was adjusted to produce approximately a 20 - 30 v % content in the deposited coating. Post-plating heat treatments were conducted at 650 F (343 C) for 2 hours to fully harden the coating. Testing for this program is divided into two sections: microstructural examination and wear/friction testing assessment. The reference nickel phosphorus coatings with the silicon carbide and boron carbide particles were examined microstructurally after heat treating at 650 F (343 C) and after an additional 1000 F (538 C), 1 hour exposure. Remaining test coatings were examined after testing at 1000 F (538 C) or 1500 F (810 C).

Wear testing consisted of using an MT-1 pin and plate friction wear tester. This machine utilizes test specimens of simple geometry and offers elevated temperature testing capability.

In brief, a 0.375 diameter pin is slid over a flat plate (Figure 1). Stroke length is set at 1 in. (25.4 mm), stroke frequency set at 1 cycle per second and the load on the pin adjusted to 32 lbs (14.54 kg). Test duration was 120 minutes and was preceded by a soak of 15 minutes at each testing temperature. Measurements included coefficient of friction and an assessment of the extent of damage in the wear track. Table I details the experimental plan.

## Results and Discussion

### 1. Microstructure and General Examination

Microstructures of the deposited and heat treated coatings were as expected. Particle enhanced coatings contained approximately 20-30% by volume of particles having a uniform distribution throughout the coating thickness.

Particle size distribution in the coatings reflects the size distribution of the particles used to make up the coating bath. Bath loadings in case of dual particles were adjusted to give approximately 15% by volume of each species used.

Mean particle diameter was 1 - 5 microns, but the calcium fluoride had a significant number of larger flakes. Silicon carbide had a more uniform size distribution than the alumina particles.

Figure 2 presents typical microstructures of the nickel phosphorus matrix coatings while figure 3 portrays the boron bearing coatings.

Exposure to 1000 F (538 C) demonstrated the instability of both silicon carbide and boron carbide in the presence of phosphorus. Under normal circumstances, one would not expect the materials to react with the matrix. It is possible that the relatively high energy state of the coating matrix, coupled with the presence of phosphorus, allowed both the solid state interface reaction to proceed and permitted significant diffusion of boron and carbon.

Metallic oxides or fluorides did not readily decompose, and this made them the prime candidates for further evaluations.

Micrographs generally confirmed that all coatings designated for wear testing, with the exception of the nickel boron systems, had approximately 0.002 in.(50 micron) deposit. The dimethylamine borane reduced nickel systems had 0.0004 in. (10 micron) to 0.0014 in. (36 micron) deposits due to the slower plating rate of these systems. Rather than extend the in-tank plating time for these preliminary evaluations, we elected to assess the performance of the thin coatings. The dimethylamine borane reduced cobalt coatings were produced using a different formulation and had significantly higher plating rates.

2. Room Temperature Testing

The short-time self-mated reference test (Table II) for the nickel-phosphorus silicon carbide particle enhanced system had significantly higher coefficient of sliding friction than did any other combination tested. Although adhesive wear resistance of silicon carbide has been shown to be excellent, the abrasive nature of the fine silicon carbide can cause some surface damage when operated under dry rubbing conditions. In this particular test definite wear track damage occurred (Table III). Nevertheless, perceived wear track damage is a function of the type of test. Cross-cylinder wear tests performed at EC Technologies demonstrated entirely different performance of this coating system.

Substitution of alumina for silicon carbide substantially reduced the coefficient of sliding friction and caused a net polishing effect to occur during the test. Similar results were observed with calcium fluoride and chromium oxide particles. Chromium oxide additions initially produced the smoothest as-deposited surface, but equivalent polishing was obtained from both samples. Coefficients of sliding friction were lowest for the calcium fluoride and chromium oxide species. Adding calcium fluoride along with alumina improved the polishing action and produced lower coefficients of sliding friction (Figure 4).

Direct semi-quantitative assessment of wear was attempted from cross-section micrographs of pins and plates for each species. Table IV summarizes these results, measured from 100X magnification microphotographs. Worst case measurements were used rather than average numbers.

The test coatings at room temperature exhibited little wear, and structures were quite uniform (Figure 5).

3. Testing at 1000 F (538 C) and 1500 F (816 C)

The nickel phosphorus matrix coatings exhibited different behavior at 1000 F (538 C). Coefficients of sliding friction were somewhat lower than at room temperature (Table II), but wear track damage was significant, as shown in Table III and illustrated in Figure 5. Although the coatings have not failed, some scoring has occurred. This could be due to additional softening of the nickel phosphorus matrix from localized friction heating or to break-

down of surface layer oxide creating more wear track debris. A further test has begun to assess different particles as well as particle volume fraction and particle size distribution on wear performance.

The borane reduced nickel systems exhibited behavior comparable to the hypophosphite reduced systems. Initial surface finish of the nickel boron systems was inferior to the nickel phosphorus systems, which led to more wear track damage. The alumina enhanced system failed at 1000 F (538 C), but was intact after 1500 F (816 C) exposure. Wear track grooves penetrated the coating. The chromium oxide enhanced nickel boron system withstood the 1000 F (538 C) exposure, but failed prior to completing the 1500 F (816 C) test. We note that coating thickness was substantially less than the nickel phosphorus systems.

Entrapped gas from the plating process not properly diffused from the cobalt samples resulted in premature failure at both temperatures. Comparing the coefficient of friction measured at 1500 F (816 C) between the nickel boron system (0.35) with the cobalt boron system (0.42) suggests that the 0.0005 in. (12 micron) nickel base coatings were still influencing the wear behavior after 30 minutes.

The preliminary wear performance results of the three borane reduced coatings is surprising since both the matrix and the particles were expected to be stable under these test conditions. A subsequent screening will be conducted to determine effects of particle chemistry, size distribution, and post-coating heat treatment on wear and friction performance, in an attempt to more closely define the metallurgical interactions that are occurring at these extreme temperatures.

In summary, of the various coating combinations, the calcium fluoride and chromium oxide enhanced nickel phosphorus coatings gave the most consistent performance through 1000 F (538 C). The nickel boron alumina system shows some promise for higher operating temperatures.

## Conclusions

Boron and silicon carbides are unstable in the presence of a nickel-phosphorus alloy matrix at elevated temperatures.

Alumina, calcium fluoride, and chromium oxide particle enhanced electroless nickel coatings survived testing at 1000 F (538 C).

Alumina or chromium oxide particle enhanced coatings reduced by dimethylamine borane did not exhibit markedly different wear characteristics from the sodium hypophosphite reduced nickel systems.

The alumina enhanced nickel boron species showed some potential for higher temperature performance.

The dimethylamine borane reduced cobalt coating did not perform well under these test conditions, possibly due to improper heat treating.

Plans for further characterization of high temperature wear performance focus on particle chemistry, particle size, volume fraction, and post-coating heat treatments.

TABLE I

High Temperature Test Program

| Coating Pin-Plate | Test Temperature RT | 1000 F (538 C) | 1500 F (816 C) |
|---|---|---|---|
| NiP+SiC | T | Heat treat only | |
| NiP+$B_4C$ | | Heat treat only | |
| NiP + $Al_2O_3$ | T | T | |
| NiP+$CaF_2$ | T | T | |
| NiP+$Al_2O_3$+$CaF_2$ | T | T | |
| NiP+$Cr_2O_3$ | T | T | |
| NiB+$Al_2O_3$ | | T | T |
| NiB+$Cr_2O_3$ | | T | T |
| CoB+$Cr_2O_3$ | | T | T |

Substrate: 304 SST except mild steel for NiP + SiC.

Coating Thickness: 0.002 in. (50 micron) except 0.0004 in. (10 micron) and .0014 in. (36 micron) for NiB coatings.

Heat Treat: 650 F (343 C) for 2 hours.

TABLE II

PIN AND PLATE FRICTION TEST RESULTS

| Coating Pin - Plate | Coefficient of Friction Room Temp 0 min | 30 min | 120 min | 1000 F (538 C) 0 min | 30 min | 120 min | 1500 F (816 C) 0 min | 30 min | 120 min |
|---|---|---|---|---|---|---|---|---|---|
| NiP + SiC | .46 (10 minute test on mild steel substrate) | | | | | | | | |
| NiP + $Al_2O_3$ | .28 | .38 | .38 | .23 | .23 | .25 | | | |
| NiP + $CaF_2$ | .28 | .32 | .32 | .28 | .23 | .28 | | | |
| NiP + $Al_2O_3$ + $CaF_2$ | .28 | .32 | .32 | .23 | .28 | .28 | | | |
| NiP + $Cr_2O_3$ | .28 | .32 | .32 | .20 | .28 | .28 | | | |
| NiB + $Al_2O_3$ (1) | | | | .30 | .35 | .35 | .30 | .35 | .38 |
| NiB + $Cr_2O_3$ (2) | | | | .28 | .33 | .34 | .30 | .35 | - |
| CoB + $Cr_2O_3$ (3) | | | | .28 | .30 | - | .30 | .42 | - |

Notes

Pin Load: 32 lb (14.54 kg)

Length of Stroke: 1 inch (1.54 cm)

Frequency: 1 cycle per second

Specimens soaked 15 min. at temperature prior to testing.

(1) Coating failed prior to completion of test at 1000 F (538 C).

(2) Coating failed prior to completion of test at 1500 F (816 C).

(3) Coating failed prior to completion of test at 1000 F (538 C) and 1500 F (815 C).

TABLE III

SURFACE DAMAGE ASSESSMENT

| Coating | Surface Roughness (Microinches CLA) Room Temp Before Test | Room Temp After Test | 1000 F (538 C) Before Test | 1000 F (538 C) After Test | 1500 F (816 C) Before Test | 1500 F (816 C) After Test |
|---|---|---|---|---|---|---|
| NiP + SiC | 22 | 350 (10 min test on mild steel substrate) | | | | |
| NiP + $Al_2O_3$ | 40 | 30 | 40 | 240 | | |
| NiP + $CaF_2$ | 20 | 11 | 20 | 250 | | |
| NiP + $Al_2O_3$ + $CaF_2$ | 28 | 12 | 28 | 260 | | |
| NiP + $Cr_2O_3$ | 15 | 11 | 15 | 270 | | |
| NiB + $Al_2O_3$ (1) | | | 50 | 300 | 55 | 350 |
| NiB + $Cr_2O_3$ (2) | | | 55 | 260 | 53 | >400 |
| CoB + $Cr_2O_3$ (3) | | | 70 | >400 | 75 | >400 |

Notes

Pin Load:

Length of Stroke:

Frequency:

Specimens soaked 15 min at temperature prior to testing.

(1) Coating failed prior to completion of test at 1000 F (538 C).

(2) Coating failed prior to completion of test at 1500 F (816 C).

(3) Coating failed prior to completion of test at 1000 F (538 C) and 1500 F (816 C).

TABLE IV

COATING WEAR SUMMARY

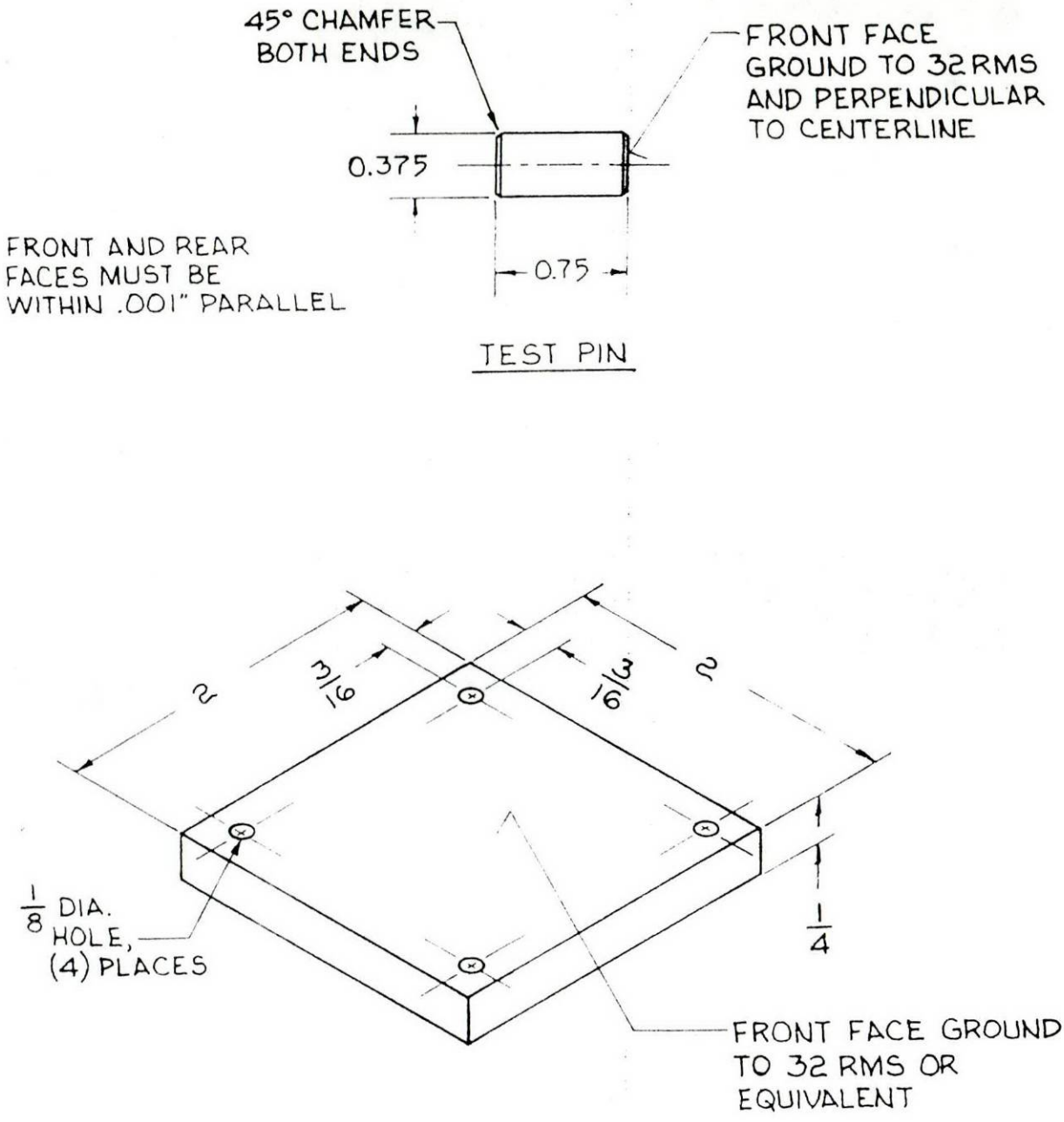
| Coating | | Minimum Coating Thickness (in.) Room Temp Untested (1) | Room Temp After Test | 1000 F (538 C) Untested (1) | 1000 F (538 C) After Test | 1500 F (816 C) Untested (1) | 1500 F (816 C) After Test |
|---|---|---|---|---|---|---|---|
| NiP + $Al_2O_3$ | pin | .0024 | .0010 | .0024 | .0000 | | |
| | plate | .0024 | .0022 | .0024 | .0004 | | |
| NiP + $CaF_2$ | pin | .0022 | .0020 | .0022 | .0012 | | |
| | plate | .0022 | .0022 | .0022 | .0012 | | |
| NiP + $Al_2O_3$ + $Ca F_2$ | pin | .0018 | .0014 | .0018 | .0014 | | |
| | plate | .0018 | .0018 | .0018 | .0016 | | |
| NiP + $Cr_2O_3$ | pin | .0018 | .0018 | .0018 | .0018(2) | | |
| | plate | .0018 | .0016 | .0018 | .0004 | | |
| NiB + $Al_2O_3$ | pin | | | .0014 | .0012 | .0014 | .0014(2) |
| | plate | | | .0014 | .0000 | .0014 | .0000 |
| NiB + $Cr_2O_3$ | pin | | | .0004 | .0000 | .0004 | .0000 |
| | plate | | | .0004 | .0000 | .0004 | .0000 |
| CoB + $Cr_2O_3$ | pin | | | .0020 | .0000(3) | .0020 | .0000 |
| | plate | | | .0020 | .0000 | .0020 | .0000 |

Notes

(1) Surface subjected to same temperature conditions without abrasive wear test.

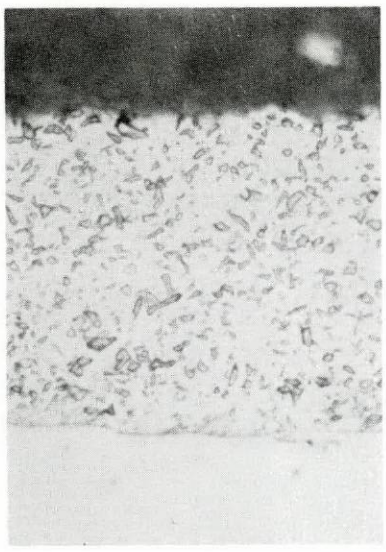
(2) Cross-section apparently missed areas of wear.

(3) Surface blistered.




FRICTION AND WEAR TEST SPECIMEN

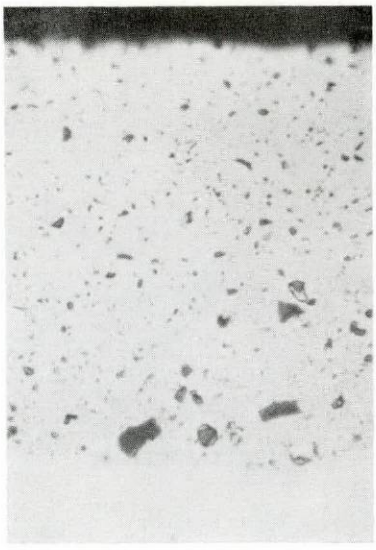
Figure 1.



As Plated



As Plated



Untested (1)



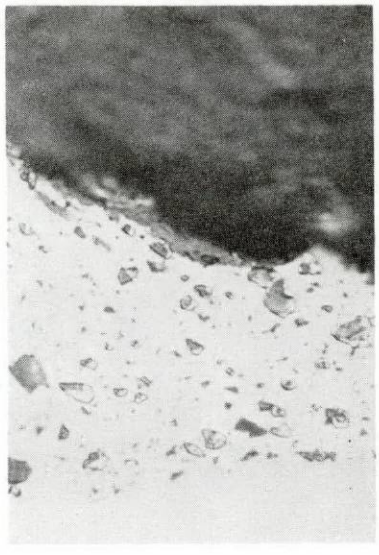
1000F (538C)
Heat Treatment, 2 hr

A. NiP-SiC



1000F (538C)
Heat Treatment, 2 hr

B. NiP-$B_4C$

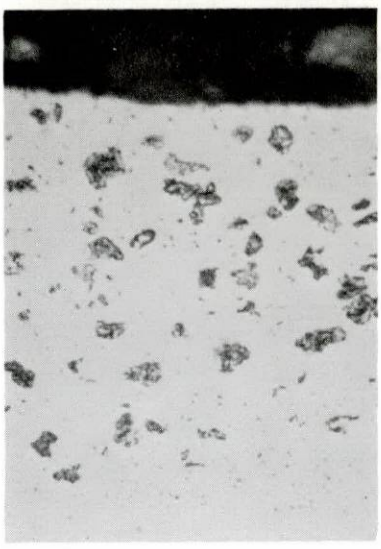


1000F (538C)
2 hr Wear Tested

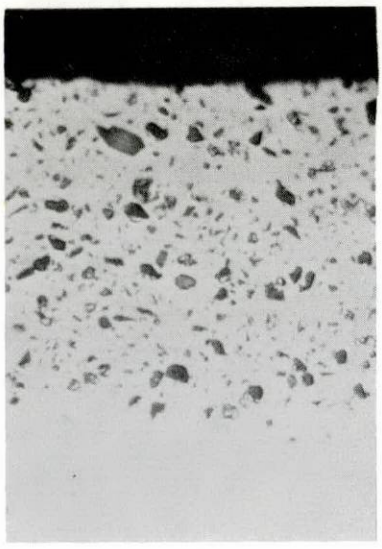
C. NiP + $Al_2O_3$

(1) Subjected to same temperature conditions without wear testing.

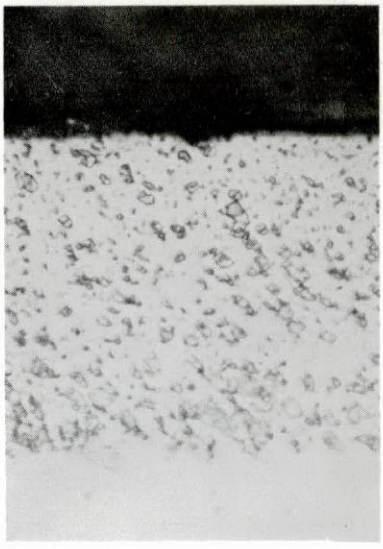
Figure 2. Nickel Phosphorus Matrix Coatings, X1000



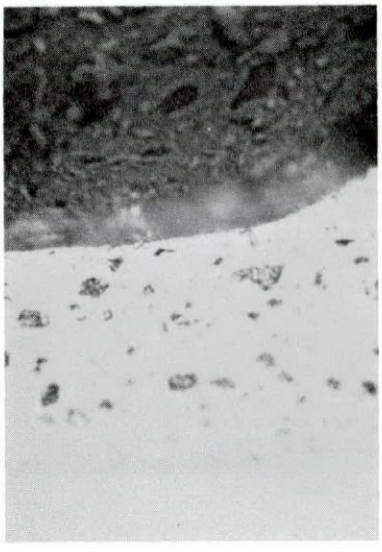
Untested (1)



Untested (1)

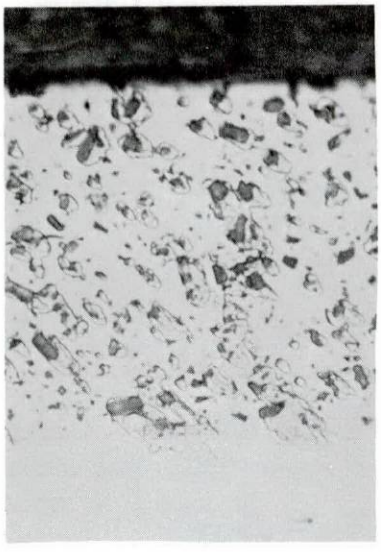


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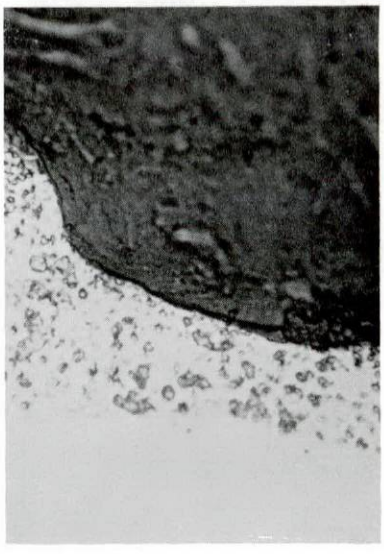
1000F (538C)
2 hr Wear Tested

D. NiP + $CaF_2$



1000F (538C)
2 hr Wear Tested

E. NiP + $Al_2O_3$ + $CaF_2$

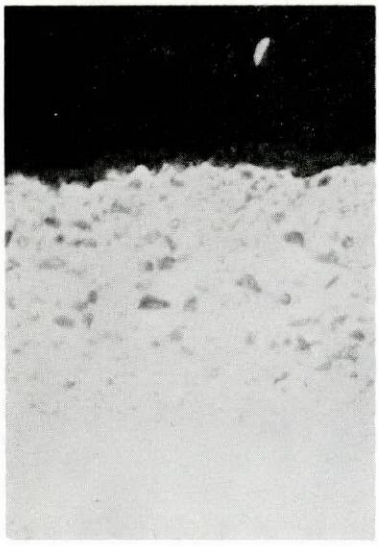


1000F (538C)
2 hr Wear Tested

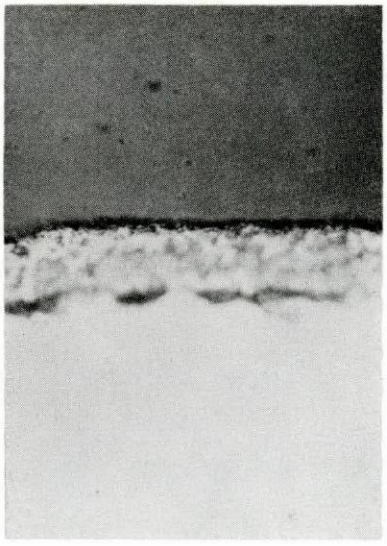
F. NiP + $Cr_2O_3$

(1) Subjected to same temperature conditions without wear testing.

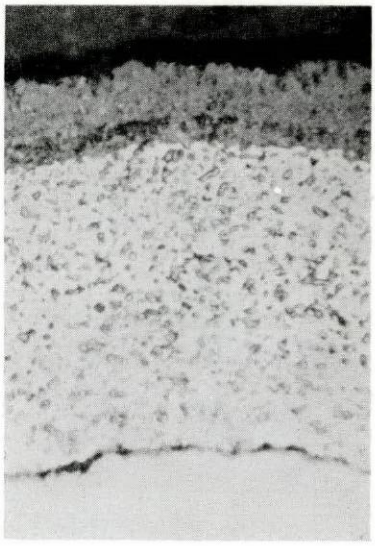
Figure 2 (Continued). Nickel Phosphorus Matrix Coatings, X1000



Untested (1)



Untested (1)

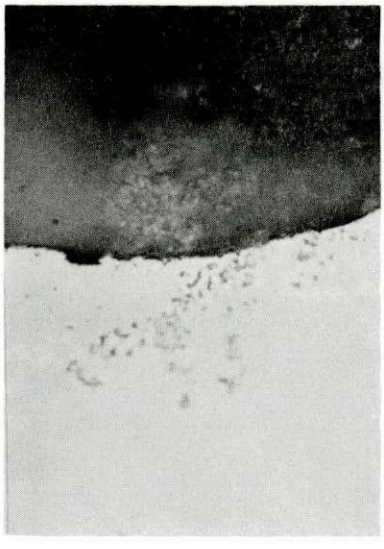


Untested (1)



1500F (816C)
2 hr Wear Tested

A. NiB + $Al_2O_3$



1500F (816C)
2 hr Wear Tested

B. NiB + $Cr_2O_3$



1500F (816C)
2 hr Wear Tested

C. CoB + $Cr_2O_3$

(1) Subjected to same temperature conditions without wear testing.

Figure 3. Nickel Boron Matrix Coatings, X1000

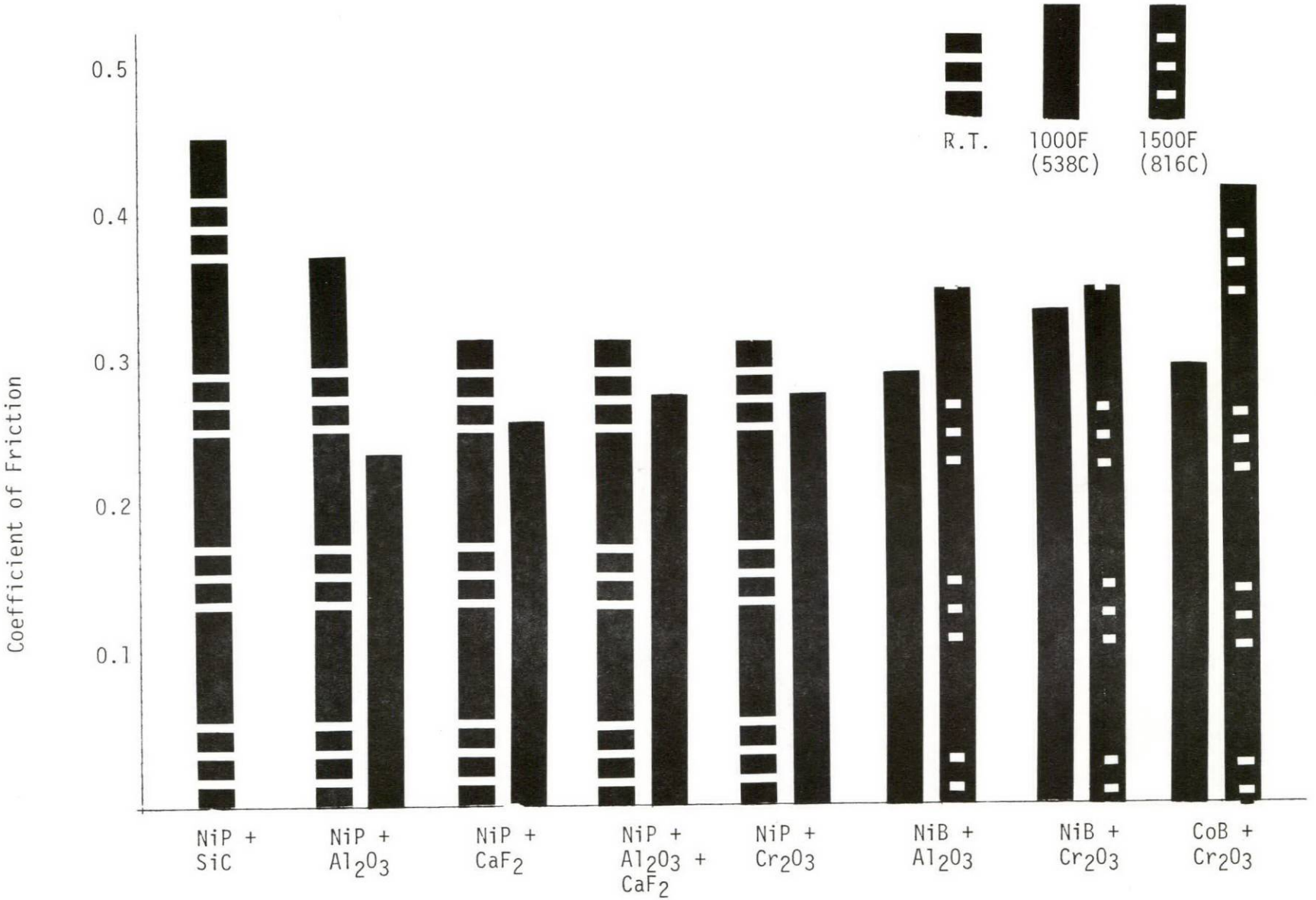
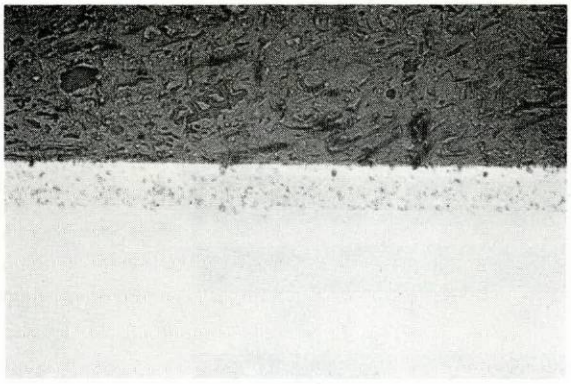
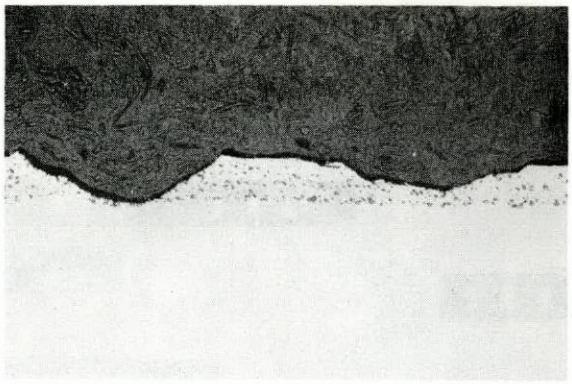



Figure 4. Self Mated Pin and Plate Friction Tests of Particle Enhanced Coatings

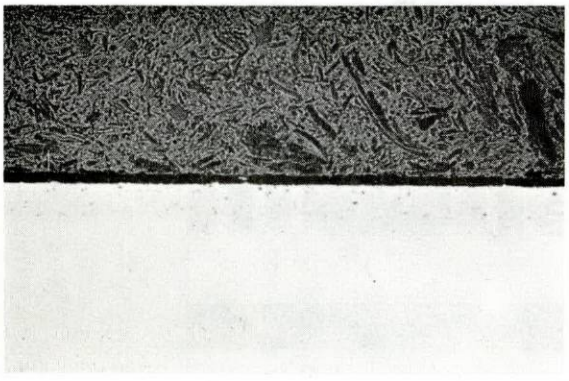


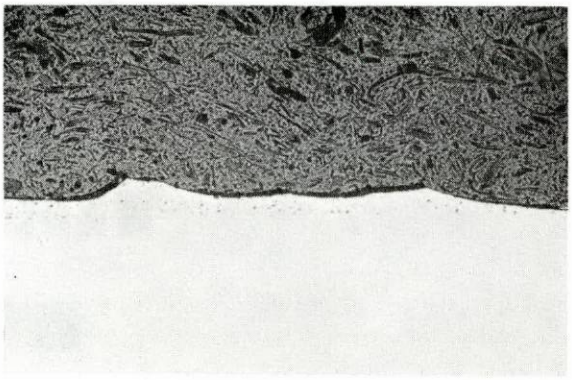


Room Temp

1000F (538C)

A. NiP + $Al_2O_3$

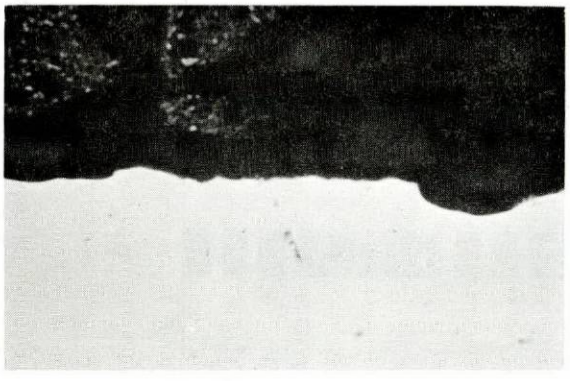


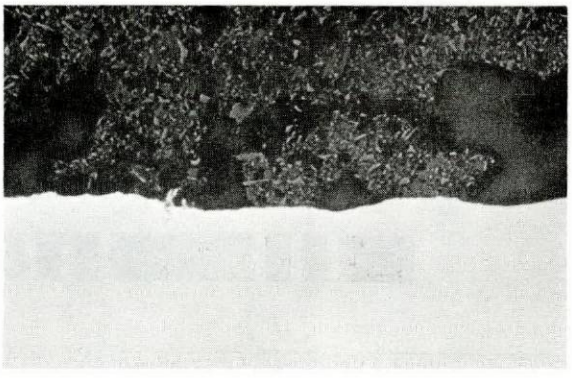


Room Temp

1000F (538C)

B. NiP + $CaF_2$





1000F (538C)

1500F (816C)

C. NiB + $Cr_2O_3$

Figure 5. Typical Plate Coating Wear Tracks, 100X

## References


1. Parker, K. "Process of Electrolessly Depositing Metal Coatings Having Metallic Particles Dispersed Therethrough" U.S.3,562,000 October 25, 1968

2. Metzger, W., et al. "Process for Electroless Metallizing Incorporating Wear-Resistant Particles" U.S.3,617,363 January 16, 1968

3. Parker, K. "Electroless Alloy Coatings Having Metallic Particles Dispersed Therethrough" U.S.3,723,078 October 25, 1968

4. Metzger, W., et al. "Articles Having Electroless Metal Coatings Incorporating Wear-Resistant Particles Therein" U.S.3,753,667 September 28, 1970

5. Feldstein, N. "Composite Coatings" Materials Engineering, pp 38-41, July 1981

6. Parker, K. "Hardness and Wear Resistance Tests of Electroless Nickel Deposits", Plating, September, 1974

7. Hubbell, F. N. "Chemical Deposited Composites - A New Generation of Electroless Coatings" Plating & Surface Finishing, December, 1978

8. Sale, J. M. "Wear Resistance of Silicon Carbide Composite Coatings," Metal Progress April, 1979


## Acknowledgement


The authors greatly appreciate the assistance of Mr. S. J. Calabrese of Rensselaer Polytechnic Institute in performing the MT-1 friction and wear testing.

# S-1

# Alloy Plating II
# Session S

## High-Speed Solder Plating at Western Electric, Richmond

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Murray Hill, NJ;
John F. Barnes and Russ R. Collins
Western Electric Co.
Richmond, VA;
Dr. Rusty R. Buckley
Bell Labs.
Murray Hill, NJ

# HIGH SPEED SOLDER PLATING AT WESTERN ELECTRIC, RICHMOND

by

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and

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A proprietary high speed solder plating system[1] was introduced into Western Electric, Richmond in 1979 and since that time considerable manufacturing expertise has been gained. In this report, the basic properties of the high speed solder plating system will be discussed along with results from manufacturing use.

Plating rates in excess of 700 $mA/cm^2$ with excellent additive stability have been obtained in laboratory usage. The system uses a fluoborate based chemistry which provides excellent conductivity and easy conversion of existing plating equipment. A two-component additive system is used in the high speed process to maximize the throwing power while maintaining excellent dendrite suppression even at high current densities. Figure 1 illustrates how the slope of the current voltage curve can be manipulated by adjusting the relative amounts of the additives. The throwing power is directly proportional to the inverse of the i-V slope. Thus, for any current density the throwing power can be maximized by changing the additive ratio. The metal content and agitation rate can be adjusted to give the desired current density or metal deposition rate. Figure 2 shows schematically how the four adjustable parameters; agitation, metal content, acid content and additive ratio, can effect the plating parameters.

Implementation of the chemistry into a manufacturing line required some modification of the plating equipment to take advantage of the increased deposition rates. Previously, printed wiring boards were plated in stand alone solder platers at low deposition rates, 15-20 $mA/cm^2$. The increased plating rate allowed one cell of a side arm copper plater to be converted to solder

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1. Solder Plating Process, P. A. Kohl, U. S. Patent 4,263,106, April 21, 1981.

plating and eliminated the need for separate solder plating equipment. The cell design is shown in Fig. 3. Solution agitation is provided by cathode rocking and by circulation through a filter pump.

Substantial reduction in solution volume, maintenance and manpower have been realized. A summary of the changes are shown in Table 1. Solder plating baths are being run at 50-140 mA/cm$^2$ on through-hole PWBs. The quality and throwing power of the solder in the holes is very good. The rate of drag out of the bath and drag in of rinse water greatly exceeds the decomposition of the additives, confirming its stability. Replenishment of the additives is based solely on the drag in and drag out of the bath. The longevity of the bath eliminates the need for carbon treatment.

A series of solder plating baths have been designed for a variety of uses. High current densities (i.e. >400 mA/cm$^2$) can easily be realized in the plating of flexible circuits where agitation is provided by the board in addition to solution pumping. Also, through-holes are no longer a concern. Barrel plating operations have benefited significantly because of the high throwing power and low coefficient of friction in the bath.

In general, the high speed process allows one to design the solder bath to meet the need of the application. The high current, low cost and virtual elimination of the unpleasant odors has allowed straightforward implementation.

**TABLE 1**

| | OLD PROCESS | NEW PROCESS |
|---|---|---|
| 1. BRIGHTENER | Peptone | Phenolphthalein/ Triton X-100 |
| 2. VOLUME (Gal) | 10,000 | 250 - 800 |
| 3. CURRENT DENSITY (ASF) | 0 - 20 | 0 - 140 |
| 4. PLATING TIME (Min:Sec) | 15:00 | 1:30 - 5:00 |
| 5. CIRCULATION (Turnovers per hr) | 2 | 10 - 15 |
| 6. ANODE AREA | Equal to Cathode Area | As Large as Possible |
| 7. CARBON TREATMENT | Required After Prolonged Peptone Adds | Not Required |

## FIGURE CAPTIONS

Fig. 1. Voltammogram of a 0.38N $Sn^{2+}$, 0.15N $Pb^{2+}$, 5N $HBF_4$ and 16 mM Triton x-100 solution with phenolphthalein concentration (mM) shown. A Pt disk electrode at 400 rpms was used and the scan rate was 10 mV/s.

Fig. 2. Schematic diagram of interaction of various bath parameters.

Fig. 3. Drawing of plating cell for solder plating.

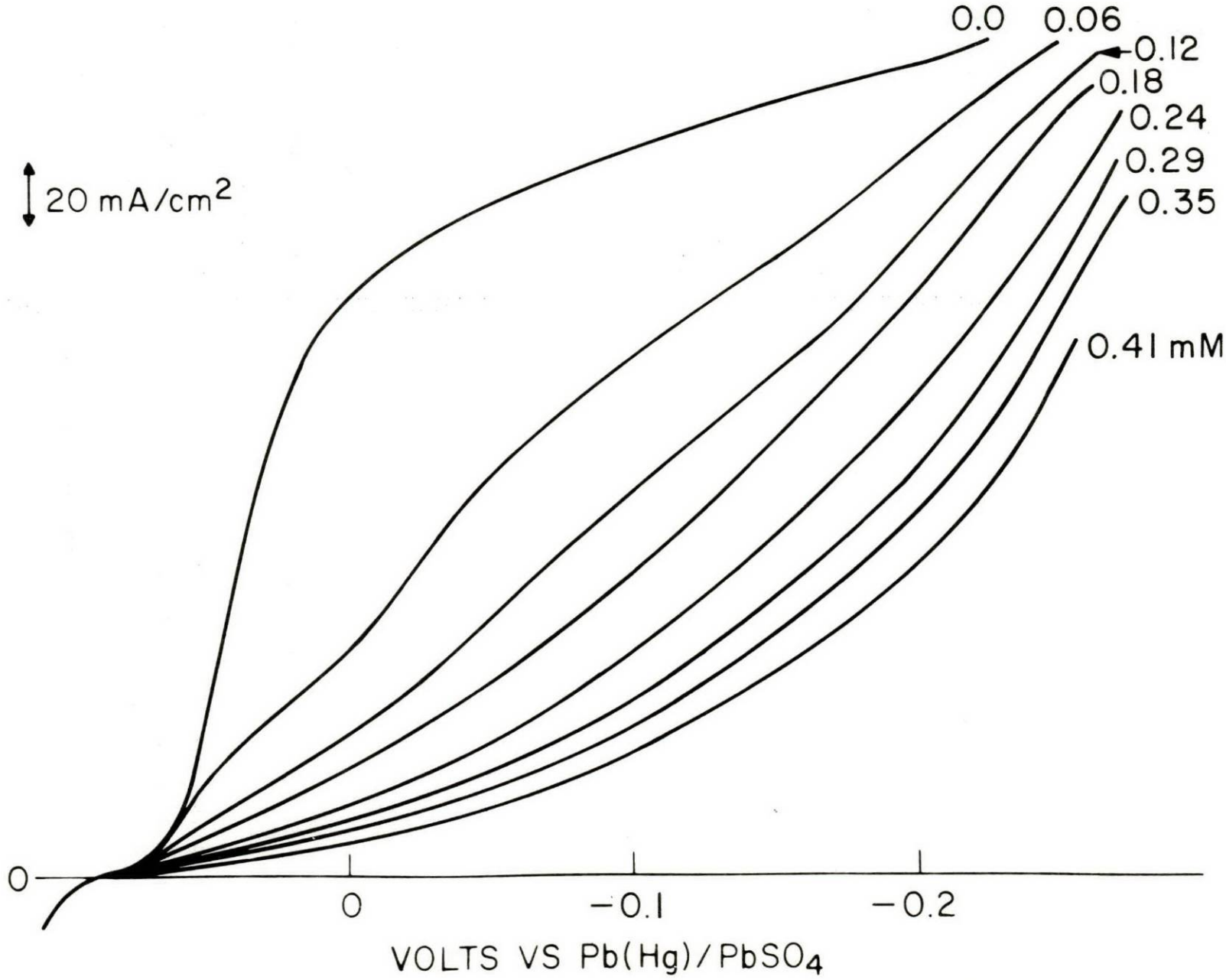

0.0
0.06
0.12
0.18
0.24
0.29
0.35
0.41 mM
20 mA/cm2
0
0
−0.1
−0.2
VOLTS VS Pb(Hg)/PbSO4

FIGURE 1

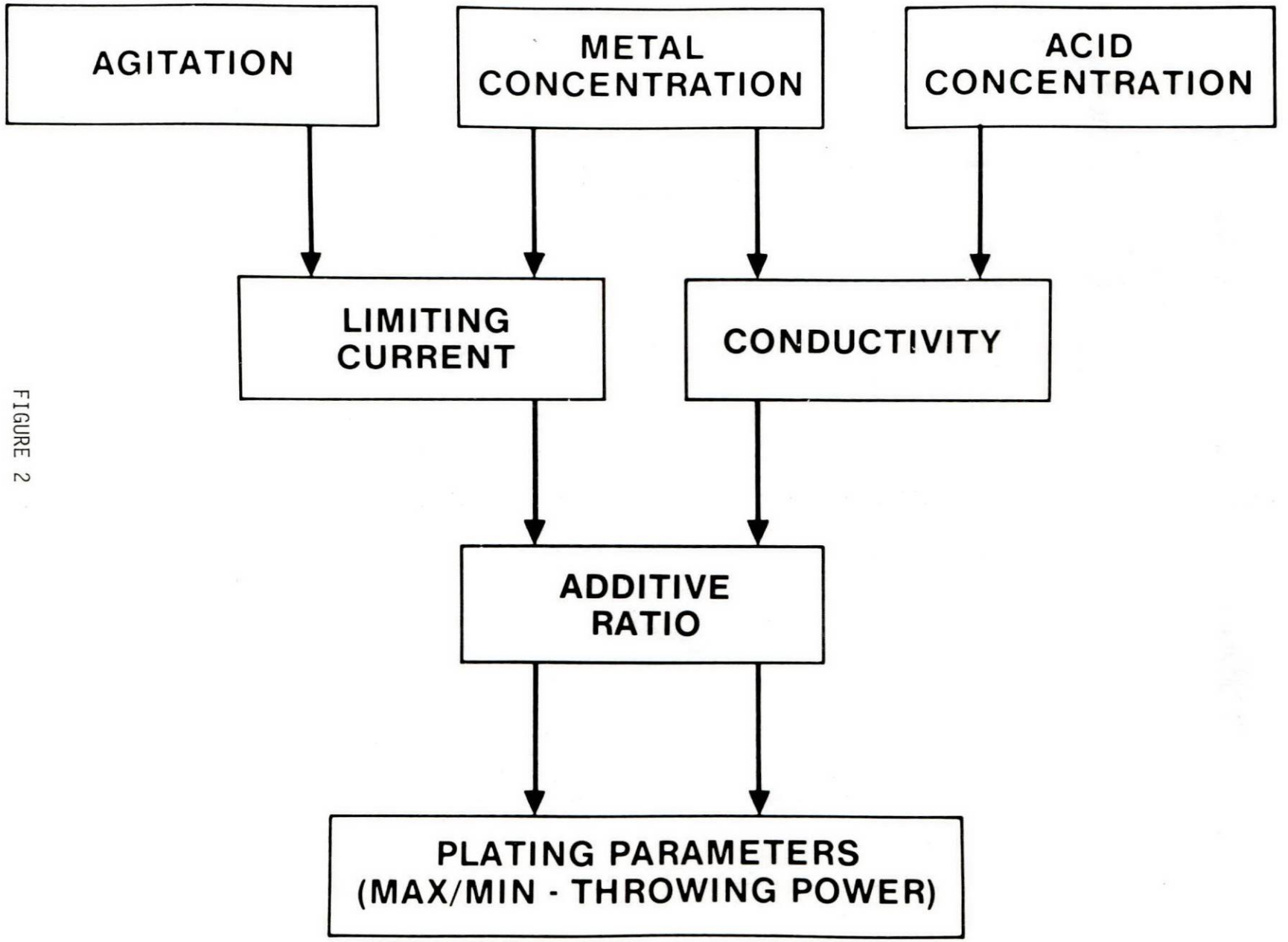

AGITATION
METAL CONCENTRATION
ACID CONCENTRATION
LIMITING CURRENT
CONDUCTIVITY
ADDITIVE RATIO
PLATING PARAMETERS (MAX/MIN - THROWING POWER)

FIGURE 2

# MODIFIED SOLDER PLATING CELL

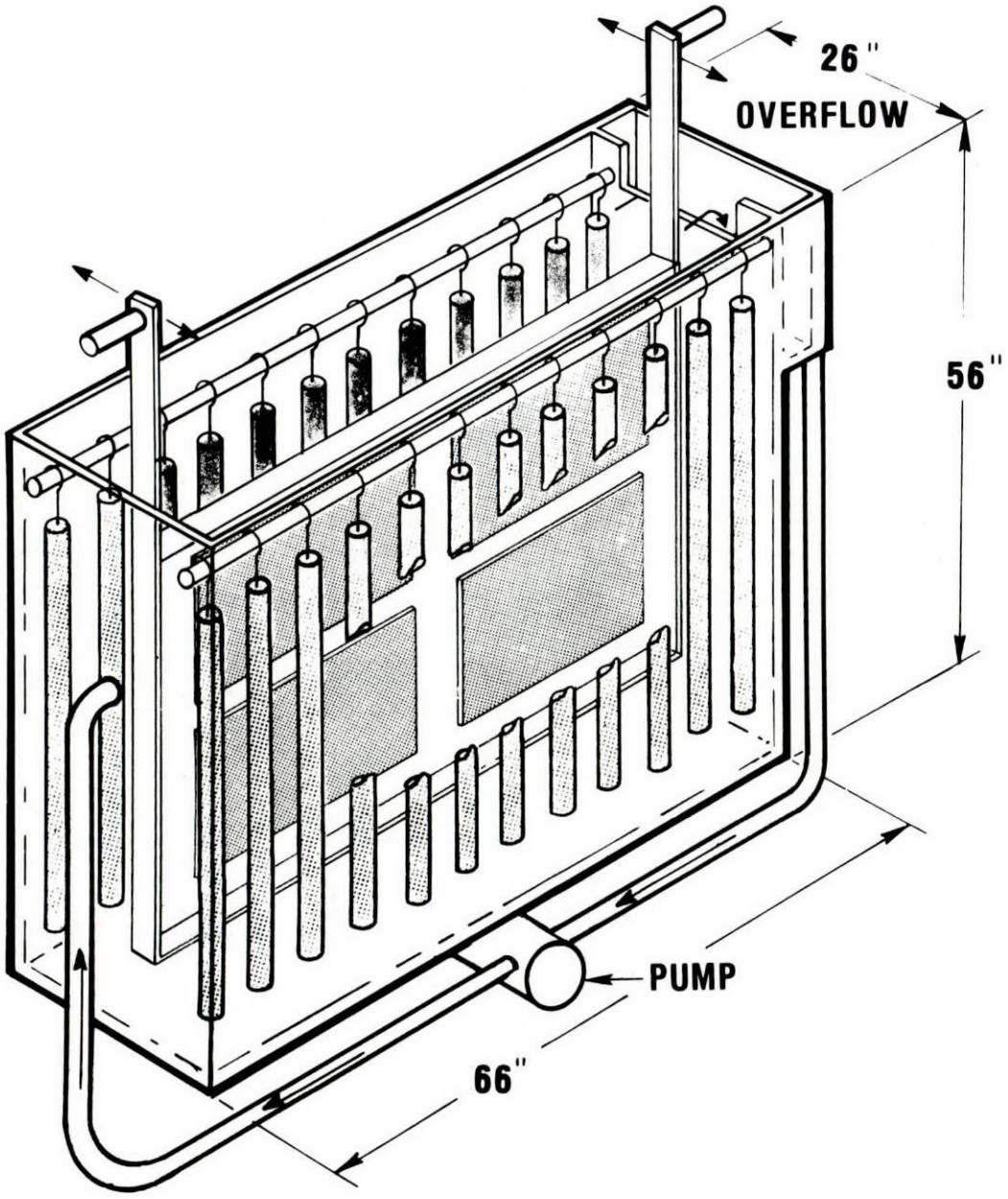



FIGURE 3

S-2

# Alloy Plating II
# Session S

## X-Ray Diffraction Studies of Precious-Metal Alloy Electrodeposits

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# X-RAY DIFFRACTION STUDIES OF ALLOY ELECTRODEPOSITS

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## Introduction

Alloy deposits are becoming increasingly important in non-precious metal plating for decorative and electronic applications. Plated alloys often possess properties that their constituent metals lack. Such properties include reduced melting points as in a eutectic alloy system, enhanced color, increased hardness, improved resistance to wear and corrosion and, in precious metal applications, reduced cost.

An alloy is simply defined as the intentional combination of two or more elements of which one is a metal. Electrodeposited alloys (1,2) generally are not in a state of thermodynamic equilibrium. They may have none, some, all, and even more phases than are predicted in phase diagrams for similar alloys thermally produced under equilibrium conditions. An initial interest in alloy deposits was the desire to establish whether such deposits were really alloys or merely gross admixtures. The results of many early studies, as compiled by Brenner (1) indicated that the simultaneous electrodeposition of two metals produced true alloys having structures similar to thermally prepared alloys. Analysis of the differences between plated alloys and their cast counter-parts reveals that:

1.) the phases in electrodeposited alloys may exist over larger or smaller compositional ranges,

2.) the presence of phases in electrodeposited alloys may occur at temperatures lower than normally found in the cast alloy,

3.) lattice parameters of the electrodeposited alloys may differ from those of the cast alloy.

Except in the case of low melting alloys, deposition occurs at temperatures far below the temperatures where detectable diffusion occurs. To obtain the required end-product properties it is often necessary to apply an additional post-treatment involving a thermal cycle in boiling water or a furnace anneal at higher temperatures. The purpose of this study is to gain an understanding of the thermal behavior of electrodeposited alloys for future specification and design by following the crystal changes that occur with these post-treatments.

## Experimental

The system initially studied was a nominal 50:50 atomic % gold-copper alloy. Under equilibrium conditions (3) this alloy possesses an ordered structure. Ordering is said to exist in substitutional solid solutions when the two kinds of atoms no longer are randomly distributed but are arranged in an orderly periodic manner develop- ing what is called a "superlattice".

Samples were fashioned from one inch square nickel-plated brass coupons plated in a cyanide bath with the operating characteristics shown in Table I. To be noted is the bath operating temperature of 50°C. Standard electroplating practices were maintained. Annealing was conducted in a Lindberg tube furnace at temperatures between 200 and 300°C for durations of between 15 and 120 minutes in a reducing atmosphere.

To study the crystal nature of the deposits, X-Ray diffractometry was employed. A Rigaku diffractometer operating at 40 KeV and 20 mA was used to scan the samples from 20 angles from 100° to 20°. The resultant traces were indexed by matching peaks to JCPDS (4) standards. Preliminary lattice parameter measurements were determined from high angle reflections so as to minimize errors (as $\theta$ increases, $\frac{d\sin\theta}{d\theta}$ decreases).

## Results and Discussions

The gold-copper system was chosen for two reasons. Firstly, the plating temperature is significantly lower than the processing anneal temperatures. The interdiffusion of copper and gold (5,6) at the plating temperature is essentially limited to grain boundary diffusion and the volume diffusion necessary to transform a mixture to an ordered structure is minimal. The specified annealing temperature (250°C) is of the proper magnitude for significant bulk diffusion to produce a material transport sufficient for ordering. Secondly the system's corrosion resistance is significantly altered upon annealing. In the as plated condition the deposit is subject to preferential dissolution of the copper in 50 vol% nitric acid solution (7) while after annealing there is no attack.

With these thoughts in mind, it was hypothesised that annealing caused the deposit to order which in turn altered the chemical activity of the deposit. Raub (8,9) reported that copper-gold alloys deposited from cyanide solutions consisted of mixtures of the individual metals. The initial X-ray results, Table II, are in striking contrast to the above idea. Both copper and gold are face centered cubic metals and have X-ray reflection for only the (111), (200), (220), (311) and (400) planes. Upon ordering all planes within the unit cell produce reflections (8). In the as-plated condition it can be seen that the deposit possesses the ordered tetragonal structure. Using the (113) and (222) peaks the lattice parameters were determined. These are compared with the reported values in Table III and appear to be somewhat distorted reflecting a non-equilibrium lattice structure. The fact that not all the reflections are present also supports this contention. Upon annealing, all the tetragonal peaks are obtained but their 2θ positions are some what altered and the resultant the lattice parameters are approaching those of the equilibrium structure.

From this data it is possible to rationalize the differences in chemical properties in the as-plated and annealed deposits. As noted above, electrodeposited alloys are not usually in a state of thermodynamic equilibrium. This non-equilibrium state is the most probable cause for increased suseptibility to corrosive environments. Such structures have higher than normal defect densities causing abnormal lattice spacings and therefore weaker metallic bonding. In highly reactive environments such as the previously noted nitric acid solution, the energy for preferential dissolution is probably greater than that of the energy binding the metal atoms. As the deposit is heated, defects are annilihated and the ordered lattice can more closely assume its equilibrium spacings.

## Conclusion

Preliminary investigations reveal that the gold-copper deposit exists as a distorted tetragonal structure. Increased chemical reactivity is attributed to this non-equilibrium state. Annealing at elevated temperatures in the range where bulk volume diffusion is predominant results in more complete ordering. As the equilibrium ordered structure is approached, the metallic bonding energy increases and thereby reduce the suceptibility to corrosion is reduced.

Future considerations will include precise measurement of the lattice parameters as a function of temperature and time. From these studies kinetic data for the ordering transformation should be obtainable. Additionally, other alloy systems representative of current alloy plating technology will be analyzed.

References:


(1) Brenner, A., Electrodeposit of Alloys (Academic Press, New York, 1963) p. 173.

(2) Raub, E., Plating and Surface Finishing 63, 30 (1976).

(3) Hansen, M. Constitution of Binary Alloys, (McGraw Hill, New York, 1958) p. 198.

(4) International Center for Powder Diffraction Data, formerly the Joint Committee on Powder Diffraction Standards, 1601 Park Lane, Swarthmore, Pa, 19081.

(5) Marx, D.R., Pickering H.W., and Bitler, W.R., Plating and Surface Finishing 64, 67 (1977).

(6) Pinnel, M.R. and Bennett, J.E., Metal Transactions 3, 1989 (1972)

(7) Duva, R. Private Communication.

(8) Raub, E. Metalloberflache 7A, 17 (1953).

(9) Raub, E. and Sautter, F., Metalloberflache 10 65 (1956).

(10) Cullity, B.D., Elements of X-Ray Diffraction 2nd Ed. (Addison-Wesly Publishing Co. Inc., Reading, MA, 1978) p. 383.

TABLE I

BATH OPERATING CHARACTERISTICS

| | |
|---|---|
| Metallic Gold Content (as cyanide salt) | 3.4 g/l |
| Metallic Copper Content (as EDTA salt) | 12.0 g/l |
| Buffer | 6.6 g/l |
| pH | 6.5 - 7.5 |
| Temperature | 50 - 60°C |
| Agitation | Vigorous |
| Current Density | 10 ASF |

TABLE II

INDEXING X-RAY DIFFRACTION DATA FROM d-SPACINGS

| Plane | JCPDS File #4-836 Copper (Ref. 4) | JCPDS File #4-784 Gold (Ref. 4) | JCPDS File #25-1220 Au-Cu (Ref. 4) | As plated | Annealed 250 for 120 min. |
|---|---|---|---|---|---|
| (001) | | | 3.670 | | 3.735 |
| (110) | . | | 2.800 | | 2.828 |
| (111) | 2.089 | 2.355 | 2.226 | 2.263 | 2.214 |
| (200) | 1.808 | 2.039 | 1.980 | 1.960 | 1.943 |
| (012) | | | 1.835 | 1.843 | 1.853 |
| (201) | | | 1.743 | 1.77 | 1.783 |
| (112) | | | 1.535 | | 1.547 |
| (220) | 1.278 | 1.442 | 1.400 | 1.386 | 1.388 |
| (202) | | | 1.346 | | 1.349 |
| (221) | | | 1.308 | 1.303 | 1.307 |
| (311) | 1.090 | 1.230 | 1.185 | 1.181 | 1.186 |
| (113) | | | 1.121 | 1.126 | 1.127 |
| (222) | 1.0436 | 1.177 | 1.113 | 1.111 | 1.113 |
| (312) | | | 1.0344 | 1.027 | 1.029 |

TABLE III

LATTICE PARAMETERS (IN ANGSTROMS)

| | Literature (Ref. 3) | As Plated | Annealed (120 min @ 250°C) |
|---|---|---|---|
| a | 3.960 | 3.929 | 3.950 |
| c | 3.670 | 3.700 | 3.692 |
| c/a | 0.927 | 0.942 | 0.935 |

S-3

# Alloy Plating II
# Session S

## Continuous Processing of Printed Wiring Boards Incorporating High Current Density Tin Lead Alloy Plating

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# CONTINUOUS PROCESSING OF PRINTED WIRING BOARDS INCORPORATING HIGH CURRENT DENSITY TIN LEAD ALLOY PLATING

By
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Worldwide, the electronics industry has sustained perhaps the largest growth in modern industrial movement. With the advent of new development within computer science, incorporation of computer automated design, numerical control for equipment, and a reach into markets of the home computer systems, there is a need for additional productivity and cost effectiveness. The key to more productivity and effectiveness is the discrete printed wiring board. The sustained growth of the electronics industry has created specific advancements and specifications for manufacturing of printed circuit boards. It has also resulted in a demand for higher productivity and yields. During the 1970's, the printed circuit board shops were often captive organizations of large computer organizations who ordered how a product was to be manufactured. Then, as the growth pattern of the electronics industry developed, production capabilities of such captive shops could not sustain the requirements on the growth curve. Soon, manufacturing firms, in order to fulfill demands of the electronics industry growth, began to purchase printed wiring boards from outside sources known as "job shops." Because of the development of the printed board processes, some standardization of manufacturing techniques has been implemented during the last ten years.

This text deals with the processes used for the manufacture on printed wiring boards, and more specifically high current density plating of the tin/lead alloy as an etch resist final coating for protection and solderability.

The development of the plating apparatus for the printed wiring industry was first incorporated in small discrete hand lines. With the advent of increased volumes, it was necessary to apply some type of automation to the manufacturing of plating processes incorporated in the industry. The level of automation presently used throughout a number of high volume shops throughout the United States and the world is an automated hoist system which transports the boards through the various process cycles. This method of automation has proved very successful within the industry and incorporated standard chemistries for the through-hole plating of printed wiring boards consisting of the basic coatings: copper, nickel, acid tin, or tin/lead deposits. These systems provide nominal current density in the area of 20-30 amps per square foot, with approximate dwell times from 12-70 minutes to deposit the required amount of plating. The specifications generally used within the industry are referenced in IPC documentation and MIL P55110C. In many facets of the printed wiring board manufacturing process specialized apparatus needed to be generated to provide additional productivity and quality as printed wiring board designs changed very rapidly. These pieces of equipment were demonstrated mostly

in the photo tool room in art work generation and the advancements of dry film plating resist along with high speed and very accurate numerical controlled drilling equipment. The plating apparatus commonly used in the industry has not changed considerably in comparison with its associated processes. The application of conventional automation has definitely shown that equipment to provide shorter dwell times in the plating cycles be developed to insure the quality and productivity necessary to keep pace with other advancements and improvements in the manufacturing processes.

Certain considerations have to be made involving high speed plating on printed wiring boards. Basically the type size of the cathodes itself is a consideration along with the specific requirements of the plating itself. The nominal specification for copper plating is 1 mil average, while the specification for the tin/lead alloy plate is 0.3 mil minimum over the entire surface of unreflowed tin/lead plating. The military specification 55110C states that the alloy shall be maintained in reference to the tin concentration in such a manner that the tin metal shall be within a 50-70% by weight of the deposit. Ideally, of course, it would be advantageous to co-deposit an alloy plate very close to the eutectic, a composition 63% tin 37% lead which has a melting point of 376°F. The primary function for high speed plating is the solution agitation and the regeneration of the cathode film while the plating process and electrochemical reactions are taking place. This high solution movement allows depleted ions within the cathode film to be removed and replenished by fresh ions for codeposition unto the substrate. In order to provide high speed or high current density plating of tin/lead alloys, a specially designed plating cell had to be constructed to allow maximum solution movement within the system to constantly replenish metallic ions at the surface of the cathode. The particular equipment involved was designed to process the panels vertically on a continuous basis to take advantage of various printed circuit board processes. This continuous process consolidates various processing steps minimizing the overall dwell times, thus eliminating the need for additional cleaners and activators prior to plating processes. This vertical concept of tanks and plating cells is shown in Figure 1.

The panels are supported on a plating rack (Figure 2) which maintains four electrical connections sufficient enough to carry the applied current in all platings including the tin/lead plating cells. The plating racks are designed specifically to requirements with relationship to the size of printed wiring board to be processed. The contact to the cathode bar is made at the top of the rack of materials that will apply pressure on carbon contacts to draw the current from a slide mechanism and transmit to the four areas of contact on the top of the part to be processed. The panels are then processed vertically through a variety of processes before entering the high speed tin/lead plating cell. The plating cell has various designs depending upon the production capabilities required of the equipment. A standard cell will be used for this discussion which has an active plating area of 4', and solution movement of approximately 150 gpm, which is equal to a turnover rate within the cell of 4 times per minute. (See figures 3 and 4).

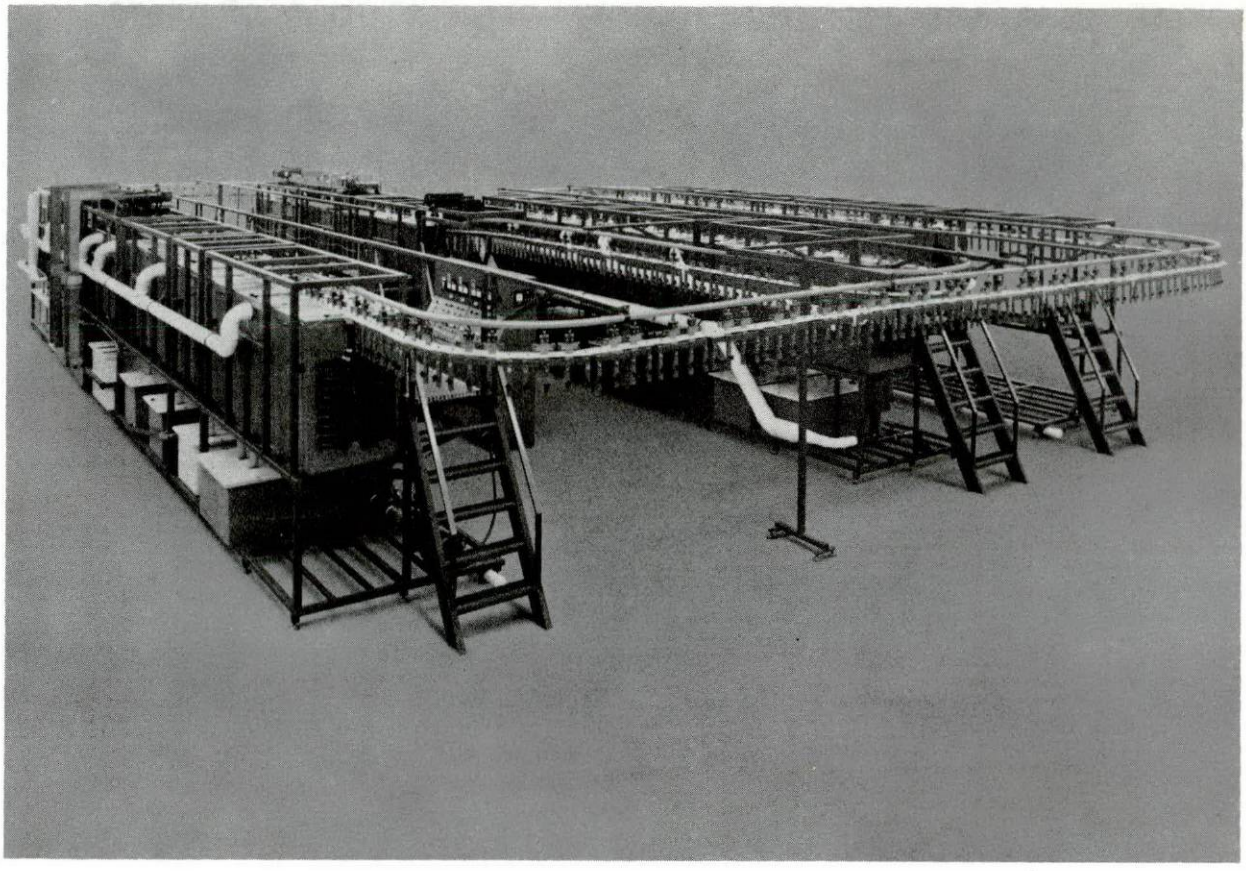
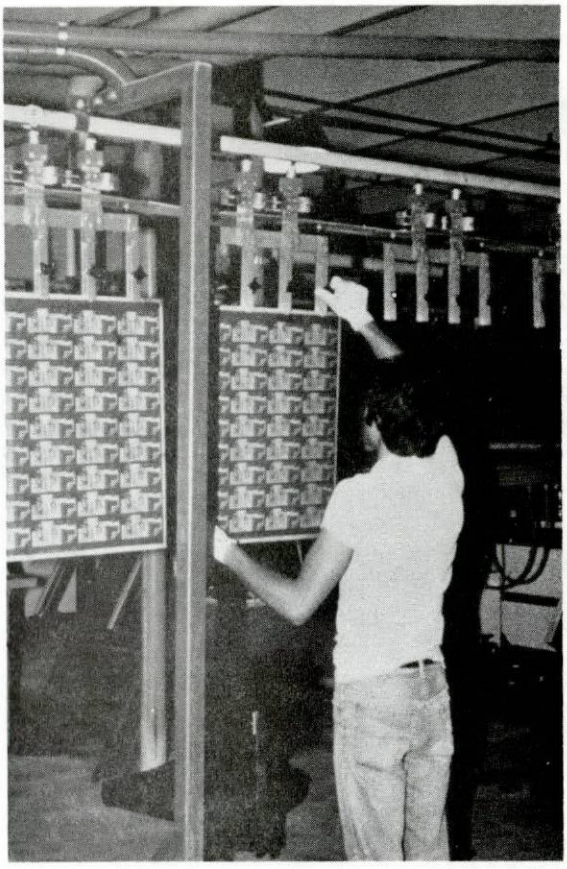


FIGURE I
MICRO-PLATE SERIES 9000 CONTINUOUS PANEL PROCESSOR

FIGURE 2

SERIES 9000 RACKING
MECHANISM



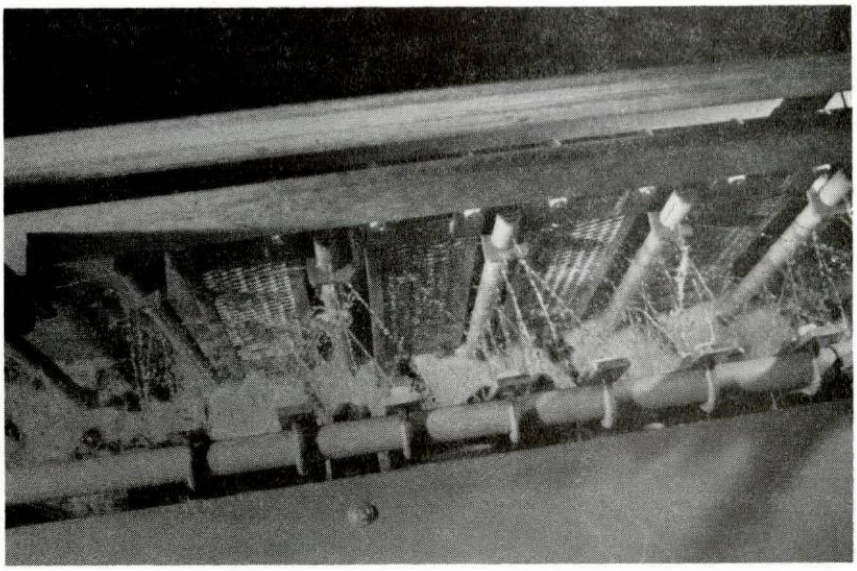
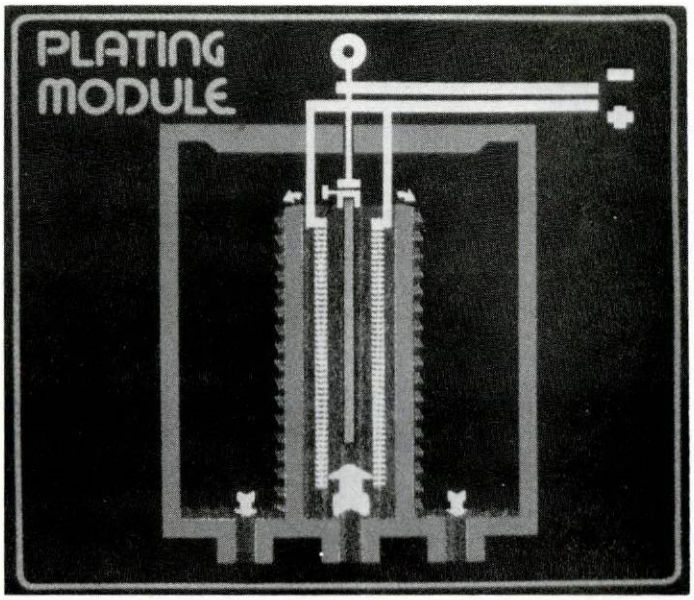


FIGURE 3
STANDARD
PLATING CELL




SOLUTION FLOW DIAGRAM IN HIGH SPEED PLATING CELL

The design thickness is 0.3 mils minimum of the tin lead alloy plate which allows a calculated dwell time within the plating cell. With a fixed dwell, standardization of applicable current density can be applied. Due to the high solution turnover rate and chemical formulations, current densities between 80 and 120 amps per square foot can be achieved. The chemical nature of the actual plating system has to be adjusted from conventional formulations to provide the correct alloy in the deposit. Some nominal values based on testing and research over the past year indicate the following chemical requirements are necessary to maintain the proper tin/lead ratio at current denisities of 80-120 amps per square foot (see Table I). Additional studies confirm that the tin/lead ratio varies throughout the nature of the printed wiring board depending upon the overall design of the board in reference to high and low current density areas. For example, a board by design may have a large ground plane which can vary in the tin concentration in the low current density area. Conversely, in a different location of the board may exist a single 10 mil wide line in an isolated area which can also vary the tin concentration because of the higher currenty density. As shown in the preceeding Table I, it is obvious that the formulation of the tin lead plating bath indica-

tes that the tin and lead ion concentration are equal, which is a marked variation compared to standard systems. Incorporating the proper grain refiners within this system, the desired tin/lead ratio can be achieved at the current densities being used for plating the deposit. As we know, the codeposition of tin favors the high current density as demonstrated by Raub and Blum[1] "that an increase in polarization will favor the discharge of the less noble metal which, in this case, is tin." To compensate for this high tin deposit at applicable current, densities the lead metal concentration was increased, thus resulting in an overall acceptable tin/lead alloy plating compostion. Presently, anodes of a configuration of 63% tin 37% lead alloy are used in the production equipment of these high speed plating cells. The anode erosion and the overall findings have not yet been confirmed in regard to incorporating other alloy composition within the system. It is expected that the need for the high volume of lead in the solution will not require a significant change in anode configuration since the deposit being plated out does meet the present requirements in the industry for tin/lead alloy ratio.

The mechanism of solution transfer incorporates a holding tank of which all the chemical make-up and solution are maintained. The solution is then pumped at the high flow rates through a main sparger mechanism which distributes the solution in a flow pattern that covers the cathode completely thus regenerating the cathode film on a frequent basis during the electrochemical reaction. The solution then overflows the vertical plating cell and is returned back to the holding reservoir. In the early days of development of this high speed system it was evident that additional design work was required to reduce the overall oxidation of the stannous to stannic tin formation. It was necessary to incorporate several mechanical devices, so that the solution overflow could be contained and gently returned back to the reservoir with a minimum oxidation with the air. This reduction was accomplished by incorporating several types of baffles in return drain systems along with eliminating the amount of overflow of the solution thus eliminating the splashing phenomena. In conventional systems one constant problem is the plating of tin/lead over the racking mechanism. This system allows the solution to be maintained below the racking system thus not codeposting on the rack tips and providing for two subsequent cleaning operations for removal of excess plating on the racks. In addition to the mechanical devices, an anti-oxidant is also present in the chemical formulation. This material has no effect on the performance of the alloy plating, while eliminating the oxidation reaction in the formation of excess stannic tin. As in conventional systems, some stannic tin is generated during the plating cycle; however, once an equilibrium is reached, stannic generation is minimal provided the anti-oxidant is maintained within the system. Current production requirements are approximately 100 grams a day of the anti-oxidant material.

[1]Blum and Hogaboom, Principles of Electroplating and Electroforming, 3rd ed., McGraw-Hill Book Company, New York, 1949.

The tin/lead plating alloy has shown marked consistency over the entire board panel and only areas of design have shown discrepancies in low or high current density areas. Distribution ranges versus current density are illustrated in Table II and demonstrates the difference in the tin concentration as the current density varies at constant parameters such as the metal concentration and operating temperatures. The normal operating temperature of this bath is 21 - 25°C. Of course, temperature is also a consideration in high speed plating because as temperatures increase, the oxidation reactions from stannous to stannic increase, while the tin ion favors high temperature and the subsequent deposition of the metal. The addition agent Micro-Brite TL is a non peptone refined animal fat. The consumption rate of this particular additive is at a 1 ML per amp hour. It has been determined that over addition of this particular additive does not cause any great deviation in the tin/lead alloy deposit; however, carbon treatment of the bath is required on a more frequent basis to remove the oxidized organics from codeposition in the deposit. As more production experience is realized on this equipment, a total amp hour per gallon figure can be generated with which recommended carbon treatment cycles can be developed.

The development of the high speed tin/lead plating for printed circuit board applications allows reduced dwell time for the plating processes from 10-15 minutes for standard processes to 1-1/2 to 2 minutes. Although this technology is new in the field of printed circuit board manufacture, it has shown large acceptance as the wave of the future for the manufacturing of printed wiring boards. Additional data is being gathered daily to determine the overall effects of metallic impurities within a high speed plating bath along with additional testing of addition agents.

The high speed processing of printed wiring boards was an evolution that had to occur, for associate industries such as the reel-to-reel plating of connectors and the continuous plating of strip, had incorporated high current density plating in the precious metal industry for a number of years. High speed plating and the quality of electrodeposited copper, nickel, tin, and tin/lead alloys are only part of the plating parameters for printed circuit boards that will have to be considered in the future. Continuous high speed plating and processing are the key manufacturing methods for the 1980's, and the implementation of these technologies will require both additional research and personnel to adopt the demands of a developing technology. Many factors which are forcing the circuit board industry to grow and produce quality products at minimum cost over a given amount of time. The processing of the past was adequate to meet the demands of the industry; however, the circuit board industry must increase its productivity and match difficult standards by applying new technologies to meet the challenge of the coming years.

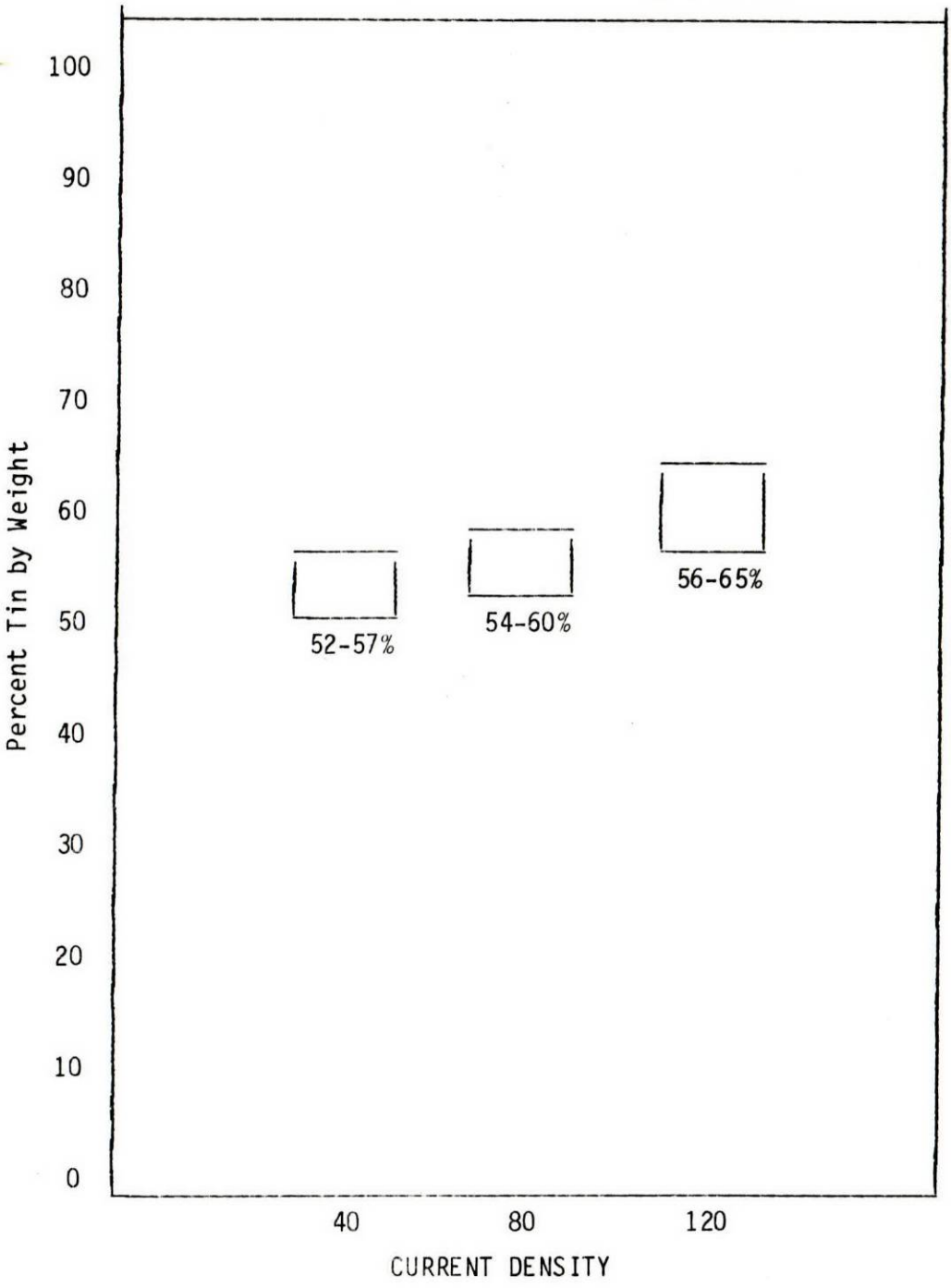
TABLE I

TYPICAL CHEMICAL FORMULATION HIGH SPEED
TIN LEAD PLATING BATH

| | Nominal | Range |
|---|---|---|
| Stannous Metal | 53 Gr/L | 45- 61 Gr/L |
| Lead Metal | 61 Gr/L | 53- 69 Gr/L |
| Fluboric Acid | 200 Gr/L | 150-250 Gr/L |
| Boric Acid | 8 Gr/L | 6- 10 Gr/L |
| Grain Refiner | 24 Gr/L | 20- 28 Gr/L |
| Anti-oxidant | 1 Gr/L | .8- 2 Gr/L |
| Temperature °C | 24 | 21- 25 |
| Agitation | As Provided by Plating Cell | |
| Anodes | 60-40 Tin/Lead | |
| Current Density | 40-120 ASF | |

TABLE II

CURRENT DENSITY VERSUS TIN DISTRIBUTION



T-1

# Electroless Plating II
# Session T

## Economics of Bulk Electroless Nickel Plating

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# ECONOMICS OF BULK ELECTROLESS NICKEL PLATING

## "Little Tricks of the Trade"

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Don't rule out bulk processing of electroless nickel for fear of excessive costs or inferior results. In many cases electroless nickel can be applied less expensively than conventional nickel plating with deposit characteristics that are far superior. This is what makes electroless nickel so attractive for many different applications. All that is necessary is strict adherence to a few rules.

The main ingredients for successful bulk electroless nickel deposition are proper equipment and solutions, excellent surface preparation, stringent bath controls and reliable operators. The following pages will attempt to give you an insight into high volume production of barrel plated electroless nickel.

### Choosing Proper Handling Equipment

Because of the unique ability of electroless nickel to plate any surface uniformly, the rules governing conventional nickel plating can almost be thrown away. Concerns over loading a barrel only half full to achieve good plating distribution can be discounted. The only limiting factors in bulk electroless nickel plating are (1) the parts must be exposed to fresh solution at all times to obtain uniform deposition, (2) the surface area to solution volume ratio must be maintained within acceptable limits, (3) the weight of the parts must not exceed the limits of the equipment.

Baskets or barrels used in bulk electroless nickel plating should be constructed of polypropylene to withstand the high plating temperatures and occasional stripping in nitric acid necessary to remove any residual deposits. They should also have as large an opening as possible to allow the greatest amount of solution flow. One way to accomplish this is to use break down barrels with interchangable panels. In this case, a few plating barrels can accommodate the wide variety of parts normally encountered in a job shop. This will keep capital expenditures to a minimum and still allow thd flexibility or running many different sizes of parts.

Good solution flow is critical, since the ability to keep fresh solution at the plating site has a direct bearing on the plating speed and deposit characteristics. A bath loading of .25-1.5 square feet per gallon is normal. It should be remembered that as the bath loading rate increases, the need for tighter controls also increases, since the depletion of the reaction chemicals proceeds at a much faster rate. ( see control section)

Plating barrels should be submerged at least 80% in the plating solution to provide intimate solution contact at all times. They should also be rotated slowly. A barrel speed of 6 rpm is sufficient to provide adequate agitation and still be slow enough to keep damage to the rotating parts to a minimum.

Most plating barrels come standard with a 115 volt A.C. motor, but for operator safety, low voltage D.C. motors should be considered. The initial cost is higher, but the increased safety level provided to the operator more than offsets the additional costs. You must remember that the electroless nickel tank operates at 185 F and the steam from the tank surface will eventually corrode the electric motors, posing a safety hazard. Air diriven motors are also an excellent choice as long as provisions are made to keep the oil laden exhaust away from all processing tanks.

Other factors such as barrel size and weight capacity must also be considered, but are really dependent on the job application and tank facilities available. The point being stressed is that you must choose your handling equipment with great care.

## Cleaning and Activation

As in all types of plating, cleanliness is of utmost importance. The first step of the cleaning cycle is the removal of heavy dirt and oil. In bulk plating there are two excellent ways to accomplish this, solvent degreasing and power spray washing. Solvent degreasing is usually confined to delicate parts or low volume runs because of the high cost of the chemicals involved. We have found that blended fluro-carbon compounds are one of the best solvents available for this purpose. Its higher price is more than offset by the ease of operation and reduction in health and safety hazards that often accompany degreasing with most chlorinated solvents.

In power spray washing, the parts are loaded into a spiral drum conveyor and taken through a hot alkaline spray manifold and clean water spray rinse to remove the oils. If sufficient volume is available to justify the high initial cost, the power spray washer is the most economical system to operate over the long run.

Once the heavy oils have been removed, the parts are loaded into a properly sized barrel and placed into the cleaning cycle. For non-ferrous parts of brass or copper, only a soak cleaner is necessary. If ferrous parts are being processed, they should be placed in an alkaline derusting solution first. There are many excellent soak cleaners and derusters on the market today, which if operated according to manufacturer's data sheets, will adequately clean the parts.

An overflow weir should be provided so that the solution

can be overflowed as required to skim any floating oil or contaminents from the top of the tank. In daily operation, a gallon of cleaner can effectively process about 200 square feet. At this point, we usually discard the solution rather than replenish, as past experience has shown that by-products that have built up in the days of use will cause poor plating. Replenishing the bath, even though it maintains the correct concentration, will not remove the contaminents. Whenever recharging, the tank bottom should be cleaned of any dropped parts or dirt accumulations.

The parts should be rotated in the cleaners not less than 5 minutes and not more than 10 minutes. Some parts left in a hot alkaline soak cleaner too long may develop oxide films which are difficult to remove and may even cause streaked, uneven plating.

The parts should be transfered from the soap thak to a warm counterflow rinse system. The water should be kept above 70 F to prevent the formation of a gel on the parts. The thermal shock of the hot, soap coated parts being immersed in cold water causes this condition. The gel, while almost invisible to the ncked eye, is very difficult to remove, and will cause poor adhesion.

After adequate rinsing, the parts are transfered to a room temperature, 50% solution of 20 Be' hydrochloric acid for 2 to 5 minutes to remove any oxides formed during prior cleaning operations. This leaves a clean active surface for nickel plating. The acid has about the same useful life as the soap, i.e. approxiametely 200 square feet per gallon, before it should be dumped.

If the components being plated are made of leaded steel or copper with large percentages of lead or tin, a 40% solution of fluoroboric acid should be used in place of the hydrochloric acid. The fluoroboric acid has the ability to disolve the tin and lead from the surface, thereby reducing the possibility of contaminating the nickel solution with these heavy metals, and leaves a much purer surface to plate.

It should be noted that there are many proprietary acid salt combinations on the market which will clean oxides from the parts, but the hydrochloric and fluoroboric acids can do the job just as well at a greatly reduced cost.

As a general rule, it is poor practice to run both copper and steel parts in the same acid tank. The steel parts will receive an immersion copper deposit which can cause peeling; while disolved iron compounds seem attracted to the copper parts and when carried into the plating bath can cause rough deposits. If it is impossible to avoid this situation, as in the processing of copper-steel assemblies, the acid should be changed frequently to avoid plating problems.

Parts should be rinsed in a counter flow rinse system similar to that described under soak cleaning, but the use of de-ionized water is recommended at this point to reduce the carry over of iron, calcium, magnesium, etc., normally found in tap water, into the plating tank. Using a sol-u-bridge to check the conductivity of the water, the conductance should be maintained at 10-15 megohms/cm. These contaminants will greatly reduce the life of the plating solution, as well as cause a wide range of plating problems.

## Nickel Plating Equipment

As the work load processed increases above .25 square feet per gallon, the need for better plating facilities will increase dramatically. A true production electroless nickel system, along with the heating, filtering, and agitation equipment must be carefully designed to allow high volume plating. A modified, steam heated, double tank system has proven to us to be the most efficient system for producing high quality, high volume electroless nickel deposits. Two of the most important features of this system are the teflon supercoils and the CPVC pumps.

The supercoils provide an extremely large heat transfer area in a very small package. This large surface area can also be used in another way. In addition to the standard hook-up to a low pressure steam boiler for heat, we have installed a cold water feed line and drain in the system which allows the rapid cool-down of the solution at the end of the day to preserve the hypophosphite content of the solution. They can also be used whenever a major problem arises which requires the rapid cool-down of the bath. If it takes 4-6 hours to heat a tank with conventional over the tank stainless steel heaters, a properly sized supercoil can do the job in two hours. The solution can also be cooled from 185 F to 130 F in as little as 20 minutes, when necessary. The supercoils also reduce many of the problems of the stainless steel heaters such as susceptibility to being plated, isolated overheating, and possible tank damage is the solution were lost while the heaters were on.

The direct drive CPVC pumps are designed so that no metal component touches the solution. They will provide rapid solution turnover and transfer, if necessary. Small particles of nickel will not jam these pumps, as is often common with magnetic impeller pumps. A properly operated pump-filter bag system is necessary for the production of smooth, fine grained nickel deposits.

These pumps also make daily bath maintence much easier, since the plating solution can be transfered to a properly prepared tank at the end of each shift, analyzed, and adjusted for the next days production. The plating tank that was in use can then be filled with 50% nitric acid to strip away and metallic deposits, and prepare it to receive the plating

solution the following day. The direct drive CPVC pump is the reliable, high volume pump that can accomplish this necessary, daily maintence with great ease.

## Control

Control is so important in electroless nickel plating that we won't allow an employee to operate the tank until they learn and completly understand the titration procedures and how they are applied to the plating solution. While it may take 3-6 months ot properly train someone, the thousands of dollars of chemical losses, excessive down time, or bad parts that can result from one simple error, makes the investment worthwhile. Titration procedures for both nickel and hypo can be found in the manufacturers' literature or plating reference book.

We use these standard titration procedures with one exception. Instead of calculating the actual nickel or hypo content of the bath, we use the mls. of reagent consumed in the titration as the control point. This eliminates the mathematical calculations,and reduces the inherent possibility of error. A graph should be constructed for each nickel tank which plots "mls" against volume of chemicals needed to bring the solution back into balance. This allows the operator to run a simple titration, look at a chart, and determine exactly how much chemicals to add to the tank.

The plating rate, and thus the nickel content will vary with changes in pH, temperature, bath loading and age of the solution. The nickel level should be checked at least once each hour on a moderately loaded, properly maintained bath. If high volume continuous production is to be carried out, the nickel level should be checked every 15 minutes to insure that the bath remains in balance and all parts receive the proper amount of plating. This is especially true in bulk plating, since dragout losses are much higher than most rack plating operations. Manufacturers' data sheets usually provide the proper replenishment schedules. Normally, the addition of the nickel and hypo solutions, based on the nickel titration, will maintain the bath in proper balance. It is advisable to titrate the solution for hypo content at the beginning of each shift, or after long idle periods at temperature, to insure that the hypo content is at the proper level.

## pH

The pH of the bath should be checked and adjusted at the beginning of each load, after all replenishments are made. While most manufacturers recommend a glass electrode pH meter, we have found that a good correlation can be established between the pH meter and most brands of narrow range pH papers. This eliminates the necessity of having expensive lab equipment in the production area, while providing a faster, easier to use check for the operators.

The pH of the bath will fall as parts are plated due to the formation of hydrogen ions in the reduction process. This must be compensated for in order to maintain a stable plating rate. The lower the pH the slower the plating rate. Below a pH of 3.8-4.0, plating almost ceases, while above a pH of 5.6, insoluable precipitates may form which affect appearance and corrosion resistance of the deposit. Too high a pH could lead to total bath destruction. The pH may be raised with small additions of a 50% solution of reagent grade ammonium hydroxide and lowered with a 10% solution of reagent grade sulfuric acid.

The addition of either sulfuric acid or ammonia should be made slowly, with good agitation to prevent shocking the bath. All pH measurements should be made at room temperature.

## Operation

After the bath has been made up and analyzed, the parts can be taken through the cleaning and activating cycle and placed in the plating tank. Transfer of the parts from the acid tank and subsequent rinses should be as swift as possible to prevent the formation of any oxides.

Once placed in the plating tank, most steel parts will start to plate immediately, while copper or brass parts must be "struck off"(initiate plating), as they are non-catalytic in most electroless nickel solutions.

Our method of striking off the parts is to use a small rectifier which can provide at least 0.25 amps/sq.ft. The positive terminal is connected to a nickel anode about 10" long and hung in the solution. The negative terminal is connected to the parts. The current flow deposits a flash of nickel on the parts. When the current is turned off, plating will continue, as the nickel layer is catalytic in the plating solution. Normally, a 30-60 second current flow is all that is required.

Electrolytic striking off eliminates the need for palladium or other type chemical acitvating solutions. It also eliminates the possibility of carrying a catalized solution into the plating tank , which can cause rough deposits.

Once plating has started, the parts are left in the solution for the required time to obtain the necessary thickness. The thickness should be checked frequently, even as often as once each batch in the case of high reliability parts. Our method of checking thickness is to plate a polished steel panel along with the parts and check its thickness with an eddy current tester. While the reading from this machine will not be exact, a corrolation factor established using cross-sectioning and high magnification will provide an easy method for a reasonably accurate thickness check. Other tests which are usually performed at the end of the plating cycle include checks for general appearance, rough deposits, blistered

plating, and in cases where corrosion resistance is extremely important, a 30 second soak in concentrated nitric acid. Since not all electroless nickel deposits can withstand the same tests the initial choice of the plating solution is very important.

Once the parts are removed from the tank, the solution is checked and replenishment of the nickel and hypo are made before the next loads are processed. Replenishment should be made slowly and with adequate agitation in the following order- nickel first, hypo second, ammonia last if required. Any additions of water to maintain proper operating level should also be made at this time.

## Trouble Shooting

Because of the many complex variables involved in electroless nickel plating, it is really more of an art than a science. Most manufacturers cannot give a quick over the phone answer to a plating problem because they require samples and sophisticated lab equipment to find a solution. Unfortunately, this may take weeks and a production line cannot lie idle waiting for an answer. Below are listed some of the oddities encountered over the years and steps taken to overcome them.

Problem: Non-adherent plating

1. Poor cleaning cycle
   a. Check cleaners and make sure they have not been used beyond recommended times. Change if necessary.
   b. Check for oil contamination in all process tanks. One drop of oil on a tank, whether it comes from the parts, overhead hoists, or other sources, will leave a thin film on the surface which will contaminate any part run through. Overflow or dump and clean the tank, then recharge with fresh solution.
   c. Check transfer time between tanks. Too long a transfer time between any tanks can cause oxides to form which are difficult to remove.
2. Nickel on nickel plating. If the area that blistered still has a nickel coating underneath, probable cause is in the plating bath. Check to see that no large chemical additions were made directly over the parts as they were plating. Any large addition would cahnge the structure of the deposit and cause stratified nickel plating. One possible remedy is to give the parts a 375 F bake for one hour to increase adhesion. This is a hit and miss situation, and is intended as a salvage operation for parts already plated. It is not a cure. Instruct operators on proper method of making addition.
3. Check parts for laminations in the raw material. There is no cure for this, other than notifying the customer and returning the parts to him.
4. Check for possible contamination of heavy metals such as iron, lead, tin, manganese, and mercury. Heavy metals are

one of the most difficult items to check for, since concentrations as low as 1 ppm can cause the plating bath to go haywire. One indication is when a relatively new bath with all the variables well within operating limits has either a low plating rate or stops plating altogether. The only cure is to pinpoint the source of the heavy metals, i.e. incoming water not run through a deionizer, contaminated reagents, hole in the supercoil introducing bad water, or operator error in placing the wrong chemical in the bath. Once the source has been located, it should be eliminated and a new bath made up. as once a plating bath has been contaminated with heavy metals, no economical way exists to remove them.

Problem: Low Plating Rate

1. Low plating temperature. Check to see that the controllers are operating properly and indicated temperature is correct.
2. Low nickel level
   a. Check to see that the tank has been analyzed and correct additions made. Adjust if necessary.
   b. Check tank for "plating out". This term defines the deposition of nicekl on the tank and heating coils. Since this is also plating, it is consuming nickel and hypo, thereby leaving less available to deposit on the parts. Plating out can be discovered by observing the tank with the air off and no parts in the tank. The solution should be dark emerald green with no evidence of gassing. If a tank is plating out, there will be significant gassing and a lightening of the solution color. Nickel metal may also be observed on the heating coils and tank walls. The best remedy is to transfer the plating solution to the properly prepared alternate tank through a double five micron filter bag, adjust nickel and hypo levels, and continue plating while stripping the plated out tank for the next days work.
3. Metallic contamination: See previous section
4. Low hypo level caused by idling bath at operating temperatures for excessive periods of time. Level should be determined through analysis and adjusted back into range.
5. Normal slowdown of the bath on aging of the solution. Slight increases in pH and temperature may provide a temporary fix, but from a cost standpoint, the plating bath should be dumped and recharged to maintain optimum efficiency.
6. Low pH. Adjust to proper range with ammonia as previously described. Note: Verify accuracy of pH papers against calibrated pH meter. pH papers may have been contaminated with solutions if good housekeeping methods are not used.

If the parts are removed from the plating tank prior to the discovery of the low plating thickness, the parts may be

recleaned and activated in a 25% solution of sulfuric acid, then replated to the required thickness.

Problem: Rough, Sandy Deposits

1. External contamination from dirt, metallic chips, etc. The particles float around in solution. Some of them are removed by the continuous filtration, but others settle on the parts and are plated over. The only way to remove the rough deposits is to strip and replate. To prevent the problem on future loads, the solution should be transfered as quickly as possible to the standby tank through a double five micron filter, and adjusted to proper limits.
2. Internal nucleation or hyperactivity caused by too high a pH, temperature or surface area/solution volume ratio. Transfer and filter as above, but correct cause of the problem before restarting.

Problem: Bath Decomposition

1. Overheating caused by insufficient air agitation or runaway temperature controller. This condition causes gross hyperactivity and seeding out. If caught early enough, the bath can be cooled down below 140F using the reverse supercoil hookup to stop activity, transfered and filtered. If the seeding out has consumed more than 40% of the nickel and hypo, it is more economical to dump and recharge.
2. Seeding out caused by too high a pH or hypo concentration. As above, if more than 40% of the chemicals have been consumed, dump and recharge; if not, transfer, analyze, and bring chemical levels back to normal.

Problem: Streaky Deposits

1. Lack of sufficient agitation. Check to see if air flow from carbon vane blower is sufficient or barrel stopped rotating. Adjust or repair as necessary.
2. Organic contamination introduced through the input of contaminated water or erroneous chemical additions. Organic, like metallic contamination, is very difficult to pinpoint without sophisticated lab equipment. It may be corrected by carbon treating, but the process is so long that it is usually more economical to discard the bath and recharge. Insure that the problem is not repeated by taking steps to prevent the addition of erroneous chemicals and run incoming water through a carbon pack to remove organics.
3. Problem in the cleaning cycle. A dirty degreaser, old or weak soap and acid, or lengthy transfer time between solutions may prevent the proper cleaning of parts.

Problem: Solution turns milky green or large white particles are seen floating in the solution.

This condition is caused by too high a pH, lack of stab-

ilizers in the bath, or a combination of both. What actually takes place is the formation of slightly soluable nickel hydroxide at a pH of 5.5 and above. Once formed, it is difficult to redisolve. A temporary cure can be effected by cooling the bath to 140 F and adding 10% sulfuric acid to reduce the pH to 3.0-3.2. This will redisolve the nickel hydroxide. Small additions of stabilizers as per manufacturers recomendations should be made and the bath brought back to normal operating levels. This will allow plating to the end of the shift, but a new solution should be made up as soon as possible as the condition will reoccur.

## Cost Control

It's true that the chemicals used in electroless nickel plating are expensive when compared to those used in standard nickel plating. While it costs approxiametly $0.25 per mil sq.ft. for conventional nickel plate, it costs, according to most manufacturers, $1.50 - 2.00 per mil sq. ft. for electroless nickel plate. This number is theoretical since it does not take into account solution transfer losses, dragout, or nominal metal plating on the tank walls and heaters during normal production. The mil sq. ft. cost in actual production can range from $1.00 per sq.ft. for home brew baths to $3.00 per sq.ft. for some proprietary nickel baths.

This is where profits are made or lost in bulk electroless nickel plating. The plater must have absolute control of his plating costs, since in many bulk electroless nickel jobs, the chemical cost can amount to 60% of the selling price. The theoretical numbers supplied by the manufacturers are good starting points, but only by actual in house cost analysis can each plater determine his own cost factors. The method we use involves comparing the number of parts processed in a given day against the amount of chemicals required to produce those parts. It can be done on a square foot basis or part count basis, as long as the method is consistent. In a short time, each plater will be able to determine his exact costs, and enable him to quote his work accordingly; as well as make comparisons among the various electroless nickels available. This method takes into account any loses or other peculiarities in a given shop and therefore, reflects a realistic rather than theoretical number.

The higher mil sq.ft. cost does not mean that electroless nickel cannot compete with standard nickel plate. Higher barrel loading rates and normally shorter plating times to achieve a given thickness gives and increased efficiency rating to any high volume operation. It must also be remembered that a much thinner deposit of electroless nickel will perform as well as a much thicker deposit of standard nickel; and this doesn't even take into account the specialized characteristics of electroless nickel, such as, lubricity, uniformity of deposit thickness, superior corrosion resistance, better

solderability, and superior electrical properties.

The secret then to successful bulk electroless nickel plating lies in the hands of the plater. If he uses careful control methods and realistic pricing, the world will beat a path to his door. If not, he may become another plater with bad memories of his experience with electroless nickel.

T-2

# Electroless Plating II
# Session T

## Minimization of Changes in Electroless Copper Bath/Deposit Characteristics with Cycling

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# MINIMIZATION OF CHANGES IN ELECTROLESS COPPER BATH/DEPOSIT CHARACTERISTRICS WITH CYCLING

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## Introduction

During operation of electroless plating baths, the bath ingredients are depleted by a combination of consumption, drag-out and bail-out. In order to keep the plating solution operational and within specification, the amounts depleted must be continuously replenished. In recent years, for economic reasons, there has been a trend in the printed cirucit industry, towards electroless copper baths which contain the replenished ingredients in the smallest volume of water practicable. These low volume replenishers lead to "no-growth" or "low-growth" baths. As a rule of thumb, we might define "low growth" as $\leq$ 10% volume replenished per cycle (a cycle is one complete metal-turnover), "medium growth" as 10-20%, and "high growth" as >20% volume per cycle.

Several factors are involved in the lower costs of low-growth baths:

1. Less freight cost because less water is shipped to the plant by the chemical supplier:

2. Less volume of bail-out means less waste of the bath chemistry;

3. Less volume of bail-out means less effluent from the plant requiring costly waste-treatment procedures.

These factors argue against the use of medium or high growth baths. However, in order that the total economic picture be understood, two countervailing forces must also be considered:

1. The percent of multilayer boards as a fraction of total printed circuit board fabrication has increased steadily over the past few years. The high cost and great complexity of MLB's require highly reliable and consistent processes, and necessitate the use of the best technology available, even if a small incremental cost is involved.

2. Increasing government regulations regarding plating shop effluent have stimulated progress in development of waste treatment procedures. As a result, treatment of electroless bath growth is greatly simplified and cost effective.

In working to develop highly reliable electroless copper processes for MLB fabrication, we have determined that moderate bath growth can offer significant advantages in terms of deposit and bath consistency with cycling, relative to low growth baths.

In this paper we will describe, from both a practical and theoretical viewpoint, the advantages in MLB processing of a medium growth vs. a low growth electroless copper bath.

Before beginning a description of all factors involved, we will describe the events leading to recognition of the benefits of medium vs. low growth baths.

The low growth bath had been formulated to satisfy a wide variety of customers and allowed fairly broad operating ranges on parameters such as temperature, hydroxide and formaldehyde content, and throughput. However, it was subsequently found that if all these parameters were simultaneously and continuously maintained at the upper limits of the recommended ranges, bath and deposit characteristics deteriorated markedly after about 8 to 10 cycles. This observation was found first in the field and was reproduced in the laboratory. It was hypothesized that higher growth in replenishment would make the bath more forgiving to continuous use at the higher limits of the operating parameters, and thus the higher growth bath was formulated. Results of the side-by-side cycling, in the laboratory, of the low and medium growth baths at high operating parameters is shown in Table 1.

These results convinced us of the need to consider the merits of a medium vs. low growth bath, and led to recognition of the numerous principles described in this paper. Closer study of bath and deposit characteristics, and minimization of changes in these characteristics with cycling, has also been carried out, and will be described herein.

## Theoretical And Observed Merits Of A Medium Growth Bath

Starting from a theoretical point of view, there are four main reasons why one would expect a medium growth bath to maintain better consistency of operation than a low growth bath.

1. Salt build-up due to replenishment is reduced.

2. Customer variations in drag-in/drag-out do not affect the chemical balance so drastically.

3. Build-up of decomposition by-products is minimized.

4. Concentration of extremely reactive ingredients in the replenisher concentrates is reduced, thus leading to less reactivity in the concentrate packages prior to usage and less shock upon replenisher addition.

We now consider each of these factors in greater detail.

In order to observe, from a practical viewpoint, the effects of these factors, a laboratory test was devised in which two electroless copper baths having identical formulations except for variation in growth rate (7 1/2% vs. 15%) were worked through 20 cycles side by side. It had already been observed in customers' shops that the 7 1/2% growth bath, which displays very good operating consistency and performance, was exceeded significantly in these areas by the 15% growth bath. Thus, in order to understand these observations more completely and be able to characterize the baths more thoroughly, this laboratory comparison was carried out, as will now be described.

1. Salt build-up is reduced.

Typical electroless copper baths employ copper sulfate or copper chloride as a source of metal, and sodium hydroxide as a source of caustic. As copper and hydroxide are consumed in the plating process, either sodium sulfate or sodium chloride is produced. These salts build up in the bath with cycling as shown in Figures 1 and 2. Because of the greater amount of bail-out in the case of the medium growth (15%) bath vs. the low growth (7 1/2%), total salt build up is reduced, and the steady state is reached at a lower number of cycles. Naturally, if growth even lower than 7 1/2% is the case, salt build-up will be even more dramatic.

Such salt build-up can produce readily observable changes in bath characteristics. The most easily observable difference is a change in specific gravity of a bath as it is cycled. In Figure 3 we show the measured specific gravities of the 7 1/2% and 15% growth baths. By comparison with the previous figures it can easily be seen that the rise in S.G. is largely due to salt build-up. In practice, in the field, it has been observed on occasion that S.G. greater than 1.10 can lead to plating problems such as reduced plating rates or poor copper adhesion. This problem is readily solved by diluting the bath with a fraction of fresh bath mixture. However, such dilution does require special operator maintenance, and a more ideal

situation would occur if the dilution were carried out automatically. Thus, the medium growth (15%) bath leads to maintenance of low specific gravity without the need for special on-site controls.

2. Customer variations in drag-in/drag-out

Every electroless plating bath is formulated in such a way that the replenishers contain all the ingredients depleted from the bath by any mechanism. Depletion can occur by three main mechanisms:

a. Chemical consumption in the plating process and associated side-reactions.

b. Bail out

c. Drag-in/drag-out

Consumption can vary from zero to 100% per cycle depending on which component is being considered. Copper metal, for example, is consumed at 100% per cycle by definition. Chelate materials, on the other hand, are usually not consumed at all, and need to be replenished only for drag-out and bail-out losses. Between these two extremes of zero and 100% consumption fall most of the other bath constituents, including caustic, formaldehyde, stabilizers, brighteners, etc. Usually the consumption figure determined during formulation of a bath is accurately carried over to operation in the field, although exceptions do exist, such as when a customer operates a bath under conditions of temperature, caustic, formaldehyde and loading which differ substantially from those recommended by the chemical supplier.

Such cases are rare, however, and we will assume for the time being that laboratory consumption figures carry over to the field.

Bail-out or growth, is the one factor in depletion which can be known with good certainty. As mentioned previously, the growth can vary from close to zero upwards to perhaps 25% for most practical electroless baths.

Drag-in/drag-out varies considerably from shop to shop depending on the type of operation. It is thought that drag-in can vary from 2% to 7% of the bath volume, per cycle, depending on the operating conditions.

The formulator cannot take into account all these variations in drag-in, but must choose arbitrarily an average, typical drag-in figure to use in preparing replenishers. Although the difference between 2% and 7% may seem small, this difference can be magnified by cycling, as we now show.

Consider the copper and chelate components only. In Table 2 we list the factors involved in determining replenishment. It will be noted that a drag-in factor of 4% was used as a working assumption. If, in fact, the customer's drag-in equals 4% per cycle, the replenishment schedule determined by the formulator will be correct. However, if the actual drag-in is either 2% or 6%, the replenishment schedule will not be accurate for the customer's shop.

It can be seen from the Table that the percent effect on the low consumption rate bath components (such as chelate) is greater than on the high consumption rate components (copper). This is because drag-in comprises a larger percent of amount replenished for a low consumption component.

It can also be observed that the effect of drag-in variation on the chelate replenishment schedule is substantially less in the case of medium to high growth baths than in the case of low growth baths. Thus the higher growth baths are more "forgiving" to variations in drag-in which may be encountered in various customers' shops.

In order to determine how this drag-in variation will affect bath component concentrations with cycling, Figures 4 and 5 were prepared. It is assumed that copper content in the bath is kept constant; the chelate concentration which results from the drag-in variation is then calculated for the 5% and 20% volume growth cases only. From these figures it is clear that the chelate to copper ratio, which is assumed to start at 3:1, goes progressively further out of balance as cycling progresses. This effect is substantially reduced for the high-growth case, and does tend toward a steady state with prolonged cycling. However, such imbalances in chelate to copper ratios are not desirable and can lead to significant variations in deposit characteristics.

For example, from the plating literature (Ref. 1) a typical study of plating rate vs. chelate to copper ratio is obtained. The particular bath involved in that study was a tartrate system[a] and data on rate vs. chelate to copper ratio are summarized in Table 3. It can be seen that as much as a 25% increase in plating rate would be observed if the tartrate/copper ratio increased from 3.00 to 3.75, as might be the case if a low growth replenishment were used, and the actual drag-in was significantly lower than that assumed during formulation.

We have considered here only effects of drag-in/drag-out on chelate to copper ratio. Obviously, all the bath components must be considered in reaching an overall conclusion about this effect; the data shown, however, do suggest the greater tolerance of higher growth baths to customer variation in operating parameters.

In Figure 6 we show the plating rates observed for the low vs. medium growth baths as a function of cycling. The decrease in rate seen over the first few cycles is normal for this formulation and is not considered, in itself, to signal any peculiarities about the growth. However, the relatively prompt leveling off of plating rate by the medium growth vs. the low growth bath does again suggest the more consistent behavior of the higher growth bath, even under laboratory conditions.

(a) The authors do not mean to imply, by the use of this literature data, either that the results of this study are applicable only to tartrate systems, or that the copper baths compared in this study are tartrate baths.

3. Build-up of decomposition products

Certain of the reactions taking place in the electroless plating process involve by-products which then tend to build up in the bath. Two examples of such by-products are methanol and formate ion, produced by reaction of formaldehyde and hydroxide in the Cannizzaro reaction:

$$2\ H\text{-}\overset{\overset{O}{\|}}{C}\text{-}H + OH^- \longrightarrow HCOO^- + CH_3OH$$

Buildup of these decomposition products is expected to be minimized in the medium growth bath vs. the low growth bath; this is now under investigation.

4. Lower concentration of reactive materials in replenisher packages

This phenomenon was unexpected initially, but had to be considered after initiation of the test program.

If the only effects of high growth were minimization of changes with cycling, then it would be expected that the two baths should behave identically on make-up. However, this was found experimentally not to be the case. Several of the tests carried out on freshly made baths were found to give results more like those from cycled baths in the case of medium vs. low growth. For example, rate tests gave significant and reproducible differences on make-up. See Figure 6 for a summary of rate test results.

In order to ascertain whether differences in deposit crystalline structure occurred between low and medium growth baths, scanning electron micrographs were obtained after one and 20 cycles. These are given in Figure 7, and show that little difference is apparent between the two baths.

Two other areas of interest in this study, where significant differences were observed between low and medium growth baths, were initiation time for plating, meaning the time required after immersion of the workpiece before vigorous gassing is observed, and stability of the bath on standing. It was found, throughout cycling, that the 15% growth bath consistently gave shorter initiation time (average 13 seconds) vs. the 7 1/2% growth bath (average 25 seconds) upon introduction of catalyzed surfaces. This shorter initiation time did not, however, seem to be correlated with lower bath stability on prolonged standing. On the contrary, it was consistently found that both the in-the-tank solution, as well as the bail-out sample collected and stored, displayed analytical and/or visual greater stability regarding plate-out or dusting, in the case of the 15% growth bath.

Thus the medium growth bath appeared to combine many desirable operating features of electroless plating solutions more consistently than a low growth bath. There were, in this study, numerous tests in which virtually no difference was observed between the low and medium growth baths or deposits. Notable among these were coverage, deposit stress and ductility. However, as a result of this work, we believe that better consistency of performance can be

achieved under a wide variety of operating parameters, by use of a moderate growth electroless plating bath. For many applications, the high overall costs of fabricating reliable multilayer boards, and the recent advances in waste-treatment of electroless bath growth will override any apparent cost advantage of low- or no- growth electroless baths.

Reference

1. M. Saito and H. Honma, 1978

Acknowledgement:

We wish to thank several members of the Shipley Technical Department who contributed either directly or indirectly towards our carrying out this study: Peter R. Rose, Edward C. Couble, Gerald J. Roelants, as well as Martin J. Harris of our Sales Department, were all quite helpful. Assistance of Gabriella Bene and Richard Carey in obtaining the analytical results is also appreciated.

Table 1 The Behavior of Plating Bath Under *Extreme Conditions

| Cycles | 1 | | 5 | | 10 | | 15 | | 20 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Growth | L | M | L | M | L | M | L | M | L | M |
| Rate/ 20 min. | 105μ" | 105μ" | 105μ" | 105μ" | 60μ" | 108μ" | - | 105μ" | - | 105μ" |
| Coverage | E | E | G | E | G | E | - | E | - | E |
| Bath Stability | E | E | G | E | P | E | - | VG | - | VG |
| Deposit Color | BMP | BMP | BMP | BMP | dark pink | BMP | - | BMP | - | BMP |
| Initiating Coverage | 15 sec | 15 sec | 25 sec | 15 sec | 25 sec | 15 sec | - | 15 sec | - | 15 sec |
| Specific Gravity | 1.05 | 1.05 | 1.08 | 1.08 | 1.11 | 1.08 | - | 1.08 | - | 1.08 |

Comments: At 6 cycles low growth bath got turbid, medium growth did not.
At 8 cycles low growth bath plated out heavily.
At 10 cycles low growth bath triggered.

E = Excellent
VG = Very good
G = good
P = Poor
- = bath not operated due to triggering
BMP = bright metallic pink
L = Low growth
M = Medium growth

*Substrate etched & scrubbed smooth FR-4, Temp. 120°F
Constant high content of $OH^-$ & CHOH through 20 cycles

TABLE 2: EFFECT OF DRAG-IN VARIATION ON REPLENISHMENT SCHEDULE

| VOLUME GROWTH | 5% | | 7 1/2% | | 15% | | 20% | |
|---|---|---|---|---|---|---|---|---|
| | Copper | Chelate | Copper | Chelate | Copper | Chelate | Copper | Chelate |
| REPLENISHMENT | | | | | | | | |
| Consumption | 100% | 0% | 100% | 0% | 100% | 0% | 100% | 0% |
| Bail-out (growth) | 5% | 5% | 7.5% | 7.5% | 15% | 15% | 20% | 20% |
| Drag-in/ Drag-out | 4% | 4% | 4% | 4% | 4% | 4% | 4% | 4% |
| Total replenished per cycle | 109% | 9% | 111.5% | 11.5% | 119% | 19% | 124% | 24% |
| % error in replenishment schedule if a 2% variation in drag-in occurs. | 1.8 | 22 | 1.8 | 17 | 1.7 | 10 | 1.6 | 8.3 |

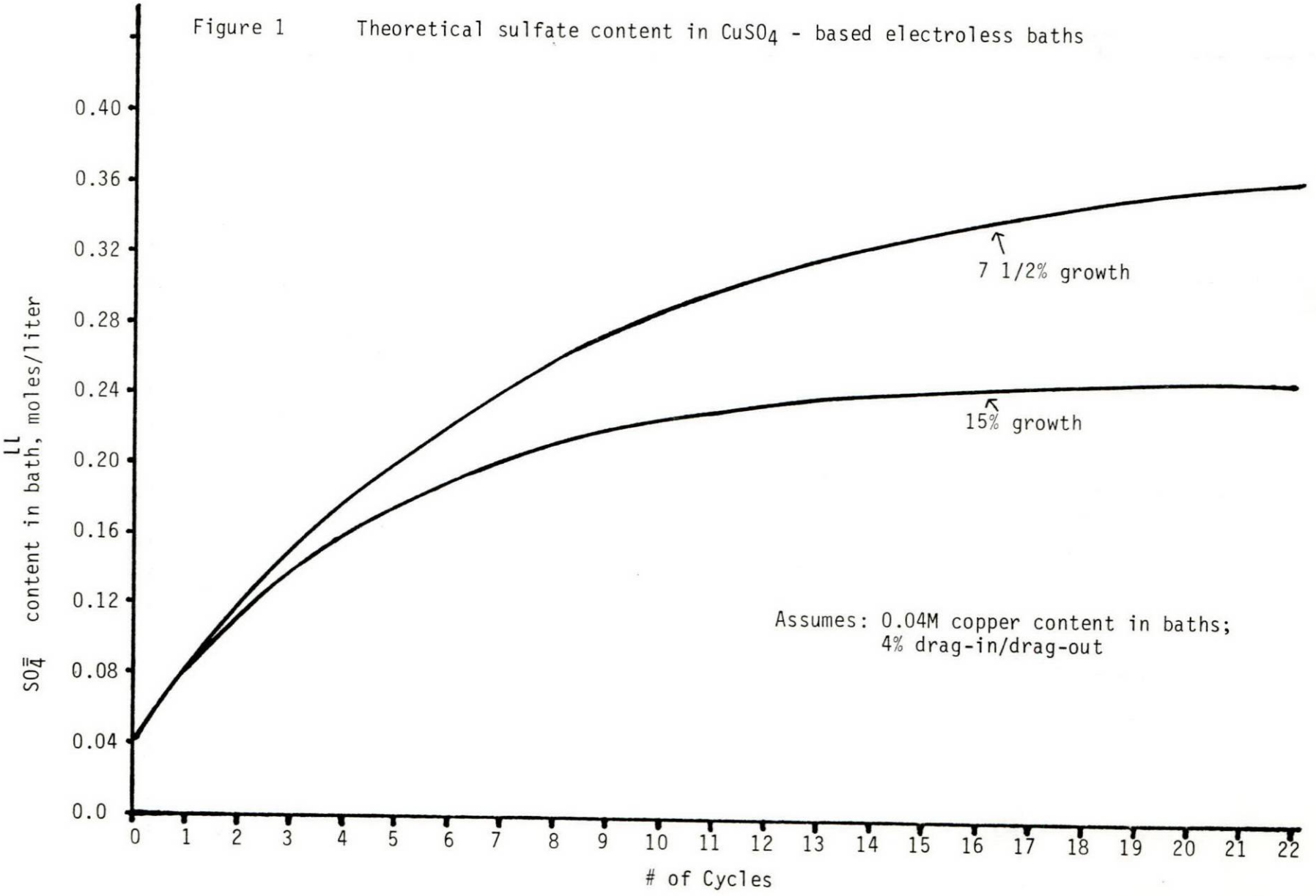
TABLE 3

Plating rates, μ in/min. for a tartrate-based electroless copper bath:

| Tartrate/copper, molar ratio | Plating rate, μ in/min. |
|---|---|
| 2.50 | 0.94 |
| 2.75 | 1.01 |
| 3.00 | 1.08 |
| 3.25 | 1.16 |
| 3.50 | 1.23 |
| 3.75 | 1.30 |
| 4.00 | 1.37 |

1. Data taken from: M. Saito & H. Honma, 1978

Figure 1 Theoretical sulfate content in $CuSO_4$ - based electroless baths



Figures 2: Theoretical Chloride content in $CuCl_2$ - based electroless baths

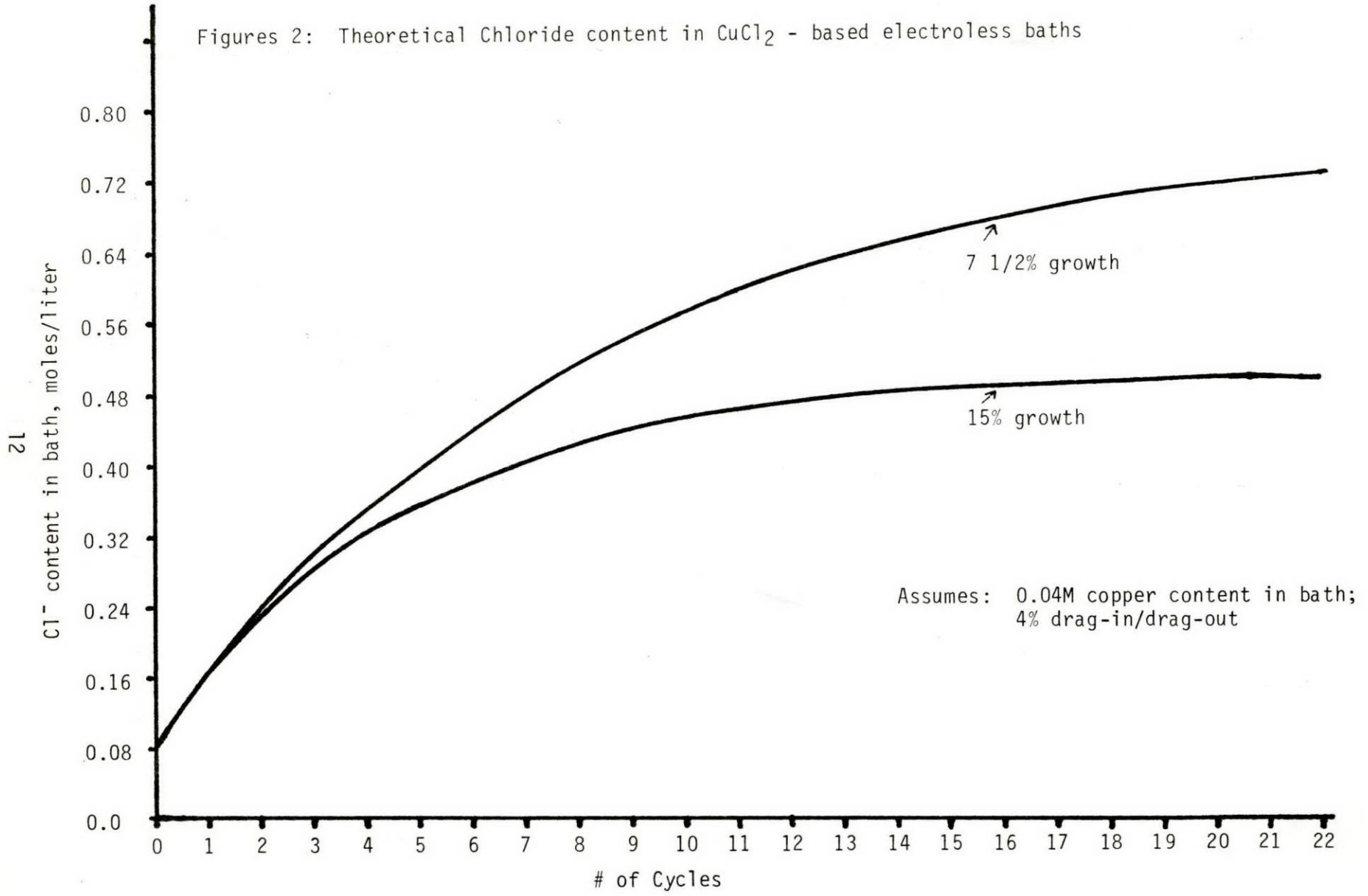


Figure 3: Specific gravity observed in laboratory cycling of low and medium-growth electroless baths.

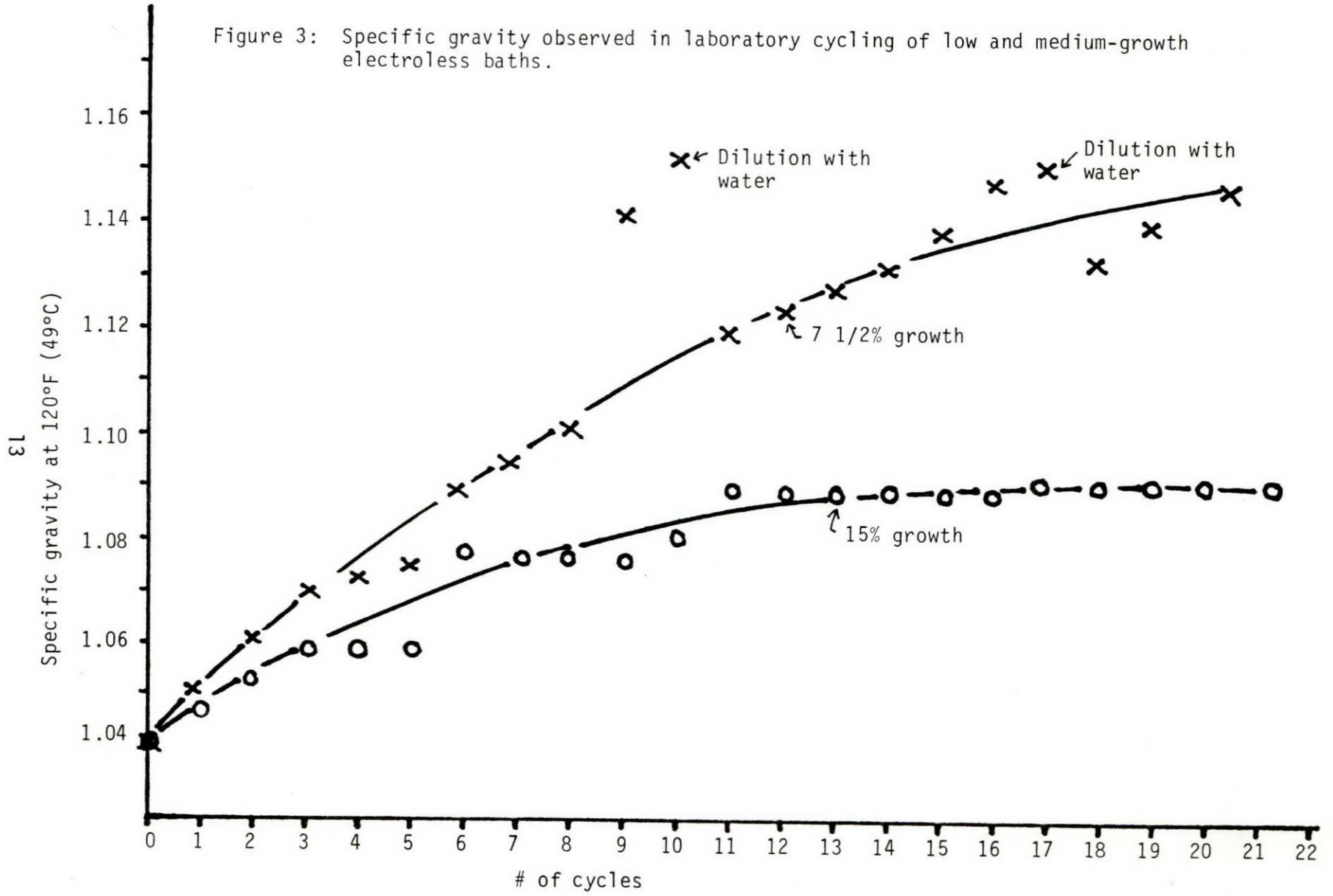


Figure 4: Effect of Volume Growth on Chelate/Copper Ratio

4% Drag-in/Drag-out assumed in formulation

2% Drag-in/Drag-out actual

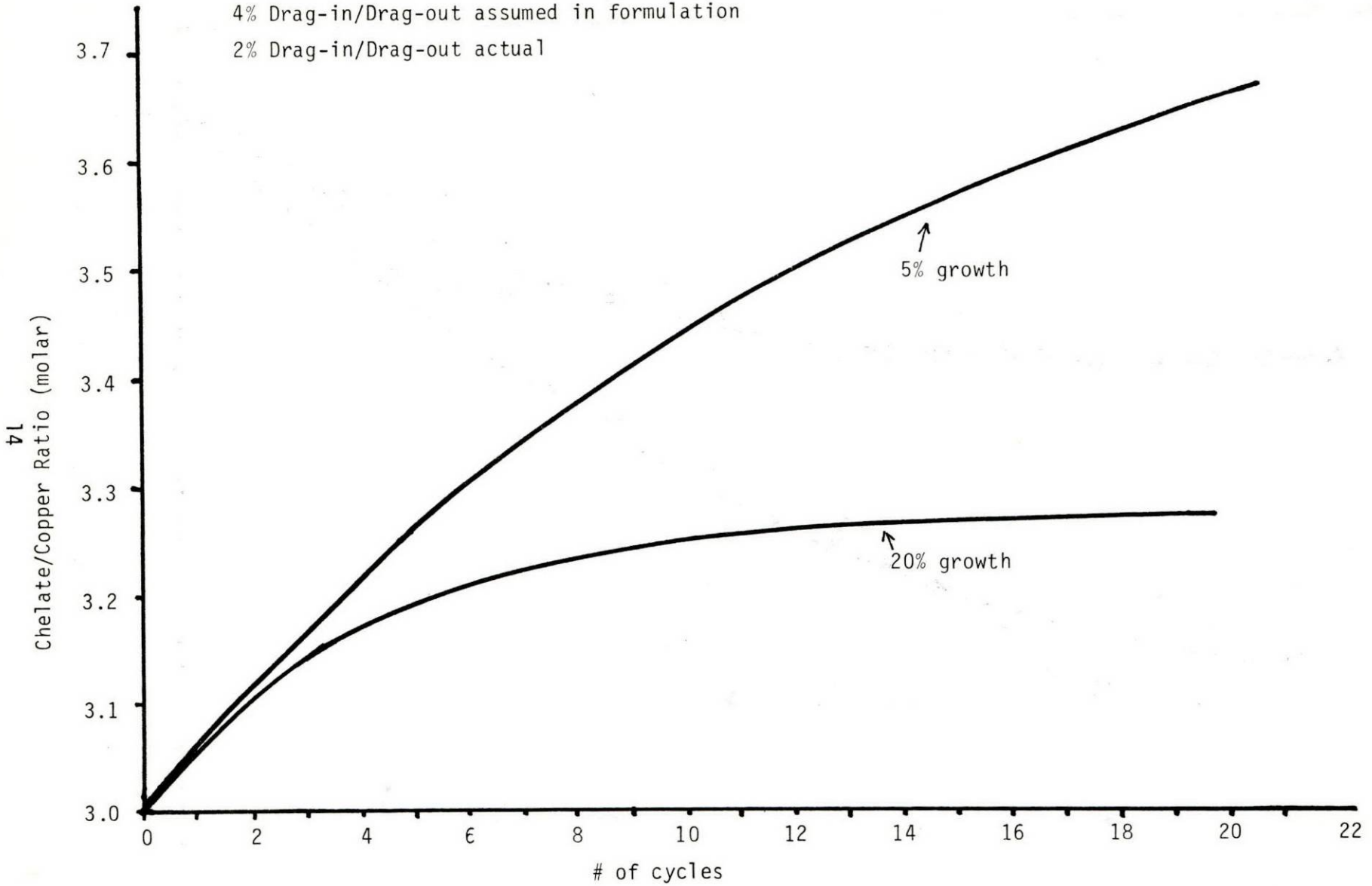


Figure 5: Effect of Volume Growth on Chelate/Copper Ratio

4% Drag-in/Drag-out assumed in formulation

6% Drag-in/Drag-out actual

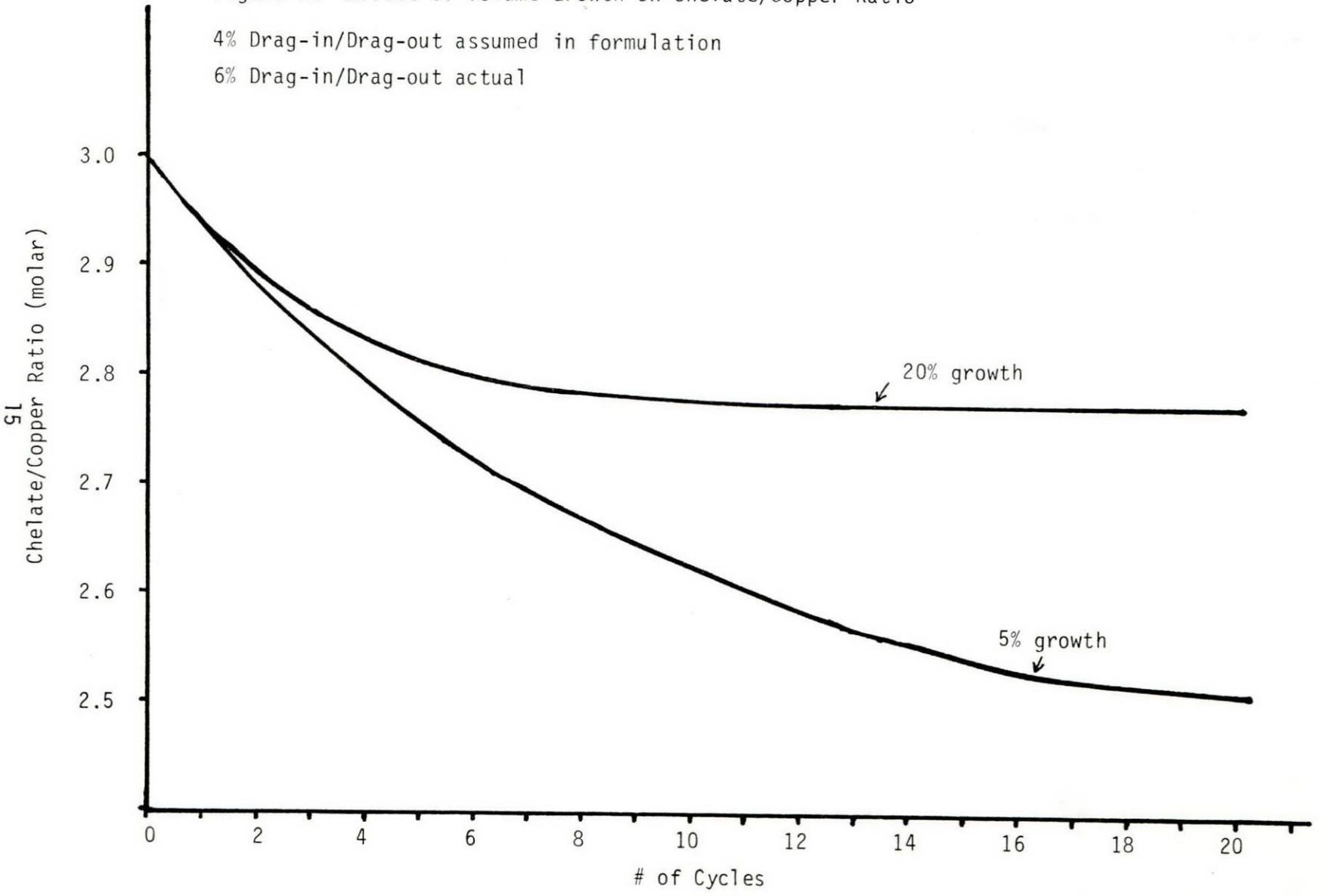
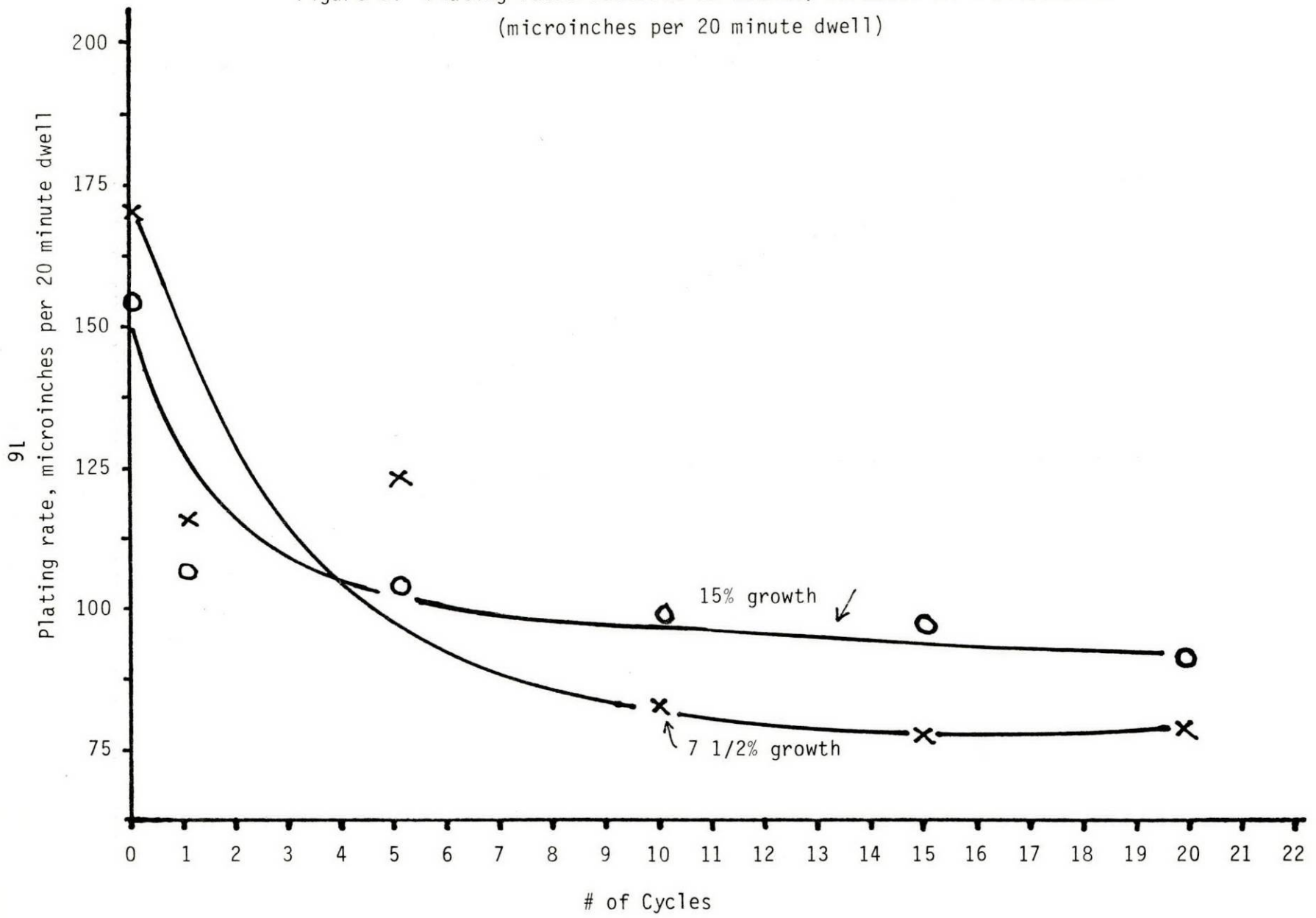
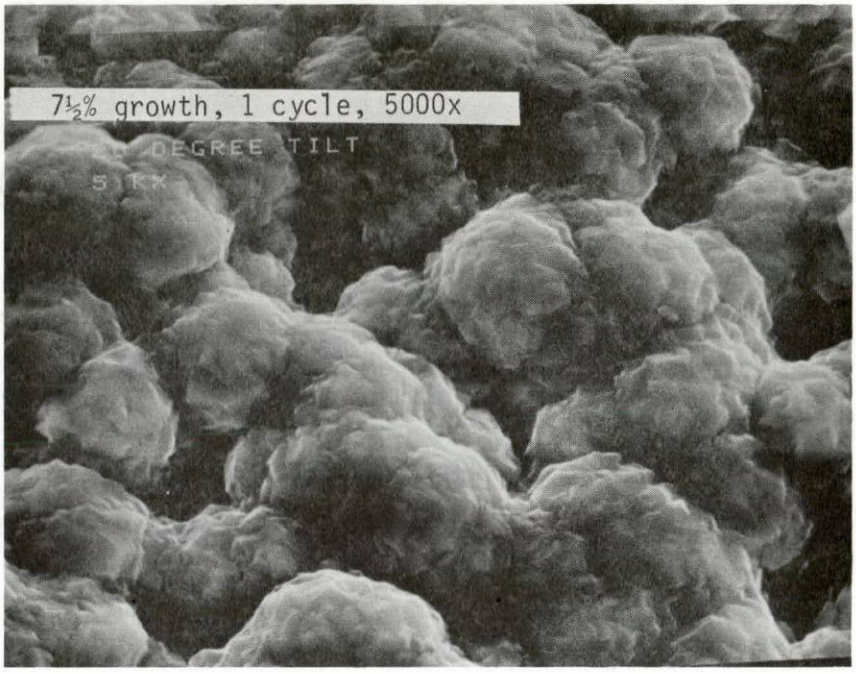
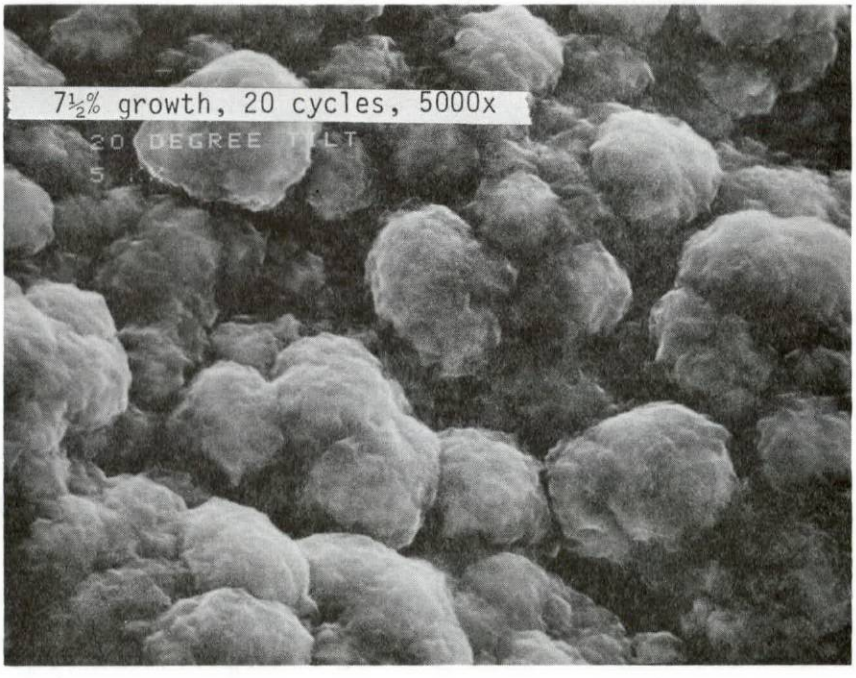


Figure 6: Plating rates observed on etched, scrubbed FR-4 substrates
(microinches per 20 minute dwell)



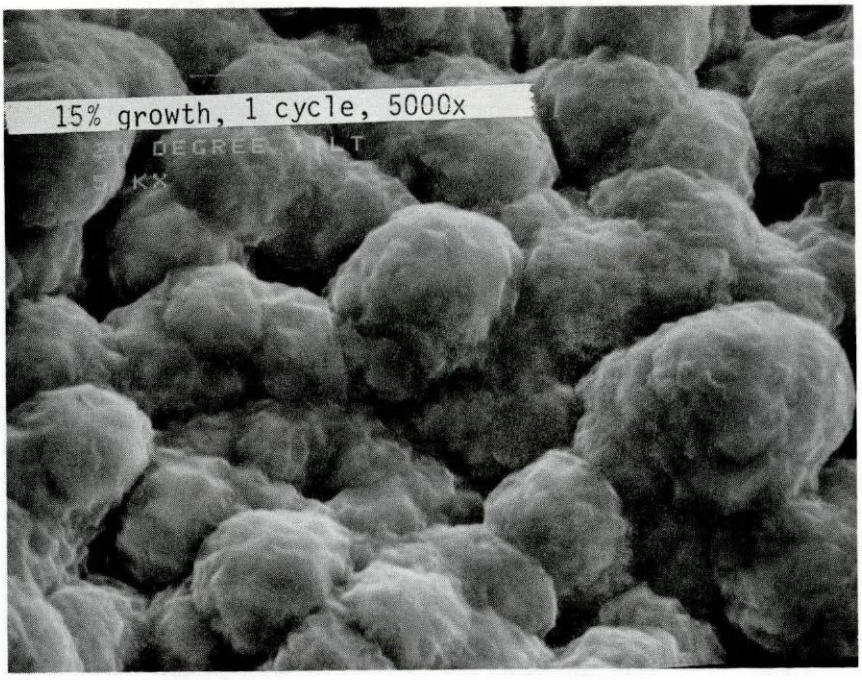



(a)

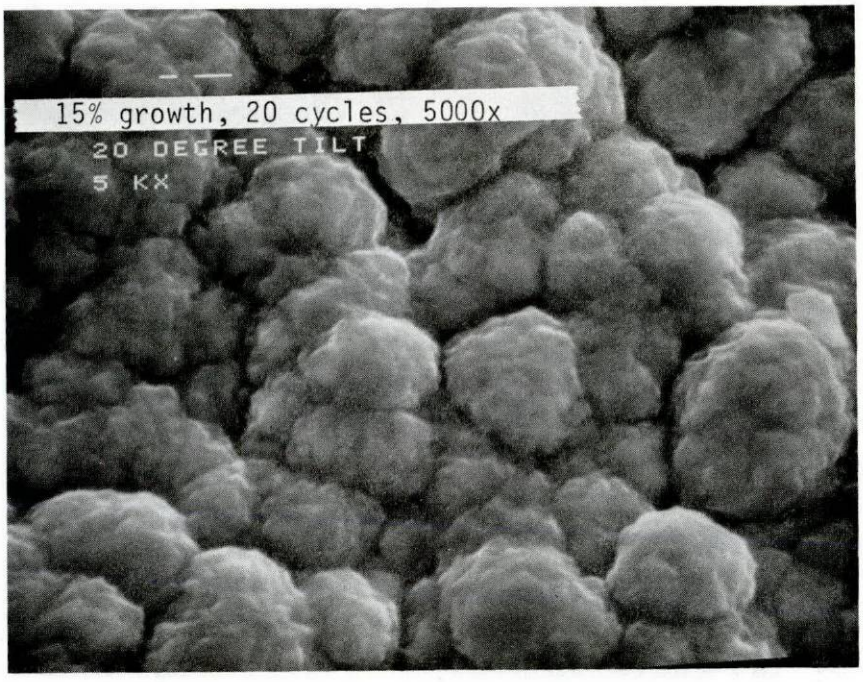



(b)

Figure 7: Scanning electron micrographs of copper deposit




(c)




(d)

Figure 7: Scanning electron micrographs of copper deposit.

# U-1

# Chromium Plating
# Session U

## High-Speed Chromium Plating on Bright Nickel Substrates: (1) Applied Studies

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# HIGH SPEED CHROMIUM PLATING ON BRIGHT NICKEL SUBSTRATES: I. APPLIED STUDIES

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## Abstract

The high speed plating (HSP) of chromium on copper and steel substrates has been successful, but bright nickel plated substrates only partially so. This work has demonstrated HSP of chromium at rates of 2.1 to 4.3 μm/min on bright nickel plated copper samples. Activation of the nickel surface by acid dipping in a 10 v/o hydrochloric acid was a necessary process step. Under no conditions could the bright nickel substrate be high speed chromium plated at a current density of 2.5 $A/cm^2$ or above without exfoliation of the chromium. Steel and copper substrates have been successfully HSP chromium plated at 30 $A/cm^2$.

## Introduction

The high speed plating (HSP) of chromium has been successful when applied to copper or steel substrates. HSP investigation was carried out on tubes (1,2,3) plated at current densities as high as 30 $A/cm^2$ with a deposition rate of 25 μm/min.

In chromium HSP on copper a minimum of cleaning was employed. This consisted of a solvent wipe of the sample followed by a one minute electrolyte flow in the HSP system without plating current. This seemed to provide sufficient cleaning for good adhesion of chromium to copper.

In chromium HSP on steel, the copper cleaning system seemed to work well with the clean steel tube samples. However, this procedure was insufficient for chromium plating steel automotive parts. It was necessary to acid dip, give the parts a reverse current electrolytic treatment in $CrO_3$ electrolyte, assemble the parts in the HSP fixture while wet with the $CrO_3$ electrolyte and then high speed plate. This procedure may be necessary whenever parts are introduced into the HSP system with considerable greases and oxides generated in previous handling.

Under some circumstances, it may be necessary to HSP chromium on plated nickel. Plating room experience indicates that plated nickel surfaces often become passive as compared to copper or steel surfaces, so some degree of difficulty could be expected. This report describes methods investigated for activating bright plated nickel prior to HSP of chromium as well as the results obtained during plating.

## Experimental

The procedure used in this investigation was the same as that used previously in HSP of chromium (2,3), with the exception of the activating procedure.

Bright Nickel Sample Preparation. Copper tube samples were plated to a thickness of 12-15 μm from a commercial bright nickel solution. The bright nickel surfaces were also lightly buffed and solvent cleaned to remove buffing residue. All samples were then electrocleaned outside of the HSP system prior to proceeding with the activating procedure.

Activating Procedures. Bright nickel plated samples were activated by acid dipping in 10, 50 or 100 v/o hydrochloric acid for 30- or 60-s intervals (Table I). In another procedure, nickel plated samples were treated cathodically at 6 V for 30 s in 10 v/o or 6 V for 30 or 90 s in 50 v/o hydrochloric acid. In yet another group, samples were treated cathodically at 6 V in 10 or 25 v/o sulfuric acid for 30 or 90 seconds.

Chromium Plating. After the activating procedure, the samples were placed in the HSP fixture and were plated at 6 V (1.2 $A/cm^2$), 7 V (1.7 $A/cm^2$), 8 V (2.1 $A/cm^2$) or 9 V (2.7 $A/cm^2$). Also, a series of nickel plated samples were chromium plated in the HSP system without activation of any kind.

The chromium plating bath composition used was as follows:

| | |
|---|---|
| $CrO_3$ | 25 g/L |
| Sulfuric acid | 0.25 g/L |

The plating system operating conditions were as follows:

| | |
|---|---|
| Voltage | 6-9 V |
| Current Density Range | 1.25 to 2.7 $A/cm^2$ |
| Temperature range | 71-82°C |
| Tank air pressure | 4.13 kPa |
| Anode-cathode gap | 3.8 mm |
| Anode-cathode area ratio | 1:1 |

## Results and Discussion

A number of bright nickel samples were plated with chromium in the HSP system. The 25 g/L $CrO_3$ electrolyte was chosen for this work because it was expected to be less passivating than the stronger 50 or 250 g/L $CrO_3$ electrolytes.

Since all samples were plated for one minute in the HSP system, appreciable chromium deposit thicknesses were obtained. These ranged from 2.1 to 4.3 μm which is much thicker than a decorative deposit of 0.2 μm normally used over plated bright nickel.

Attempts to chromium plate on bright nickel without any activation were not successful as can be seen in Figs. 1 and 2. Either misplate or exfoliation or both were encountered at 6 V (1.2 $A/cm^2$), 7 V (1.7 $A/cm^2$) and 8 V (2.1 $A/cm^2$) at temperatures of 71 or 82°C.

The best results in chromium plating on bright nickel were obtained after activating for 30 s in 10 v/o hydrochloric acid. As shown in Fig. 3,

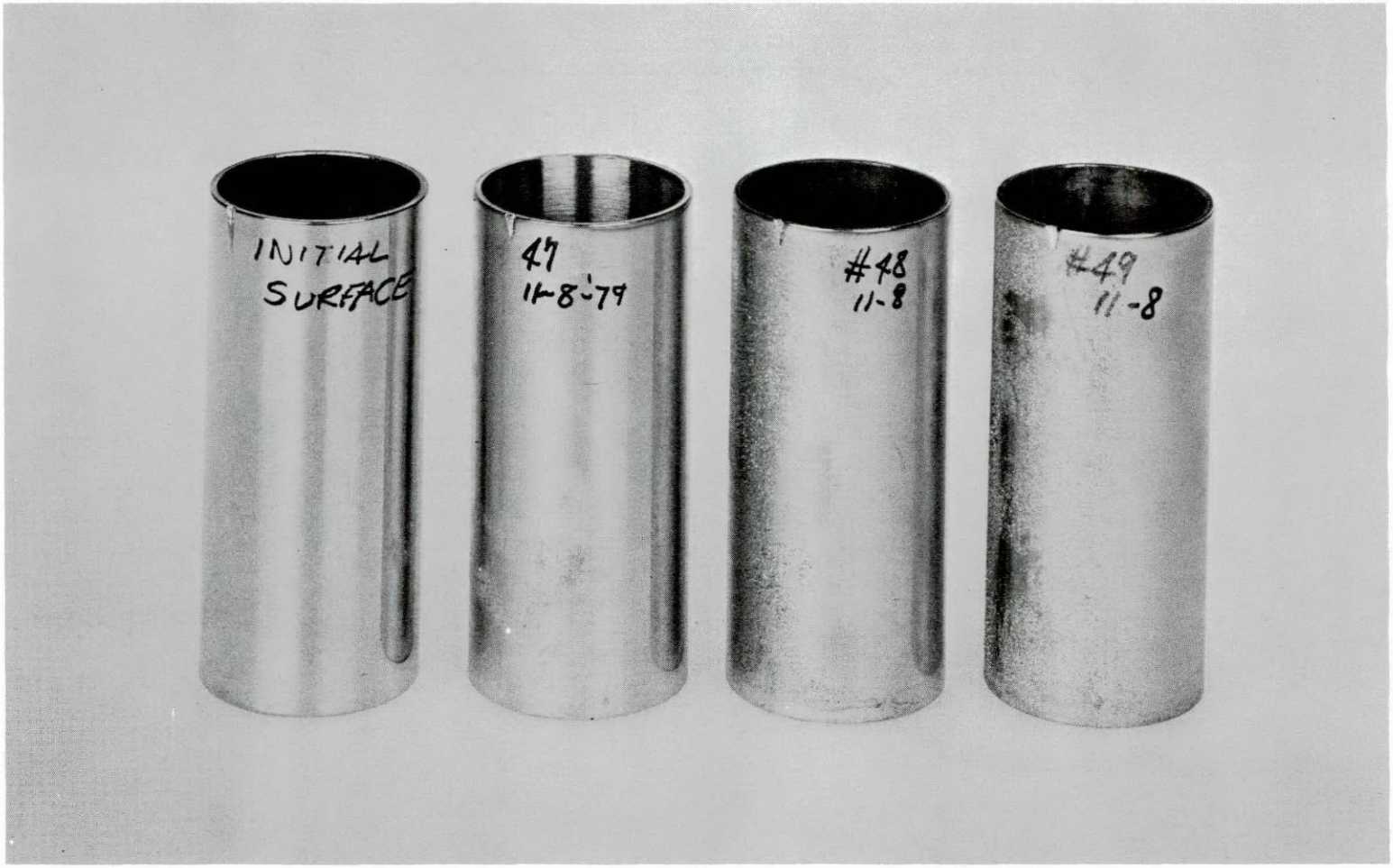



Fig. 1. No sample activation, temperature 71°C. Plated: #47, 6 V; (1.1 A/cm$^2$) # 48, 7 V; (1.6 A/cm$^2$) #49, 8 V (2.0 A/cm$^2$).

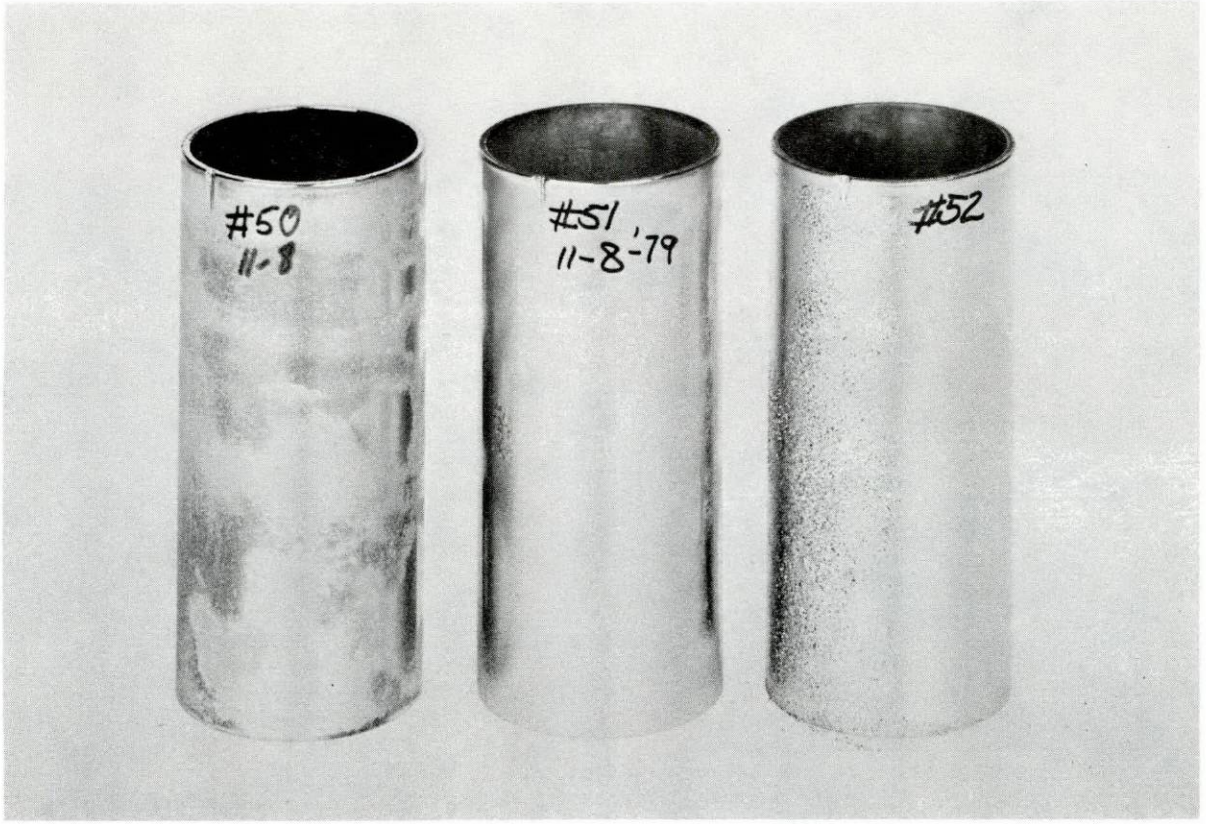



Fig. 2. No sample activation, temperature 82°C. Plated: #50, 6 V; (1.2 A/cm$^2$) #51, 7 V; (1.7 A/cm$^2$) #52, 8 V (2.1 A/cm$^2$).

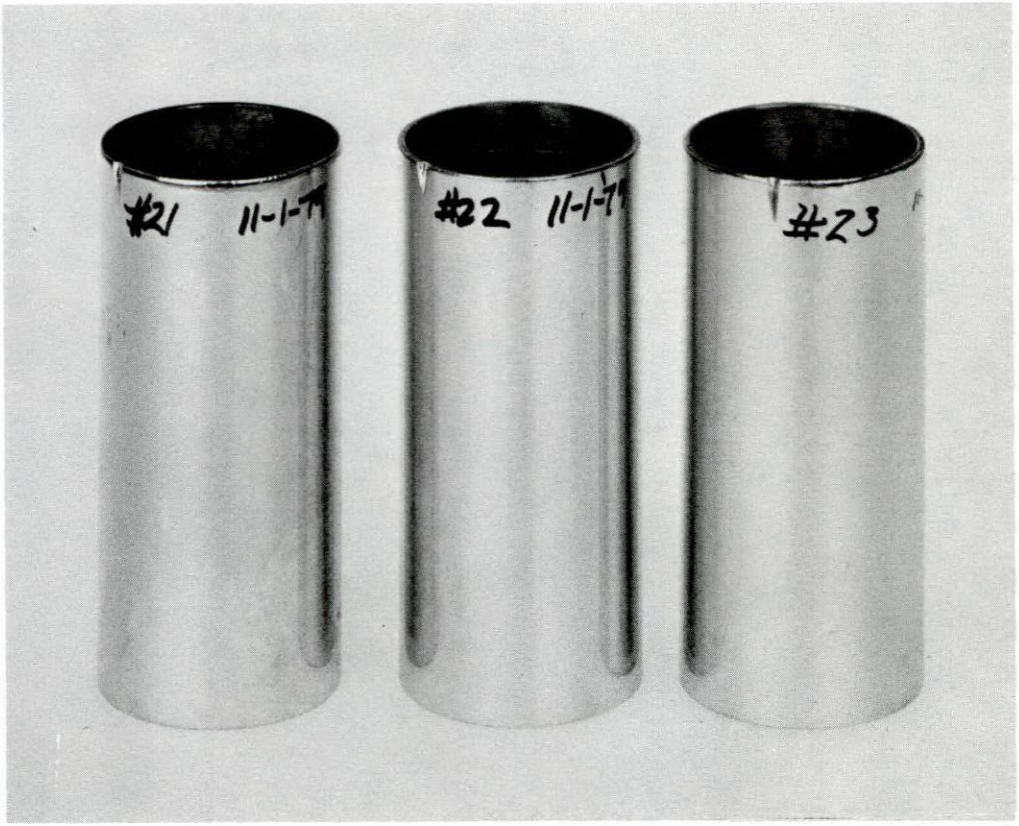



Fig. 3. Activated 30 s in 10 v/o hydrochloric acid, temperature 82°C. Plated: #21, 6 V; (1.2 A/cm$^2$) #22, 7 V; (1.7 A/cm$^2$) #23, 8 V (2.1 A/cm$^2$).

bright smooth, adherent chromium deposits were obtained at 7 V (1.7 A/cm$^2$) and 8 V (2.1 A/cm$^2$) at a temperature of 82°C. Under no circumstances could the bright nickel substrate be plated at 9 V (2.7 A/cm$^2$). Attempts to use stronger acid (50 v/o hydrochloric) to activate the nickel substrate for chromium plating were not an improvement, as seen in Fig. 4. The stronger acid presents more of a fuming problem and would only be used if it led to substantial improvement in sample preparation.

Experience indicates that activation can be accomplished by cathodic treatment of substrates in various mineral acids (4). From this view, activation attempts were carried out using sulfuric and hydrochloric acids as the activating electrolyte. Figure 5 shows samples chromium plated after cathodic activation of bright nickel surfaces under various conditions using sulfuric acid. It can be seen that only one condition, that represented by sample #34, of six depicted is acceptable. Samples from all the other condition variations such as time of treatment and sulfuric acid concentration had either misplate or exfoliation of the deposit or both. Samples shown in Fig. 6 were activated by treating the nickel surface cathodically in hydrochloric acid. The only difference between results after the sulfuric acid treatment and after the hydrochloric acid treatment is that the latter are less exfoliated.

It is often standard practice in hard chromium plating to use a short interval reverse current treatment in the chromium plating solution to promote adhesion (5). It was not thought to be advantageous to anodically treat nickel substrate in this manner because of the ease with which nickel passivates in chromic acid. Several samples were, however, plated employing this technique, but the deposits obtained were unsatisfactory due to heavy exfoliation as expected.

In summary, bright nickel substrates can be chromium plated in the HSP system from low concentration electrolyte at cell voltages between 6-8 V (1.2-2.1 A/cm$^2$) at deposit rates of 2.1 to 4.3 μm/min, provided the bright nickel substrates were given an activation treatment. In this work it was determined that the most effective activation treatment for HSP on bright nickel substrates was a 30 s immersion in 10 v/o hydrochloric acid.

References


1. M. A. LaBoda, Plating and Surface Finishing, 66, 10 (1979).

2. M. A. LaBoda, A. H. Holden, and J. P. Hoare, J. Electrochem. Soc., 127, 1709 (1980).

3. M. A. LaBoda, Surface Technology, 11, 91 (1980).

4. N. Hall, "Preparation of Basis Metals for Plating," Metal Finishing Guidebook and Directory, January, 1979, Vol 77, No. 13, pp. 171, 175.

5. P. Morisset, J. W. Oswald, C. R. Draper and R. Pinner, Chromium Plating, Robert Draper, Ltd., Teddington, England, 1954.

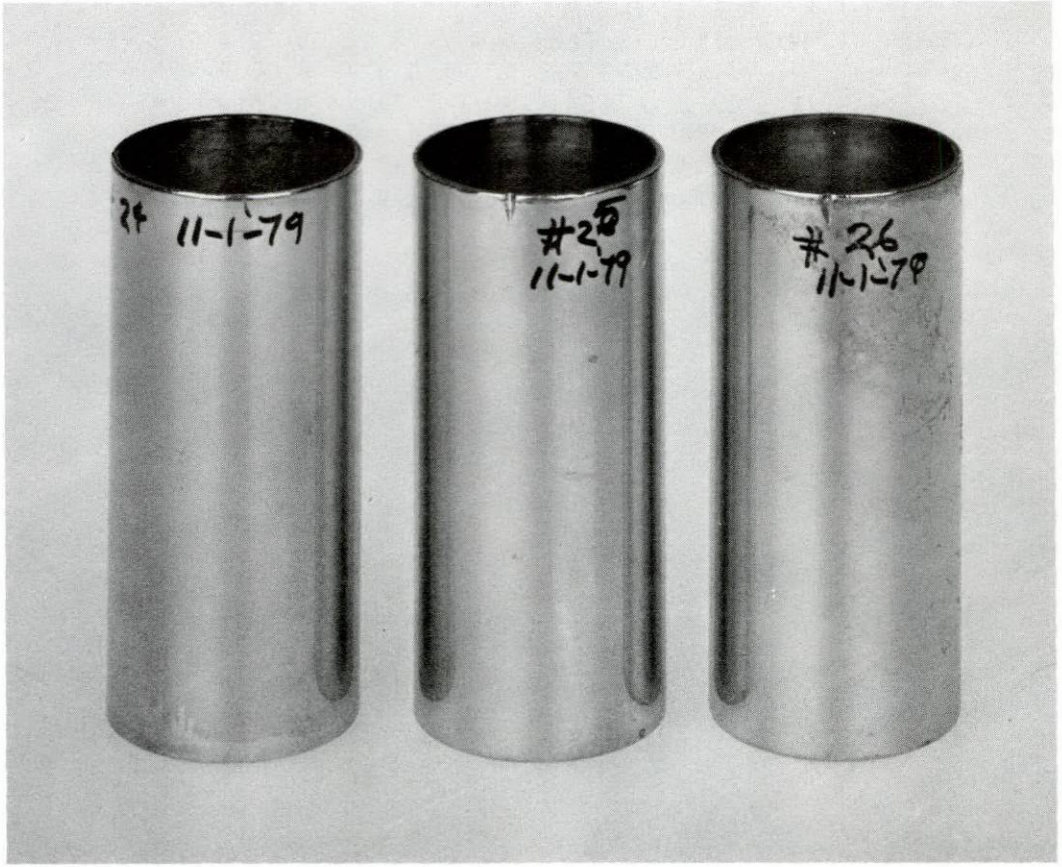



Fig. 4. Activated 30 s in 50 v/o hydrochloric acid, temperature 82°C. Plated: #24, 6 V; (1.2 A/cm$^2$) #25, 7 V; (1.7 A/cm$^2$) #26, 8 V (2.1 A/cm$^2$).

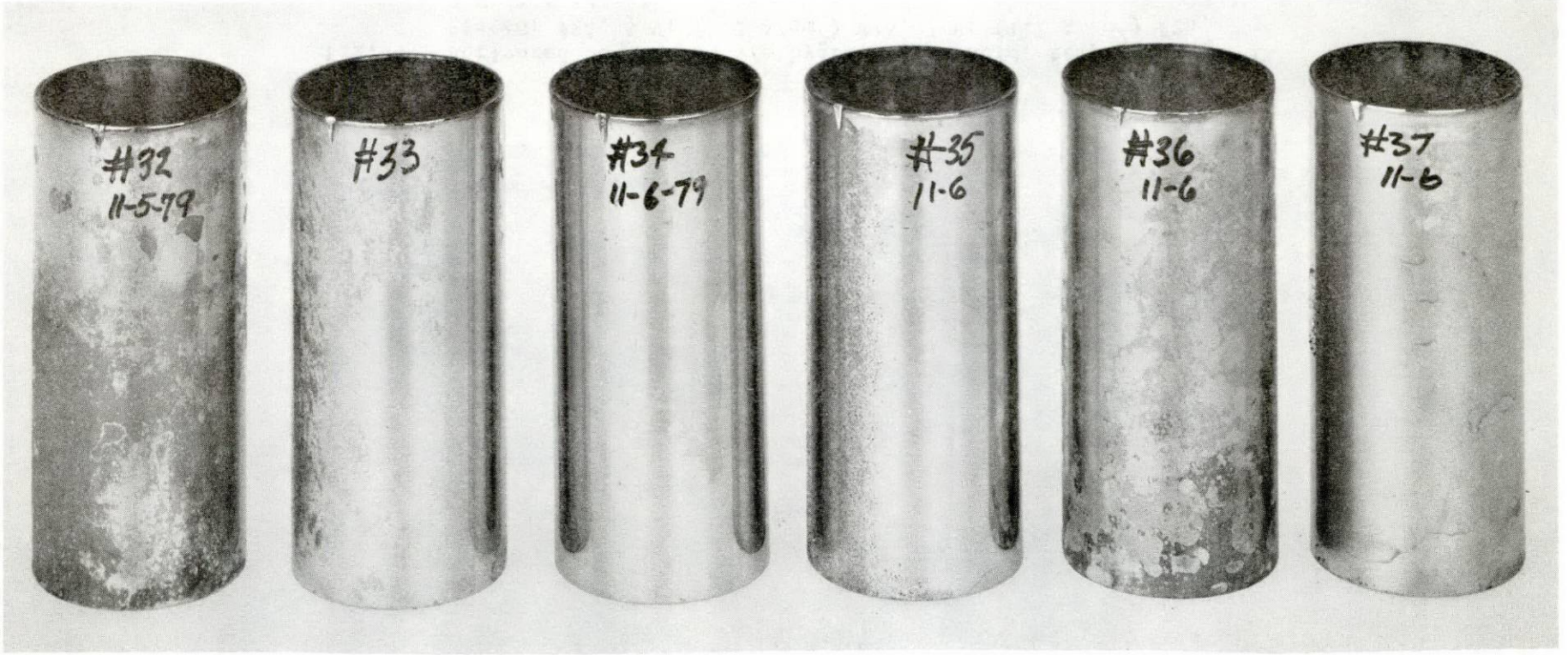



Fig. 5. Activated 30 s at 6 V in 10 v/o sulfuric acid, temperature 82°C.
Plated: #32, 6 V; (1.2 A/cm$^2$) #33, 7 V (1.7 A/cm$^2$).
Activated 30 s at 6 V in 25 v/o sulfuric acid, temperature 71°C.
Plated: #34, 6 V; (1.1 A/cm$^2$) #35, 7 V (1.7 A/cm$^2$).
Activated 30 s at 6 V in 25 c/o sulfuric acid, temperature 82°C.
Plated: #36, 6V (1.2 A/cm$^2$) #37, 7 V (1.7 A/cm$^2$).

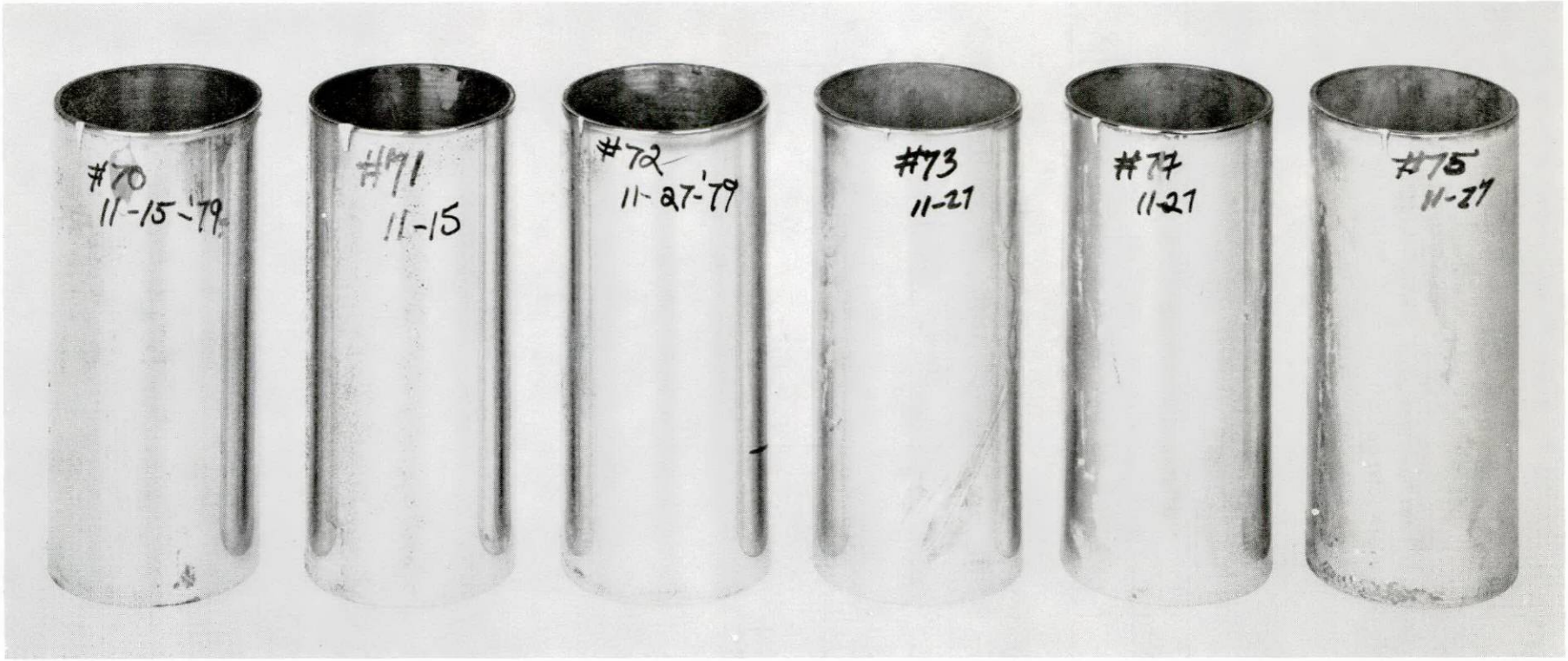



Fig. 6. Activated 30 s at 6 V in 10 v/o hydrochloric acid, temperature 71°C. Plated: #70, 6 V; (1.1 A/cm$^2$) #71, 7 V (1.5 A/cm$^2$). Activated 30 s at 6 V in 50 v/o hydrochloric acid, temperature 71°C. Plated #72, 6 V; (1.1 A/cm$^2$) #73, 7 V (1.1 A/cm$^2$). Activated 90 s at 6 V in 50 v/o hydrochloric acid, temperature 82°C. Plated #74, 6 V; (1.7 A/cm$^2$) #75, 7V, (1.7 A/cm$^2$).

Table I

Various Activation Systems Employed in
HSP of Chromium on Bright Nickel Deposits

Hydrochloric Acid

| 10 v/o | | 50 v/o | | 100 v/o | |
|---|---|---|---|---|---|
| 30 s | 60 s | 30 s | 60 s | 30 s | 60 s |

Hydrochloric Acid Cathode Treatment @ 6 V

| 10 v/o | 50 v/o | |
|---|---|---|
| 30 s | 30 s | 90 s |

Sulfuric Acid Cathode Treatment @ 6 V

| 10 v/o | | 25 v/o | |
|---|---|---|---|
| 30 s | 90 s | 30 s | 90 s |

# U-2

# Chromium Plating
# Session U

## High-Speed Chromium Plating on Bright Nickel Substrates: (II) Mechanisms

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# HIGH SPEED CHROMIUM PLATING ON BRIGHT NICKEL SUBSTRATES: II. MECHANISMS

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## Abstract

From an analysis of the steady-state polarization curves obtained on nickel wire microelectrodes in various chromate solutions, it was determined that a deposit of Cr could not be layed down on the normally oxidized Ni surface. Nickel can be activated (oxide layer removed) either chemically by treating, for example, in HCl solution or electrochemically by cathodizing in certain acid solutions. Actual plating of Cr on Ni-plated Cu tubes in the high speed plating machine showed that the range of acceptable Cr deposition was limited to current densities below 2.5 $A/cm^2$. This is compared to Cr on steel or Cu at 6.5 $A/cm^2$. Exfoliation of the Cr deposit on the Ni layer at current densities above 2.5 $A/cm^2$ is due to the release of hydrogen gas at the Cr-Ni interface at high currents and temperatures.

## Introduction

A model for the deposition of metallic chromium from conventional chromic acid baths has been proposed (1,2) which accounts for many of the well-known observations made during the operation of commercial chromium plating baths. This model was then used to account for the observations made during the high speed plating (HSP) of bright, hard Cr on iron and copper substates at high (2) and low (3) chromic acid concentrations in the HSP machine described by LaBoda (4,5). Although a considerable amount of Cr plating involves the deposition of Cr on Ni substrates, particularly in decorative Cr plating, a need may arise under certain circumstances for depositing Cr at high rates on Ni plated surfaces. This report describes an investigation of the passivation and activation of Ni surfaces and the electrodeposition of bright Cr on the active Ni. In a series of experiments, steady-state, polarization curves were obtained on Ni wire microelectrodes. From these data it was possible to propose a possible mechanism for the observations made during HSP of bright chromium on bright, nickel-plated, copper tubes.

## Experimental

The Ni microelectrode cathodes were made from Ni wire (99.97+% pure) 0.0785 cm in diameter, and were cleaned by abrading the surface with fine emery paper, followed by degreasing in trichloroethylene, washing with acetone, soaking in triply distilled water, and drying in air. After the wire had been covered with tight fitting teflon spaghetti with about 0.5 cm of wire exposed, the exposed end was potted in molten polyethylene to prevent solution from creeping up the wire under the teflon spaghetti. The polyethylene coating was cut away so that about 0.2 cm of wire was exposed and the active area was about 0.05 $cm^2$.

The anode was made from a piece of lead wire 0.32 cm in diameter which was abraded and cleaned in the same way as the Ni wire was. This lead anode was also covered with teflon spaghetti such that 1 cm of wire was exposed to the electrolyte. Since the Pb electrode was not being studied, no attempt was made to prevent electrolyte from creeping up the inside of the teflon spaghetti. After a run, the exposed portion of the Pb anode was coated with a brown layer of $PbO_2$, but under the teflon spaghetti where current was restricted, yellow $PbCrO_4$ accumulated.

A description of the polarization cell, the filling of the salt bridge connecting the polarization compartment with the reference compartment which contained a saturated calomel reference electrode (SCE), and the preparation of the solutions and cells was presented previously (1). The solutions examined were 1M $Na_2CrO_4$, 1M $Na_2Cr_2O_7$ and 1M chromic acid (100 g $CrO_3$/L) (designated from now on as $H_2Cr_3O_{10}$) with and without additions of 0.01M $HSO_4^-$ ion as $H_2SO_4$. All solutions were stirred with purified nitrogen at flow rates between 180 and 230 $cm^3$/min to minimize mass transfer effects.

In addition, polarization curves were obtained on Ni cathodes in 0.5M chromic acid + 0.005M $HSO_4^-$ and 0.25M chromic acid + 0.0025M $HSO_4^-$ to show that the shape of the polarization curve was not changed with dilution as long as the solution is red (presence of trichromate ion and the ratio of $CrO_3$ to $H_2SO_4$ is 100 to 1).

After the cell had been filled with the solution of interest and sealed with molten polyethylene, the Ni test electrode, which had been activated by dipping in concentrated HCl for 15 s followed by rinsing in triply distilled water, was inserted through the cell top into $N_2$-stirred chromate solution. Both galvanostatic and potentiostatic, steady-state, polarization curves were determined. In each case, some runs were made in which polarization measurements were begun at open circuit with increasing current, and others at the highest cathodic current studied with decreasing current. One is referred to an earlier report (1) for the techniques in obtaining the polarization data.

All potential values are recorded with respect to the saturated calomel reference electrode (SCE) unless otherwise noted and were obtained at the ambient temperature of 23 $\pm$ 1°C. The composition of the deposits was analyzed with Auger electron spectroscopy (AES).

## Results and Discussion

Steady-state polarization curves for Ni cathodes in $N_2$-stirred 1M $Na_2CrO_4$ (squares), 1M $Na_2Cr_2O_7$ (triangles) and 1M $H_2Cr_3O_{10}$ (circles) are plotted in Fig. 1 at constant current and in Fig. 2 at constant potential. In all cases, the Ni wires were activated in concentrated HCl solution and allowed to rest in contact with the chromate solution at open circuit until a steady rest potential was recorded. When standing on open circuit in chromate solutions, the Ni wire becomes coated with an oxide film (most likely a mixture of hydrated oxides of Ni and Cr) (6) by the oxidation of the Ni surface by chromate ions. Initially, the potential of the activated

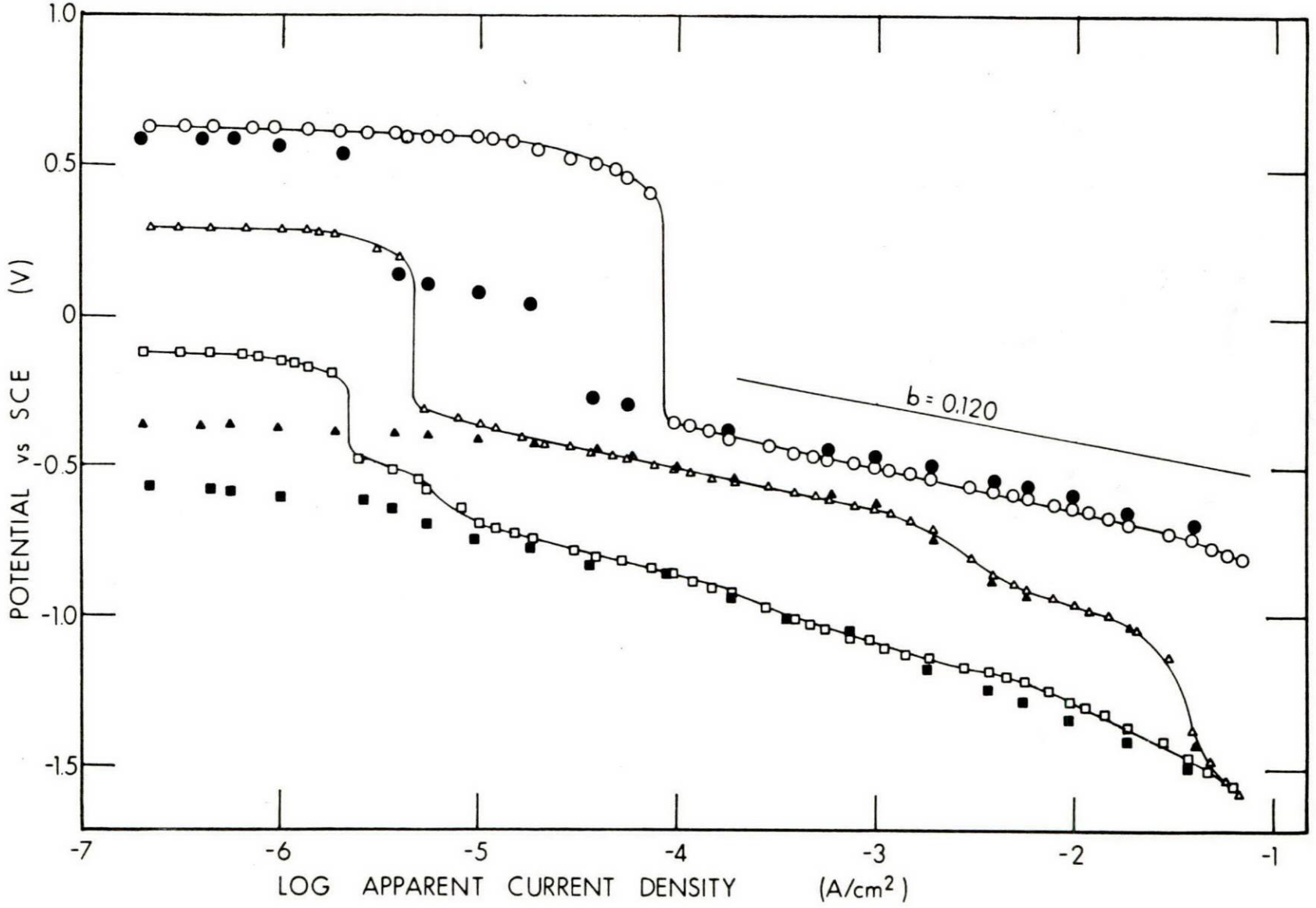



Fig. 1 Steady-state galvanostatic polarization curves obtained on Ni wire cathodes from open circuit conditions in $N_2$-stirred 1M $Na_2CrO_4$ (squares), 1M $Na_2Cr_2O_7$ (triangles) and 1M chromic acid (circles) solutions; open symbols for increasing cathodic current, filled for decreasing current. A line with a slope of 0.120 is drawn as a reference standard.

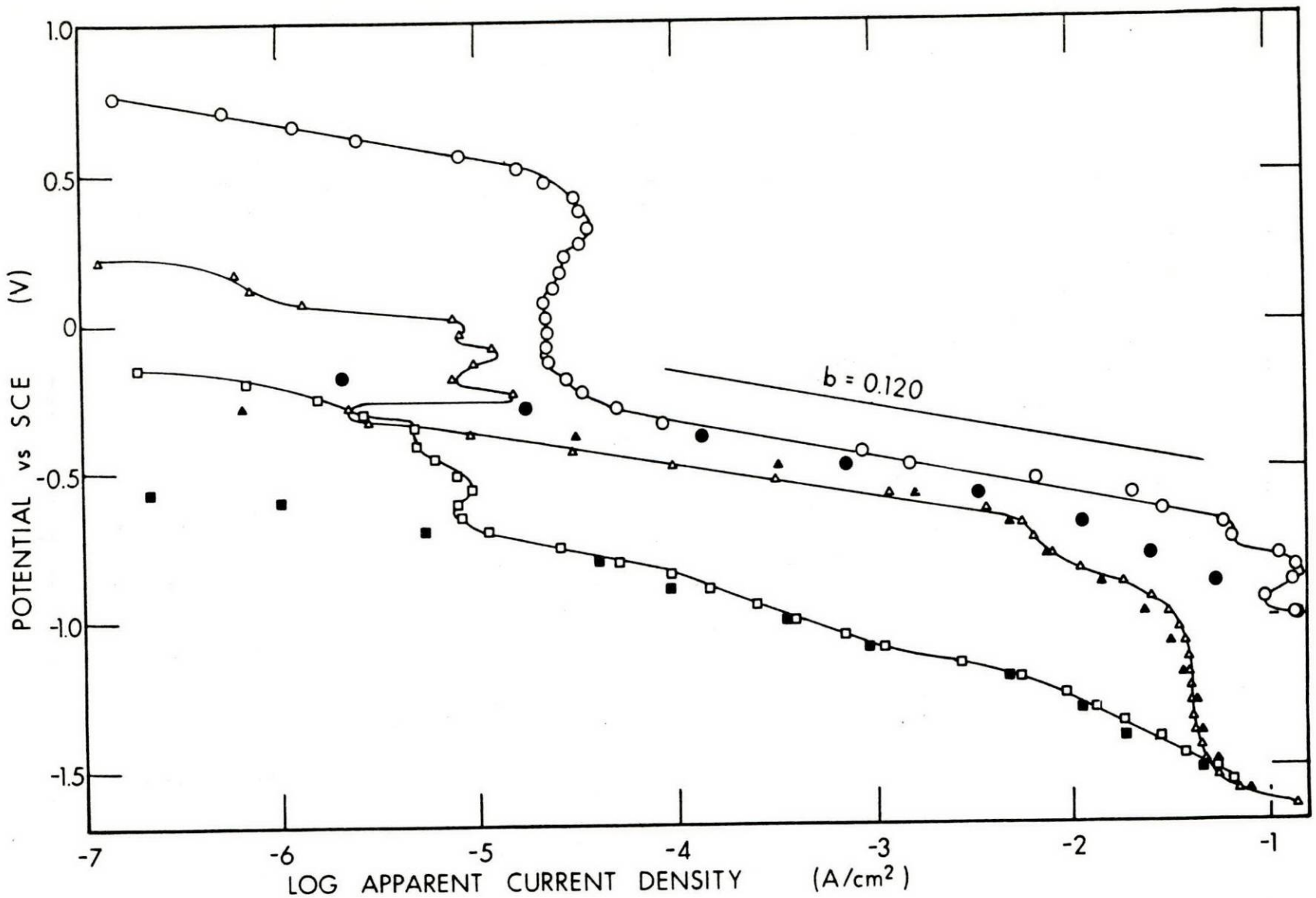



Fig. 2 Steady-state potentiostatic polarization curves obtained on Ni cathodes in the same solutions as in Fig. 1 with the same notation.

Ni in chromic acid was near zero V, but with time (about 2100 s) the potential rose to a virtually steady value of about 0.5 V. This rest potential is similar to that for non-activated Ni in chromic acid.

In the first part of the polarization curves at low current densities, the applied cathodic current is consumed in the reduction of this oxide surface film. As the film is being reduced by the cathodic current, it is also being replaced by oxidation of the Ni surface with adsorbed chromate ions. As a result, a steady state is set up where the rate of oxide film reduction equals the rate of oxide film formation. With increasing cathodic current, the reduction rate increases and the steady state oxide film becomes thinner. Eventually, a point is reached where the rate of reduction becomes greater than the rate of formation of the oxide film and the potential falls rapidly to a value where another cathodic process can support the demanded current (or rate of reaction).

This abrupt drop in potential or limiting current region may be accompanied by significant changes in the electrode area due to the reduction of the surface oxide layer. For the potentiostatic curves in Fig. 2, area changes are observed as shown by the negative resistance regions (current decreases for increasing potential) corresponding to the limiting current region in Fig. 1. From $Na_2CrO_4$ to chromic acid, the curves are shifted towards more noble potentials, which action reflects the decrease in pH as one proceeds from $Na_2CrO_4$ to $H_2Cr_3O_{10}$ (1). In addition, the length of the oxide reduction plateau lengthens with decreasing pH (1M $Na_2CrO_4$, pH~7; 1M $Na_2Cr_2O_7$, pH~2; 1M $H_2Cr_3O_{10}$, pH~-14 (1)). Such behavior reflects the increase in the oxidizing power of the chromate solution as the pH decreases. It requires a higher current density to be reached before the rate of oxide reduction can overtake the rate of the Ni surface oxidation and initiate the limiting current region for solutions of lower pH.

Following the limiting current region, a linear region appears which corresponds to the evolution of hydrogen. On Ni cathodes, the Tafel slope for hydrogen evolution is 0.12 (7-10). In Figs. 1 and 2, a line with a slope of 0.12 is drawn to show that the data are consistent with a 0.12 slope. The $H_2$-overvoltage is much higher on Ni than on Pt as compared with the curves obtained on Pt in chromate solutions (1).

In the absence of sulfate catalysts, Fig. 1 and 2, the hydrogen region extends to the highest values of the current density studied. At the higher values of the current density, some current is consumed in the reduction of Cr VI to Cr III which causes deviations from the 0.12 slope. As the pH is increased ($H_2Cr_3O_{10}$ to $Na_2Cr_2O_7$ to $Na_2CrO_4$), the hydrogen region is shifted to less noble values, and since the $H_2$-evolution reaction is inhibited with increasing pH, the fraction of current consumed in Cr VI reduction is increased. Consequently, deviations from the 0.12 slope begin earlier at lower current densities for solutions with higher pH, Fig. 1 and 2.

Once the highest current density studied was reached, polarization of the Ni cathode was continued in the direction of decreasing currents and the data are recorded as the filled symbols in Fig. 1. Agreement between these data for decreasing currents and those for increasing currents (open symbols

in Fig. 1) is very good in the $H_2$-evolution region (high and intermediate currents). In the oxide reduction or low current density region, however, a hysteresis exists.

It is known (11) that hydrogen can be dissolved in Ni and may be referred to as a Ni-H alloy. This effect may account for the observed hysteresis. The Ni-H alloy is a good catalyst for the hydrogen reaction and tends to behave as a hydrogen electrode even at low current densities. There is, however, another process that can take place at open circuit or at very low current densities and that is the oxidation of the electrode surface by the chromate solution. When a surface site becomes oxidized, it can be reduced by the hydrogen dissolved in the Ni metal. As long as the rate of reduction of oxidized sites is the same or greater than the oxidation of surface sites, the rest potential will remain in the hydrogen region. Until the hydrogen dissolved in the Ni-H alloy is oxidized by adsorbed chromate ions, the Ni surface will not be oxidized and the potential will not rise to the steady-state value initially observed on an oxidized Ni wire in a chromate solution. In solutions of high pH such as 1M $Na_2CrO_4$ where the oxidation rate is low, it may require up to 48 h under open circuit conditions before the initial, steady-state, rest potential of oxidized Ni is recovered as noted by the filled squares in Fig. 1. For a low pH solution such as chromic acid the oxidation rate is so fast that the dissolved hydrogen of the Ni-H alloy is rapidly depleted, and consequently, the rest potential of oxidized Ni is recovered within an hour or two (filled circles in Fig. 1). The behavior in 1M $Na_2Cr_2O_7$ solution is intermediate between that in 1M $Na_2CrO_4$ and that in chromic acid.

After polarizing the Ni at the highest current density, the circuit was broken and the electrode was removed. Visual examination of the Ni wire cathodes revealed that those from the $Na_2CrO_4$ and $Na_2Cr_2O_7$ solutions were bright. Auger electron spectroscopy (AES) analysis of these samples showed the presence of only adsorbed chromate ions on the Ni surface polarized in 1M $Na_2CrO_4$ solution and a very thin (14 nm) layer of an oxide or hydroxide of chromium on that in 1M $Na_2Cr_2O_7$ solution. In the case of Ni polarized in chromic acid, the wire was velvety black, and AES analysis detected a thick layer (>1600 nm) of hydrated chromium oxides on the Ni surface. Such a deposit would produce large changes in the surface area corresponding to the prominent negative resistance region at high current densities in the open circles of Fig. 2. According to the proposed model (1, 2) of Cr deposition, only Cr black and $H_2$ in the trichromate ($H_2Cr_3O_{10}$), and $H_2$ and Cr VI to Cr III reduction in di- ($Na_2Cr_2O_4$) and mono-($Na_2CrO_4$) chromates will be deposited in the absence of the sulfate catalyst in agreement with the above observations.

If, now, one activates Ni wires in concentrated HCl, and after rinsing, plunges these electrodes into the chromate solution at the highest current density studied, the polarization curves obtained (open symbols in Fig. 3) are nearly identical to those obtained for decreasing current densities in Fig. 1 (filled symbols). As soon as the open circuit is reached, the current is increased, and the polarization curve obtained (filled symbols in Fig. 3) is virtually identical to the one obtained for decreasing current

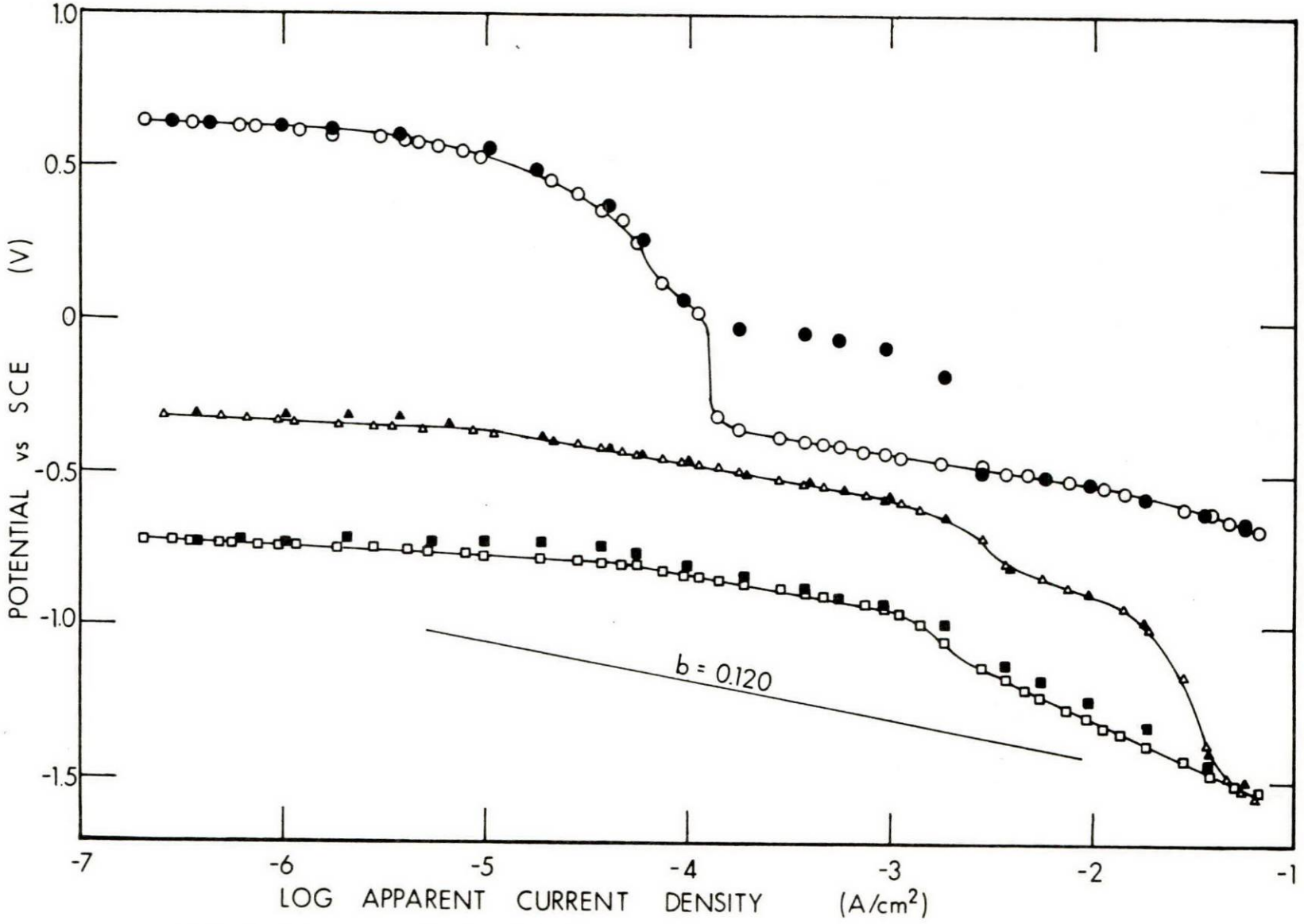



Fig. 3 The same polarization data as Fig. 1 except that the run was begun hot at the highest current densities studied and obtained for decreasing current (open symbols). Filled symbols represent data obtained for increasing current.

(open symbols in Fig. 3). In this case, initial polarization at high current densities converts the Ni cathode to a Ni-H alloy cathode and its polarization behavior is the same as the data (filled symbols) in Fig. 1. Only in the case of chromic acid is an oxidized Ni surface obtained. Accordingly, one concludes that strong cathodic polarization (Fig. 1 data) activates the Ni surface electrochemically as well as does chemical reduction of the surface in HCl (Fig. 3 data).

In Fig. 4 is plotted the galvanostatic (circles) as well as the potentiostatic (squares) polarization curves obtained on Ni wire cathodes in $N_2$-stirred chromic acid to which the sulfate was added as sulfuric acid. In this case, the plateau in the galvanostic curve is longer so that it appears that Cr is deposited almost as soon as the oxide layer is reduced since a negative resistance region appears shortly thereafter. This behavior is produced by a metallic deposit being laid down on the Ni surface causing large changes in the surface area which are reflected in the polarization curve as a negative resistance. This is so because the true current density is lower than the apparent current density due to the increase in area of the deposit. On visual inspection, the Cr deposit on the Ni wire was gray and porous, and AES analysis identified a deposit of metallic Cr >200 nm thick. Such observations support the conclusion obtained from the proposed model that a very low pH is required to bring about decomposition of the cathodic film by an acid catalyzed hydrolysis. At high pH a metallic Cr deposit is not obtained even though a catalyst and a cathodic film are present. An AES analysis of the Ni surface in the high pH solutions reveals the presence of only thin layers of oxides or adsorbed chromates.

It was found in Part I of this work that the region of acceptable bright Cr deposits on the bright Ni substrate was severely limited as compared to that obtained on copper or steel substrates. On the Ni-plated Cu tubes frosty patches and exfoliation of the deposits were encountered at current densities above ~2.5 $A/cm^2$. In contrast, acceptable bright Cr deposits can be obtained up to 6.5 $A/cm^2$ on Cu or steel.

When Cr is deposited on any basis metal from a conventional Cr plating bath, a large fraction of the applied current is consumed in hydrogen evolution (12). In the $H_2$-evolution mechanism, a hydrogen atom is adsorbed on the cathode surface by the transfer of an electron from the cathode to a specifically adsorbed (13) hydrogen ion. This H atom has a choice of two actions. In one, it may combine with another adsorbed H atom and be desorbed as a $H_2$ molecule. Or, it may dissolve in the metal of the cathode which can cause the embrittlement of the electrode metal.

For Cr deposition on Cu, the hydrogen can only be evolved as $H_2$ molecules since Cu virtually does not dissolve hydrogen. Nickel, however, does dissolve hydrogen although not as well as iron or palladium (11). Consequently, during the Cr deposition on bright, Ni-plated Cu tubes, hydrogen dissolves in the Ni and diffuses through the Ni layer to the Ni-Cu interface where it can penetrate no further. With continued plating, the Ni layer becomes saturated and eventually supersaturated with dissolved hydrogen. At certain nucleation centers in the surface layers of the Ni just below the Cr deposit, the dissolved H atoms combine and a burst of $H_2$ gas is

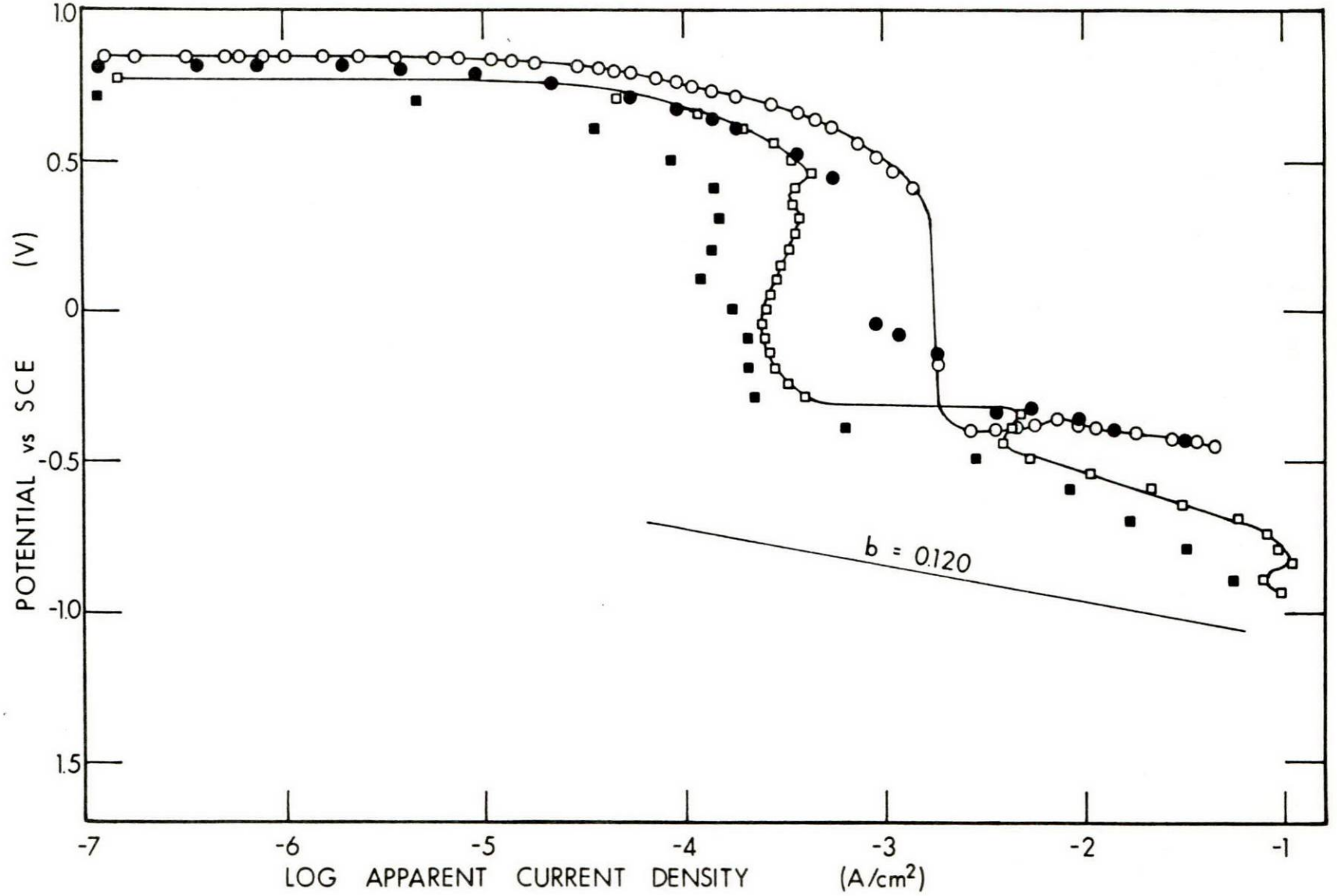



Fig. 4 Steady-state polarization curves obtained on Ni were cathodes in $N_2$-stirred 1M chromic acid solution which was also made 0.01M in $H_2SO_4$; galvanostatic data (circles); potentiostatic data (squares); open symbols, increasing current; filled, decreasing current.

liberated with near explosive violence. The liberated $H_2$ gas causes a separation of the Ni and Cr layers in an incipient blister at the Ni-Cr interface. Because the deposited Cr layer is very brittle, cracks develop which free the liberated $H_2$. It is known (14) that the Cr deposit is under tensile stress which causes the loosened Cr layer to curl and bend away from the Ni surface. If the burst of gas is great enough it produces an exfoliation of the Cr deposit and exposes the underlying Ni surface.

Scanning electron micrographs (SEM) of these Cr deposits are presented in Fig. 5. The bright smooth Cr deposit is given in Figs. 5A and 5B at two magnifications whereas the frosty patches are given in Fig. 5C and 5D at two magnifications. The deposit thickness on both was 3.1 μm. In Fig. 5E, an SEM of an exfoliated deposit is presented which shows that pieces of the Cr deposit have flaked off the Ni surface. Places where the $H_2$ evolution has begun to push through the Cr deposit appear in the center and lower center of Fig. 5F. Where the Cr deposit is loosened from the Ni substrate, the flakes curl away from the interface showing that the Cr deposit is under tensile stress.

To support the $H_2$ eruption model of the exfoliated deposit, flakes of deposit were removed from the sample surface with transparent tape and analyzed in the AES chamber. The top side of the flakes is composed of metallic Cr, and the bottom side, of metallic Cr plus traces of metallic Ni. Signals for the presence of Cu were not detected by AES on the underneath side of the flakes. This observation indicates that separation of the deposit occurs at the Cr-Ni interface and not at the Ni-Cu interface, nor either within the Ni or within the Cr layers. Analysis shows that the region where flakes of deposit have been removed is Ni without traces of Cr or Cu.

Above an applied current density of ~2.5 $A/cm^2$ (>8V applied) the Ni layer becomes supersaturated with dissolved hydrogen so rapidly, it is not possible to obtain a Cr deposit on bright, Ni-plated Cu without exfoliation. Such behavior sets an upper limit to the rate at which Cr can be deposited on this basis metal system.

With electrochemical activation, not only is the surface oxide barrier to electrodeposition removed but also the Ni sample is charged with dissolved hydrogen. As a result, it requires less H deposition during Cr plating to supersaturate the Ni layer and the range of acceptible non-exfoliated Cr deposits is further limited to operation below a current density of ~1.4 $A/cm^2$ (>7V applied). Chemical activation does not cause large amounts of hydrogen to be dissolved in the Ni metal thus giving the wider range of operation.

In the case of Cr deposition on the steel tubes where hydrogen is dissolved in iron or steel to a much greater extent than in Ni (11), the dissolved hydrogen never builds up to saturation since it can diffuse through the iron sample and escape through the surface on the back side. For this reason Cr can be deposited at a rate of ~15 μm/min at about 6.5 to 7 $A/cm^2$ without exfoliation of the Cr deposited.

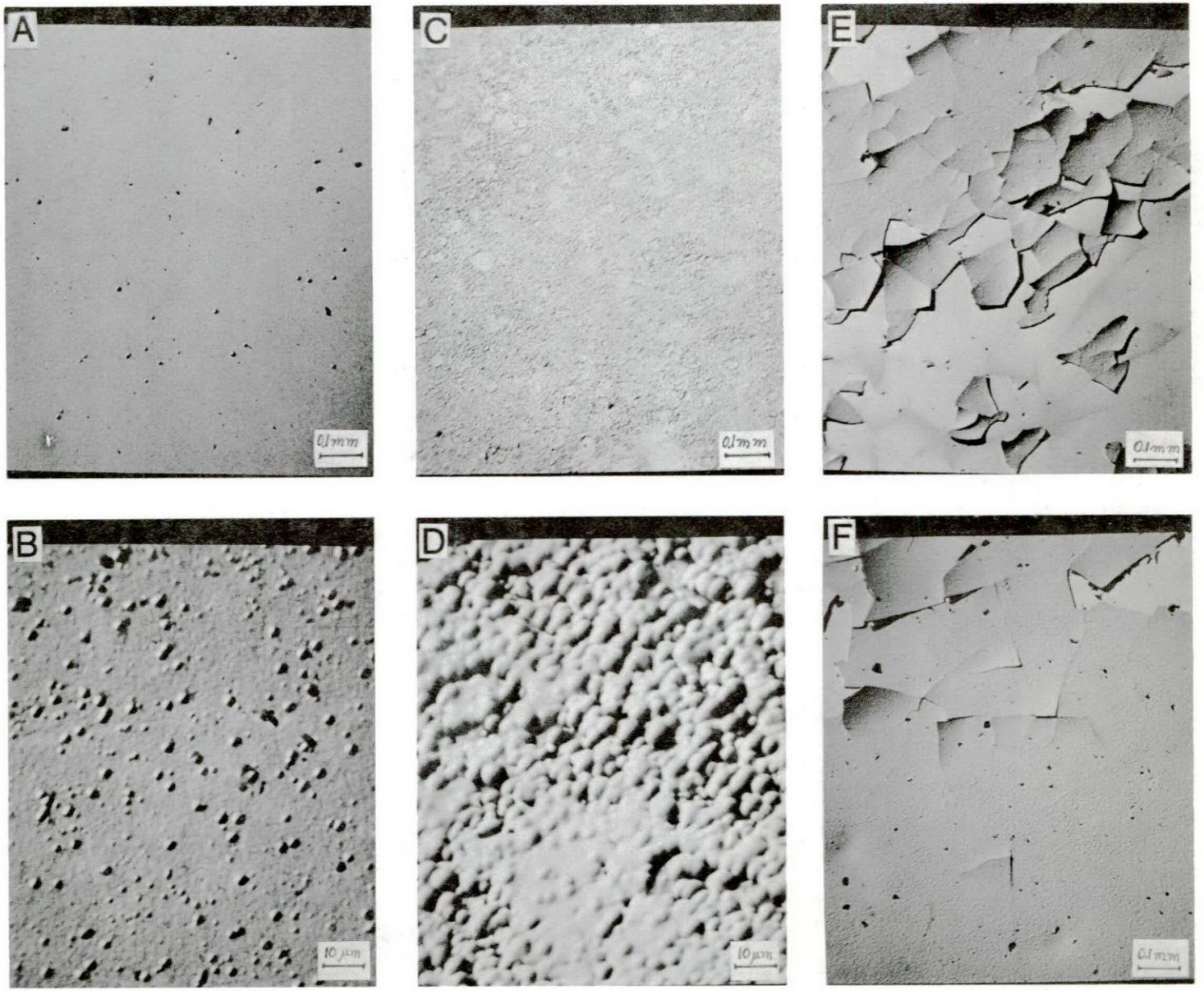



Fig. 5 Scanning electron micrographs of bright (A,B), frosty (C,D) and exfoliated (E,F) deposits of bright Cr on Ni-plated Cu tubes.

Since Ni is an endothermic occluder (11) of hydrogen (solubility increases with temperature), the deposition behavior of Cr on bright Ni may be affected by changes in temperature. Although the correlation is not clear, some evidence for temperature effects may be detected in the samples shown in Part I.

In summary one concludes from these data that the Ni surface exposed to the atmosphere is covered by a tenacious oxide over which Cr cannot be deposited. This passivating oxide layer is removed or the Ni surface is said to be activated either chemically by treatment in HCl solutions or electrochemically by cathodic polarization in certain acid solutions. In general, the chemical activation is preferred because it produces a more even oxide removal, is more economical (no electrical energy usage) and does not charge the basis metal with dissolved hydrogen as the electrochemical process does. Compared to Cr deposition on Cu or steel the operating region for smooth bright Cr deposits on Ni-plated Cu is severely limited, because at high current densities and high temperatures, the Ni layer becomes supersaturated with dissolved hydrogen. The explosive release of $H_2$ gas at active sites at the Cr-Ni interface separates the Cr deposit from the Ni causing exfoliation of the deposit. It appears that one of the major differences between the Cr deposition behavior on various basis metals may be traced to the interaction of the basis metal with hydrogen.

References


1. J. P. Hoare, J. Electrochem. Soc., 126, 190 (1979).

2. J. P. Hoare, A. H. Holden and M. A. LaBoda, Plating Surf. Fin., 67, 42, No. 3 (1980).

3. M. A. LaBoda, A. H. Holden, and J. P. Hoare, J. Electrochem. Soc., 127, 1709 (1980).

4. M. A. LaBoda, U. S. Pat. #4,111,751, Sept. 5, 1978.

5. M. A. LaBoda, Surf. Tech., 11, 91 (1980).

6. M. Cohen and A. F. Beck, F. Elektrochem., 62, 696 (1958).

7. P. Lukovtsev, S. Levina and A. Frumkin, Acta Physicochim USSR, 11, 21 (1939)

8. P. Lukovtsev and S. Levina, Zhur. Fiz. Khim., 29, 1508 (1955).

9. J. O'M. Bockris and E. C. Potter, J. Chem. Phys., 20, 614 (1952).

10. J. P. Hoare and S. Schuldiner, J. Phys. Chem., 62, 229 (1958).

11. J. D. Fast, Interaction of Metals and Gases, Barnes and Noble, New York, 1972, p. 67.

12. J. L. Griffin, Plating, 53, 196 (1966).

13. D. C. Grahame, Chem. Rev., 41, 441 (1947).

14. J. E. Stareck, E. J. Seyb and A. C. Tulumello, Proc. Am. Electroplater's Soc., 41, 209 (1954).

U-3

# Chromium Plating Session U

## Improved Electrodeposited LC Chromium

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# IMPROVED ELECTRODEPOSITED LOW CONTRACTION CHROMIUM

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## ABSTRACT

A systematic study was made to optimize the parameters for plating high quality LC chromium using standard chromic acid solutions and solutions containing vanadium additions. The results indicate that deposit strengths were improved substantially by aging the plating solution at 250 A hr/liter and by using current densities in excess of 120 $A/dm^2$. Under these conditions, hydrogen incorporation was reduced five-fold while hardness, strength, and cathode efficiency were maximized. A further improvement in deposit strength was obtained by adding vanadium as $V_2O_5$ at a concentration of 10 g/l to standard chromic acid solutions. At higher concentrations, inferior deposits were produced that showed surface roughness, porosity, low strength, and higher hydrogen content.

## INTRODUCTION

The use of electrodeposited chromium coatings to protect metals is a well established industrial practice. For example, coatings of bright or hard chromium are routinely applied on various products to reduce galling, friction, wear, and erosion. For corrosion protection, a softer, crack-free variety of electrodeposited chromium has been used with good results [1]. This type of chromium, designated "LC" for low contraction, may be readily plated from a standard chromic acid bath.

Thick coatings of LC chromium have been used in ordnance [2,3] and other applications [4,5] such as gun tubes and engine cylinders where extreme conditions of corrosion and wear are encountered. The results, while encouraging, were inconsistent and improvements may be effected by optimizing the quality of the deposits.

In the present study, experiments were carried out to upgrade the LC chromium plating process. Major emphasis was directed towards improving deposit strength through the use of optimum plating parameters and of adding electroactive chemicals to the plating solutions. The selection of $V_2O_5$ for this purpose was based on an earlier report where $V_2O_5$ showed a beneficial influence on the electrodeposition of cobalt [6] and the subsequent voltametric measurements which revealed its potential to diminish the reduction of hexavalent chromium and the formation of hydrogen in chromic acid solutions.

## EXPERIMENTAL

### Plating Procedure

All chemicals are of reagent grade and used without further purification. A chromium stock solution was prepared and stored in two portions by dissolving 250 g/l of chromic acid and 2.5 g/l of sulfuric acid in double distilled water. The first was used without additional refinements while the second was pre-electrolyzed (aged) 250 A hr/l prior to use. $V_2O_5$ at concentrations of 10, 15, and 20 g/l was added to the aged solutions.

Because of the brittleness of electrodeposited chromium, tensile test specimens were electroformed in the shape of cylinders. The electroforms were plated at a solution temperature of 85 ± 0.5°C using current densities ranging from 60 to 150 A/dm$^2$. The plating was conducted in one liter Pyrex beakers using Teflon-coated magnetic stirrers for agitation. Rotating brass tubes having a masked area of 10 cm$^2$ were used as cathodes. A platinum anode with a surface area of 20 cm$^2$ was formed in a convex shape with respect to the cathode to provide constant current density throughout the cathode surface. Electroformed chromium tubes were obtained for evaluation by dissolving the brass in dilute nitric acid solutions.

### Physical and Mechanical Property Measurements

Tensile strengths were measured with a table model Instron tensile machine. To minimize damage through handling and during testing, special fixtures were devised to grip the brittle chromium tubes. PVC end caps were machined to accommodate the tubular samples and quick setting epoxy was used to cement them in position. The total length of the assembled test sample and the gage section were 7.5 and 3.5 cm respectively. The test sample was mounted on the universal coupling of the Instron tester by passing a pin through the sample end cap and the coupling. Stress was applied to the specimen by lowering the movable Instron grip until its opened jaws engaged the shoulders of the lower end cap, Figure 1. A cross head speed of 0.05 cm/min was used in all the tests.

The hardness was measured with a Knoop diamond indenter at a load of 50 g.

Codeposited hydrogen and oxygen were determined using vacuum fusion and nitrogen by semi-micro Kjeldahl analysis.

## RESULTS AND DISCUSSION

Figure 2 shows the plating rate of LC chromium as a function of current density for deposits plated from unaged solutions (2A), pre-electrolyzed solutions (2B), and solutions containing 10 g/l $V_2O_5$ (2C). The plating rates were determined from the weights of the deposits and the use of an average LC chromium density value of 7.15 g/l. In all cases, the plating rate increased with increasing current density. The higher plating rates were obtained with pre-electrolyzed solutions. At a current density of 150 A/dm$^2$, the deposition

rate was as high as 3.5 times that associated with conventional bright chromium.

The results of the cathode efficiency measurements as a function of current density for the three different chromium plating solutions are given in Figure 3. The cathode efficiency is obtained from the weight of the chromium deposited on the basis that hexavalent chromium ion is reduced to metallic chromium. The cathode efficiency obtained with pre-electrolyzed solutions, Figure 3B, varies between 11.1 and 13.1 percent and is 2 to 3 percent higher than that obtained with the unaged solutions, Figure 3A. In both cases, the efficiency increases with current density from 60 $A/dm^2$ and reaches a plateau at a current density of 120 $A/dm^2$. With solutions containing 10 g/l $V_2O_5$, the efficiency also increased with current density. However, unlike the two previous solutions, a maximum efficiency of 12.5 percent is reached at a current density of 90 $A/dm^2$. Solutions containing 15 and 20 g/l $V_2O_5$ showed maximum efficiencies of 8.0 and 5.0 percent respectively.

The hardness, tensile strength, and codeposited oxygen, hydrogen and nitrogen for LC chromium are given in Table 1. At a given current density, the hardness decreases in the order of deposits from unaged solutions > deposits from pre-electrolyzed solutions > deposits from solutions containing 10 g/l $V_2O_5$. In all three cases, the hardness ranged from 525 to 668 KHN for current densities between 60 and 150 $A/dm^2$. Chromium deposits plated from solutions containing 15 and 20 g/l $V_2O_5$ are softer by as much as 174 KHN.

LC chromium plated from unaged solutions exhibits very low tensile strengths. From Table 1 and Figure 4, the tensile strength is seen to increase from 7.1 to 29.1 ksi with increasing current density from 60 to 150 $A/dm^2$. Pre-electrolyzing the plating solution raises the tensile strength of all deposits appreciably. For the same current density range, the tensile strength increases from 32.8 ksi to a maximum of 48.2 ksi (at 135 $A/dm^2$) followed by a decrease to 44.0 ksi. The addition of $V_2O_5$ to the plating solution at a concentration of 10 g/l improves the tensile strength to between 54.1 and 56.3 ksi. The use of higher concentrations of $V_2O_5$, 15 and 20 g/l, had the negative effect of lowering the tensile strength.

The codeposition of oxygen, hydrogen, and nitrogen is very much affected by the various plating parameters. With increasing current density, deposits plated from pre-electrolyzed solutions demonstrate that nitrogen content decreases from 0.006 to 0.004 wt.% while oxygen and hydrogen increase from 0.014 to 0.050 and from 0.0115 to 0.0137 wt.% respectively. In comparison, the magnitude of gas codeposition is considerably higher in coatings plated from unaged solutions; hydrogen and nitrogen levels as high as 0.0513 and 0.009 wt.% were observed. Deposits plated from solutions containing 10 g/l $V_2O_5$ show the lowest content of gas incorporation for all three gases. However, at $V_2O_5$ concentrations of 15 and 20 g/l, the trend reverses and large amounts of hydrogen and oxygen as occluded electrolytes are introduced into the deposits. The severity of the occlusions increases with current density and $V_2O_5$ concentrations as illustrated in Figure 5. A consequence of occlusions is the reduction of hardness and tensile strength mentioned earlier.

The codeposition of gases can have both beneficial and detrimental effects on the properties of LC chromium deposits. For example, the presence

of oxygen in the form of basic inclusions can increase deposit hardness through the mechanism of dispersion-strengthening in a manner similar to that observed in the precipitation hardening of metals. The increase in hardness with oxygen content reported in Table 1 can be explained in this fashion.

The process of electrodeposition can introduce large quantities of nitrogen in chromium deposits apart from that dictated by solubility data. It was reported that the nitrate ion concentration in a conventional chromic acid plating solution was reduced from 2.7 to 0.008 g/l after an electrolysis of 25 A hr/l. The corresponding nitrogen content in the chromium was reduced from 0.24 to 0.025 wt.% [7]. The presence of nitrogen is known to increase the ductile-brittle transition temperature. It was reported that by water-quenching chromium samples containing 80 ppm nitrogen the transition temperature is increased upwards of 250°C [8].

Although the equilibrium solubility of hydrogen in chromium is extremely small, electrodeposited chromium can retain a large quantity of hydrogen. The mode of occurrence has been the subject of considerable speculation and the consensus is that hydrogen most probably exists in the form of hydrides and hydrated chromic oxides [6]. While both forms contribute to the build up of stress, the unstable hydride formation and the shrinkage effect accompanying the hydride decomposition is believed to play a major role. Figure 6 shows an LC chromium deposit where the stress build up is sufficient to cause spallation. This spallation is commonly obtained in deposits plated from unaged solutions at a current density of 60 $A/dm^2$. Spallation does not occur in deposits plated at either a higher current density or from pre-electrolyzed solutions. It is of interest to note that the hydrogen content between spalled and coherent samples differ by factors of 2 to 5.

It was mentioned earlier that the increase in deposit hardness with increasing oxygen content is consistent with the view of dispersion-strengthening by codeposited basic inclusions. According to Brenner [9], the basic inclusions most probably occur in the form of hydrated chromic acid, $Cr_2O_3 \cdot xH_2O$. Depending on the water of hydration, the weight ratio of oxygen to hydrogen can vary from 32 ($Cr_2O_3 \cdot xH_2O$ where $x = 1$) to a limiting ratio of eight for large values of x. Assuming the weight ratio of eight applies for combined hydrogen, the lower limit of all other "free" hydrogen in the deposits can be estimated. Table 1 shows that the estimated "free" hydrogen content is largest in deposits plated at low current densities and particularly from unaged solutions. A graph of "free" hydrogen versus tensile strength is given in Figure 7 showing the excellent correlation obtained with deposits from pre-electrolyzed solutions and from solutions containing 10 g/l $V_2O_5$. The graph indicates that the tensile strength of LC chromium can be optimized by reducing the concentration of "free" hydrogen in the deposits. In the present investigation, this was accomplished by solution aging and the addition of vanadium to the plating electrolyte. Other procedures such as the use of current modulation may also be effective. The relationship between tensile strength and "free" hydrogen is believed to be applicable to all chromium deposits which are free of plating defects; deposits with cracks, i.e. conventional hard chromium, spallations, voids or occluded electrolyte, do not fit in the correlation.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. Richard Carter for preparing the chromium electrodeposits and performing the necessary mechanical tests and to acknowledge Mrs. Theresa Brassard for the metallographic work and hardness measurements.

REFERENCES

1. W. H. Safranek, The Properties of Electrodeposited Metals and Alloys, American Elsevier Publishing Co., Inc., (1974), p. 33.

2. J. P. Young, NBS Report No. 3B101, August 1, 1954.

3. V. A. Lamb and J. P. Young, NBS Technical Note 46, May 1960.

4. W. H. Safranek, The Role of Coatings in the Prevention of Mechanical Failures, (1976), pp. 56-63.

5. The Iron Age, Y. 175, No. 2D, (1955), p. 140.

6. G. R. Lakshminarayanan, E. S. Chen, J. C. Sadak, and F. K. Sautter, J. Electrochem. Soc., Vol. 123, No. 11 (1976), p. 1612.

7. N. Ryan and E. J. Lumley, J. Electrochem. Soc., Vol. 106, No. 5 (1959), p. 388.

8. A. H. Sully and E. A, Brandes, Chromium, New York Plenum Press (1967), p. 47, p. 170.

9. A. Brenner, P. Burhead, and C. Jennings, Res. Nat. Bur. Stand., 40 (1948), p. 31.

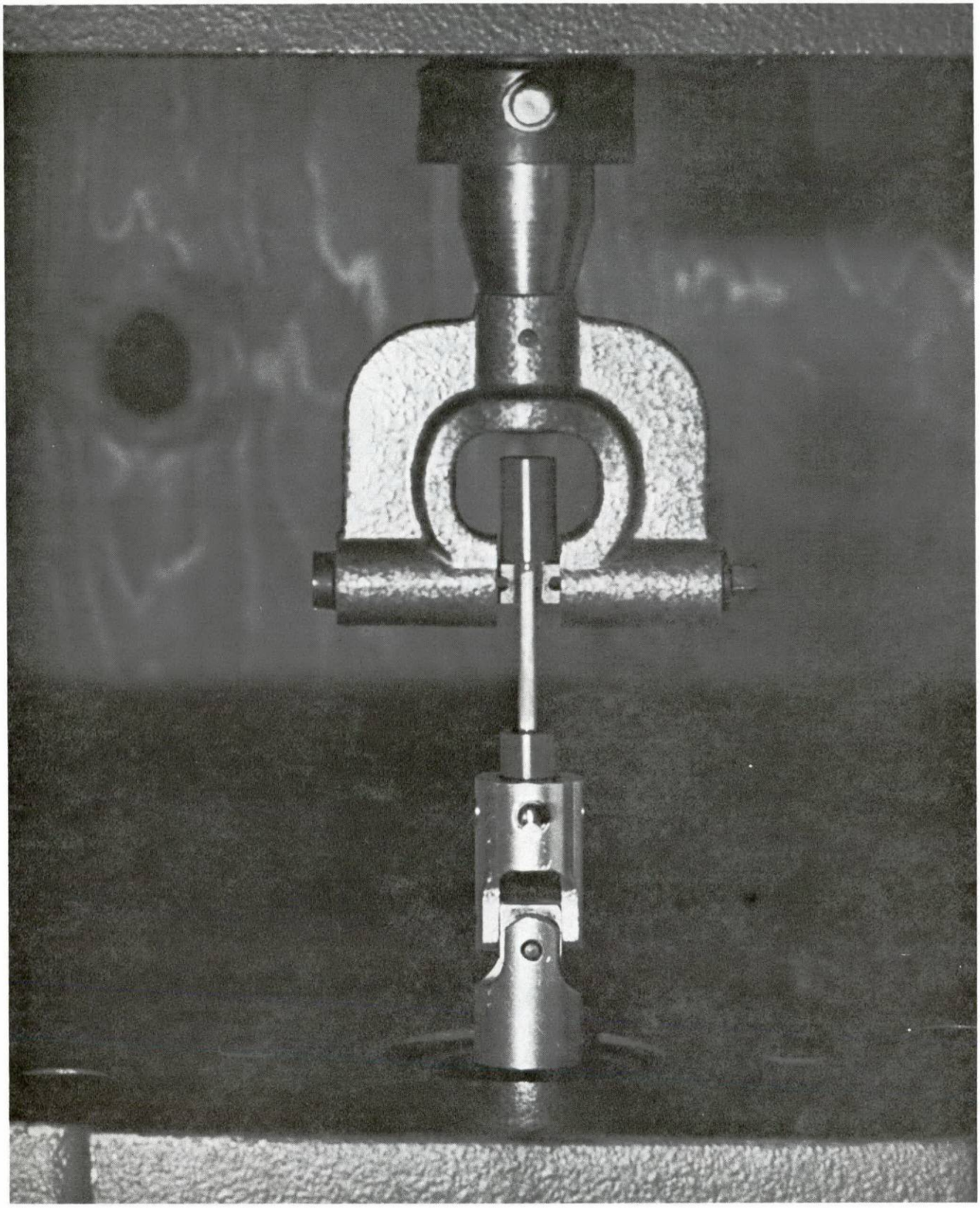


Figure 1. Tensile strength test.

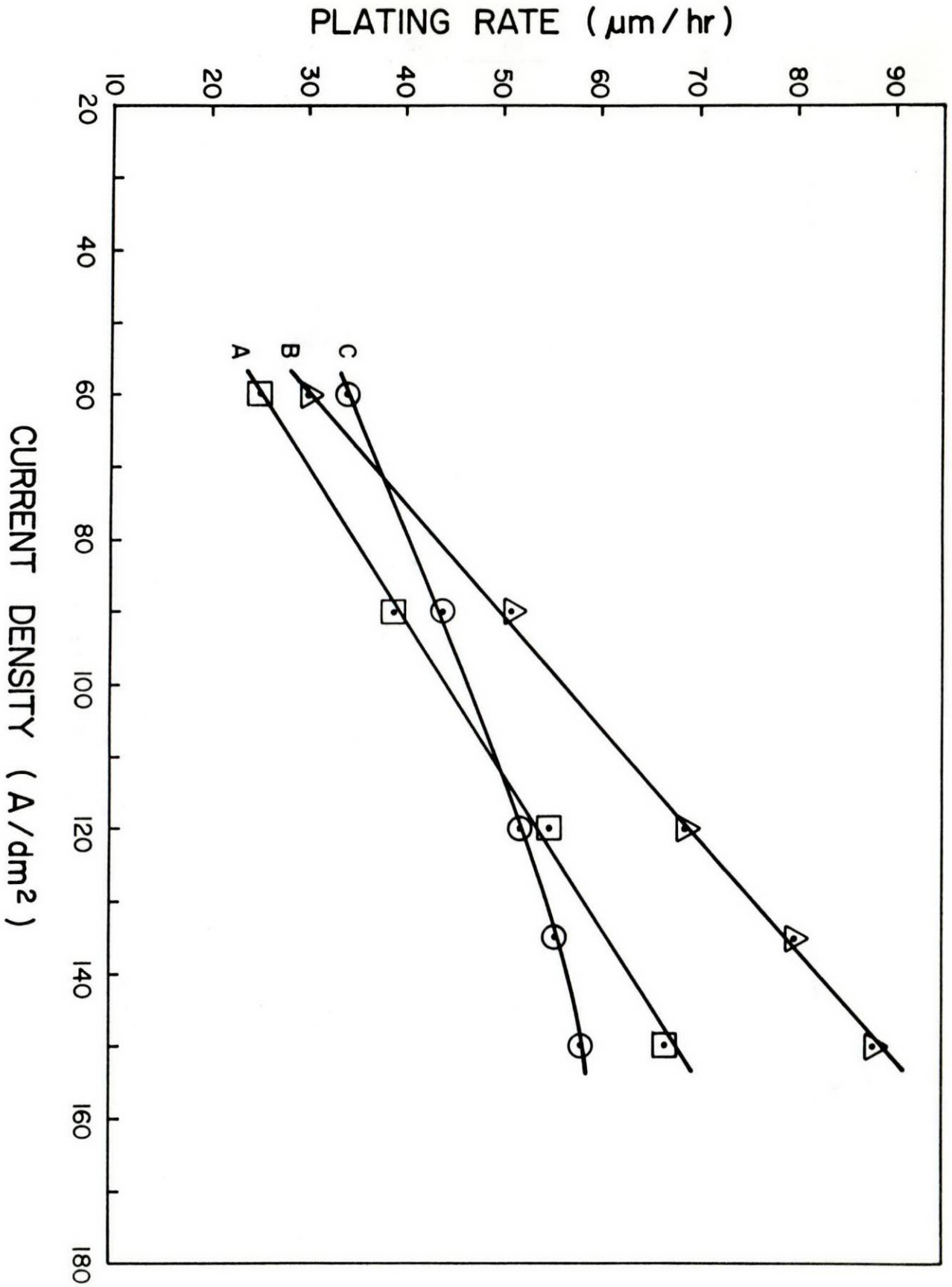



Figure 2. Plating rate of LC chromium with current density at 85°C. A - unaged solution, B - pre-electrolyzed solution, C - solution with 10 g/l $V_2O_5$.

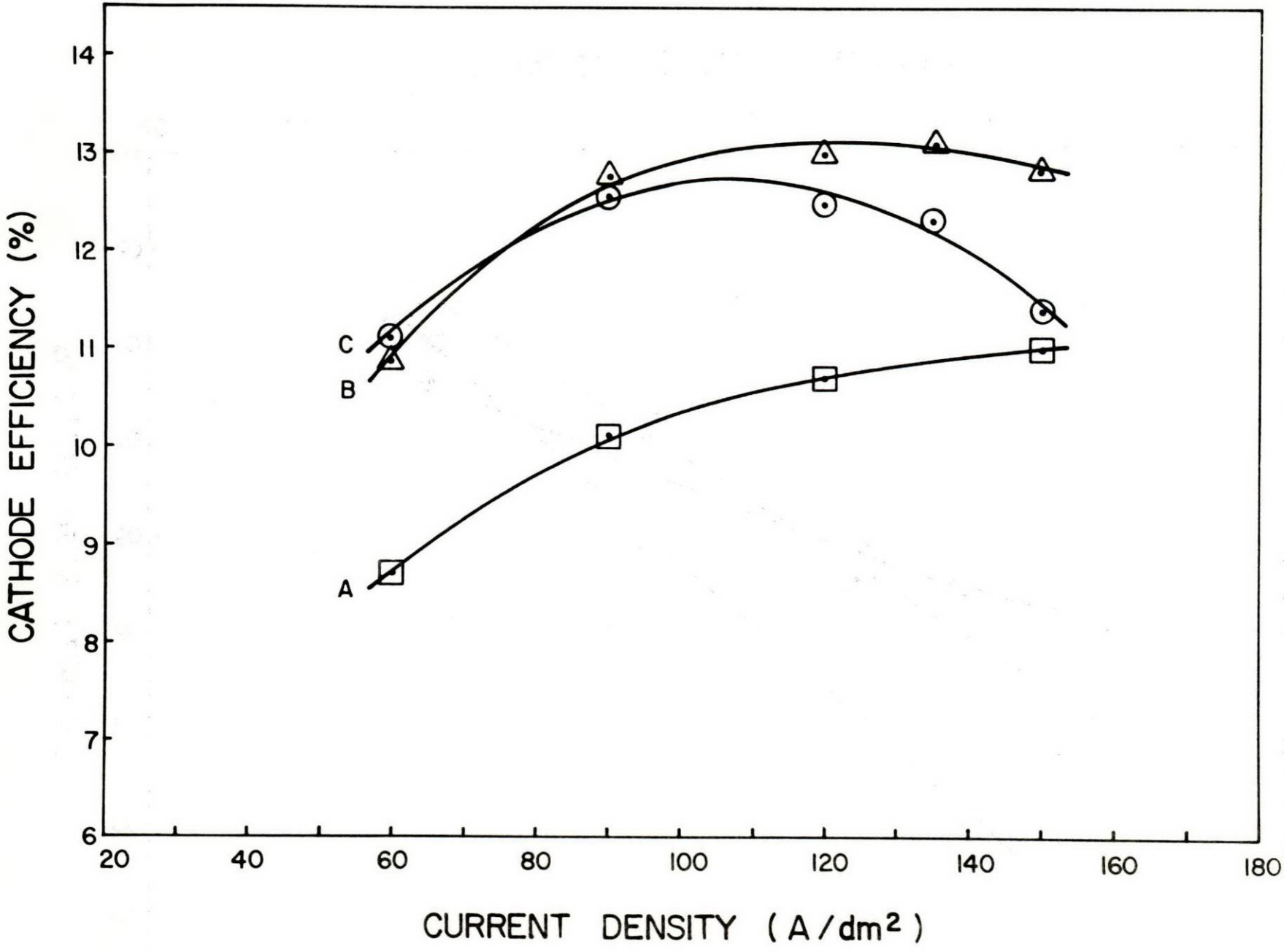



Figure 3. Cathode efficiency of LC chromium with current density at 85°C. A - unaged solution, B - pre-electrolyzed solution, C - solution with 10 g/l $V_2O_5$.

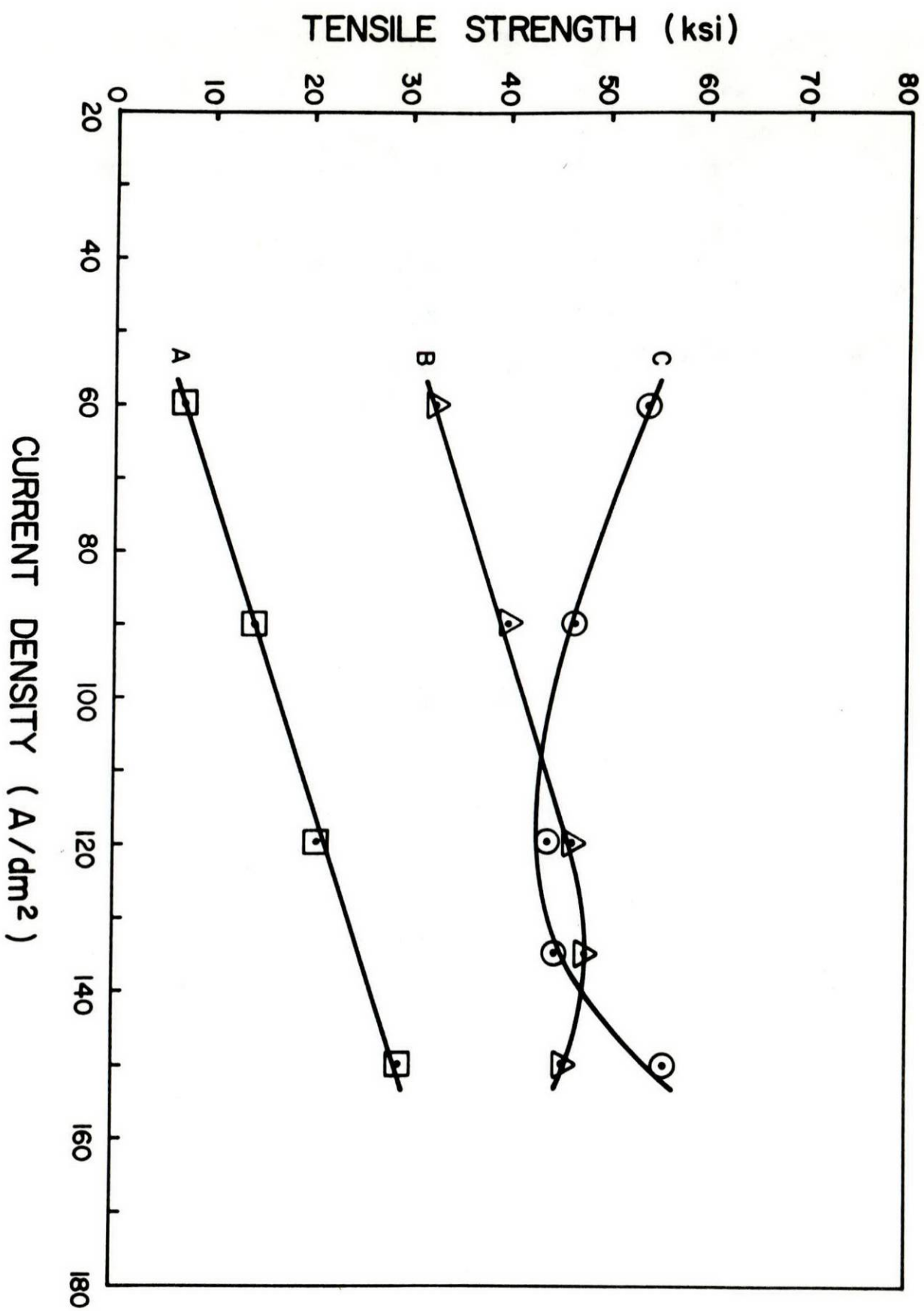



Figure 4. Tensile strength of LC chromium with current density at 85°C. A - unaged solution, B - pre-electrolyzed solution, C - solution with 10 g/l $V_2O_5$.

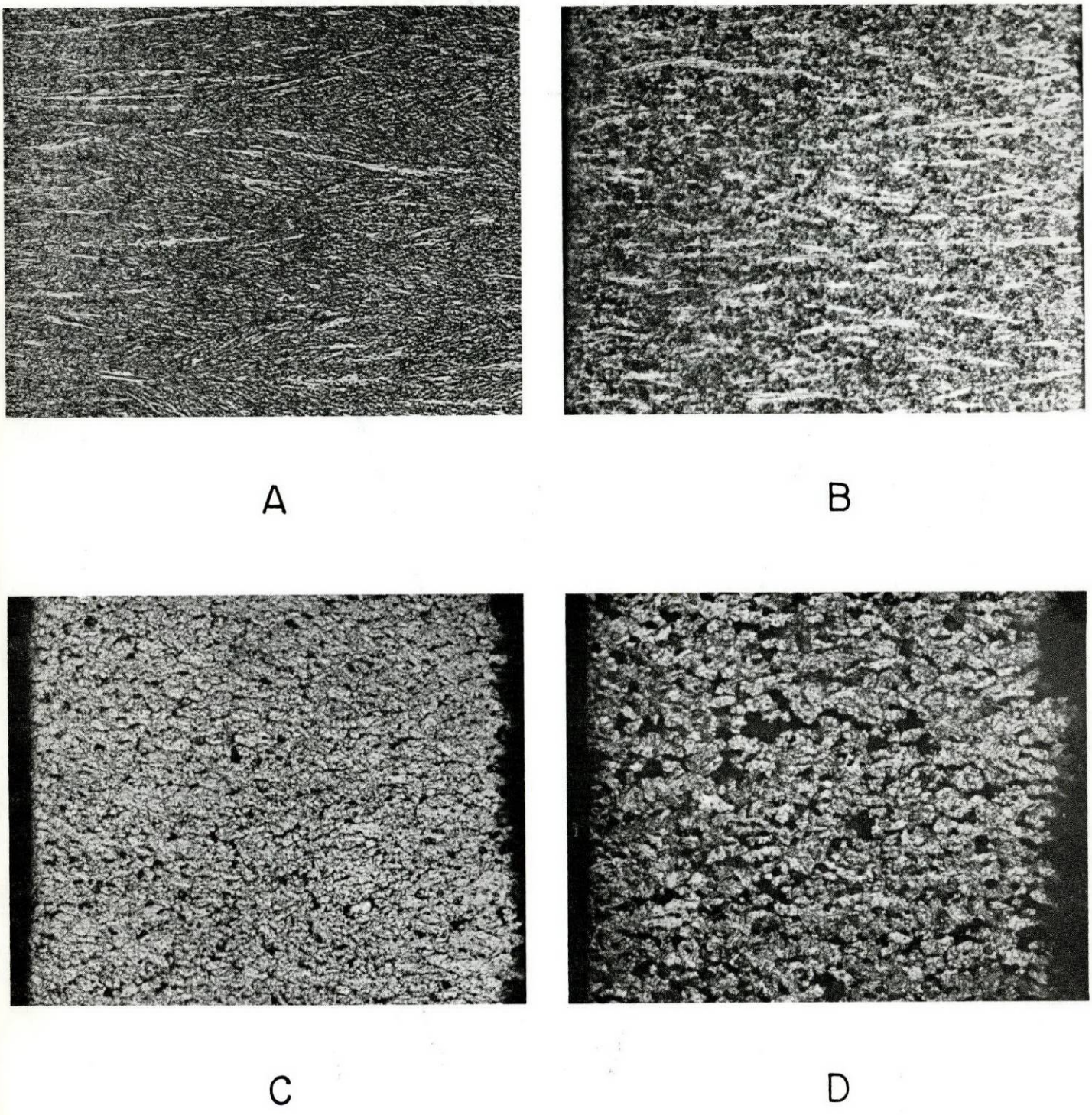



Figure 5. Microstructure of LC chromium deposited from solutions containing $V_2O_5$ at 85°C. A 10 g/l $V_2O_5$ , 135 A/dm$^2$, B - 15 g/l $V_2O_5$, 120 A/dm$^2$, C - 20 g/l $V_2O_5$, 90 A/dm$^2$, D - 20 g/l $V_2O_5$, 135 A/dm$^2$.



Figure 6. LC chromium plated from unaged solutions at 85°C. Left - good deposit, 120 A/dm$^2$, Right - spalled deposit, 60 A/dm$^2$.

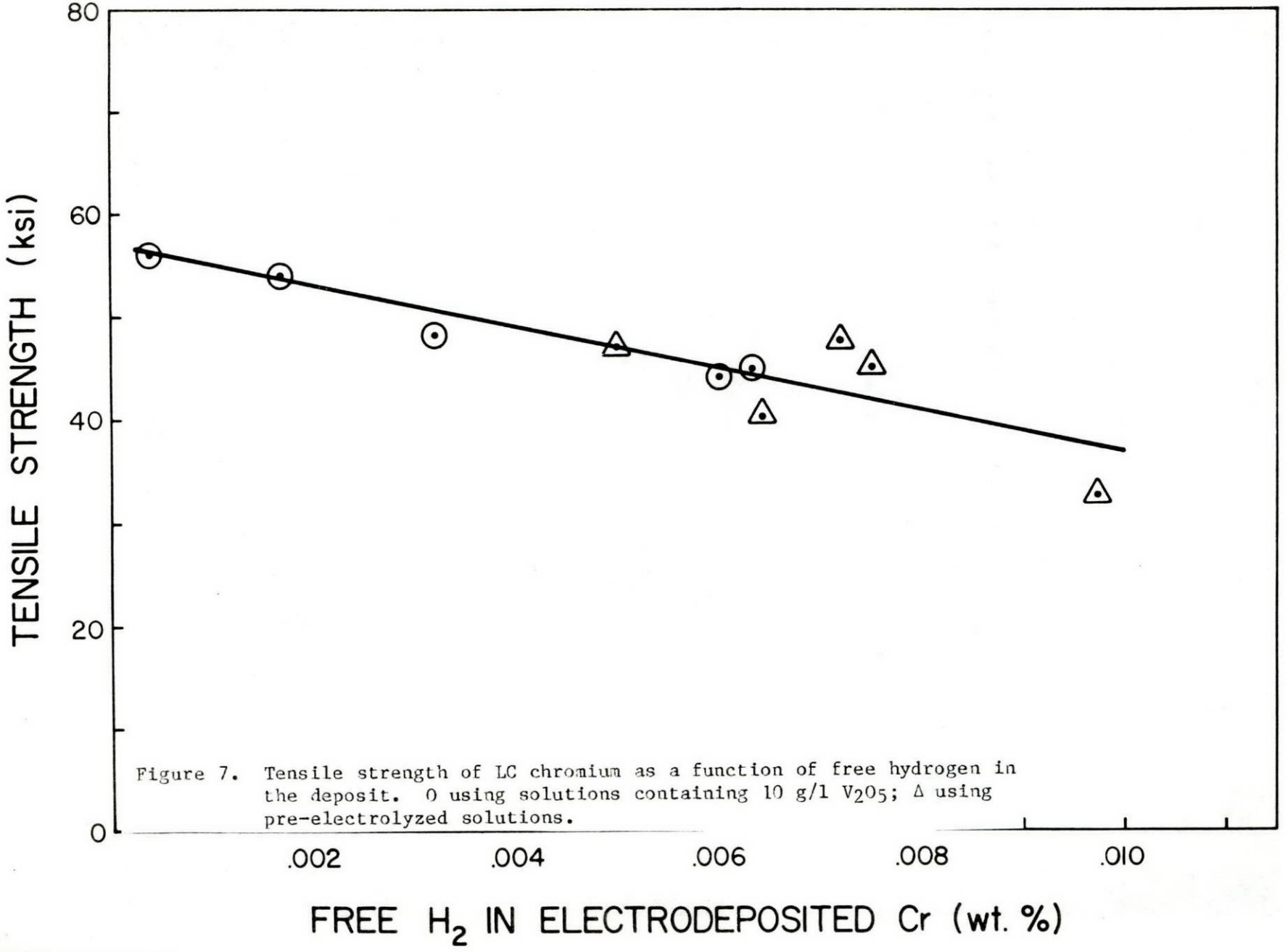



Figure 7. Tensile strength of LC chromium as a function of free hydrogen in the deposit. O using solutions containing 10 g/l $V_2O_5$; Δ using pre-electrolyzed solutions.

TABLE 1. HARDNESS, TENSILE STRENGTH AND CODEPOSITED OXYGEN, HYDROGEN, AND NITROGEN CONTENT IN LC CHROMIUM ELECTRODEPOSITED AT 85°C.

| Standard Chromium Bath | Current Density ($A/dm^2$) | Oxygen (wt.%) | Hydrogen (wt.%) | Nitrogen (wt.%) | Weight Ratio $O_2/H_2$ | Free[c] Hydrogen (wt.%) | Hardness (KHN) | Tensile Strength (ksi) |
|---|---|---|---|---|---|---|---|---|
| Unaged[a] | 60 | 0.036 | 0.0513 | 0.007 | 0.7 | 0.0468 | 562 | 7.1 |
| | 90 | 0.021 | 0.0244 | 0.009 | 0.9 | 0.0218 | 620 | 13.6 |
| | 120 | - | - | - | - | - | 655 | 20.1 |
| | 150 | 0.031 | 0.0304 | 0.006 | 1.0 | 0.0265 | 668 | 29.1 |
| Pre-electrolyzed[b] | 60 | 0.014 | 0.0115 | 0.006 | 1.2 | 0.0097 | 540 | 32.8 |
| | 90 | 0.033 | 0.0105 | 0.006 | 3.1 | 0.0064 | 578 | 40.0 |
| | 120 | 0.034 | 0.0096 | 0.005 | 3.4 | 0.0050 | 646 | 47.0 |
| | 135 | 0.048 | 0.0132 | 0.004 | 3.6 | 0.0072 | 643 | 48.2 |
| | 150 | 0.050 | 0.0138 | 0.004 | 3.6 | 0.0075 | 657 | 45.5 |
| With $V_2O_5$ at 10 g/l | 60 | 0.020 | 0.0042 | 0.002 | 4.8 | 0.0017 | 525 | 54.1 |
| | 90 | 0.028 | 0.0067 | 0.001 | 4.2 | 0.0032 | 562 | 46.7 |
| | 120 | 0.038 | 0.0108 | 0.001 | 3.5 | 0.0060 | 581 | 47.0 |
| | 135 | 0.031 | 0.0102 | 0.001 | 3.0 | 0.0063 | 617 | 44.8 |
| | 150 | 0.040 | 0.0054 | 0.001 | 7.4 | 0.0004 | 640 | 56.3 |
| With $V_2O_5$ at 15 g/l | 60 | 0.075 | 0.0090 | 0.001 | 8.3 | 0.0000 | 495 | 9.5 |
| | 90 | 0.062 | 0.0112 | 0.001 | 5.5 | 0.0034 | 549 | 38.1 |
| | 120 | 0.101 | 0.0148 | 0.001 | 6.8 | 0.0022 | 586 | 44.2 |
| | 135 | 0.087 | 0.0112 | 0.001 | 7.8 | 0.0003 | 596 | 34.4 |
| | 150 | 0.096 | 0.0159 | 0.001 | 6.0 | 0.0039 | 609 | 30.4 |
| With $V_2O_5$ at 20 g/l | 60 | 0.062 | 0.0080 | 0.001 | 7.8 | - | 535 | 15.5 |
| | 90 | 0.137 | 0.0101 | 0.001 | 13.6 | - | 526 | 33.1 |
| | 120 | 0.182 | 0.0120 | 0.001 | 15.2 | - | 520 | 43.4 |
| | 135 | 0.311 | 0.0231 | 0.001 | 14.8 | - | 480 | 23.4 |
| | 150 | 0.365 | 0.0234 | 0.002 | 15.6 | - | 466 | 21.5 |

[a]The values of oxygen, hydrogen, and nitrogen content in these deposits are the result of a single measurement.

[b]Each value of oxygen content represents an average of three determinations. The values of hydrogen and nitrogen represent an average of two determinations.

[c]The free hydrogen was calculated on the basis of oxygen combining with hydrogen in a weight ratio of eight.

U-4

# Chromium Plating
# Session U

## Improving Efficiency of Cr Plating With Higher Sulfate and Cn (III)

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# IMPROVING EFFICIENCY OF Cr PLATING WITH HIGHER SULFATE AND Cr(III)

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## Abstract

By increasing the concentration of sulfate in chromic acid baths, it is possible to increase the tolerance for Cr(III) without deterioration of Cr deposits. In addition, current efficiency increases with concentration of Cr(III) up to a certain limit, which depends on the temperature of deposition. Data obtained at temperatures in the range 40 to 64°C are presented.

## Introduction

Beginning in 1856 many different plating baths have been proposed for chromium electrodeposition.[1] The most successful of these are chromic acid bath containing sulfate catalyst or a mixture of catalysts (usually sulfate and silicofluoride). The current efficiencies of these baths are approximately in the range 10 to 25%, depending on the catalyst and plating conditions.[2]

The concentration of trivalent chromium (Cr(III)) in the chromic acid bath is an important factor in chromium plating. Cr(III) accumulates in industrial plating baths by cathodic reduction of Cr(VI) and poor anodic oxidation. If the concentration of Cr(III) becomes too high, plating of chromium may cease.

Plating Cr at high current densities (0.6 $A/cm^2$ and higher) from a solution containing 250 g/l $CrO_3$, 10 g/l $H_2SO_4$, and 20 g/l Cr(III) was reported to give 25% higher current efficiency without any harmful effects on the properties of the deposits.[3] These workers obtained the desired concentration of Cr(III) by adding hydrogen peroxide to the chromic acid bath. We have performed similar research, using methanol to produce the desired concentration of Cr(III) in the chromic acid bath. We report here our results on current efficiency and appearance of the deposits as functions of concentration of Cr(III) and temperature.

## Experimental Methods

Experiments were performed with two water-jacketed cells connected in series to a constant temperature circulating bath,

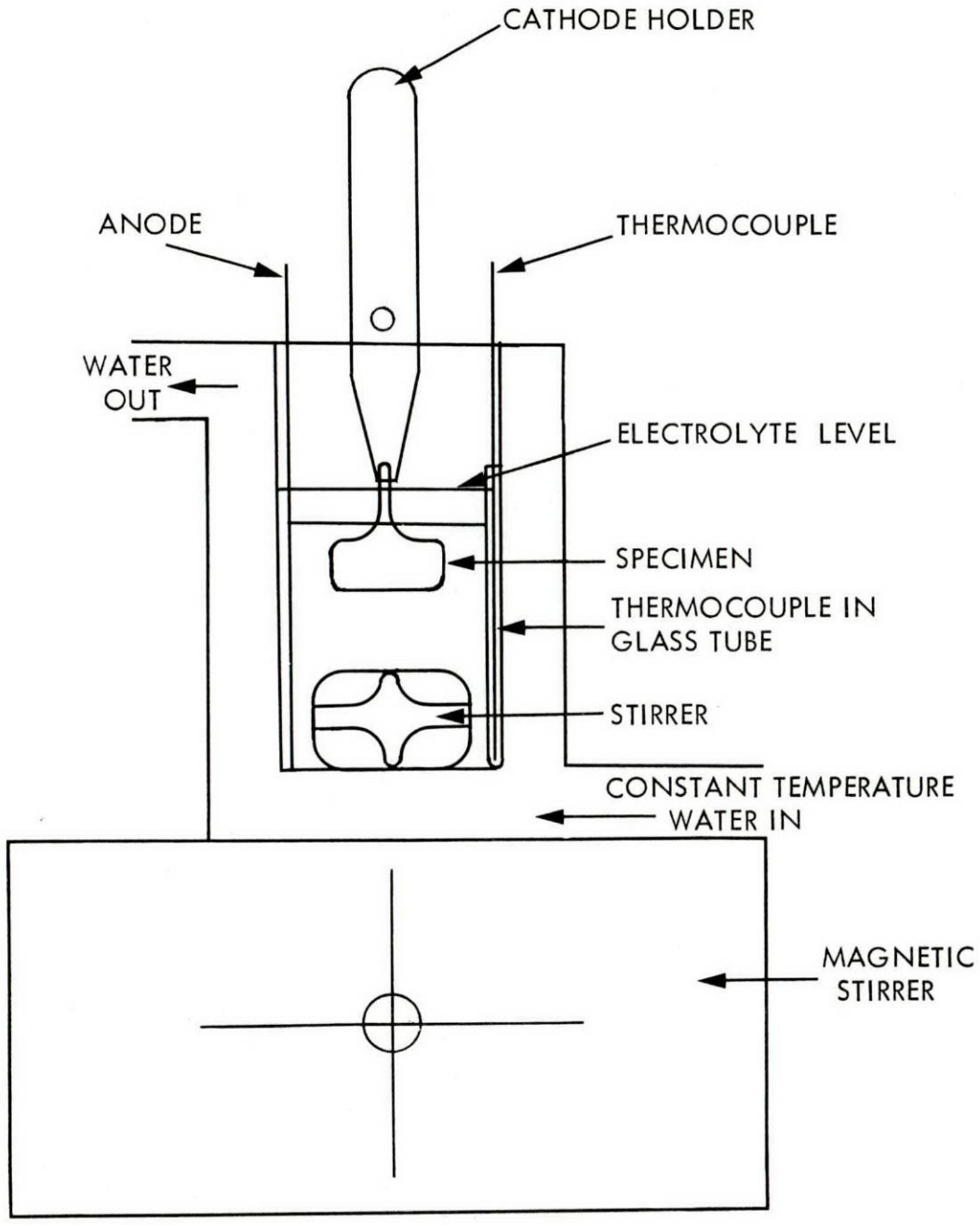



Fig. 1. Cell used for plating experiments (actual size).

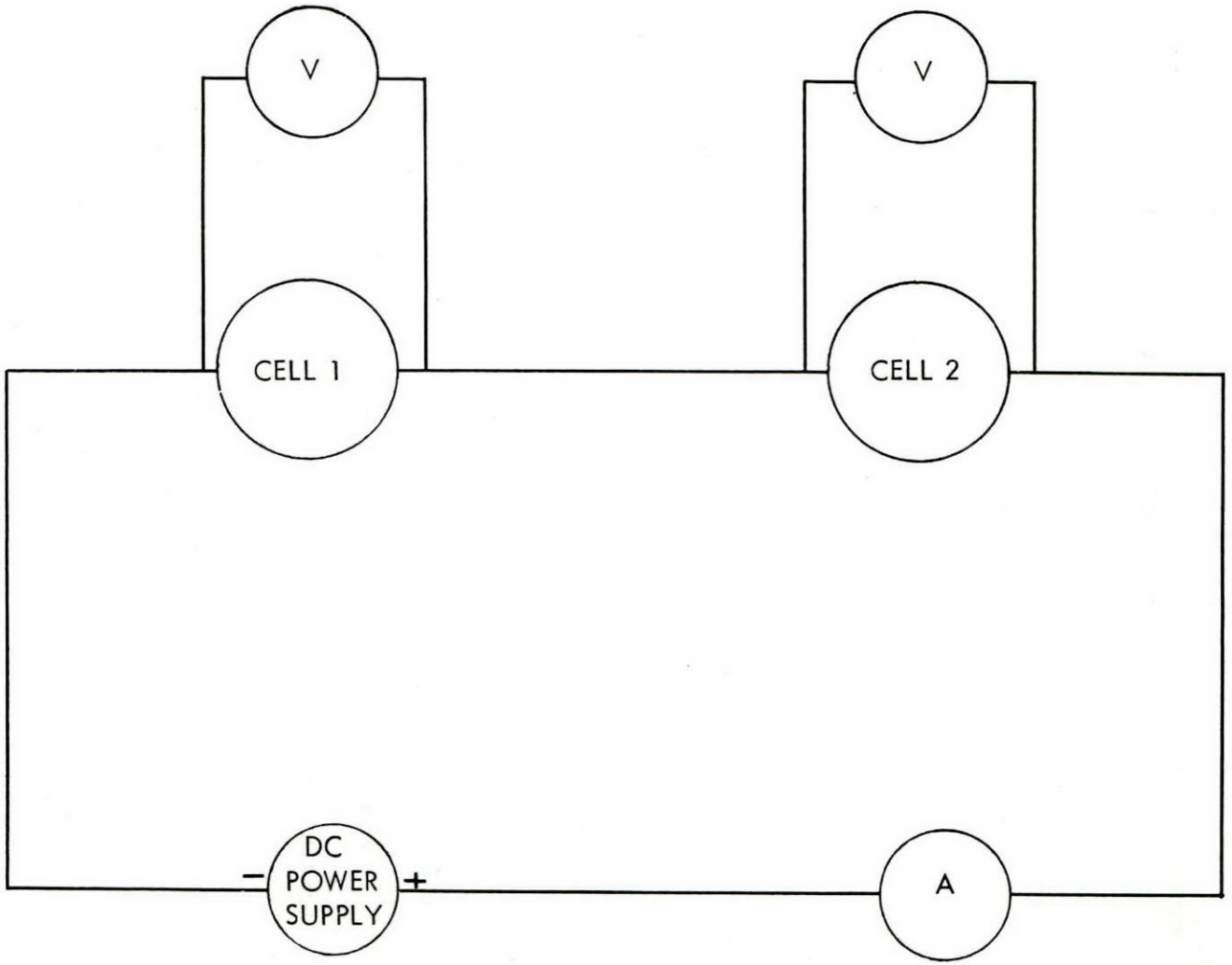



Fig. 2. Electrical curcuit used for plating experiments.

which maintained the desired temperature in both cells. Pure lead cylindrical anodes surrounded the rectangular cathodes, each of surface area $2cm^2$ (Fig. 1). The cells were connected in series to a constant current power supply (Fig. 2) which maintained a current density of 25 $A/dm^2$ for all experiments. With this arrangement it was possible to obtain data on two cells which were identical except for composition of the electrolyte. Cell voltages were recorded on a 2-pen strip chart recorder. For each experiment the plating time was one hour (unless otherwise mentioned), and the initial concentration of $CrO_3$ (analytic reagent) was 250g per liter of purified water. The concentration of Cr(III) was measured with a spectrophotometer. The baths were stirred during plating with magnetic stirrers.

## Experimental Results

Our initial experiments determined the effect of concentration of sulfuric acid on current efficiency. These results (Fig. 3) were obtained at 40°C. This figure shows that current efficiency increases to a maximum of about 21% at about 2.5 g/l $H_2SO_4$ and this maximum efficiency is maintained up to a concentration of about 4.0 g/l $H_2SO_4$. Further increases in $H_2SO_4$ concentration cause reduced current efficiency.

The next series of experiments determined the effect of increasing concentration of Cr(III) on current efficiency of plating from baths containing three different concentrations of $H_2SO_4$ at 40°C. The Cr(III) was produced in the solution before plating by adding suitable amounts of methanol. Fig. 4 gives these results. Here it is shown that a concentration of 3.7 g/l $H_2SO_4$ together with 2.9 g/l Cr(III) increases current efficiency by about 20% compared with the results from a solution with no initial Cr(III). The appearance of the deposits changes from slightly shiny with no Cr(III) present in the initial solution to light gray matte at all concentrations of Cr(III) exceeding 2.4 g/l. At other concentrations of sulfate, additions of Cr(III) to the solution before plating also increase current efficiency but by lesser amounts (Fig. 4).

Experiments have also been performed for 15 min. and 30 min. plating times at 40°C. The current efficiency results for these experiments are given in Fig. 5. Appearance of the 15 min. deposits is dark gray matte. This becomes increasingly lighter gray with increasing time of deposition. Maximum current efficiency (28%) was obtained for the 30 min. plating time.

The above increases in current efficiency by additions of methanol to chromic acid baths with sulfate present raised questions about the role of methanol. Experiments were performed to determine if chromium deposits from sulfate-free

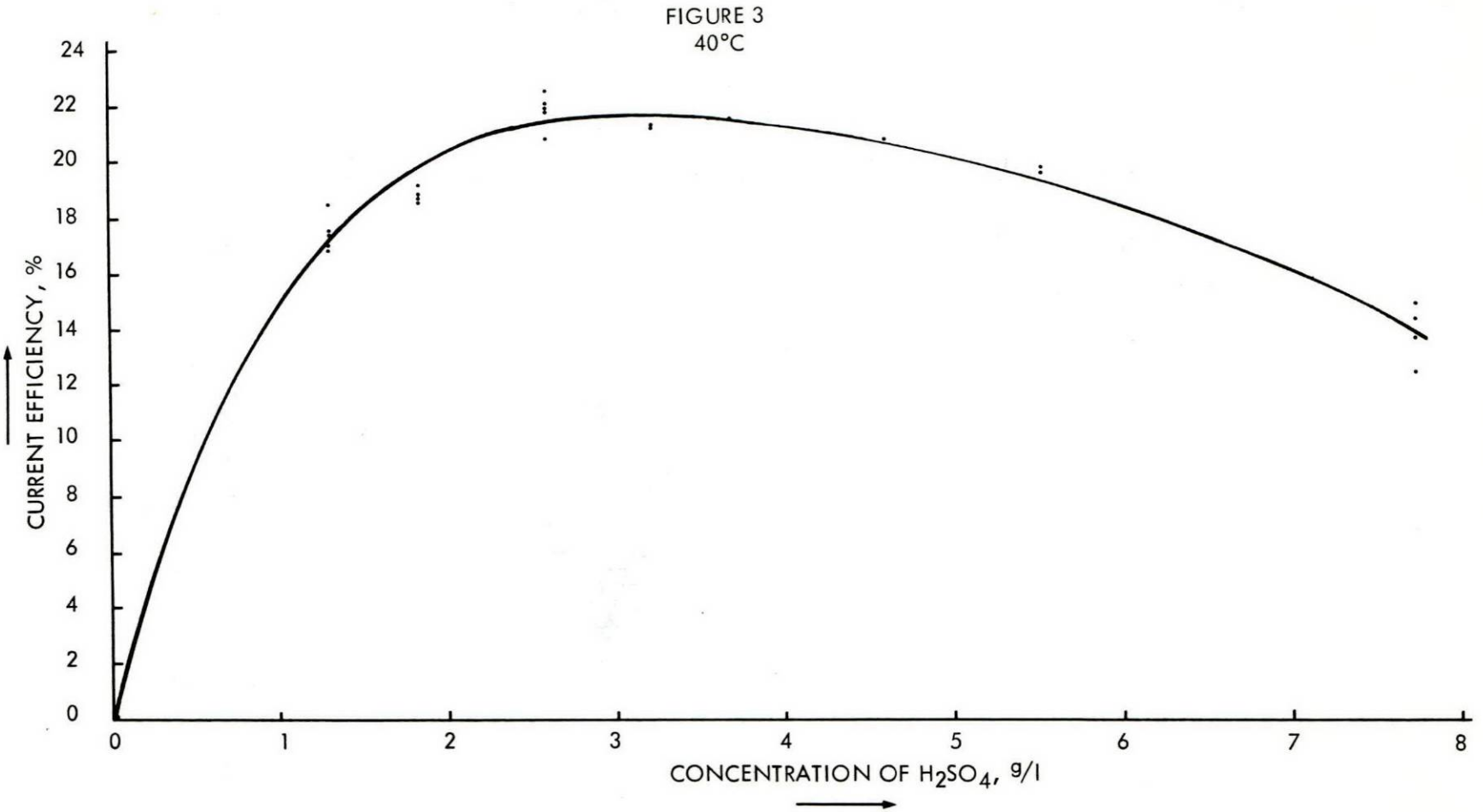



Fig. 3. Effect of increasing $H_2SO_4$ concentration on the current efficiency of plating from a solution containing 250 g/l $CrO_3$ at 40°C. Each point on the graph represents one experimental result.

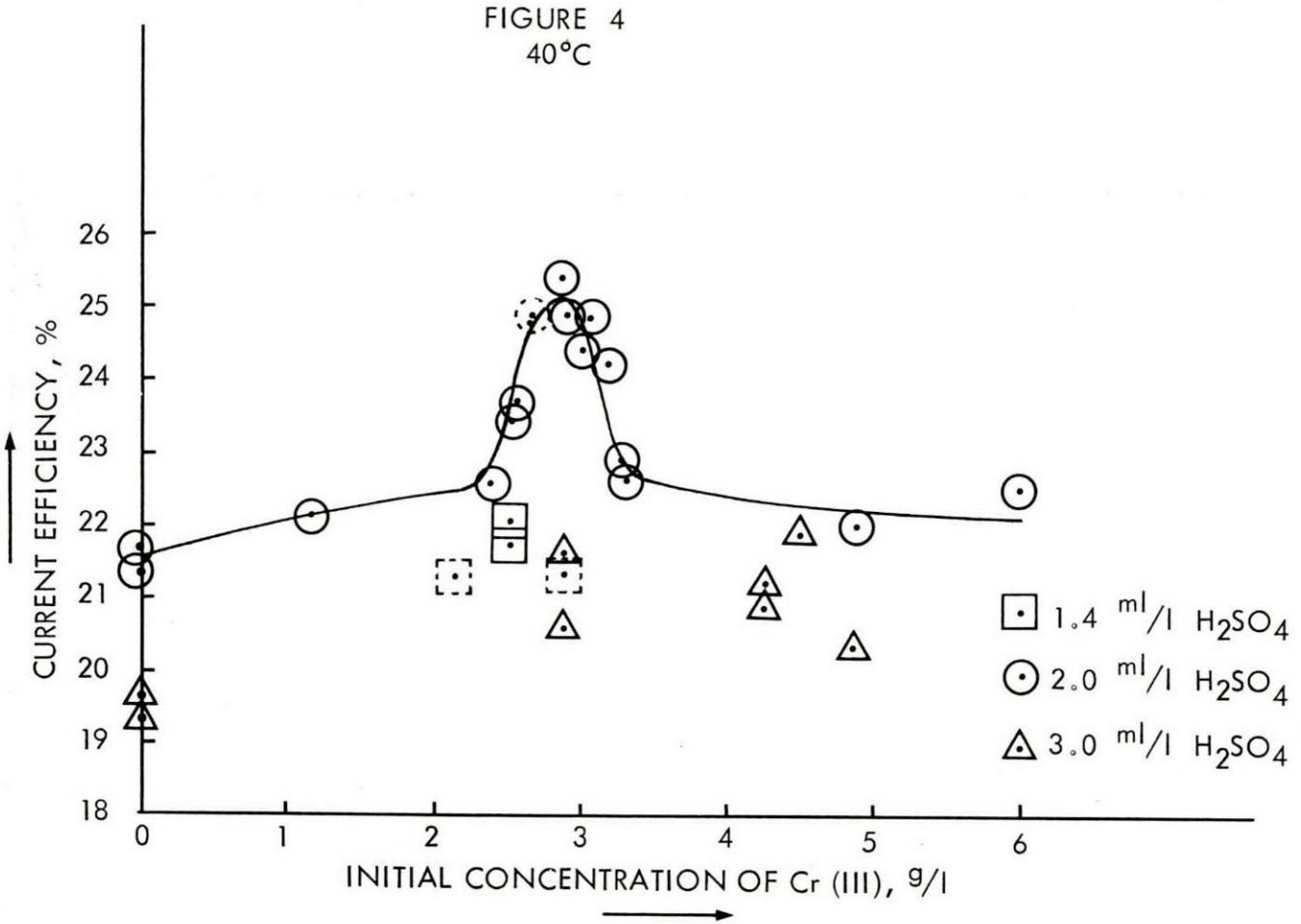



Fig. 4. Effect of Cr(III) concentration on current efficiency of plating at 40°C from three solutions with different concentrations of $H_2SO_4$. The dotted circle and squares indicate points where two experimental results coincided exactly.

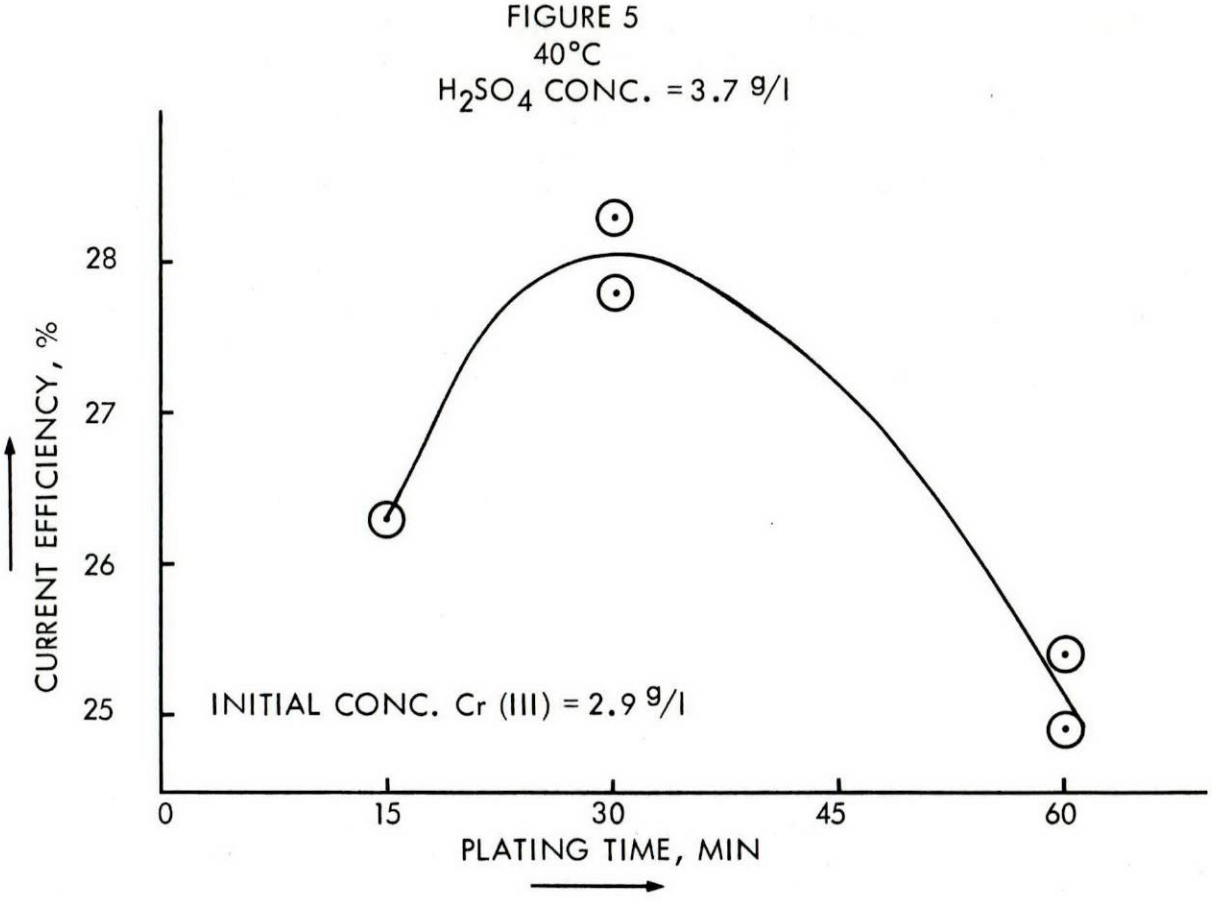



Fig. 5. Effect of plating time on current efficiency of plating at 40°C from a solution with an initial concentration of 2.9 g/l Cr(III).

chromic acid baths with added methanol or ethanol. The results are given in Fig. 6. Deposits were obtained at up to 10% current efficiency from a solution of 250 g/l $CrO_3$ to which 20 to 35 ml/l methanol had been added. These deposits were dark gray and sometimes non-adherent. Deposits were also obtained from the sulfate-free solutions to which ethanol had been added. These were also of poor quality, and current efficiency was always less than 2% for the range tested (20 to 120 ml/l ethanol). However, these results demonstrate that these alcohols produce Cr(III) in a form from which chromium can be deposited.

The effects of methanol additions to baths containing 250 g/l $CrO_3$ and 3.7 g/l $H_2SO_4$ was also studied for chromium plating experiments at 48, 54, and 63°C. Fig. 7 gives the current efficiency results obtained at 48°C. These depostis are shiny, but the specimen edges become increasingly gray with increase in Cr(III). At 54°C, the deposits are shiny over the entire range of Cr(III) shown in Fig. 8a. Current efficiency increased by about 10% for 16 experiments with Cr(III) in the range 6 to 20 g/l, and there was no change in the appearance of the deposits. Scanning electron micrographs were taken to show the entire specimen and a smaller area at higher magnification. Fig. 8b and 8c show a specimen plated at 54°C with no added Cr(III), and Fig. 8d and 8e show a specimen plated at 54°C with 12.3 g/l Cr(III) added before the start of plating.

It is well known that there are three competing cathode reactions in chromium plating[4]:

(a) production of $H_2$ gas,

(b) production of Cr(III) ions, and

(c) production of chromium metal.

The results presented above show that the addition of Cr(III) to the solution enhances reaction (c). The effect on reaction (a) was not measured. The next experiments determined the Cr(III) concentration before and after plating times of 15, 30, and 60 min. at 54°C in solutions with 4ml methanol/l added to produce an initial concentration of 12.3 g/l Cr(III). Simultaneously, plating was performed for the same time from solutions of the same composition except that no methanol was added, so there was no Cr(III) present initially in these solutions. Fig. 9 shows that there is a rapid, linear decrease in Cr(III) from the initial 12.3 g/l to less than 2 g/l after 60 min. plating. This figure also shows a small accumulation of Cr(III) during the first 30 min. of plating in the solutions with no initial Cr(III). This remains constant during the period from 30 to 60 min. plating time.

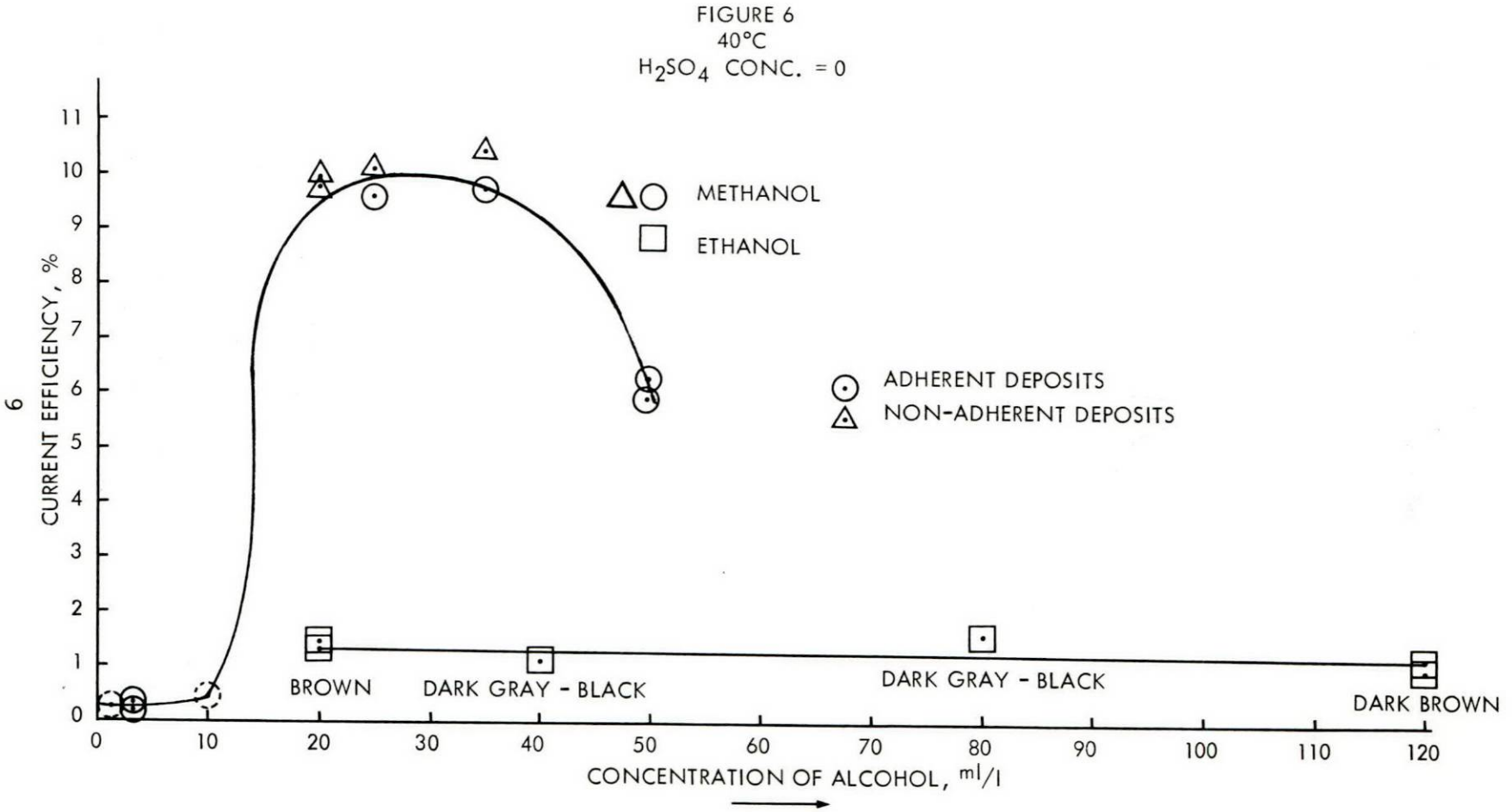



Fig. 6. Catalytic effect of alcohol on chromium deposition. The deposits made from the solutions containing methanol were dark gray.

FIGURE 7
48°C
$H_2SO_4$ CONC. = 3.7 g/l

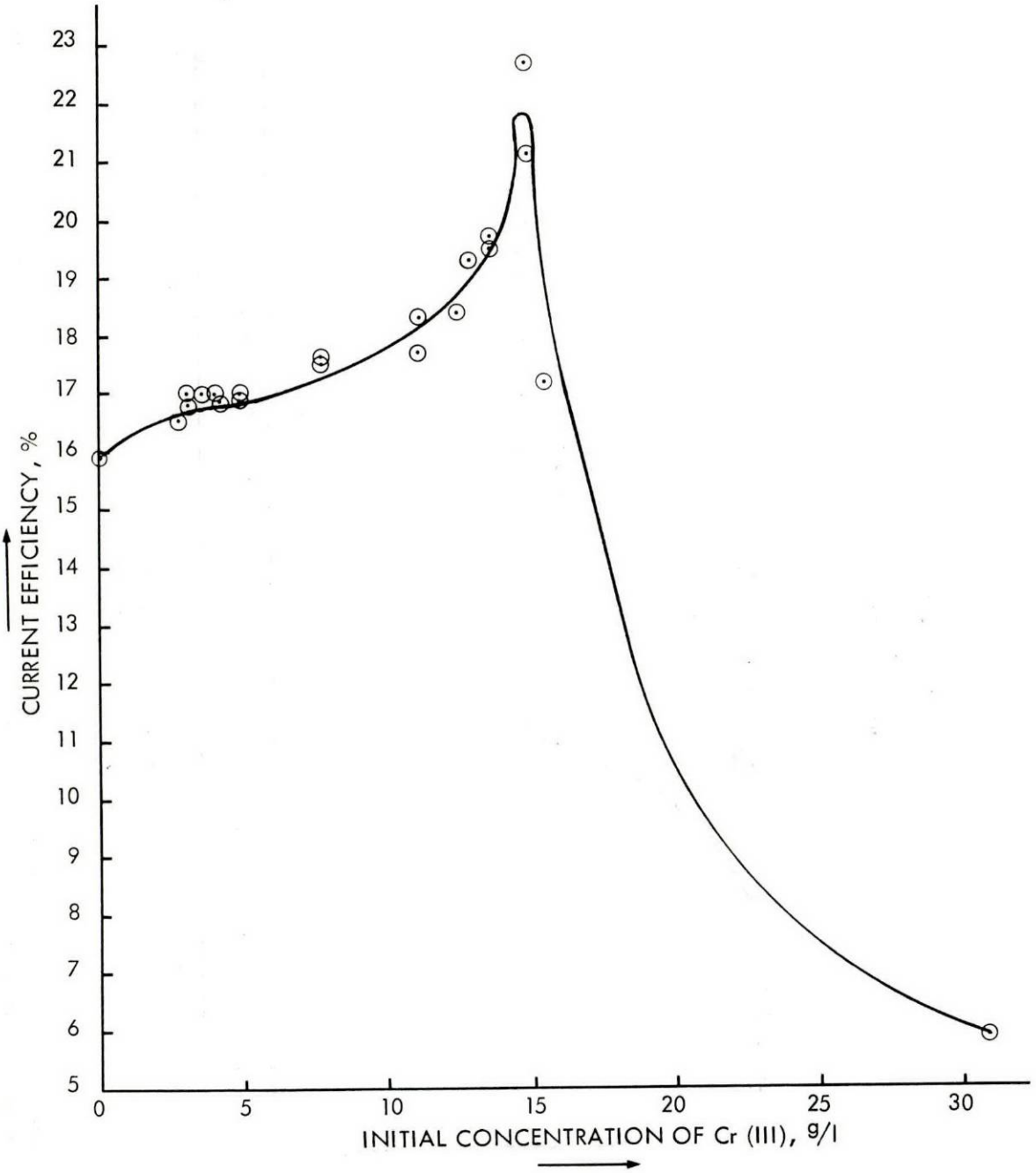



Fig. 7. Effect of Cr(III) concentration on current efficiency of plating at 48°C. Deposits were shiny with no added Cr(III), but edges became increasingly gray with increasing Cr(III).

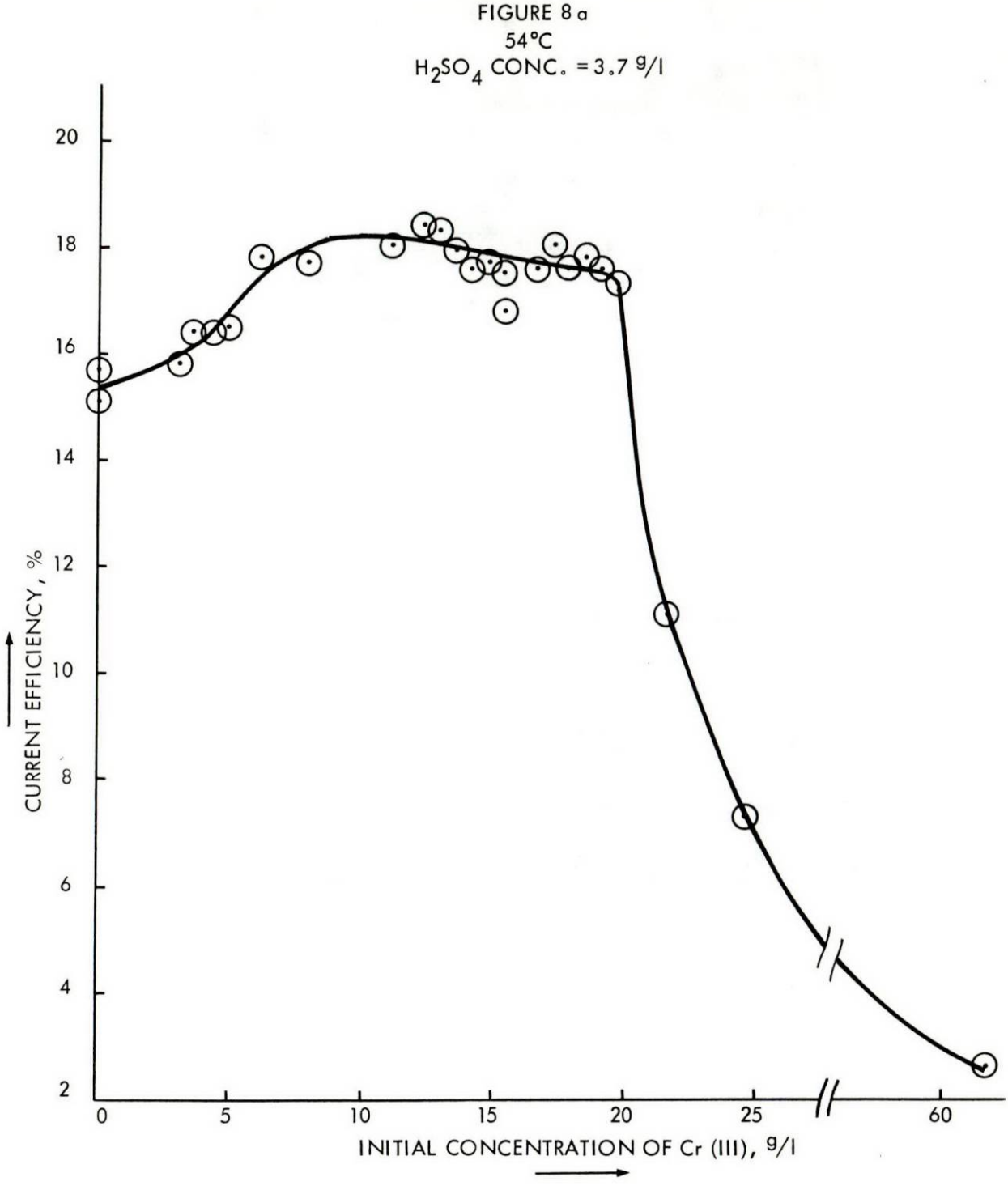
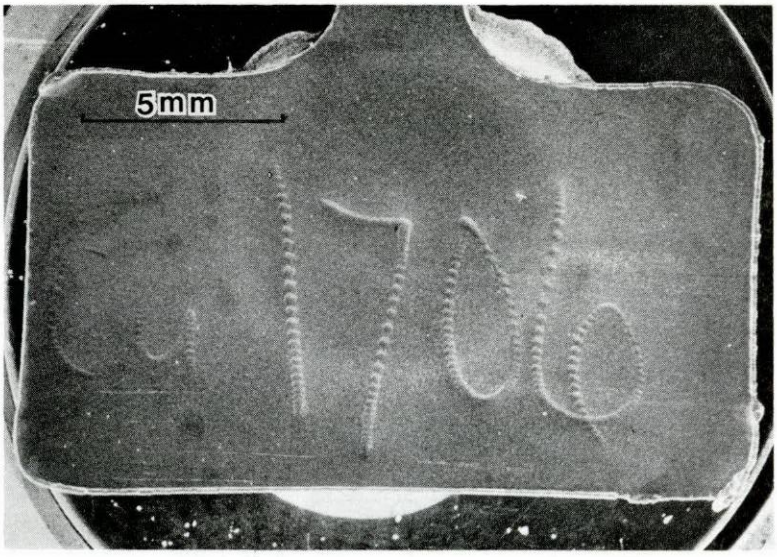
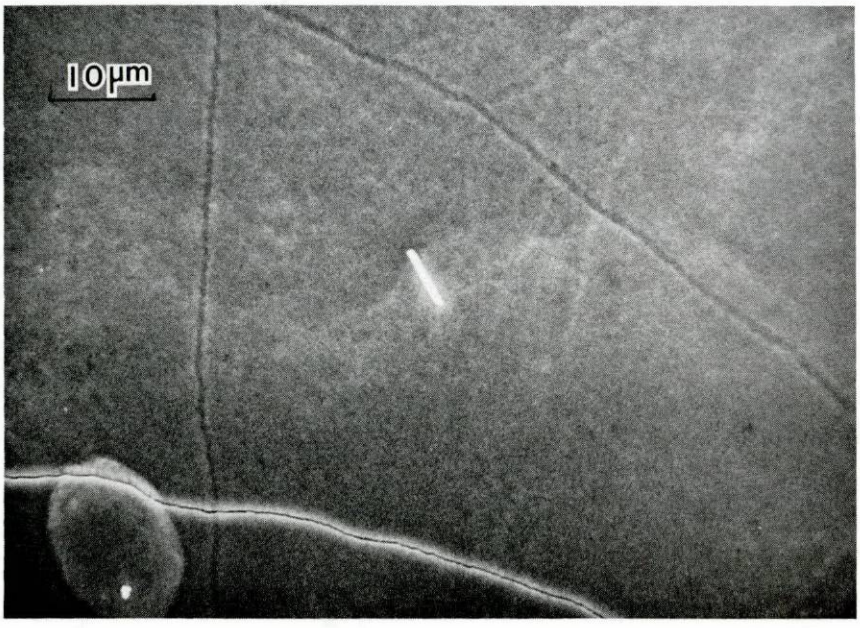


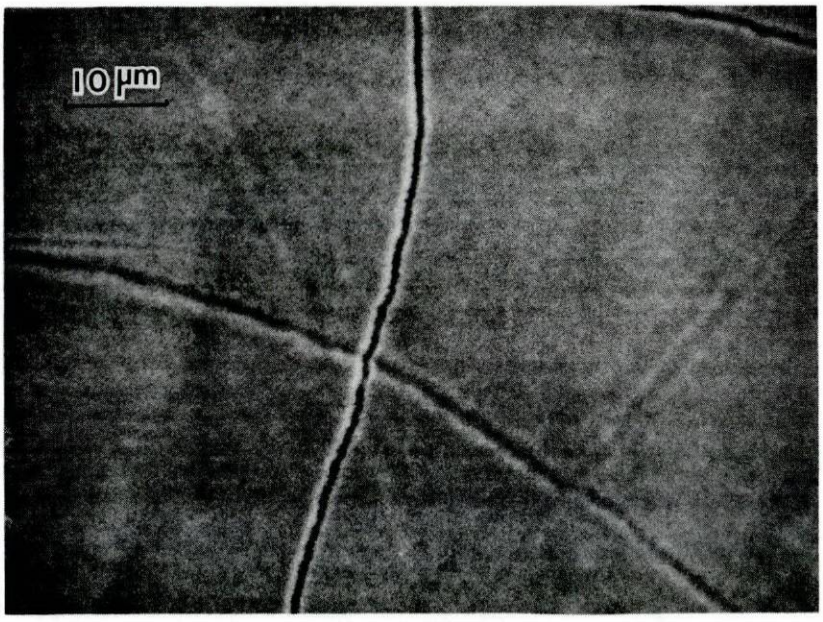

Fig. 8a. Effect of Cr(III) concentration on current efficiency of plating at 54°C.




Figs. 8b and 8c. Scanning electron micrographs of specimen plated at 54°C with no added Cr(III).




Figs. 8d and 8e. Scanning electron micrographs of specimen plated at 54°C with 12.3 g/l Cr(III) added before the start of plating.

FIGURE 9
54° C
$H_2SO_4$ CONC. = 3.7 g/l

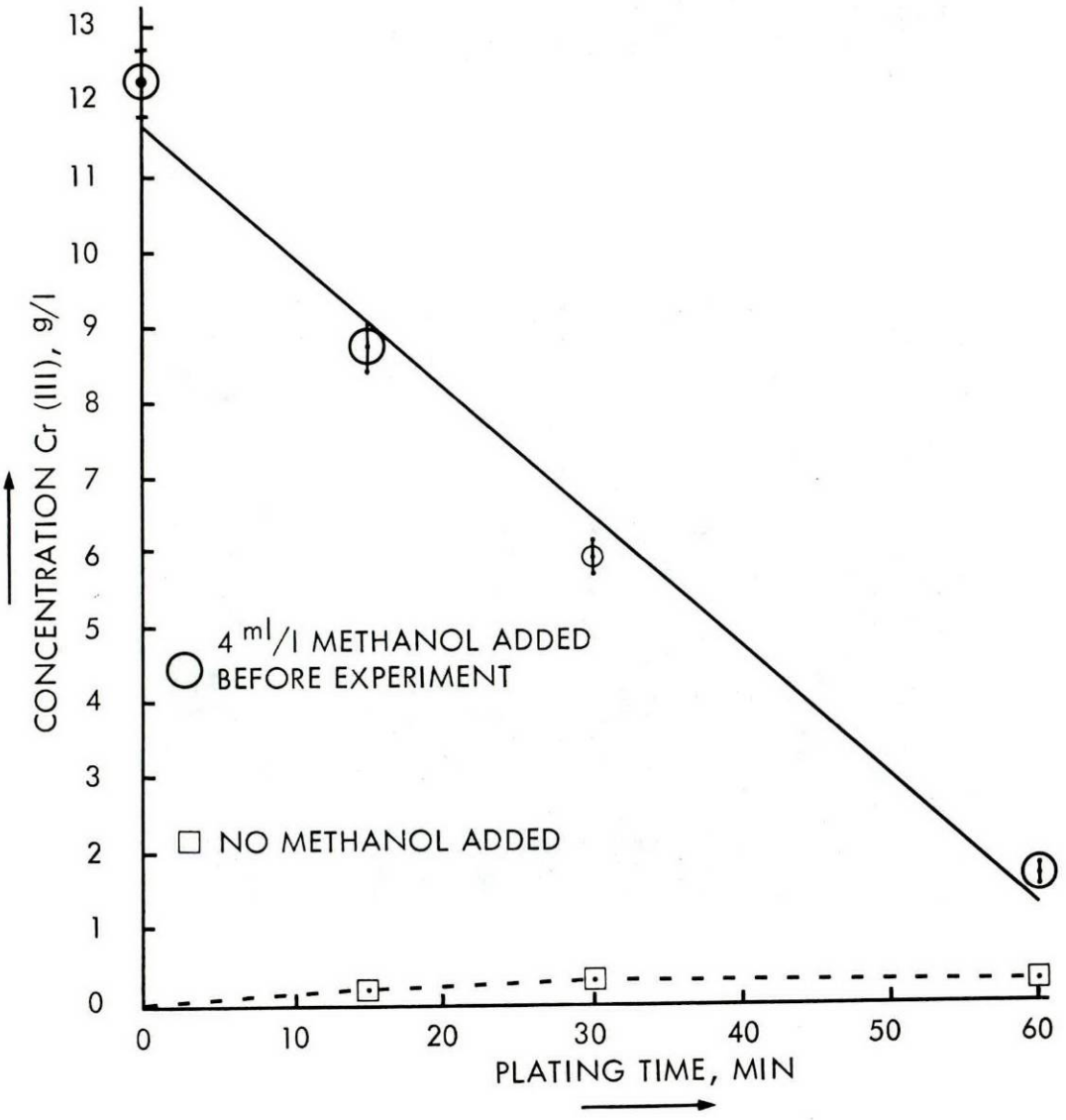



Fig. 9. Changes in concentration of Cr(III) during plating at 54°C.

The results at 63°C (Fig. 10) are similar to those at 54°C in that Cr(III) additions over a broad range increase current efficiency without changeing the appearance of the deposits, which all appear milky at this temperature. This figure also shows that increasing the current density from 0.25 A/cm$^2$ to 1.25 A/cm$^2$ greatly increases current efficiency. The largest increase was observed for an experiment with an initial Cr(III) concentration of 6 g/l.

FIGURE 10
63° C
$H_2SO_4$ CONC. = 3.7 g/l

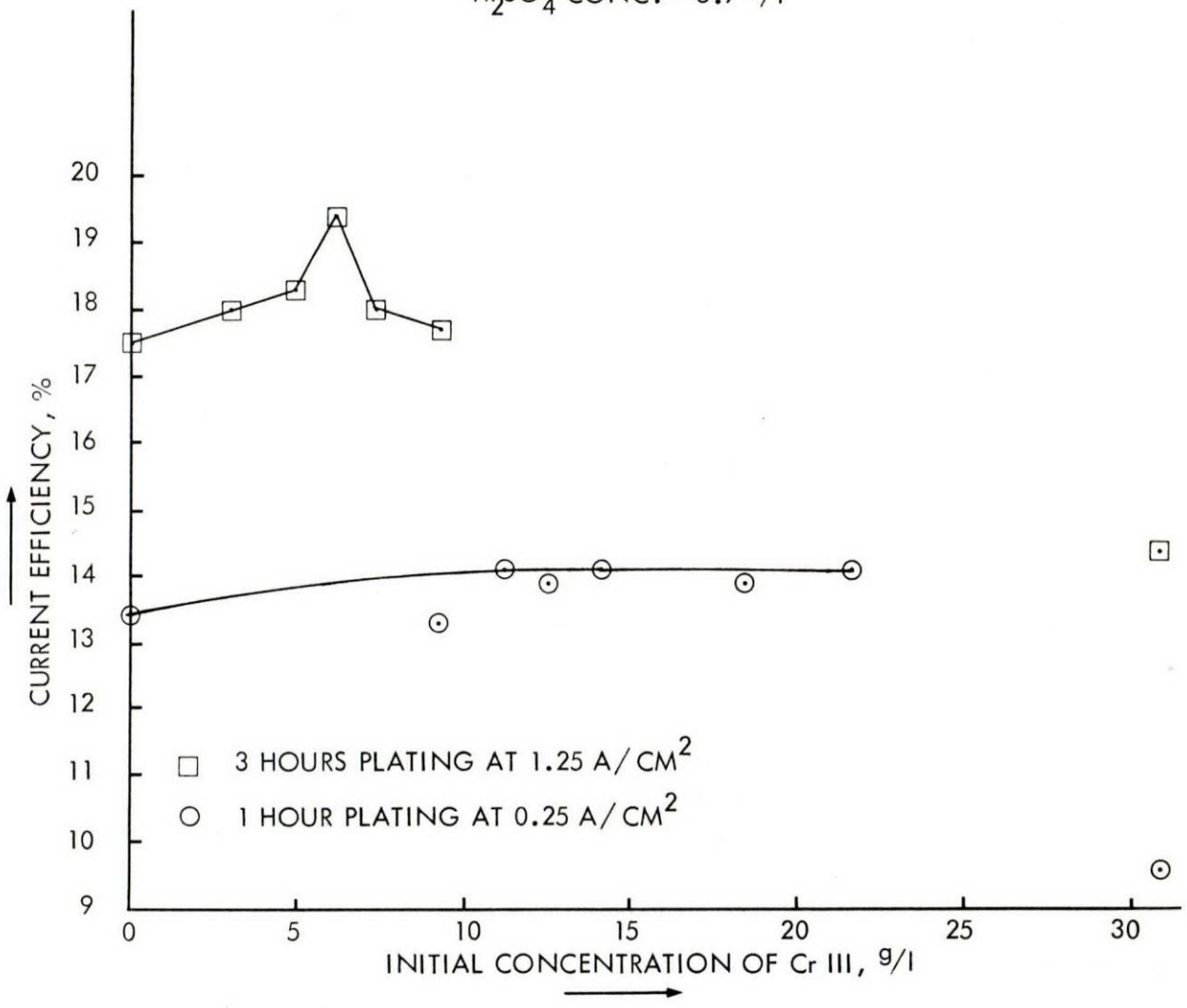



Fig. 10. Effect of Cr(III) concentration on current efficiency of plating at 63°C.

## Discussion of Results

The addition of methanol ($CH_3OH$) to chromic acid solutions is expected to cause the following chemical reactions:

(1) $4CrO_3 + 3CH_3OH + 12H^+ = 3HCOOH + 4Cr(III) + 9H_2O$

(2) $3HCOOH + 6H^+ + 2CrO_3 = 2Cr(III) + 6H_2O + 3CO_2$

When there are large amounts of methanol, reaction (2) may not go to completion. The formic acid (HCOOH) remaining in the solution may catalyze the deposition of chromium as shown in Fig. 6.

When ehtanol is added to chromic acid solutions the expected reactions are:

(3) $4CrO_3 + 3C_2H_5OH + 12H^+ = 3CH_3COOH + 4Cr(III) + 9\ H_2O$

(4) $3CH_3COOH + 4CrO_3 + 12H^+ = 6CO_2 + 4Cr(III) + 12H_2O$

Notice that reaction (4) requires twice as much $H^+$ as reaction (2). Thus, it is less likely to go to completion, and acetic acid ($CH_3COOH$) should remain in the solution. The results in Fig. 6 indicate that acetic acid is not as effective as formic acid in catalyzing chromium deposition. The deposits from solutions to which ethanol was added are darker, and the current efficiency was much less. With a concentration of 40ml/l ethanol, the deposit is gray in the high current density areas (specimen edges) and quite black in the low current density areas.

In the presence of sulfate catalyst, the increase in current efficiency obtained by adding methanol is believed to be caused by suppression of the cathode reaction,

(5) $Cr(VI) + 3e = Cr(III)$,

due to high concentration of Cr(III) at the start of plating. This conclusion is supported by several of our experiments in which Cr(III) was produced in the initial solution by the addition of $H_2O_2$. The current efficiency in these experiments was increased by the same amount as in the case of Cr(III) produced by methanol.

## Acknowledgment

This research was supported by the U. S. Army Research Office. We are grateful to C. Cousins for his assistance in obtaining the data for Fig. 3.

References

1. J. P. Hoare, J. Electrochem. Soc. 126, 190 (1979).

2. G. Dubpernell, in "Modern Electroplating," 3rd ed., F. A. Lowenheim, Editor, p. 88, John Wiley & Sons, Inc., N. Y. (1974).

3. R. A. Ignat'ev, et al, Protection of Metals 9, 417 (1973).

4. J. L. Griffin, Plating 53, 196 (1966).