AMERICAN ELECTROPLATERS' SOCIETY, INC. 67TH ANNUAL TECHNICAL CONFERENCE— MILWAUKEE, WI

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CLEANING
SESSION A

New Developments in Alkaline Cleaning

L. J. Durney and K. Frey
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NEW DEVELOPMENTS IN ALKALINE CLEANING

L.J. Durney and Keith Frey
Frederick Gumm Chemical Co., Inc.

Historically, the major emphasis in metal cleaning formulations has been toward cleaning by emulsification and saponification. Attention was generally focused on the solution/oil interface and efforts were directed at reducing this interfacial tension. Although the work of Linford, Saubestre and others had indicated that the spreading coefficient of the oil on the substrate could be correlated with the ease or difficulty of cleaning, the importance of this fact was not appreciated. Development of the HLB system of classifying surfactants and soils permitted relatively easy matching of soils and surfactant combinations to give emulsification characteristics adequate for good cleaning. Operating temperatures were held fairly high to provide the energy needed for emulsification and to approach the cloud point of nonionic systems, thereby promoting migration of the surfactant system into the oily soil. Reclaim of surfactant and discharge of oil to the surface to promote longer cleaner life were obtained by periodic cooling of the system during shutdown, or locally at the surface or in oil separation units. Cleaner concentrations were maintained relatively high to maintain desireable transfer rates across the interface.

The energy crises of the early 1970's resulted in an urgent demand for reduced operating temperatures for all cleaning processes. Two immediate options suggested themselves, the incorporation of hydrotropic solvents in the cleaner formulations, and the substitution of mechanical energy for thermal energy to produce emulsification.

Hydrotropic solvents reduced the required operating temperature by thinning

the oily soils; reducing the energy required for emulsification, and improving the penetration of the surfactant system into the oily soil. Unfortunately, increased emphasis and restrictions were placed on hexane solubles in effluents. Since both emulsification and the incorporation of solvents contribute to hexane solubles, this method of approach became less desireable.

While mechanical energy worked well as a substitute for thermal energy in spray washing units and certain bulk washing units, the amount of agitation possible on an automatic rack plating machine for example, severely limited the progress possible in this direction.

Review of the spreading coefficient work previously mentioned led to the conclusion that it might be possible to alter this spreading coefficient in the cleaning solution, thereby reducing the energy required for cleaning, and permitting operation at considerably lower temperatures.

Attention was first turned to soak cleaners and a series of these materials were successfully formulated. Slide #1 shows a comparison of the general operating conditions between conventional cleaners and the new low temperature type. Note especially that not only has the temperature, but also the concentration, been reduced. This results in lower dragout losses, and reduced waste disposal costs as well as energy savings.

Needless to say, these advantages are not gained without some sacrifice. The new principles work best when used to formulate displacement type cleaners, that is cleaners that float the oil rather than emulsifying it. We will discuss the relative advantages and disadvantages of displacement cleaners later in the paper. Emulsifying type materials can be formulated, but only

by increasing concentrations and/or temperatures somewhat - concentration to 4-8 oz/gal. and temperature to 80-120°F. It was also found that while the concentration and composition of the alkali portion of the cleaner was relatively unimportant as long as proper buffering is maintained, concentration of surfactant is critical, and there is an interaction between the two. Control of cleaner concentration therefore becomes somewhat more critical - excess concentration can affect performance; so also can low concentration.

Surfactant composition and in particular, structure, becomes extremely important. Additionally, the principles are operative only on liquid soils. Soils that contain higher melt materials such as paraffin, may require somewhat higher temperatures. Even in this case however, savings in energy are generally possible. Although the materials tend to be somewhat specific in application, it has been possible to formulate materials effective for job shop use, and in captive shops where a narrower range of soils is encountered, the results can be outstanding.

In electrocleaners, additional factors have to be taken into consideration. Lower temperatures reduce the conductivity of the solutions, so the normal cleaning current densities are more difficult to attain. Fortunately, measurements of cleaning ability as a function of current density, concentration, and temperature have shown that the required current density for cleaning, mainly smut removal, is dependent on the concentration of certain key ingredients. Furthermore, the required concentration and minimum current density, generally increase with temperature. Reductions of concentration are not as dramatic as with soak cleaners, but can still be appreciable. Slide #2 compares the operating conditions for conventional and low temperature electrocleaners.

Again, these gains are tempered by some restrictions. Adequate buffering at the part solution interface must still be maintained and may become more difficult at low temperatures due to mass transfer considerations. Inhibition of sensitive metals such as zinc becomes more difficult. The key to success lies in closer control of the cleaning solution, and granted this, successful operation even under job shop conditions can be attained.

Electrocleaners have the advantage that in many cases, once heated to operating temperature, no further heating is necessary. The required heat to maintain operating temperature is provided by the heating effect of the current used for cleaning.

Spray cleaners, because of the agitation produced by impingement, can be readily formulated. Modest gains in reducing concentrations are possible as well as reducing temperatures.

The main disadvantage of low temperature cleaners is that some problems may be encountered in dissolving the material for use. In some instances it is possible to formulate liquid products to eliminate the problem. In other cases it is possible to utilize the more readily soluble hydrated alkalies rather than the anhydrous materials. Raw material manufacturers, recognizing the problem, are attempting with some success, to vary the crystal size and form of the anhydrous materials to promote easier solubility. However, the problem must be faced and provisions made to properly dissolve the materials.

The advantages of low temperature cleaners are shown in Slide #3. Energy savings are of course paramount and will be discussed further. The improved working conditions, while not measurable in dollar terms, contribute to improved employee relations. The elimination of dry down problems and resultant staining can materially reduce rejection rates, particularly on

automatics with moderate to long transfer times. Not listed on the slide are the savings in waste disposal costs and material consumption due to the reduced concentrations used.

Slide #4 shows the reduction in heat loss from each square foot of solution surface obtained in going from high temperature to low temperature cleaning. At 150°F the loss is approximately 900 BTU per ft.^{2}/hour, at 170°F approximately 1600 BTU/ft.^{2}/hour. In contrast, the loss at 100°F is only 200 BTU/ft.^{2}/hour. Since foam is an excellent insulator, the loss from the surface of an electrocleaner is considerably lower, and the savings correspondingly reduced.

Slide #5 gives similar data for tank walls.

Slide #6 utilizes this data to calculate the savings for a 450 gallon tank, 4' x 5' x 3' deep. Reducing the operating temperature from 160°F to 90°F reduces the heating requirement by 90%. Note that in this case, no effort has been made to incorporate the savings resulting from not heating the work processed. This, expressed in BTU's per hour would be 9 x pounds per hour processed for steel, and 14 x pounds per hour processed for aluminum and copper alloys.

As previously mentioned, most of the low temperature cleaners clean by displacement. Since this is a departure from common practice, we should consider the advantages and disadvantages of this type of operation.

Slide #7 lists the advantages.

Displacement types generally operate at somewhat lower concentrations than do emulsifying types. This gives reduced makeup costs, and since

dragout is dependent on concentration, dragout losses are reduced, thereby reducing replenishment costs. Waste disposal costs are correspondingly reduced. As an offsetting penalty, if cleaner disposal and/or dragout are being utilized to neutralize acids in a waste disposal system, it may be necessary to provide additional alkalie in the form of liquid caustic or soda ash. However, since these basic materials cost less than the dragged out cleaner they replace, there is still a net saving.

Hexane soluble restrictions on effluents are becoming increasingly common. Removal of oils by emulsification contributes substantially to the hexane soluble content of the effluent. Displacement cleaners materially reduce this problem since the oil is separated from the cleaner by virtue of the way it operates. The problem is not completely eliminated since it is difficult to completely eliminate all drag over into the rinses.

Longer working life is the natural result of the separation of the oil from the cleaner. The cleaner no longer becomes saturated with oil and ceases to function. Cleaner life is not infinite however, because in most cases a gradual imbalance in ingredients occurs as a result of selective absorption and removal.

Finally, the separated oils can often be reused. In one case, a company processing screw machine parts was able to separate and reuse approximately 80 gallons of screw machine oil per week. In another instance, a job shop recovers approximately 150 gallons of oil per week which is added to their fuel oil and used to produce process steam.

Displacement cleaners unfortunately have disadvantages as well. These are shown in Slide #8.

Since the oils are displaced, and float on top of the cleaner, a suitable grease trap and skimming system is required to keep the surface relatively free of oil. A slide of such an arrangement will be shown next. Since this system removes from the cleaner almost all the oil taken off the parts, it greatly reduces the hexane soluble content of the effluent.

In the absence of a suitable skimmer-grease trap, redeposition of the displaced oils and consequent drag down may occur. This can be overcome by matching a suitable electrocleaner with the soak cleaner to form an integrated system.

Slide #9 shows a schematic of a suitable skimmer-grease trap system. Certain points should be emphasized. The dam overflow must be level and the edge relatively smooth so good skimming action is obtained. The dimensions of the dam and overflow pipe should be adequate to avoid flooding of the dam. The flow through the header pipe should be adequate to provide good skimming action, but not so violent that it causes emulsification or excessive foaming. Dimensions of the outboard tank should be adequate to allow complete separation of the oil. The drop from the dam to the grease trap can result in some emulsification and/or foaming. Additional separating partitions are sometimes helpful in overcoming this and providing good separation. In this case, each chamber should have provisions for trapping off separated oil.

To sum up -
Low temperature, low concentration soak and electrocleaners can be formulated and are available.

They are only effective on liquid oils, therefore the minimum operating temperature is determined by the melting point of the oil to be removed.

They are somewhat specific in performance, but can be effective even in job shop operation.

They offer tremendous savings in energy costs, as high as 90%.

They require more careful control, and the use of a skimmer-grease trap is recommended.

COMPARISON OF GENERAL SOAK CLEANER WORKING CONDITIONS

	Conventional	Low Temp
CONC.:	8 - 12 oz./gal.	2 - 4 oz./gal.
TEMP.:	150 - 170°F.	*70 - 90°F.
TIME:	1 - 5 minutes	1 - 5 minutes

* *Slightly higher for emulsifying type*

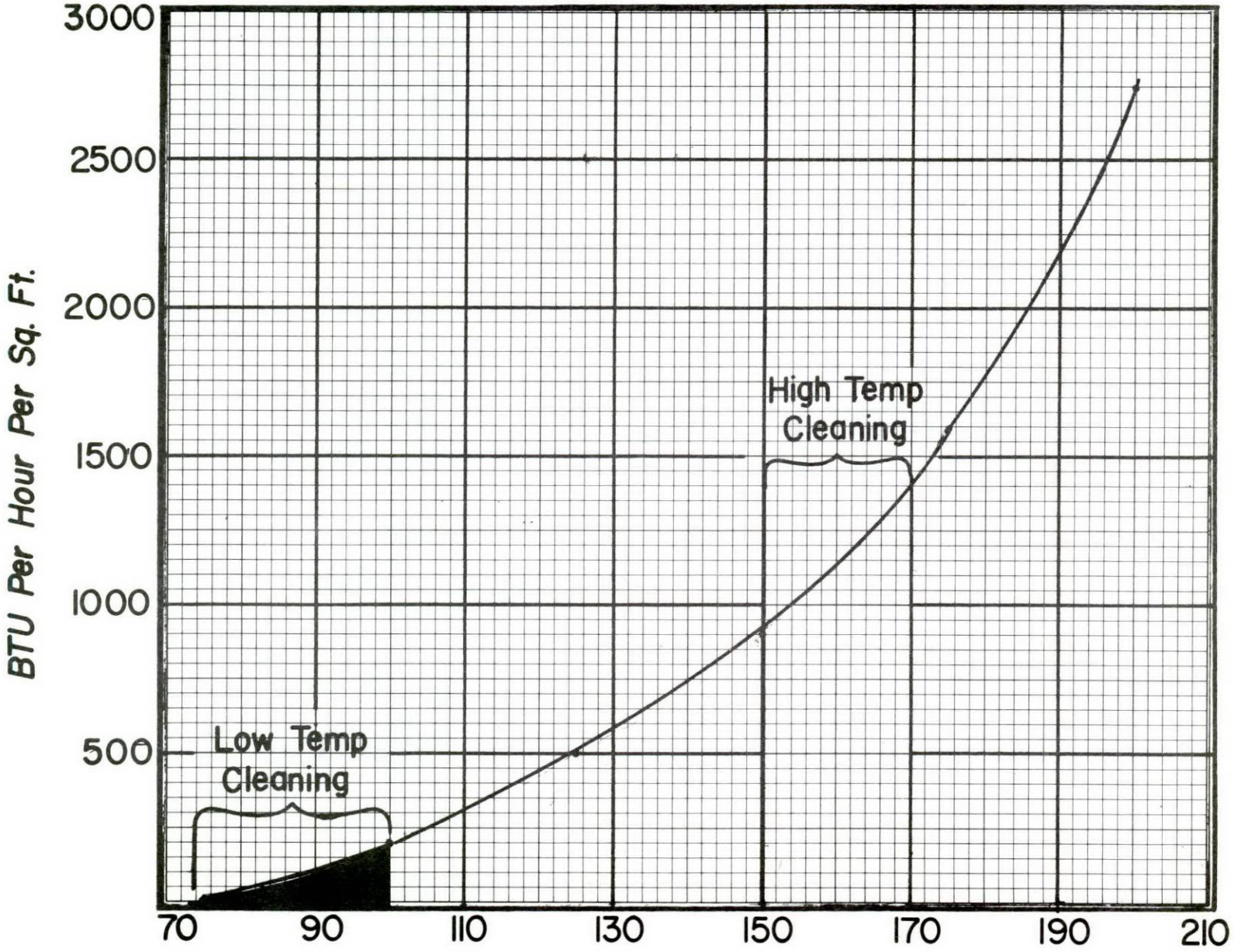
COMPARISON OF GENERAL ELECTROCLEANER WORKING CONDITIONS

	Conventional	Low Temp
CONC:	8-12 oz./gal.	6-10 oz./gal.
TEMP:	170-190 F.	75-85 F.
TIME:	30 sec.-2 min.	30 sec.-2 min.
POLARITY:	Anodic	Anodic
VOLTAGE:	6-10 volts	6-10 volts
C.D.:	50-100 ASF	30-70 ASF

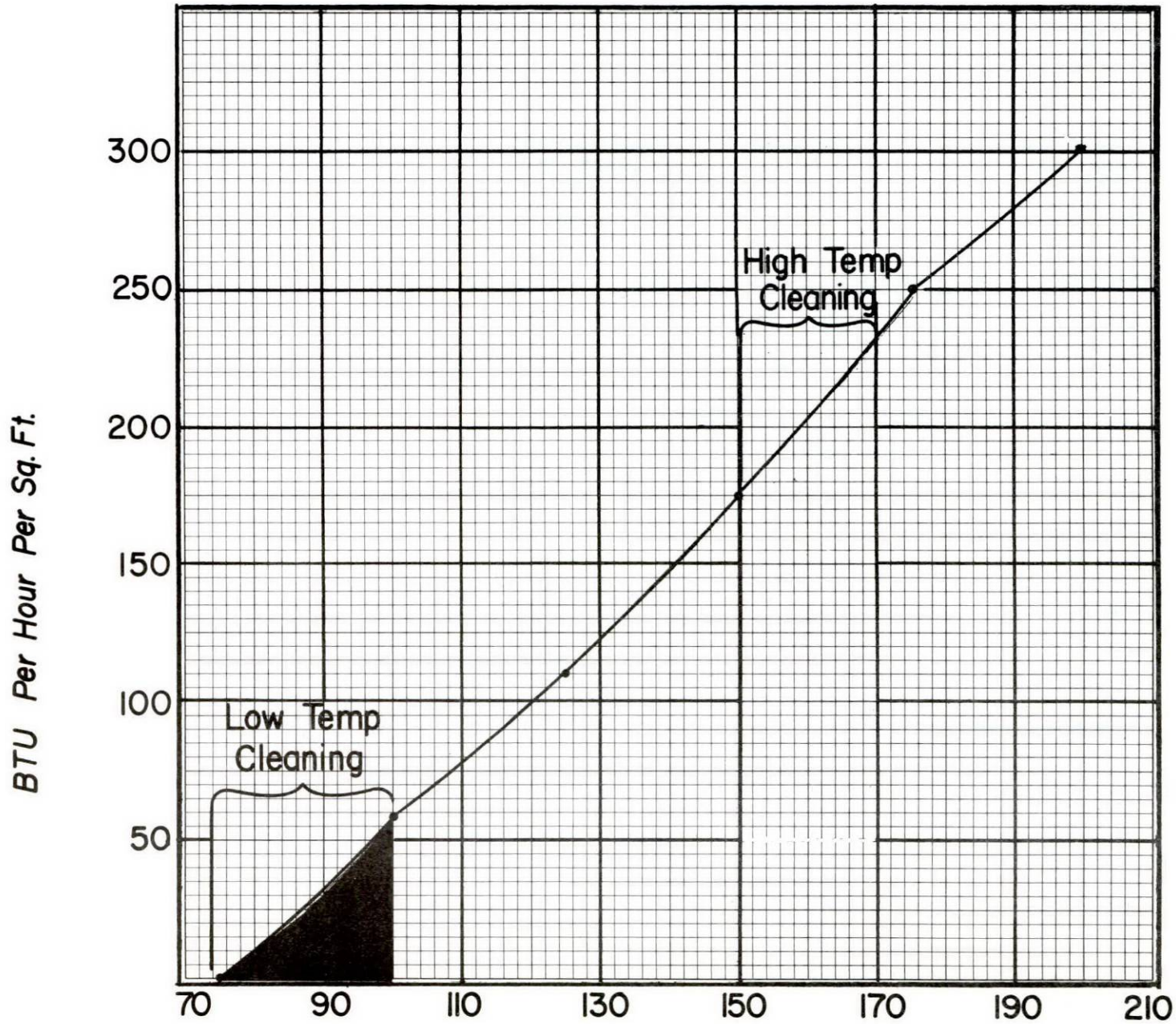
ADVANTAGES OF LOW TEMP CLEANERS

1. Energy Savings
2. More Pleasant Working Conditions
3. No Hazard from Hot Solutions
4. Eliminates Dry Down Problems

HEAT LOSS FROM WATER SURFACE



HEAT LOSS FROM TANK WALLS



TYPICAL 4FT. by 3FT. by 3FT. DEEP TANK
450 GALLON

TANK WALL AREA = 54 sq. ft. · SOLUTION SURFACE AREA = 20 sq. ft.

At 160° F. Operating Temperature:

Solution Surface Area = 1100 BTU/hr./sq. ft. x 20 sq. ft. = 22,000 BTU/hr.
Tank Wall Area = 200 BTU/hr./sq. ft. x 54 sq. ft. = 10,800 BTU/hr.

TOTAL BTU LOSS ..... 32,800 BTU/hr.

At 90° F. Operating Temperature:

Solution Surface Area = 100 BTU/hr./sq. ft. x 20 sq. ft. = 2,000 BTU/hr.
Tank Wall Area = 35 BTU/hr./sq. ft. x 54 sq. ft. = 1,890 BTU/hr.

TOTAL BTU LOSS ..... 3,890 BTU/hr.

Approximate Energy and Fuel Cost Savings 90%

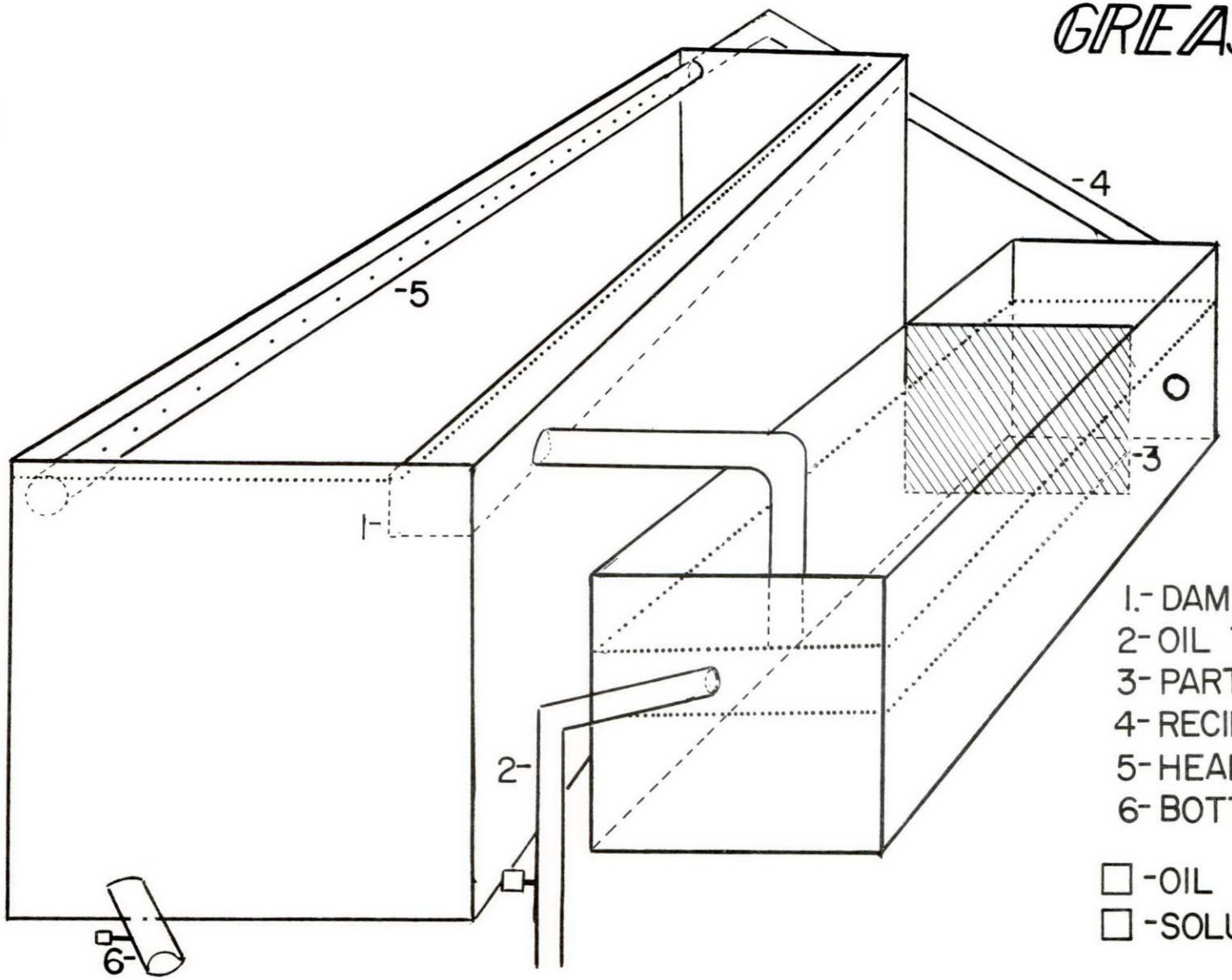
ADVANTAGES OF DISPLACEMENT CLEANERS

1. Lower Working Concentrations
2. Reduced Hexane Solubles
3. Longer Working Life
4. Reuse of Reclaimed oils

POSSIBLE DRAWBACKS
of
DISPLACEMENT CLEANERS

Drawback	Cure
1. Grease Trap Needed	Maybe a Plus
2. Redeposition of Displace oils	Matched Electrocleaners Available
3. Dragdown of Displaced oils	Matched Electrocleaners Available

CLEANING TANK WITH OUTBOARD GREASETRAP



1.- DAM OVERFLOW
2- OIL TAP OFF
3- PARTITION (within 2" of bottom)
4- RECIRCULATING PUMP
5- HEADER PIPE
6- BOTTOM DRAINER

□ -OIL
□ -SOLUTION

A-2

CLEANING SESSION A

Low-Temperature Cleaning—A Study in Applications

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LOW TEMPERATURE CLEANING
(A Study in Applications)

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Abstract

This paper is intended to review some case studies of conversion from high to low temperature cleaning. We will attempt to reveal the facts relative to the success or failure of the conversions. We will attempt to answer the questions of how much energy was saved; what overall dollar effect occurred and was productivity affected.

Introduction

As you might recall, the National Gas Policy Act was enacted as part of the omnibus energy bill passed in 1978. This act provided for graduated increases in the wellhead price of new interstate gas moving to total decontrol by 1985. As a result, there seems to be an ample supply of natural gas supplies at this time. Congress provided under this act for an incremental pricing structure. What this means, in effect, is that industrial users of interstate gas are required to bear a disproportionate share of the higher wellhead gas prices to therefore hold down rates of residential and commercial consumers. This is Phase I of the regulation. This became effective January 1, 1980.

Phase II is a three-tier system designed to bring the cost up to the BTU equivalent price of your standby or alternate fuel, namely No. 6 fuel oil or No. 2 fuel oil. If you have another alternate (such as propane), your gas would be set at the No. 2 fuel oil equivalency price. This applies as of November 1, 1980 to all non-exempt industrial users of gas.

Right now, all users of less than 300 MCF per day would be exempt. However, in order to hold down residential and commercial rates, 95% of all interstate pipeline gas would have to be incrementally priced. The regulation also states that if the total exemptions add up to more than 5% of the total then the 300 MCF would be lowered to reduce the number being exempt.

The impact in short could mean that your gas costs could rise over 90% by November 1, 1980.

The only reason I bring this brief discussion into this paper is to point out that there are innumerable untested federal regulations effecting the costs of doing business that the general public are completely unaware of let alone understand. While the business community tends to feel the brunt of new regulations first you can bet on the certainty that we all will pay the price eventually.

Everyone has become energy conscious, particularly in the last few years, probably, because of how the increased energy costs have effected our daily lives. If we would save ten percent of our gas or electric bill these days we would save some real dollars. Five years ago a ten percent savings in dollars would not have been as meaningful to us. Of course this applies in like fashion to the gasoline we buy today versus what we paid five years ago. However, the real moral of the story is that if we had all saved ten percent of the energy we were consuming five years ago, we wouldn't be paying so much for energy now.

In any event, we have all awakened to the fact that there is an energy shortage and there is a limit to the sources of energy, and the more we continue to consume energy resources, not only will energy become more costly but there will be less of it available.

Therefore, rather than damn the past, we should engage in the opportunities of the present so we don't have to dread the future.

Consistent with this line of thinking we must not only do what we can do in conserving energy individually but also where we work. If every industry saved ten percent or more of the energy they consume, we, as a nation, would soon have a surplus. Of course, industries are nothing more than a whole bunch of people being employed to accomplish the same or similar work. So what we do individually on the job is extremely important.

One of the obvious consumers of energy in the electroplating industry is the heating of cleaning solutions. Imagine, if you will, that energy was free and inexhaustible. Question. Would there be any interest in low temperature cleaners? The point is, that if energy was indeed free, heating a cleaning

solution would nearly always be desired. The reason being that in most cases the efficiency rate of alkaline cleaners doubles for every 20°F above 140°F with respect to conventional formulas. Unfortunately, the forms of energy available today are not free and are in short supply. In particular, the thermal units consumed in heating tanks over a temperature of 130°F. It takes a lot more energy to raise the temperature from 130° - 180°F and maintain it than it does to raise it from 80°F - 130°F and maintain it. We will get into some of those figures a little later.

Let's briefly discuss the principles of cleaning in general terms.

Historically, the best rate of removal and the best cleaning has been achieved by operating at the highest practical temperature. The obvious reason is that the rate of cleaning, is directly affected by heat. For example, some soils cannot be removed at all without reaching a certain temperature. An example of this is buffing compounds whereby it is advantageous to operate the cleaner at a temperature above the melting point of the compound so that the compound will be much more readily removed. Certain oils react in the same manner. Heat will reduce its viscosity thereby allowing it to flow for easier and quicker removal. However, without surface active agents the application of heat alone would take too long to remove any soil by today's standards, and it wasn't that long ago that surface active agents were initially developed. Although a major portion of cleaning is due to the inorganic materials in a cleaner, the surface active agents, commonly referred to as wetters and/or surfactants play a significant role, and with regard to low temperature cleaners, even a more prevalent role. It is within this area of technology that most of the research has been occurring. In order for a surfactant to be effective, it must have an affinity for the substrate. It must be able to pull water molecules through and under the layer of oil and wet the surface. In addition, the surfactant must be only slightly soluble in the soil to be removed. Anything less would not be effective.

The technology particularly with regard to cloud points or solubility of surface active agents and emulsifiers has vastly

improved in the last five years. Here we are talking about long chained materials which lend themselves to heavy duty applications as opposed to lighter duty applications such as hair shampoos or dishwashing compounds. There are additional synthetic materials that lend themselves to the synergism necessary in producing low temperature heavy duty products. We will not go into the specifics but suffice it to say that the technology is available to produce a line of products for soak, spray or electrocleaning applications that will perform in many low temperature applications where up to the recent past only a high temperature product would do the job.

We set up our testing in a manner that would best show the effects of direct comparison. We chose, for that reason, to restrict our study to only soak cleaners. We selected parts that are commonly seen in a job shop. The parts were steel and contained the usual variety of soils -- cutting compounds, drawing compounds, stamping compounds and buffing compounds.

Twelve installations were involved in our study and eight of those were able to convert from high temperature cleaners to low temperature cleaners. Our slides will show the types of parts, types of soil, time limitations, concentrations of the solution, size of tanks, and of course, operating temperatures.

The eight successful conversions varied in the energy and dollars saved, primarily on the basis of the volume of solution.

For the purpose of this paper, we are defining low temperature as being from ambient to 130°F and high temperature being from 160°F to 210°F.

We assumed that if we could do the job at less temperature, we would save energy and money.

To arrive at the probability of doing the job, we have prepared some typical examples of what, in fact, has occurred when the high to low temperature cleaning conversion has been attempted.

CASE STUDY A

Job Shop - Rack & Barrel Plating

Equipment:	Hand Line - Barrel - Zinc Plating
Type of Work:	Stampings
Tank Size:	800 gallons (4' x 6.5' x 4')
Time Limitation:	3 min. soak (3 min. electro)
Type of Soil:	Stamping oils and rust preventatives
Operating Conditions:	High Temp. Low Temp.
	10 oz/gal. 6 oz/gal.
	170°F 130°F
Source of Energy:	Electric (emersion heaters)
Hours in Operation:	20 hrs./day 6 days/wk.
BTUs Saved Per Hour:	101,825 BTUs
Savings:	$18.90/day

Study A shows the saving was significant because of the electric heat source. We draw your attention to the lower concentration used by the low temperature cleaner. You may find this to be true in many cases but certainly not in every case as you will see in later slides.

CASE STUDY B

Job Shop - Rack & Barrel Plating

Equipment:	Oblique Automatic Barrel Line - Zinc Plating
Type of Work:	Various - mostly fasteners & stampings
Tank Size:	660 gallons (5.5' x 4' x 4')
Time Limitation:	2½ min. soak (2½ min. electro)
Type of Soil:	Cutting and stamping oils; rust preventatives, drawing lubes, etc.
Operating Conditions:	High Temp. Low Temp.
	10 oz/gal. 6 oz/gal.
	185°F 130°F
Source of Energy:	Natural gas
Hours in Operation:	16 hrs./day 5 days/wk.
BTUs Saved Per Hour:	179,320 BTUs
Savings:	$8.90/day

The rate you pay for natural gas depends on your area and

the cubic feet consumed. Generally, it is 1/3 that of electricity and 1/2 that of fuel oil on a comparative cost basis. The savings on this line will save approximately $2200.00 per year based on a 16 hour day for 250 days.

(Again note the lower concentration of the low temperature cleaner.)

CASE STUDY C

Job Shop - Barrel Line

Equipment:	Automatic Horizontal Barrel - Zinc Plating	
Type of Work:	Fasteners	
Tank Size:	960 gallons (4' x 8' x 4')	
Time Limitation:	5 min. soak	
Type of Soil:	Quench oils, cutting oils, drawing lubes, and shop dirt	
Operating Conditions:	High Temp.	Low Temp.
	10 oz/gal.	10 oz/gal.
	180°F	165°F
Source of Energy:	Natural gas	
Hours in Operation:	16 hrs./day	6 days/wk.
BTUs Saved Per Hour:	92,995 BTUs	
Savings:	$4.60/day	

The utility rate for this shop differs from the previous slide because of its quantity of consumption of gas. As you can see, the savings in dollars here is modest when one considers that low temperature cleaners quite often are 20% to 30% more costly than conventional high temperature cleaners. The over-all dollars saved was slight. However, the number of BTUs saved here would be significant enough to heat a home or two for an entire year.

CASE STUDY D

Job Shop - Rack & Barrel Plating

Equipment:	Return Type Automatic Barrel - Zinc Plating

Type of Work:	Various - bolts, washers, lug nuts and some stampings
Tank Size:	1200 gallons (4' x 10' x 4')
Time Limitation:	4 min. soak (3 min. electro)
Type of Soil:	Drawing lubes, cutting oils, stamping and quenching oils, etc.
Operating Conditions:	High Temp. Low Temp. 10 oz/gal. 6 oz/gal. 165°F 90°F
Source of Energy:	No. 6 fuel oil
Hours in Operation:	10 hrs./day 5½ days/wk.
BTUs Saved Per Hour:	271,100 BTUs
Savings:	$16.80/day

The soil on these parts was more easily removed in this case primarily due to the fact that the line was fed by only two customers. The soil conditions remained rather constant which was an advantage in formulating to meet those conditions. On another line in this same shop, a low temperature cleaner failed to offer any BTU savings as the next slide shows.

CASE STUDY E

Job Shop - Rack & Barrel Plating

Equipment:	Automatic Horizontal Barrel - Zinc Plating
Type of Work:	Fasteners
Tank Size:	1200 gallons (4' x 10' x 4')
Time Limitation:	5 min. soak (2½ min. electro)
Type of Soil:	Heat treat scale, burnt on oils, drawing lubes, rust preventatives, etc.
Operating Conditions:	High Temp. Low Temp. 10 oz/gal. 10 oz/gal. 180°F 180°F
Source of Energy:	No. 6 fuel oil
Hours in Operation:	16 hrs./day 5½ days/wk.
BTUs Saved Per Hour:	-0-
Savings:	-0-

In this case, the lower temperature cleaner did the job on many parts at reduced temperature. However, approximately 30% of the work on this line required elevated temperatures.

Therefore, a low temperature cleaner conversion did not work in this instance.

CASE STUDY F

Job Shop - Rack Plating

Equipment:	Return Type Automatic Rack - Zinc Plating	
Type of Work:	Furniture parts (tubing & flatware)	
Tank Size:	1500 gallons (4' x 10' x 5')	
Time Limitation:	4 min. soak (4 min. electro)	
Type of Soil:	Buffing compounds, cutting and polishing compounds	
Operating Conditions:	High Temp.	Low Temp.
	12 oz/gal.	8 oz/gal.
	185°F	185°F
Source of Energy:	Natural gas	
Hours in Operation:	16 hrs./day	5 days/wk.
BTUs Saved Per Hour:	-0-	
Savings:	-0-	

The buffing compounds would not separate from the part without high temperature. Although in this case, there was no BTU savings, the company chose to keep the low temperature cleaner in the line, even though it was more costly per pound. The lower concentration reduced the cleaner costs.

CASE STUDY G

Job Shop - Rack & Barrel Plating

Equipment:	Barrel Hand Line - Zinc Plating	
Type of Work:	Various - fasteners, washers, stampings, etc.	
Tank Size:	1000 gallons (4' x 10' x 3.5')	
Time Limitation:	6 min. soak	
Type of Soil:	Various - rust preventatives, coolants, cutting compounds, etc.	
Operating Conditions:	High Temp.	Low Temp.
	12 oz/gal.	8 oz/gal.
	175°F	110°F
Source of Energy:	Fuel oil	

Hours in Operation:	20 hrs./day 5½ day/wk.
BTUs Saved Per Hour:	242,325 BTUs
Savings:	$30.00/day

The large surface area of this tank contributed greatly to the heat loss differential particularly because of the 65° drop in operating temperature. In this case, the company saved a substantial amount of BTUs and dollars.

CASE STUDY H

Job Shop - Rack Plating

Equipment:	Hand Rack Line - Zinc Plating	
Type of Work:	Mostly steel springs of various sizes	
Tank Size:	650 gallons (4' x 6' x 3')	
Time Limitation:	3 min. soak (3 min. electro)	
Type of Soil:	Various stamping and cutting oils	
Operating Conditions:	High Temp.	Low Temp.
	8 oz/gal.	8 oz/gal.
	165°F	130°F
Source of Energy:	Furnace oil	
Hours in Operation:	16 hrs./day	5 days/wk.
BTUs Saver Per Hour:	87,595 BTUs	
Savings:	$10.70/day	

The above case only allowed for a degree drop of 35°F. Even this amount is meaningful as you can see. $2000 per year.

CASE STUDY I

Job Shop - Rack Plating

Equipment:	Hand Rack Line - Nickle Plating	
Type of Work:	Stampings	
Tank Size:	1080 gallons (4' x 6' x 6')	
Time Limitation:	10 min. soak	
Type of Soil:	Rust preventatives, stamping and drawing compounds	
Operating Conditions:	High Temp.	Low Temp.
	10 oz/gal.	10 oz/gal.
	180°F	180°F
Source of Energy:	Natural gas	

Hours in Operation:	12 hrs./day 5 days/wk.
BTUs Saved Per Hour:	-0-
Savings:	-0-

Another case where low temperature wasn't applicable. High temperature was necessary because one of the compounds contained a paraffinic type, that required melting before it could be removed.

CASE STUDY J

Job Shop - Rack Plating

Equipment:	Automatic Rack Line - Nickle Plating
Type of Work:	Automotive Trim
Tank Size:	2400 gallons (4' x 10' x 8')
Time Limitation:	4 min. soak (6 min. electro)
Type of Soil:	Buffing and polishing compounds
Operating Conditions:	High Temp. Low Temp.
	14 oz/gal. 8 oz/gal.
	190°F 165°F
Source of Energy:	Fuel oil
BTUs Saved Per Hour:	242,840 BTUs
Savings:	$30.00/day

This company buffed and polished the parts on the premises and quickly got them into the plating line and which we all know is an important factor in cleanability considerations. A significant savings in BTUs and dollars was achieved.

CASE STUDY K

Job Shop - Barrel Plating

Equipment:	Oblique Type Automatic Barrel Line - Zinc Plating
Type of Work:	Fasteners
Tank Size:	1350 gallons (4' x 15' x 3')
Time Limitation:	5 min. soak (2½ min. electro)
Type of Soil:	Scale, quench oil, drawing lubes, etc.
Operating Conditions:	High Temp. Low Temp.
	10 oz/gal. 10 oz/gal.
	170°F 170°F
Source of Energy:	Natural gas

BTUs Saved Per Hour:	-0-
Savings:	-0-

Another case where a significant percentage of soils needed both higher temperature and concentration.

CASE STUDY L

Job Shop - Rack & Barrel Plating

Equipment:	Automatic Barrel - Zinc Plating	
Type of Work:	Various stampings mostly caster parts	
Tank Size:	960 gallons (4' x 8' x 4')	
Time Limitation:	3½ min. soak (2 min. electro)	
Type of Soil:	Rust Preventatives and stamping oils	
Operating Conditions:	High Temp.	Low Temp.
	10 oz/gal.	6 oz/gal.
	170°F	120°F
Source of Energy:	Fuel oil	
Hours in Operation:	24 hrs./day	5 days/wk.
BTUs Saved Per Hour:	150,428 BTUs	
Savings:	$22.35/day	

As illustrated in this case and others, with agitation, there is a better chance that low temperature cleaners will work. A nice savings for this company.

The method of calculating the potential savings can be simplified by applying the following formula. While this formula does not consider all the factors involved it does allow one to make a reasonable estimate.

We remind you that each attempted conversion should be approached individually to first find if it is possible to clean the parts in a time cycle practical for production. Next, how much energy is saved and then how much money is saved.

In order to apply the formula to a given situation, it is necessary to determine the heat loss from the surface of the solution at the various temperatures and air velocities. We used the chart developed by Samuel J. Friedman of Du Pont. This chart lends itself nicely for our application.

Slide 13 -

HEAT LOSS FROM WATER SURFACE AT VARIOUS WATER TEMPERATURES AND AIR VELOCITIES.

Air Temperatures, 60° F. Relative Humidity, 70%

Fig. 70-2

Water Temp. F.	Air Velocity--Feet per Second							
	0	0.5	1	2	5	10	20	50
	Heat Loss--BTU/Hour (Square Feet)							
60	7	18	21	26	34	56	95	180
70	33	52	60	78	105	170	270	580
80	78	110	125	150	210	315	510	1050
90	130	180	210	240	330	490	780	1600
100	205	270	320	350	480	710	1150	2300
110	290	370	420	480	670	1000	1600	3300
120	400	500	570	660	930	1350	2200	4400
130	550	660	750	890	1240	1800	3000	6000
140	710	870	970	1150	1600	2400	4000	8000
150	950	1130	1260	1510	2100	3200	5300	10500
160	1230	1450	1600	2000	2700	4050	6900	13700
170	1600	1900	2100	2600	3700	5200	9100	18500
180	2050	2600	2900	3550	5000	7200	12500	25000
190	2600	3550	4000	4950	6900	10300	17500	35000
200	3300	5200	5700	7000	9700	14600	25000	50000

From "Heat Losses from Tanks, Vats and Kettles" by Samuel J. Friedman, E. I. DuPont De Nemours and Co., Heating and Ventilating, Apr. 1948.

Referring to the chart, we can see that as the air velocity increases over a solution the heat loss per square foot increases dramatically. When related to the temperature of the solution, the heat loss is very significant. For Example, if the air velocity was 5 ft./sec. and the solution was 200°F the heat loss per square foot is 9700 BTUs per hour.

Now let's apply this to our formula.

Slide 14

Formula for calculating potential BTU and dollar savings relevent to low temperature soak cleaners.

Step I — Refer to "Heat Loss From Water Surfaces" Chart. Determine the air velocity over the tank. (5 ft./sec. is considered average). Locate the present operating temperature for the heat loss per square foot. Subtract from this number the heat loss per square foot at the lower temperature. (A lab evaluation will indicate at what degree the temperature can be lowered and still clean).

Step II — Multiply the answer obtained in Step I by the area of the tank. This figure gives the heat saved, due to lower operating temperatures, in BTUs per hour.

Step III — Subtract the temperature of the incoming water from the present operating temperature. Do the same for the lower operating temperature. Subtract these differences from each other and multiply that total by the gallons of the tank.

Step IV — Multiply the final figure in Step III by 8.33 (the weight of water). The answer is in BTUs relating to the heat savings to heat-up the tank.

Step V — Divide the answer in Step IV by the hours in operation. This gives the BTU savings per hour.

Step VI — Total answers obtained in Step II and Step V.

This figure is the total heat savings in BTUs per hour for the heating up and maintaining the solution.

Step VII Divide the answer in Step VI by 0.7, the typical boiler efficiency. This is the over-all BTUs per hour saved.

Step VIII Multiply Step VII by the fuel rate in your situation. Example; natural gas is $.32 per 100 ft.^{3}, fuel oil .85 per gallon, electricity .06 a kw-hour. If your source of energy is natural gas, divide the answer obtained by 1,033,000 (1000 ft.^{3} of gas produces 1,033,000 BTUs). If fuel oil, divide by 139,000 (one gallon of furnace oil produces 139,000 BTUs). If electric divide by 3412 (BTUs in one kw-hr.) This figure gives the cost of energy per hour.

Step IX Multiply the above cost/hr. by the number of hours in operation for the cost per day.

Slide 15

Example of Calculations:

A 650 gallon cleaner tank with a surface area of 4' x 6', operates at 165°. Air travels over the tanks at about 5 feet per second. The temperature can be reduced to 130°. The system operates 20 hours per day including the hours to reach the operating temperature starting from 60°F. Source of energy - oil; source of heat - boiler.

Computation

Step I 3400 - 1240 (heat loss at 165°F vs. 130°F; air velocity at 5 ft./sec. = 2160 (BTUs in heat loss/ sq. ft. difference)

Step II 4 ft. x 6 ft. (surface area) x 2160 = 51,840 (total BTUs/hr. saved from surface loss)

Step III (165°F - 60°F) ambient vs. high temp. - (130°F -

60°F) ambient vs. low temperature times 650 gal. (solution volume) = 22,750

Step IV — 22,750 x 8.33 (wt. of water) = 189,507 (total BTUs saved by operating at lower temperature)

Step V — 189,507 ÷ 20 (hours of operating) = 9475 (BTUs per hour)

Step VI — 51,840 + 9475 = 61,315 (Total BTUs saved)

Step VII — 61,315 ÷ 0.7 (boiler efficiency) = 87,593 (adjusted total)

Step VIII — 87,593 x $0.85 (cost of fuel/gal.) ÷ 139,000 (BTUs/gal) = $0.535 (savings per hr. of operating)

Step IX — $0.535 x 20 = $10.70 (savings per day)

Conclusion

Conversion from high temperature cleaning to low temperature cleaning was possible in 2/3 of the cases studied. The amount of savings was slight in some cases and very substantial in others.

There are many, many factors that affect just how much is saved. Just to name a few, volume of the tank, type of fuel used to heat the cleaners, surface area of the tank, velocity of air movements over the tank solution, drag-in, temperature of parts entering the cleaner, type of soil, the volume of parts, operating hours, temperature of make-up water, heat of the area surrounding the cleaning tanks, the efficiency of burner and boiler equipment, and last but not least, whether the tanks are insulated or not.

Our studies would indicate that the possibility of making a low temperature cleaning conversion should be evaluated.

A-3

CLEANING SESSION A

Low-Temperature Chemical Processes

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LOW TEMPERATURE CHEMICAL PROCESSES

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ABSTRACT

A detailed discussion will be presented covering introduction of "low temperature cleaning" to the manufacturing and finishing process. In particular specific mention of integrating lubrication and forming compounds with post fabrication cleaning prior to organic finishing are detailed. Basic concepts of formulating along with specific advances in organic detergents and additives will be outlined in order to clarify why "low temperature cleaning" can in practice be realized. Misuse of low temperature processes are discussed in order to clarify why users must tread carefully when evaluating results and expected savings.

Introduction

As we all know, low temperature processes including cleaning, phosphatizing, plating and painting have been in vogue for the last five years gaining substantial momentum with government edicts requiring 8 to 10% cut backs in manufacturing and over-all plant energy consumption. In order to implement energy savings in the manufacturing sector of plant operations the appropriate responsible authorities from department foremen to industrial or process engineers have looked exclusively at temperature reductions in plant processes as a means of reducing energy usage. Often times the simple replacement of an existing process with a new process with stated lower energy requirements produced higher over-all manufacturing costs and sometimes a sacrifice in quality.

It is this very problem of compromising a manufacturing process for the sake of lower energy consumption which will be addressed in this paper along with the design intent of low temperature chemical processes. Any in plant finishing process must incorporate with it an "integrated approach" of all processes prior to and including the final finished product. All plant operations tied together intelligently, such as stamping oils and their easy cleanability with low temperature soak or spray cleaning follow on processes, allow energy reductions which are meaningful as well as cost effective.

Low Temperature Process: Designs and formulations

The question is sometimes asked whether the low temperature process employed is simply a renamed older process at a higher price or truly a redesigned system with new innovations. It is true that some processes sold are not what they seem, for example, using phosphoric acid as an accelerator for low temperature iron phosphating baths while simultaneously

corroding the welds, tank walls and burner tubes of mild steel tanks. This type of low temperature process design is not desirable no matter what application or energy savings.

In actuality the latest designs and formulations sold for cleaning, phosphating, plating and painting, which are intended for low temperature operation, are based on complex organics and catalysts which have only been developed in the last 5 to 8 years and are continuing to be developed to meet specific manufactures needs along with general formulation trends.

These complex organics and catalysts are more often than not sold in the market place with specific formulations and chemical reactions in mind. However, with a talented staff of research chemists kept in tune to the changing manufacturing needs by an enthusiastic sales staff, innovations such as incorporating catalysts from petroleum and rubber manufacturing to accelerate the chromating of aluminum at room temperatures are a reality.

Metal stamping lubricants have been redesigned to incorporate a wide variety of entirely new synthetic compounds that are not only biodegradable but offer unique extreme pressure characteristics. Also the user is offered easy cleanability with these compounds when co-designed with new synthetic organic detergents in room temperature alkaline and acid cleaners.

The complete redesigning of the basic nickel sulfate and decorative chrome plating processes have yielded outstanding finishes at substantially lower temperatures. With the use of newly conceived organic brighteners, improved leveling and throwing power has occurred at temperatures 30°F. below previous nickel plating processes while maintaining brightness and ductility. The corresponding use of a blend of inorganic metallic catalysts is used in decorative chrome plating to eliminate passivity in prior nickel deposits. This innovation has improved throwing power and coverage all at a temperature 20°F. below conventional decorative chrome processes.

These technical modifications in otherwise long standing processes demonstrate another active energy savings program. However, with careless maintenance of contacts, poor cleaning of racks, and improper rebuilding of hangers the benefits of such processes are negated with higher currents used in plating leading to the very possibility of using greater energy in the over-all operation.

Perhaps the greatest innovations, without detracting from the prior discussion has occurred in the area of organic coatings i.e. paint films. This field, if properly investigated by a paint user, is abound with new organic films applied in various fashions with little or no solvents at lower curing temperatures than anything contemplated in the finishing field 5 years ago. The organic finish offers the manufacture the area of greatest potential for the reduction in energy consumption in his plant. However, these new films cost more, require new equipment and greater technical know how by the operator and finishing foreman.

In answer to the lead question of this section we can say without hesitation that the products exist for low temperature cleaning, phosphatizing, plating and painting. They must more often than not be selected carefully and with specific end results in mind. The promoter and user of these products must communicate well so as to insure proper control and maintenance of each process to a greater extent than in years past, and additionally must be willing to integrate processes such as stamping, cleaning and finishing to achieve the over-all end result of less energy used with equal to or higher quality at economical costs.

Selection and Design of Low Temperature Systems

It is not possible here to discuss all processes used in the forming and finishing of metals etc.; but it is possible to present the most basic concepts in equipment and temperatures to be used as a starting point in planning and realizing goals of reducing energy.

As a starting point we must of course outline the manufacturing steps used to produce our end product. Each area of operation should be detailed to:

1. Specify lubricants and coolants used and modify the products thru suppliers for ease of cleaning.

2. Check designs to minimize trapping lubricants in welded areas or in roll formed areas.

The next detailing should include a complete survey of equipment used in the finishing steps. Modifications to equipment to lower operating temperatures and conserve energy will include:

1. Insulate all exposed existing or proposed metal tanks from spray washer walls to soak tank sides.

2. Modify or add spray nozzles after appropriate soak tanks using water pressure to insure efficient rinsing of key operations. Modify spray equipment to include:

    A. More efficient spray nozzles.
    B. Add spray nozzles where appropriate.
    C. Increase pressures for a more efficient and complete spray pattern.

3. Baffle ovens to promote more thorough mixing of heated air to insure better heat transfer to finished parts.

4. Investigate and install infra-red heating units to improve energy usage where appropriate.

A final detailing should incorporate an engineering study to see if final finishes can in some way be combined with other processes to eliminate the recycling of finished parts several times thru the same oven. For example, the very effective new one coat porcelain enameling system

where the prior two coat system require two firings and thus twice the energy for each finished product.

Now with these changes either contemplated or implimented what can we expect from typical cleaning operations using the latest highly refined low temperature cleaners and phosphatizers.

Barrel Plating Lines:	
Soak Cleaning	100°F.
Electro Cleaning	100°F.
Spray Washers:	
Spray Cleaner	100°F. - 120°F.
Iron Phosphate	100°F. Non-chlorated.
Iron Phosphate	110°F. Chlorated.
Zinc Phosphate	140°F.
Rack Plating Lines:	
Soak Cleaner	100°F.
Electro Cleaner	100°F.

The temperatures employed in plating baths, curing paint films, and firing porcelain frits are more specific and set for the particular finish desired and cannot be stated here. However, as outlined earlier the low temperature processes do exist and are presently being employed.

What results in terms of quality can we expect from our energy reduction program? I can say without question that the finished product will meet or exceed that of the highest quality finished products. In particular metal surfaces will be exceptionally clean and accept plating and phosphate coatings readily with supreme uniformity. Energy savings in gas, electricity or oil consumption will easily surpass 30 to 40% in each of the processing operations.

Misuse of Low Temperature Processes

The misuse of low temperature cleaning and finishing processes starts with the insistance on needing them without understanding the preliminary requirement for having them, namely integrated manufacturing operations.

For example any attempt to employ a low temperature cleaning process in a high production job shop plating operation with its myrid of soils, oils and waxes is by enlarge ill conceived. The variety of films to be removed from various metal parts to be processed may absolutely require higher temperatures to offset the deficiencies inherent in alkaline and detergent system designs. The end result will be the use of low temperature cleaning in an environment in which it cannot succeed.

Another poor choice is to attempt to clean a highly chlorinated of sulfurized oil with a low temperature cleaner phosphatizer in a 3-stage spray washer. As you may know a phosphatizing solution is mildly acidic, however, with careful formulating excellent organic additives may be

blended into the product to maximize its cleaning efficiency. This product, however, will have continued trouble cleaning these types of oil blends no matter what the temperature or concentration. It is unquestionably the best bet to completely redesign your lubricating oils. The previous highly chlorinated and sulfurized oil blend is simply not soluble in acid solutions and is likewise not easily blasted off with high pressures in a spray washer.

As with most processes, we desire the most for the least. This, once again, may not be feasible if we understand our needs and requirements. Such is the case of requiring a low temperature phosphating process in a 5-stage spray washer but simultaneously requiring high coating weights with superb corrosion resistance. Low temperature may necessitate a minimum of 130° F. to insure an excess of 40 mgs./sq. ft. and an excess of 1000 hours salt spray. To require lower temperatures because of outside sales or inside management pressures may be entirely ill conceived and a misuse of low temperature phosphatizing will undoubtedly take place.

The greatest and most frequent misuse of the concept of low temperature processes was illuded to earlier, namely the lack of maintenance and control of equipment and solutions. The use of lower temperatures in any or all of the processes mentioned necessitate careful and controlled steps to insure proper equipment operation and chemical concentrations. This must be coupled with appropriate prescribed dumping cycles. To carry on, as many have done in the past with a disregard to maintenance and control, may yield to disappointment and frustration.

Conclusion

The low temperature cleaning, phosphatizing, plating and painting processes which are of high quality and marketed successfully are both a formulators and end users dream and delight. They incorporate the latest in sophisticated technology with superb end results when applied properly and perform consistently with lower over-all costs than products of the past. In addition they enhance the working environment by reducing in plant heat, fumes and humidity.

My suggestion is get involved with your metal finishing needs thru the installation of one or more low temperature processes and energy saving equipment designs. Your efforts will be rewarding to you and your company.

B-1

DECORATIVE PLATING
SESSION B

The Use of Acid Copper in The Electroplating of Plastic

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THE USE OF ACID COPPER IN THE ELECTROPLATING OF PLASTIC

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ABSTRACT

A practical article for platers reviewing the benefits and problems of decorative acid copper in plating on plastics industry, as well as the bath specifications and requirements.

Particular emphasis will be placed on the new innovative acid copper strike for plating directly over electroless deposits. The outline will also touch on the differences between the use of acid copper, pyrophosphate copper, and nickel strikes.

INTRODUCTION

Acid copper electroplating was first reported in the early 19th Century.[1] These early baths were difficult to control and did not exhibit the leveling and brightness qualities associated with modern decorative copper deposits.

The introduction of thiourea[2]-type additives improved leveling characteristics and brightness, but organic breakdown products made the bath difficult to operate and required frequent treatment. Discovery of the beneficial effect of wetting agents or medium to high molecular weight polymers along with dyestuffs,[3] as low current density brighteners and levelers, and improvements in organic thiourea type brighteners resulted in better leveling, stability and ductility. These developments are the basis of the modern decorative acid copper processes.

Along with improvements in organic additives, it was found that varying the electrolyte formulation resulted in increased throwing power of acid copper solutions.[4] These solutions, which contain higher amounts of sulfuric acid and lower copper sulfate concentrations, have been used mostly in the electronics industry because of the need for uniform metal distribution. The decorative bath, while having a relatively poor distribution of metal thickness, can be plated at higher current densities, provides better leveling,[5] and will be less corrosive to equipment and the environment because of the lower concentrations of sulfuric acid.

Plating on plastics requires an extremely bright and ductile deposit, which will expand and contract with the thermal expansion of the plastic without cracking, blistering or peeling, a condition which can develop due to the expansion difference between the electrodeposited metal and plastic substrate. A bright decorative acid copper bath will provide a ductile deposit which meets these requirements.

The plastic substrate must be processed through various pretreatment steps and finally a conductive coating is applied from an electroless process before it is ready to be electroplated. The very thin electroless deposit requires the use of a low voltage strike solution. The strike process builds metal around the contact points, preventing dissolution or loss of electrical conductivity (burn off) of the electroless deposit, due to the higher voltage requirements of decorative plating baths.

The strike solutions used to deposit the initial thin electrolytic deposit have heretofore been based on Watts nickel or pyrophosphate copper electrolytes. The recent introduction of proprietary high throw acid copper solutions for plating the initial deposit have resulted in improved quality as well as reduced cost.

Decorative Copper Plating

A typical electrolyte formulation for bright decorative copper contains:

140 - 250 g/l	Copper Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$)
40 - 75 g/l	Sulfuric Acid (H_2SO_4)
30 - 150 ppm	Chloride (Cl^-)

The copper sulfate provides metal ions in the solution. Sulfuric acid prevents anode polarization and improves electrolyte and cathode film conductivity. Small amounts of chloride (or any member of the halogen family) are needed to make the brightener system function.

Because of the myriad of sizes and shapes of plastic parts, organic brightener systems are needed to extend the high current density plating range and provide a bright lustrous ductile deposit with leveling or smoothing characteristics.

Plateable plastics such as ABS have higher coefficients of expansion than typical metal parts. Because of this expansion, the plated deposits on plastic surfaces must have a high degree of ductility.

An acid copper deposit is soft, ductile and has the ability to expand and contract with the plastic substrate, acting as a buffer for the relatively brittle nickel and chromium deposits.

In order to pass thermocycle testing, the ratio of copper to nickel metal thicknesses should be maintained at least 1 to 1 with higher ratios preferred. These ratios are maintained in the following ASEP guidelines.

Thickness Requirements (ASEP Guidelines)

	Minimum Service (μm)
Acid Copper	5 - 10
Bright Nickel	5 - 7.5
Chromium	0.13
	Medium Service (μm)
Acid Copper	10 - 15
Bright Nickel	10 - 15
Chromium	0.13
	Heavy Duty Service (μm)
Acid Copper	15 - 20
Semi-Bright Nickel	7.5 - 12.5
Bright Nickel	5 - 7.5
Microdiscontinuous Chromium	0.25 - 0.5

Operational Parameters

The optimum operating temperature range for decorative acid copper baths is between 20 - 35°C. Temperatures below 20°C will reduce the high current density range, while temperatures above 35°C result in loss of low current density brightness.

Anodes should have a high phosphorus content of .04 to .06% phosphorus. The phosphorus content helps maintain a tight anode film which prevents copper particles from the anodes contaminating the solution, causing roughness or speckling.

Like many other plating solutions, a decorative copper bath should be continuously filtered. The filter should only be packed with inert filter media since carbon will remove the organic additives, causing high brightener consumption and variable plating results.

Strike Solutions

The plating of a plastic part involves the use of a preplate system to condition the substrate for the initial electroless metallic deposit, followed by an electrolytic strike and conventional copper, nickel and chromium electrolytic deposits. The strike deposit is used to protect the relatively thin electroless coating and to build metal thickness at the contact points. This prevents stripping of the electroless deposit when higher voltages are used in the plating tanks.

Nickel Strike Solutions

Various formulations of nickel strike solutions are used in the plating on plastics industry. Examples of different formulations are as follows:

Watts Nickel[7]

300 - 315 g/l	Nickel Sulfate ($NiSO_4$) . $6H_2O$
82 - 90 g/l	Nickel Chloride ($NiCl_2$) . $6H_2O$
22 - 40 g/l	Boric Acid (H_3BO_3)
pH	3.5 - 4.0
Temperature	50 - 60°C
Moderate air agitation	

Woods Nickel Strike[8]

100 g/l	Nickel Chloride ($NiCl_2$) . $6H_2O$
100 ml/l	Hydrochloric Acid (HCl)
Temperature	Room
Moderate air agitation	

Proprietary Nickel Strike[9]

300 g/l	Proprietary Salts
Temperature	50 - 60°C
pH	4.0 - 4.5
Moderate air agitation	

Plating current is usually around 1 - 2 A/dm^2 with plating times of 2 - 12 minutes.

The various nickel strikes will provide activation of the electroless deposit, and good plate thickness at contact points, thereby reducing the tendency for burn off in subsequent plating tanks. Because of the poor throwing power of most nickel strikes, low current density areas away from the contact points may have little or no plate. The exposed electroless deposit thus may be passive enough to cause adhesion difficulties with the bright acid copper deposit.

Copper Pyrophosphate Strikes

Complex parts with extreme low current density areas may be successfully plated using a copper pyrophosphate solution. Pyrophosphate copper solutions have high throwing power, which will result in more uniform plate thicknesses over wide current density ranges. These copper deposits will result in improved thermocycle performance, and the copper metal thickness acquired in the strike deposit is additive to the total copper thickness required for the copper specification.

Typical Pyrophosphate Copper Solutions[8]

5 - 30 g/l	Copper Metal (Cu°)
P_2O_7/Cu ratio	7.4 to 8.1/1
NH_3 as NH_4OH	1.4 to 8.6 mls/liter
Temperature	42 - 56°C

Acid Copper Strikes

Decorative acid copper sulfate solutions have been used to plate the initial strike deposit with varying degrees of success. Operating conditions and/or solution composition have been modified as follows: 1) reduced entry voltage in the acid copper plating tank followed by gradual increase to full plating voltage, 2) reduced concentrations of sulfuric acid, 75 - 112 g/l, and copper sulfate, 30 - 45 g/l, when plating over electroless copper. These systems, which have had only limited success, have resulted in extended plating time, thereby reducing capacity. Furthermore, they have very poor throwing power, resulting in reduced copper thicknesses in the low current density areas.

The new high throw acid copper solutions developed in the present study can be used for depositing an initial strike on the electroless plated parts.

A typical electrolyte formulation and operating conditions are as follows:

Typical Formulation

60 - 90 g/l	Copper Sulfate Pentahydrate ($CuSO_4 \cdot 5H_2O$)
150 - 225 g/l	Sulfuric Acid (H_2SO_4)
40 - 100 mg/l	Chloride (Cl^-)
Proprietary Brighteners	
Current	0.8 to 2 A/dm
Time	2 minutes minimum
Voltage	1 to 3 V

The high throw acid copper formulations offer the advantages of a pyrophosphate copper strike, namely uniform coverage and excellent throwing power, plus many distinct advantages of their own. A comparison of the characteristics of different types of strike processes is made in the following table.

Comparisons of Strike Solutions

	Nickel	Pyrophosphate Copper	Acid Copper	High Throw Acid Copper
Cost	high	high	low	low
Waste Treatment	yes	yes	no	no
Throwing[4] Power	poor	62	14	87
Adhesion Between Strike & Copper Plate	Possible low current density area problems	good	good	good

A comparison of typical make-up costs are given in Figure 1. These costs are accurate as of January, 1980.

FIGURE I

COST TO MAKE-UP STRIKE PER LITER

WATTS NICKEL		PYROPHOSPHATE COPPER		HIGH THROW ACID COPPER	
300 g/l NICKEL SULFATE	$0.68	12 g/l POTASSIUM PYROPHOSPHATE	$0.03	75 g/l COPPER SULFATE	$0.07
80 g/l NICKEL CHLORIDE	$0.24	336 g/l COPPER PYROPHOSPHATE	$1.29	195 g/l SULFURIC ACID	$0.04
	$0.92		$1.32		$0.11
+ BORIC ACID		+ BRIGHTENERS		+ BRIGHTENERS	
NICKEL ANODES	$3.48/lb	COPPER ANODES	$1.66/lb	COPPER ANODES	$1.66/lb
COST/1000 GALS.	$3496	COST/1000 GALS.	$4973	COST/1000 GALS.	$418

The typical cycle detailed below indicates that it is possible to go directly from the strike solution into the acid copper plating tank.

Typical Cycle for High Throw Copper Strike

1. Preplate
2. Electroless deposit
3. Rinse
4. Rinse (optional)
5. Sour rinse * 1.5% HCl
6. Rinse
7. Conditioner **
8. Acid Copper Strike Solution
9. Copper plate

* May be needed if the transfer times between electroless nickel and strike tank are longer than about 10 minutes.

** Optional, as discussed in Section on Conditioner (below).

Since the strike solution is high in sulfuric acid, it will probably result in the increase of the sulfuric acid concentration in the copper plating bath. Rinsing can be used between copper strike and copper plate with no loss of adhesion, but rinse waters will then have to be treated before disposal. Higher sulfuric acid concentration (90 - 112 g/l) can be tolerated in a decorative plating bath with no adverse effects, but it should be noted that a common ion effect can take place with high copper sulfate and high sulfuric acid concentrations, causing copper sulfate to precipitate out of the solution. If direct transfer is being used, copper sulfate concentrations should be kept below 165 g/l, while the sulfuric acid concentration should reach equilibrium (drag-out equals drag-in) at values no higher than 115 g/l. Most proprietary brightener systems developed for high throw copper strikes are compatible with the bright acid copper brighteners, resulting in less consumption of brightener in the acid copper plating tanks.

Conditioner

When an electroless nickel surface is introduced into any acid copper solution the nickel can be displaced by the following reaction:

$$Ni^{\circ} + Cu^{+2} \rightleftharpoons Ni^{+2} + Cu^{\circ}$$

When coverage is slow, the electroless nickel deposit in low current density areas or in areas that are remote from the contact points can be dissolved.

The use of a conditioner will activate a passive electroless nickel deposit resulting in faster covering rates. It is desirable to use a conditioner even on a relatively active electroless nickel to eliminate the possibility of immersion deposits, which result in striations in subsequent electrolyte copper plating. The size of the part and the location and number of contact points can influence the tendency for the formation of immersion deposits (see Figure 2).

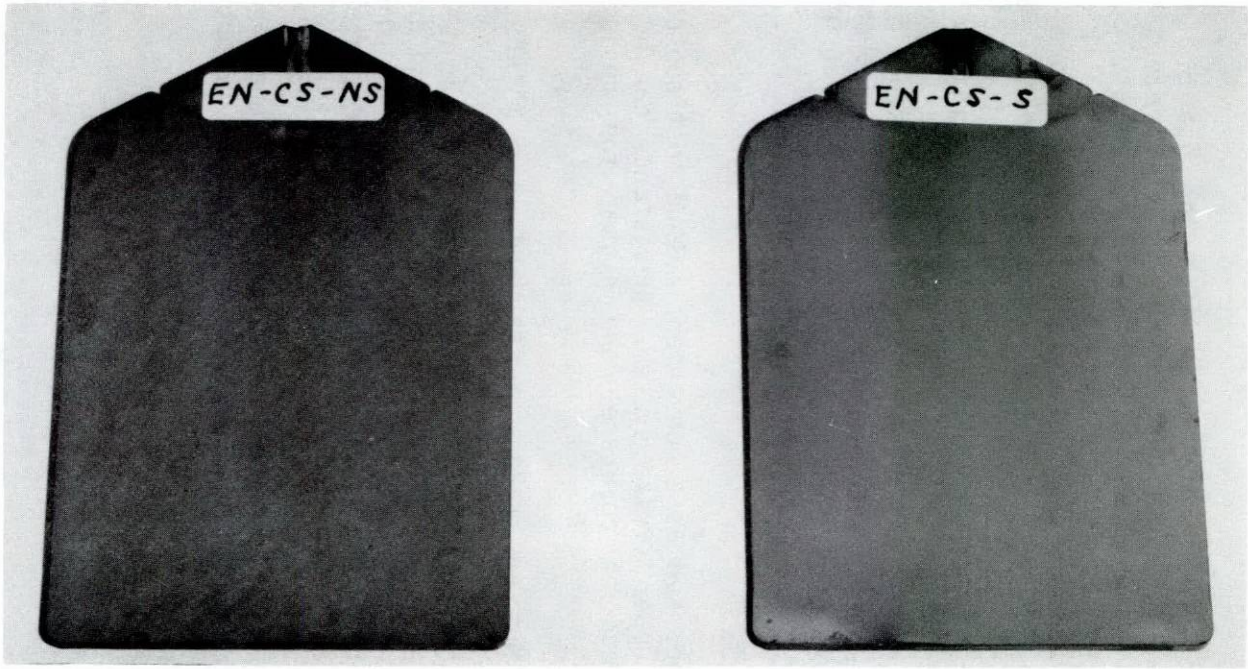
Very passive electroless nickel deposits, even with the use of a conditioner, can result in slower covering rates. On an active electroless nickel deposit, complete coverage, even on very complex shapes, can be expected within 2 minutes. Plating or coverage rates will vary slightly depending on the number and position of contact points. One hundred percent coverage is extremely important. Parts that show electroless nickel after the copper strike can be expected to result in dissolution of the electroless nickel in the bright copper plating tank, resulting in bare plastic exposed on the completed work. It should be remembered that under optimum conditions, a certain amount of the electroless nickel deposit will dissolve (see Figure III). A minimum thickness of 0.2 um is needed to insure that there will be no loss of adhesion due to the dissolution of the electroless deposit.

The Use of Resistance Measurements

Resistance measurements can be used as a convenient method to troubleshoot the electroless nickel and copper strike system. Resistance can be used to evaluate the rate or speed of coverage, the higher the resistance reading the slower the rate of coverage.

Experimental resistance readings are taken on standard 4" x 3" ABS test panels. A series of panels are processed through the preplate system and removed after each significant bath (electroless nickel, sour rinse and conditioner). After each bath, a test panel was removed, rinsed and dried. A one-inch strip was then electrically isolated from the rest of the panel. Resistance measurements were taken at one-inch intervals at the center of each strip, as shown in Figure IV, with the tabulated results indicated.

Since readings can vary from one production bath to another depending on the composition of the electroless nickel bath, a history of the production bath should be maintained.



The use of a conditioner.

Both panels were processed through the preplate line and given an electroless nickel deposit. The panel on the left was immersed in a copper strike for 30 seconds with no current. The dark irregular surface shows heavy immersion deposits. The panel on the right was immersed in a conditioner for 30 seconds and then immersed in the acid copper strike for 30 seconds with

FIGURE III

THICKNESS LOSS OF ELECTROLESS NICKEL DEPOSIT IN PROCESSING

THICKNESS = W/k A

WEIGHT = WEIGHT OF DEPOSIT IN GRAMS

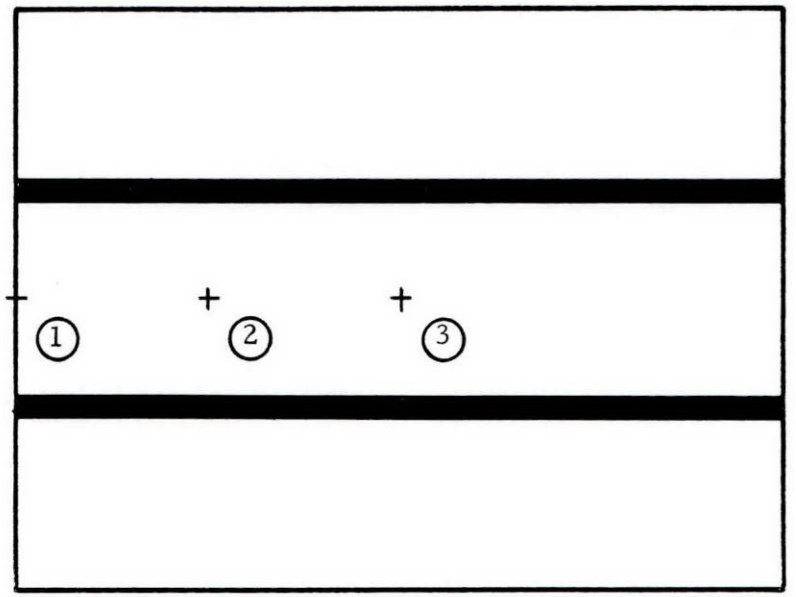
k = CONSTANT

A = AREA OF PART IN SQUARE CENTIMETERS

PROCESS STEP	THICKNESS OF ELECTROLESS NICKEL DEPOSIT (µm)
ELECTROLESS NICKEL	0.38
HYDROCHLORIC ACID 1%	0.33
CONDITIONER (30 SECONDS)	0.28
DIRECTLY INTO ACID COPPER STRIKE (30 SECONDS - NO CURRENT)	0.28

FIGURE IV

RESISTANCE MEASUREMENTS



BATH	TYPICAL RESISTANCE OF PRODUCTION BATHS (Ω)		
	1 - 2	2 - 3	1 - 3
ELECTROLESS NICKEL	6 - 20	5 - 20	8 - 30
HYDROCHLORIC ACID 1%	6 - 20	5 - 20	6 - 28
CONDITIONER	4 - 15	4 - 15	6 - 20
COPPER STRIKE	< 1	< 1	< 1

Temperature Limits

The optimum temperature range for an acid copper strike is between 22 - 30°C. Temperatures below 22°C can result in burning which reduces the high current density plating range. Temperatures above 30°C will result in a slower rate of coverage (Refer to Figure V).

Loss of Peel Strength

Loss of peel strength can develop when coverage of the electroless nickel by the copper strike takes an excessive period of time. It has been observed that some production parts which successfully pass thermocycle tests will, when broken, show little or no peel strength. In extreme cases, the peel strength is so poor that blisters will appear in low current density areas, particularly in the areas that are last to be covered in the strike solution. This is due to apparent attack on the palladium anchoring sites on the plastic surface.

Figure VI illustrates the loss of peel strength when an electroless nickel surface is introduced into a strike solution with high acid content (180 g/l H_2SO_4). To obtain these results, a series of six panels was processed through the preplate line. Panel 1 was processed in the optional manner by going directly into the strike with live entry and no current interruption; while panels 2 through 6 were left in the strike solution with no current for periods of up to 5 minutes (1 minute/samples) before plating at 1 A/dm^2, for 5 minutes, followed by bright copper plating for two hours at 6 A/dm^2, which provides a total thickness of about 100 um. Peel strengths were determined using an Instron™ Tensile Tester. The results show a sharp decrease in peel strength after 2 minutes.

Problems of this nature can be corrected by modifying process parameters or operating conditions as follows:

1. Increase the activity of the electroless nickel deposits, for example, by correcting solution imbalance or increasing temperature.

2. Increase thickness of electroless nickel deposits (minimum thickness of the electroless deposit should be greater tha 0.2 um).

3. Use or increase concentration of the conditioner.

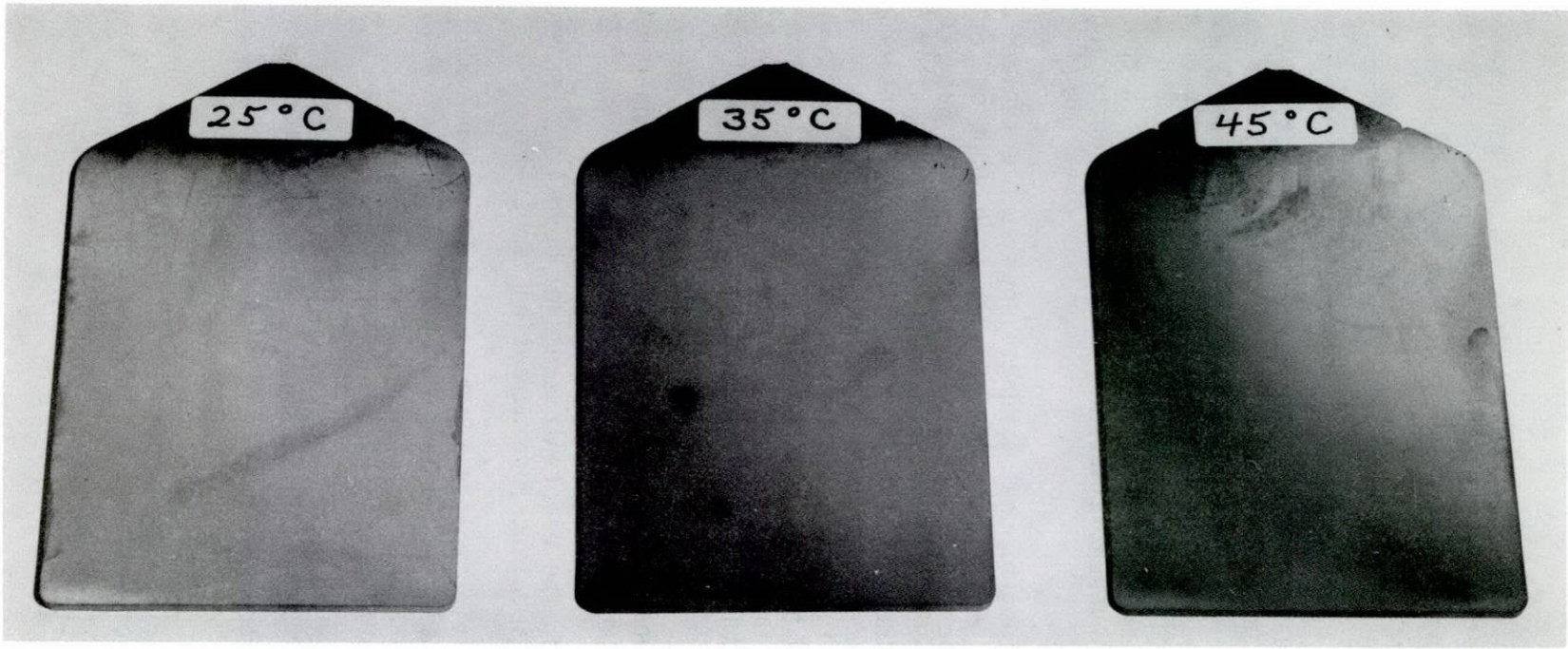
4. Increase current density in the strike.

5. Use a sour rinse activator.

6. Increase the number or change positions of contact points.

7. Increase concentration of sulfuric acid in the copper strike solution.

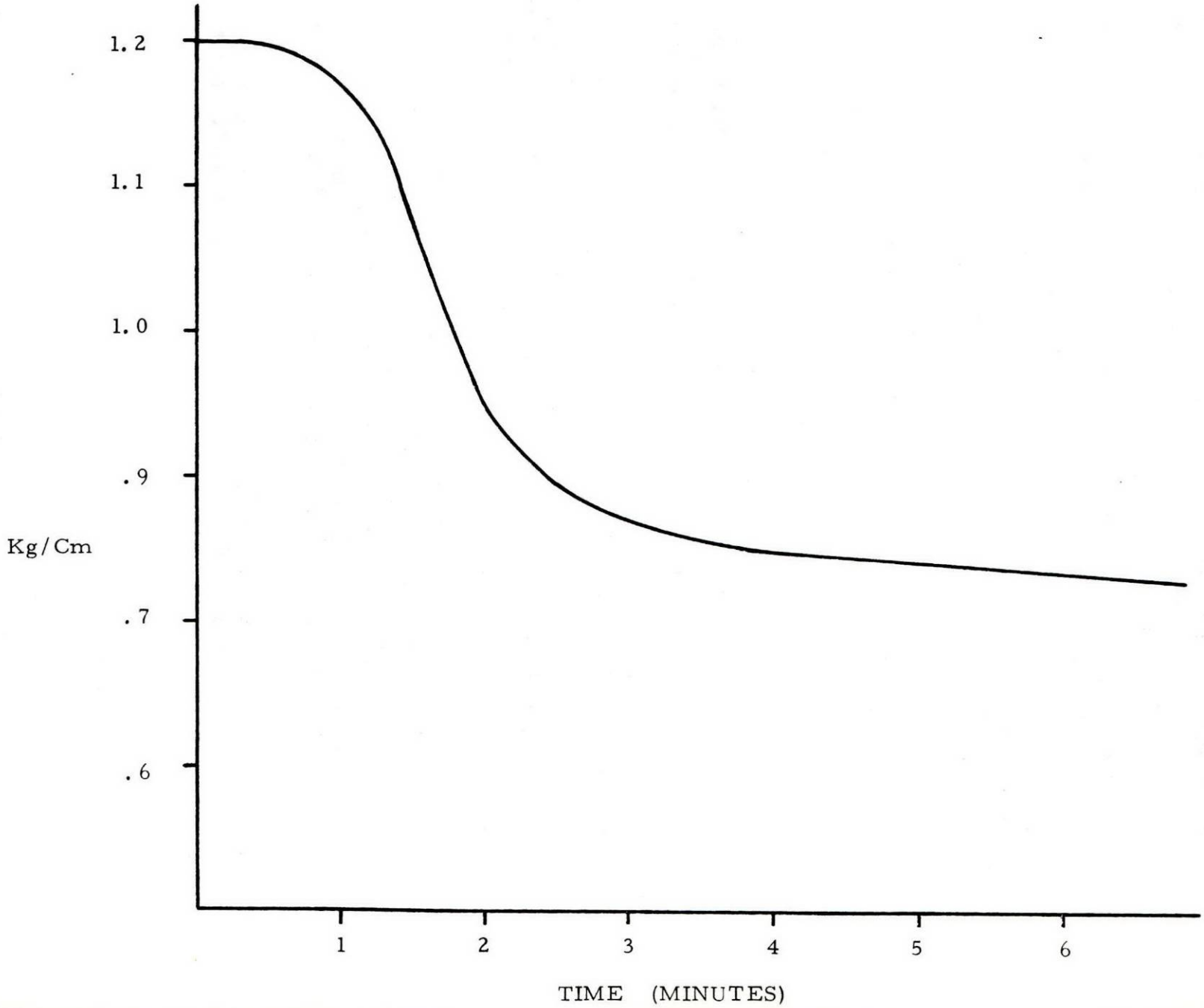
8. Correct deficiencies in the etch.



Effect of temperature on rate of coverage.

Three panels were processed through the preplate line and given a electroless nickel deposit. The panels were processed through a conditioner and then plated in series at 1 A/dm^2 for 2 minutes. The temperature of the strikes were 25, 35, 45° C. The dark surface on the 35° and 45° C panels show no coverage from the copper strike.

PEEL STRENGTH VS TIME



When the system is correctly operated, strikes using the high throw acid copper formulation can give equal if not superior peel strengths to other types of strikes.

Electroless Copper

A conditioner is not required when using the acid copper strike after electroless copper deposits because no potential difference exists to produce immersion deposits.

Electroless copper is successfully plated in production by: 1) Reduced entry voltage into the decorative copper plating tank allowing metal thickness to increase at the contact points before attaining normal plating voltage; 2) Using a dilute acid copper electrolyte formulation, thereby reducing the tendency to dissolve the thin electroless copper deposit before coverage. While functional, this system gives poor plate distribution and a slower rate of coverage than a high throw copper strike.

Electroless copper can be successfully plated using 75 g/l copper sulfate with a sulfuric acid concentration of 150 g/l. Higher sulfuric acid concentrations than 150 g/l can result in dissolution of the thin electroless copper.

Conclusion

The use of a high throw acid copper strike is a very effective method to improve quality by increasing the copper thickness in low current density areas, especially at the contact points, while also reducing cost and waste treatment requirements when compared to a nickel or pyrophosphate copper strike.

When using a high throw acid copper strike over electroless nickel, it is important to cover the electroless deposit as quickly as possible. Extensive covering times can result in dissolution of the electroless nickel deposit and/or loss of peel strength. The rate of covering can be increased by the ue of a conditioner and/or increasing contact points or other methods, as discussed in this paper.

The copper strike can be controlled by routine analysis and brightener additions, but it should be remembered that the electroless deposit has a direct influence on the performance of the strike. Passive electroless nickel deposits will result in slower rates of coverage. Resistance measurements and thickness checks of the electroless deposit should be maintained so that potential trouble can be corrected before production is lost.

An all copper underlayer for plastic surfaces (copper strike, copper plate) will provide a bright, lustrous, ductile and leveled deposit, perfectly suited for a plastic substrate.

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B-2

DECORATIVE PLATING SESSION B

Development of and Experiences with the Chrysler "STEP" Test

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DEVELOPMENT OF AND EXPERIENCES WITH THE CHRYSLER "STEP" TEST

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ABSTRACT

It is now possible to simultaneously measure the relative electrochemical potential difference between, and the thickness of, the individual layers in multilayer nickel deposits using the Chrysler "STEP" test. The test is rapid and, in many cases, obviates the need for microscopic thickness measurements. The corrosion performance of duplex nickel deposits is related to the interlayer electrochemical potential difference between the bright and semibright nickel. This value can now be determined by testing finished parts rather than individual nickel foils. Equipment and operating conditions for carrying out the test are described. Precautions, limitations and various other characteristics of the test are discussed. Examples of typical results obtained on various multilayer nickel deposits are presented. The relationship of potential difference, corrosion performance and sulfur contamination of semibright nickel deposits is explored.

Introduction

The development and growth of plating over the years has been responsible for a concurrent growth in test procedures and instruments for evaluating deposit thickness and corrosion resistance. The need to measure nickel plate thickness has resulted in the development of thickness testers based on coulometric[1], magnetic[2], beta back scatter[3], X-ray[4] and other chemical and physical methods. The referee thickness test, however, relies on the microscopic[5] examination of a carefully prepared cross section of the deposit to be tested. In the case of multilayer nickel deposits, the microscopic method has until now provided the only means of measuring the thickness of the individual layers. Unfortunately, the microscopic method is time consuming and requires expensive equipment and a skilled person to carry out the test.

The need to evaluate the corrosion resistance of plated parts has similarly resulted in the development of a variety of accelerated corrosion tests. The most widely used accelerated corrosion tests for nickel-chromium deposits are the Corrodkote[6] and CASS[7] tests, both of which require about twenty four hours per cycle.

With the recent development of the Chrysler "STEP" * test[8,9] the measurement of individual nickel layer thicknesses in multilayer deposits can be carried out much more rapidly and with less difficulty than before. Of even greater significance than thickness measurements is the ability of the "STEP" test to measure the relative electrochemical potential difference between layers in multilayer nickel (and other metal) deposits. Hospadaruk[10], Safranek[11], and Petrocelli[12] have shown that the superior corrosion resistance of duplex nickel deposits is a function of the electrochemical potential difference between the active sulfur containing bright nickel and the noble essentially sulfur-free semibright nickel. Although this fact has been known and appreciated for almost twenty years, most duplex nickel electroplaters have ignored measuring the potential difference of their deposits because of the inconvenience of the test procedure suggested by DuRose[13]. Duplex nickel deposits with inferior corrosion resistance resulting from inadequate electrochemical properties have consequently often been, and continue to be, put into service where they prematurely fail despite a presumed adequate total nickel thickness. The "STEP" test can drastically shorten the time required to evaluate deposit quality with respect to thickness and electrochemical potential and is presently being used by a growing number of plating establishments.

* "STEP" is an acronym for Simultaneous Thickness and Electrochemical Potential.

Equipment and Data Format

A diagramatic representation of the basic "STEP" test apparatus is shown in Fig. 1. The test is based on the coulometric dissolution of a portion of the deposit while measuring the voltage between the deposit and a reference electrode as a function of time. A well regulated, constant current D.C. power supply, capable of providing about 15 to 40 milliamperes at about 5 to 10 volts supplies the electrical energy for stripping the deposit. Anodic stripping takes place in a special cell which confines the stripping to a known area of deposit (generally, a circle one eight of an inch in diameter). The metal cell, which is the cathode in the circuit, also contains a suitable electrolyte and a glass or plastic agitator tube connected to a pulsating, closed air supply. The pulsating column of air pumps electrolyte back and forth against the deposit being stripped to prevent concentration polarization at the anode surface. A reference electrode (e.g., silver-silver chloride) is housed inside the agitator tube where it is physically protected, but in electrical contact with the electrolyte.

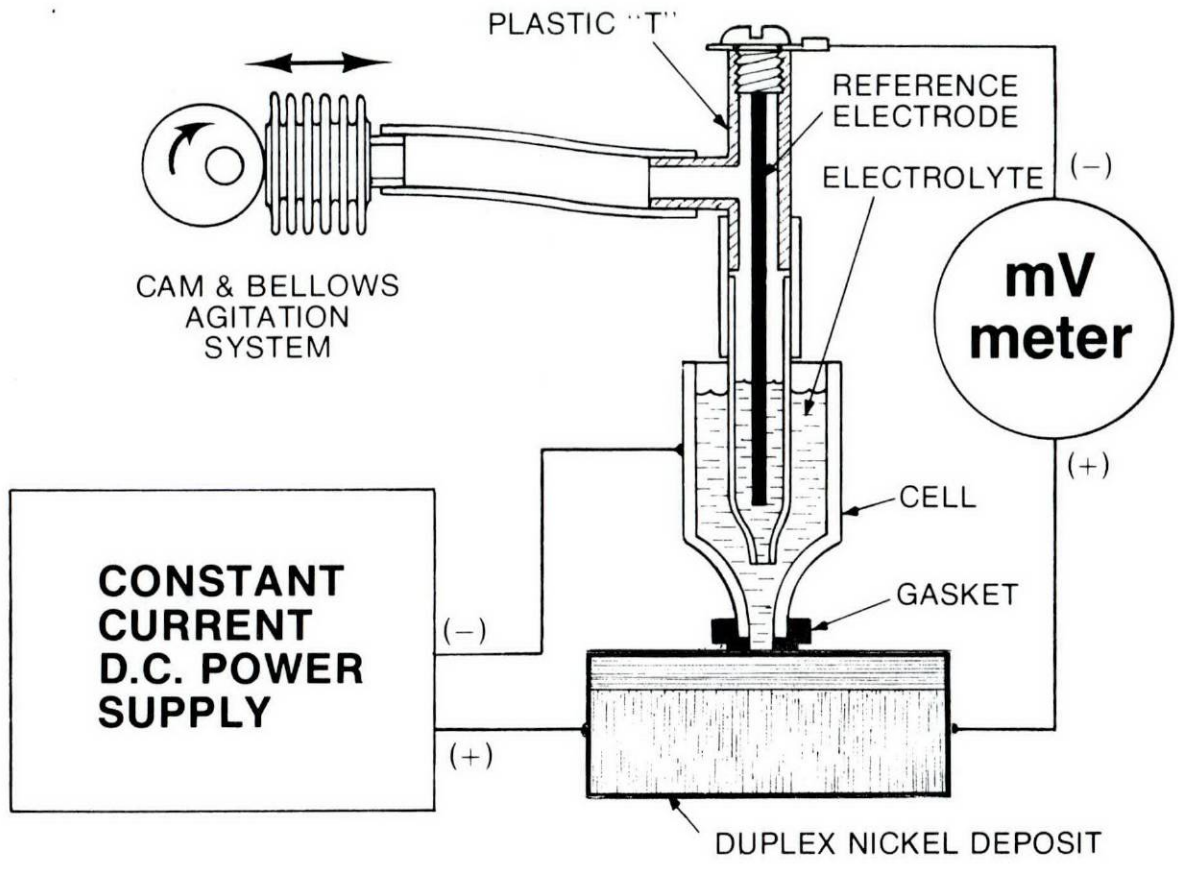

Fig. 1. Basic circuit for "STEP" test apparatus.

The voltage between the deposit being anodically stripped and the reference electrode is measured as a function of time or deposit thickness. The voltage can be measured with a millivoltmeter having an input impedance of at least one megohm and a full scale reading of about one to two volts. A pH meter, set to read millivolts is satisfactory. However, the use of a recording potentiometer (X-Y or strip chart recorder) is more desirable because rapidly changing potentials and other subtle variations can be readily observed. Reference 8 gives more detailed descriptions of the construction and operation of a "STEP" test apparatus.

Typical data that can be obtained from the "STEP" test of a duplex nickel deposit is shown in Fig. 2. In this example, the duplex nickel has a thin top layer of nickel designed to produce a microdiscontinuous chromium deposit. Stripping time, which can be expressed in deposit thickness units using Faraday's Laws, is displayed along the horizontal axis. Millivolts are recorded along the vertical axis with the more noble deposit having the more positive (higher) voltage.

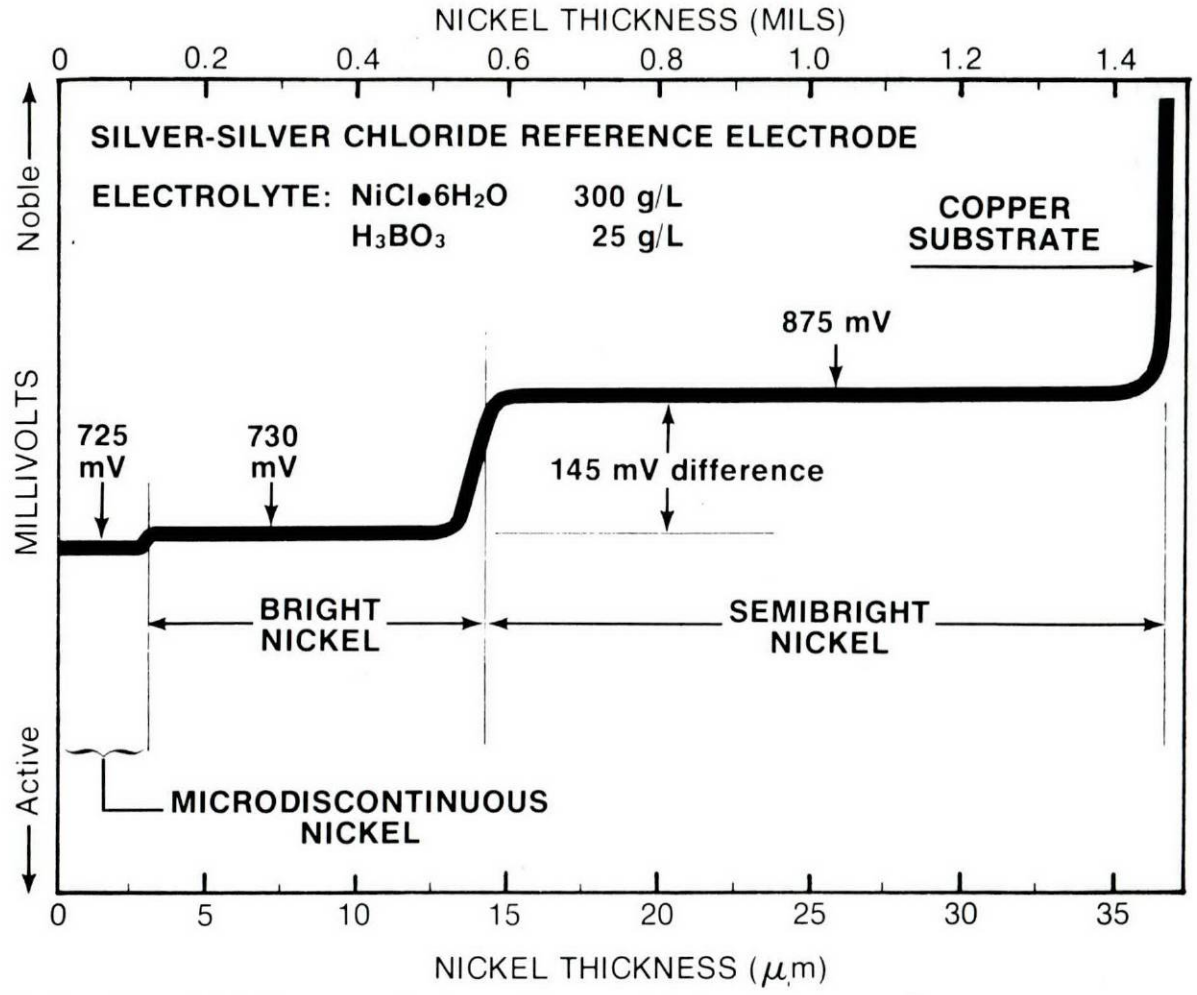

Fig. 2. Potential-thickness graph of a multilayer nickel deposit consisting of semibright, bright and microporous nickel layers.

A rapid change in potential, evident as a break in the curve, signifies a change in the relative electrochemical potential of the deposit, which implies the presence of a different deposit layer. The point along the horizontal axis where the change occurs indicates the thickness of the layer, while the magnitude of the potential change can be related to the corrosion resistance of the total deposit. The potential of bright nickel and a "microdiscontinuous" nickel (for producing microdiscontinuous chromium) would normally be expected to be identical. However, in practice there is often a slight potential difference which makes it possible to determine the thickness of the very thin "microdiscontinuous" nickel deposit.

A photograph of an actual "STEP" test plot obtained on a production plated multilayer nickel system is shown in Fig. 3. The deposit sequence consisted of a semibright nickel (directly on steel), a very active nickel*, bright nickel and an inert particle containing microporous nickel top layer.** The entire test was completed in less

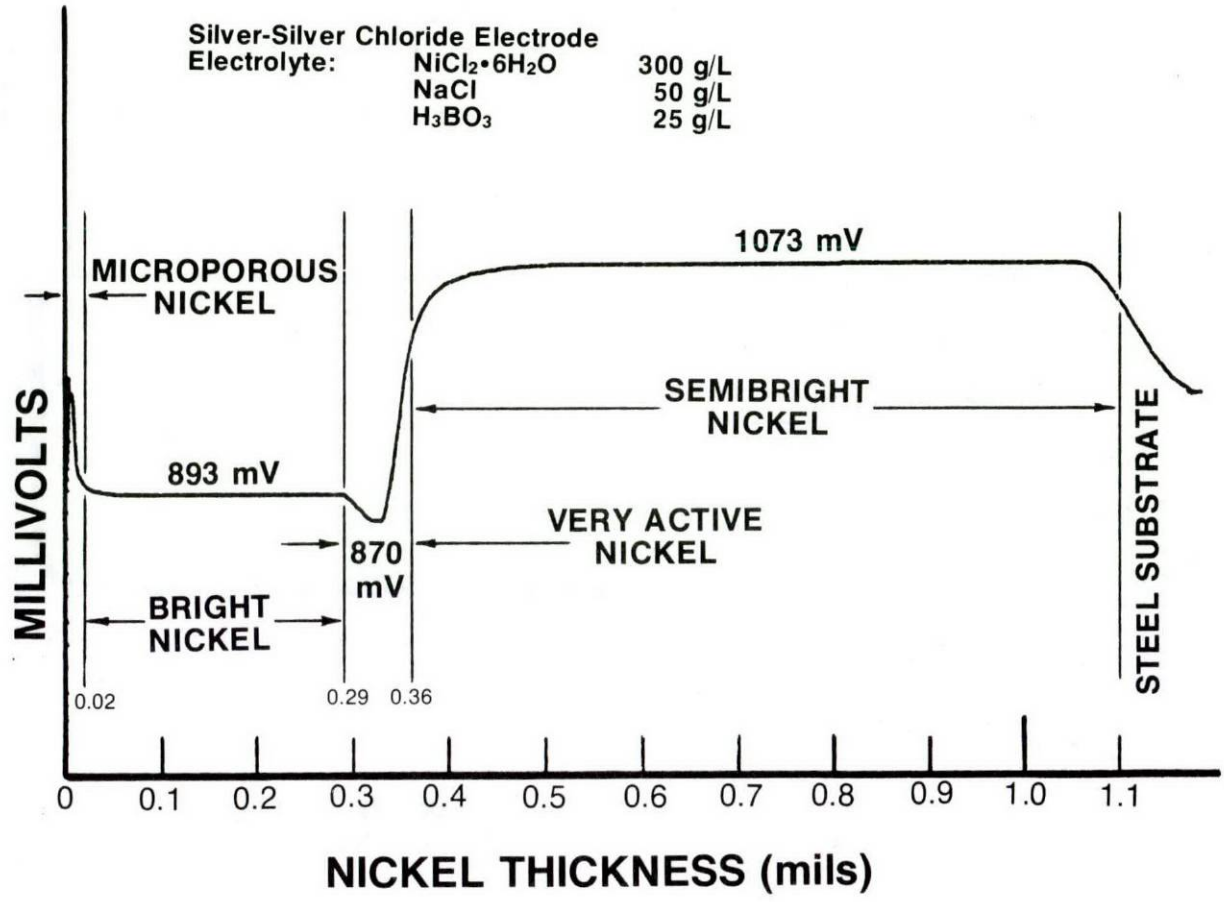

Fig. 3. Photograph of actual "STEP" test potential-thickness graph showing a four layer nickel deposit with a very active nickel layer between the semibright and bright nickel layers.

than ten minutes, including the time required to prepare the sample. The test results indicated that the total nickel deposit was about 1.1 mils thick and the semibright, very active, bright and microporous nickel layers were about 0.74, 0.07, 0.27 and 0.02 mils thick respectively. The semibright nickel layer was 180 millivolts more noble than the bright nickel and the very active nickel was about 23 millivolts less noble than the bright nickel. The microporous nickel in this case is atypical in that it is far thinner than it should have been and the electrochemical potential is about 75 millivolts more noble than the bright nickel. In most cases the microporous nickel layer is normally about 5 to 20 millivolts more active than the bright nickel. the thickness of the top layer of microporous nickel should have been about 0.05 to 0.1 mil.

The "STEP" test is quite useful for monitoring the thickness of thin deposits like very active or microdiscontinuous nickel because the microscopic method becomes less reliable as deposit thicknesses fall below about 0.3 mil. The very active nickel deposit must be electrochemically more active than the bright nickel in order to be effective. The "STEP" test may provide an easier means of controlling the process than analyzing the plating bath for the sulfur contributing additive or analyzing a nickel foil for its percent sulfur content.

*Oxy Metal Industries Corp. (Udylite) "Tri Ni:"
**Oxy Metal Industries Corp. (Udylite) "Dur Ni"

Experimental Observations, Results and Discussion

If the electronic equipment required for the "STEP" test is in good working order and solid electrical connections are present between the test sample, cell, reference electrode, etc., there are very few things that can adversely affect the test results. The main variables that must be controlled are the electrolyte composition and the condition of the cell and reference electrode.

The basic requirements for the electrolyte are that it preferably provide 100 percent anode efficiency, uniform deposit dissolution and not interfere with the reference electrode or deposit being tested. Although many electrolytes might be found that fulfill these conditions, satisfactory results were obtained with some of the first electrolytes tested. As a result, extensive testing of electrolyte compositions was not carried out. Table I lists some of the electrolyte compositions investigated along with observations of their effectiveness.

Table I

ELECTROLYTE FORMULATIONS TESTED FOR USE WITH "STEP" TEST

FORMULATION	COMPOSITION	g/L	REMARKS
A	$NiCl_2 \cdot 6H_2O$	300	Gives good results
B	$NiCl_2 \cdot 6H_2O$ H_3BO_3	300 25	Gives good results
C	$NiCl_2 \cdot 6H_2O$ NaCl H_3BO_3	300 50 25	Gives good results; possibly too aggressive for some nickel deposits
D	HCl	10 vol %	Works on nickel but not copper; gases excessively
E	HCl	5 vol %	Works on nickel but not copper; gases excessively
F	HCl $NiCl_2 \cdot 6H_2O$	5 vol % 25 - 50	Works on nickel but not copper
G	HCl $NiCl_2 \cdot 6H_2O$	5 vol % 150	Works well on nickel, also strips copper
H	NaCl $Cu(NO_3)_2 \cdot 3H_2O$	30 0.2	Used for open circuit potential measurements; too dilute for "STEP" test
I	NH_4NO_3 NaSCN	750 90	Strips well, but does not give potential differences

Electrolyte compositions with low concentrations of chloride ion (e.g., formulations D, E and F in Table I) are not very effective in stripping copper. If a very thin copper strike is present between a ferrous substrate and a nickel deposit, a large voltage will be observed as stripping proceeds through the nickel and the copper layer is exposed. The copper will eventually be dissolved, but not as efficiently as when an electrolyte with higher

chloride concentrations is employed (e.g. formulations A, B, C and G in Table I). With a thin copper strike and a high chloride electrolyte, the presence of the copper strike may be essentially undetectable. Fig. 4 shows the difference chloride concentration in the electrolyte can have on the shape of the "STEP" test curve when a thin copper strike is present. Of course, if the copper layer is thick enough, even a high chloride electrolyte will result in a large voltage when the copper layer is reached because the stripping potential of copper is notably greater than that of nickel.

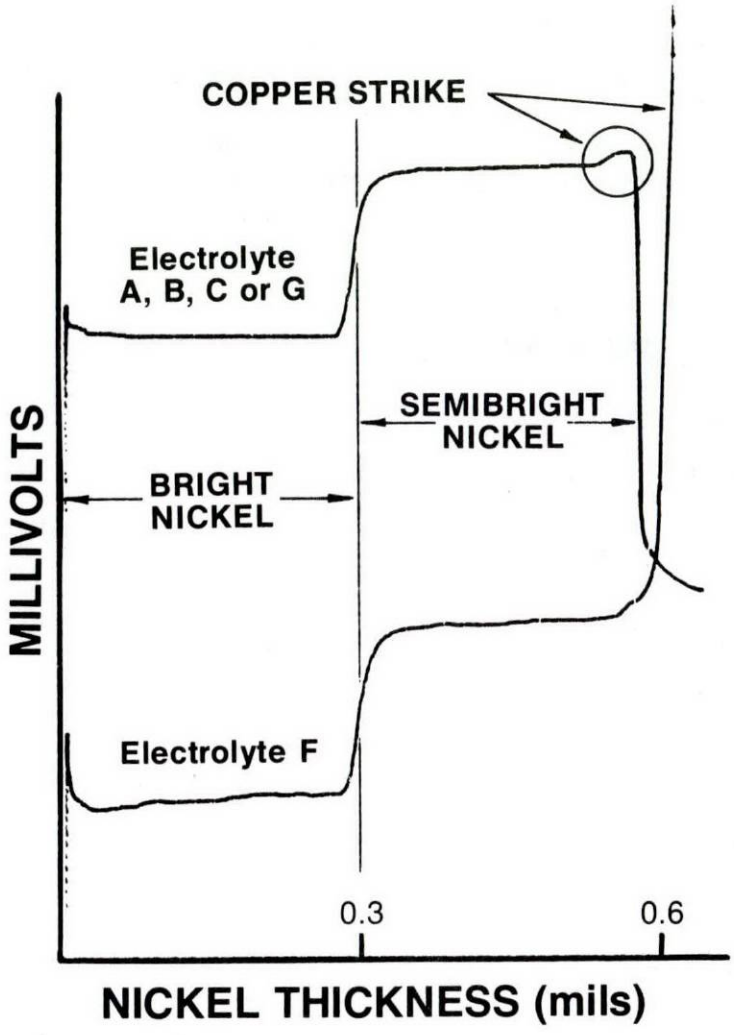

Fig. 4. Two potential-thickness graphs of the same duplex nickel deposit over a copper strike illustrating the response of the copper layer to different electrolytes.

Under some conditions, electrolytes containing high chloride ion concentrations can promote particularly aggressive and nonuniform dissolution of some nickel deposits. This can result in thickness errors if the nickel layers are not stripped evenly. Underlying nickel layers may be prematurely exposed, resulting in anomalous potential changes even though significant amounts of the upper layer(s) are still present. Nonuniform stripping of deposit layers can also lead to errors in potential difference measurements between layers, because the combined potential of more than one layer may be measured. This situation should be suspected when indistinct potential changes between layers, or unusual potential drift or variations are observed. A photograph (20X) of a test spot, taken on a duplex nickel sample after about half of the semibright nickel

deposit had been stripped away, is shown in Fig. 5. Electrolyte F from Table I was used and stripping across the entire eighth inch diameter test spot was quite uniform. Fig. 6 is a similar photograph of a test spot on the same duplex nickel sample using electrolyte C from Table I. In this case, it can be seen that dissolution of the semibright nickel was not uniform, and while not evident in a black and white photograph, the underlying copper deposit has been exposed in the more deeply stripped areas. The combined potential of both the semibright nickel and copper will be observed in this case rather than just the semibright nickel.

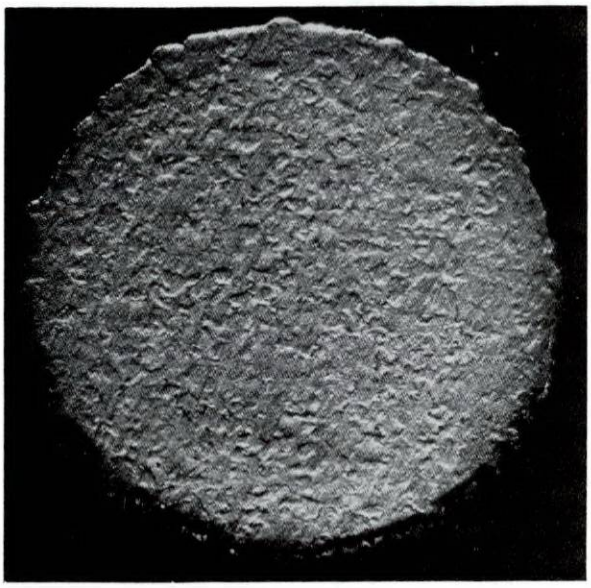

Fig. 5. Test spot of uniformly stripped semibright nickel using a low chloride electrolyte, 20x.



Fig. 6. Test spot of unevenly stripped semibright nickel using a high chloride electrolyte, 20x.

The semibright nickel deposit discussed in the preceding paragraph was plated from a coumarin-free bath* and seems to strip more uniformly than a semibright nickel plated from a coumarin-containing bath. If a coumarin type semibright nickel is tested, electrolyte C from Table I (i.e., high chloride type) gives good results, while a less aggressive electrolyte may not, as is shown in Fig. 7. The implication is that it might be possible to distinguish between a semibright nickel deposit plated from a coumarin-containing bath and a semibright nickel plated from a coumarin-free bath by using electrolytes of different compositions. The preferred electrolytes for use with the Chrysler "STEP" test are A, B and C from Table I which all give essentially identical results. If these electrolytes are too aggressive for the particular nickel deposit being tested, then electrolyte F should be used. Although all the electrolytes in Table I, except for H and I, give potential difference values for a given duplex nickel deposit within ± 10 percent, formulations D and E are not recommended because they do not contain nickel ions. If these electrolytes are used, gassing occurs at the cathode due to hydrogen generation. This can cause a slightly noisy recorder signal.

Nonuniform dissolution of the deposit can also occur if the deposit surface has not been completely stripped of chromium or if the surface has not been adequately cleaned, Dirt or grease can partially mask areas of the test spot and increase the anodic current density over the remainder of the test area. The deposit may then strip in a nonuniform manner which may result in severe localized attack and erratic results.

*Oxy Metal Industries Corp. (Udylite) "N2E"

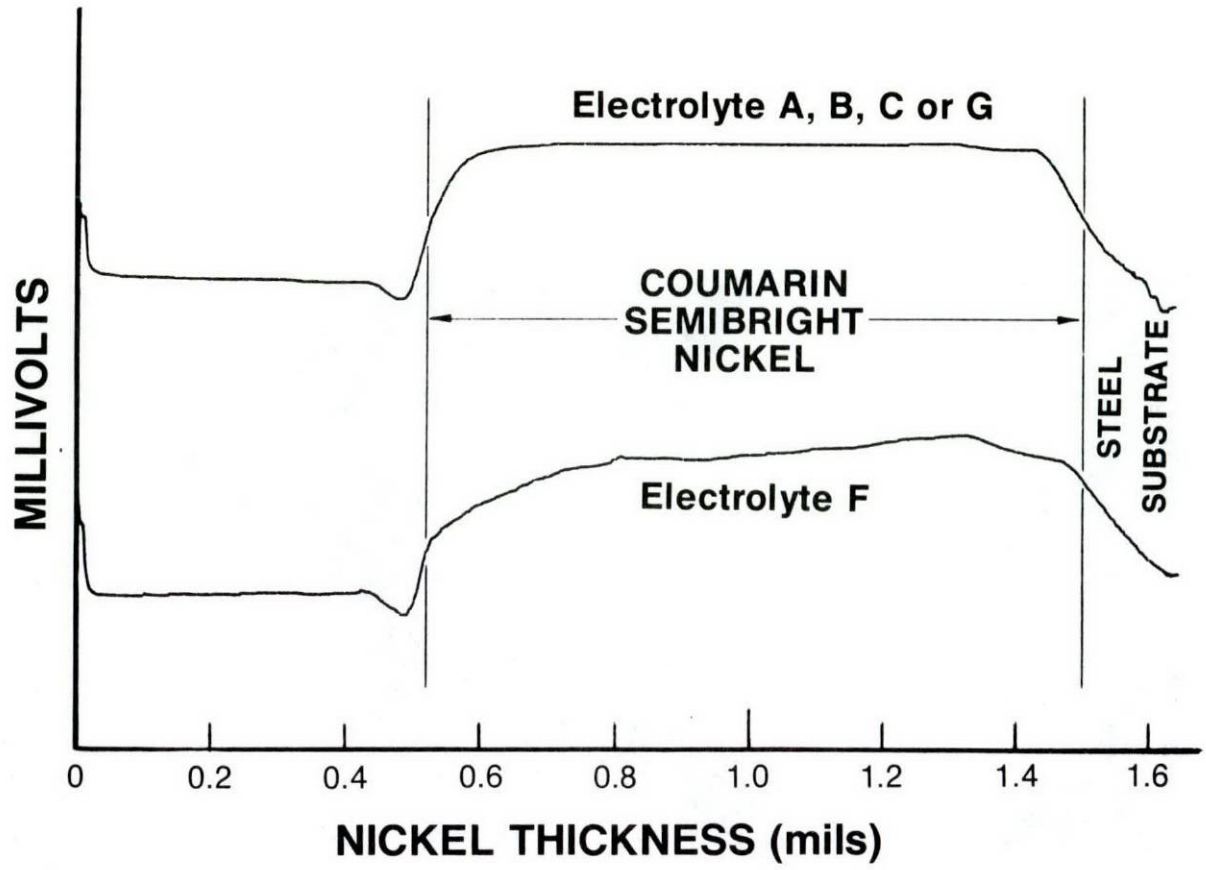

Fig. 7. Potential-thickness graphs of identical multilayer nickel deposits with a coumarin semibright nickel showing the effect of low and high chloride electrolytes.

It is *absolutely imperative* that the cell (cathode) be kept clean and free of excessive plate build up. If the small orifice at the bottom of the cell is allowed to excessively build up with plated metal, stripping of the test deposit will not proceed uniformly because of the changing anode to cathode distance."Whiskers" can grow on the cathode and cause localized high current density areas on the anode which in turn can give inaccurate results. The recorded signal becomes erratic and noisy when deposits build up on the cathode. As a general guide, the cell should be cleaned at least daily, or more often if necessary, using suitable acids or mechanical means.

If the test spot is inadvertently located over a small pit or crack which extends to an underlying layer, the results can also be very erratic. Usually a very noisy signal will be observed on the recorder until solid metal is reached. An air bubble adhering to the deposit surface may also produce a noisy signal. If noisy or erratic signals are observed, the cause should be investigated and eliminated. When everyting is working properly, a clean curve with well defined potential steps should be obtained as in Fig. 3.

Variations in anodic stripping current were also investigated. The first "STEP" test apparatus was built by modifying a commercial coulometric thickness tester.* Setting the metal selector switch of the commercial tester to different settings makes it possible to obtain different cell currents. Table II lists the millivolt potential differences obtained on the same duplex nickel deposit using various metal settings and cell currents. It can be seen that the electrochemical potential difference between the semibright and bright nickel

*Kocour Electronic Thickness Tester, Model S-77, Kocour Company, Chicago, Ill.

layers remains essentially constant even though a twofold change in cell current may occur. The deposit thickness appears to have changed but it is actually stripping time that changed. Knowing the actual cell current and stripping time, the correct thickness values could have been calculated. In any event, the actual cell current, provided it is not excessive, is not a variable which significantly affects the electrochemical potential difference observed between deposit layers.

Table II

Millivolt Difference vs. Cell Current for Duplex Nickel Deposit

THICKNESS TESTER SELECTOR SWITCH SETTING	CALCULATED CELL CURRENT (mA)	APPARENT NICKEL THICKNESS (mils)	"STEP" VOLTAGE DIFFERENCE (mV)
NICKEL	33.6*	0.60	140**
COPPER	31.0	0.65	142
BRASS	28.9	0.68	142
ZINC	24.2	0.83	142
CADMIUM	16.9	1.20	141

* measured value
**"standard" deposit = 140.5 mV

The preferred reference electrode for the "STEP" test is a silver-silver chloride electrode. Although not ordinarily prepared in situ, a satisfactory silver-silver chloride electrode can be prepared by using a clean silver wire as the reference electrode. A film of silver chloride will form on the silver wire when it is used in combination with an acidic chloride containing electrolyte. The silver wire electrode must therefore be conditioned to form the silver chloride film when it is put into use for the first time, after cleaning, or if it has not been used for a day or so. To assure that a satisfactory film of silver chloride has formed, several trial determinations should be made on a standard duplex deposit until consistent and reproducible results are obtained. Ordinarily, the electrode will be in good operating condition after about five to ten minutes of actual use. Until the silver-silver chloride reference electrode is in proper operating condition, the observed potential difference values may be too large or too small.

Other precautions are necessary when using the silver-silver chloride reference electrode. The electrolyte must not contain an active sulfur compound such as NaSCN, or the surface of the electrode may be "poisoned" and may not respond to voltage changes of less than about 250 millivolts. Safranek[11] and DuRose[13] have both pointed out that the electrochemical potentials of nickel deposits are severely affected by SO_2 and sulfite ion. It is therefore advisable to avoid electrolytes containing active sulfur compounds (e.g. formulation I in Table I) even if reference electrodes other than silver-silver chloride are used. Fig. 8 shows two "STEP" test plots of the same duplex nickel deposit carried out under identical conditions except for the electrolyte composition. The curve showing both the bright and semibright layers was made using electrolyte formulation C from Table I. The trace in which only the total nickel thickness could be determined was obtained with electrolyte I from Table I. Similar results were obtained with a platinum reference electrode which indicates that active sulfur compounds can also interact with the nickel as well as the silver-silver chloride reference electrode.

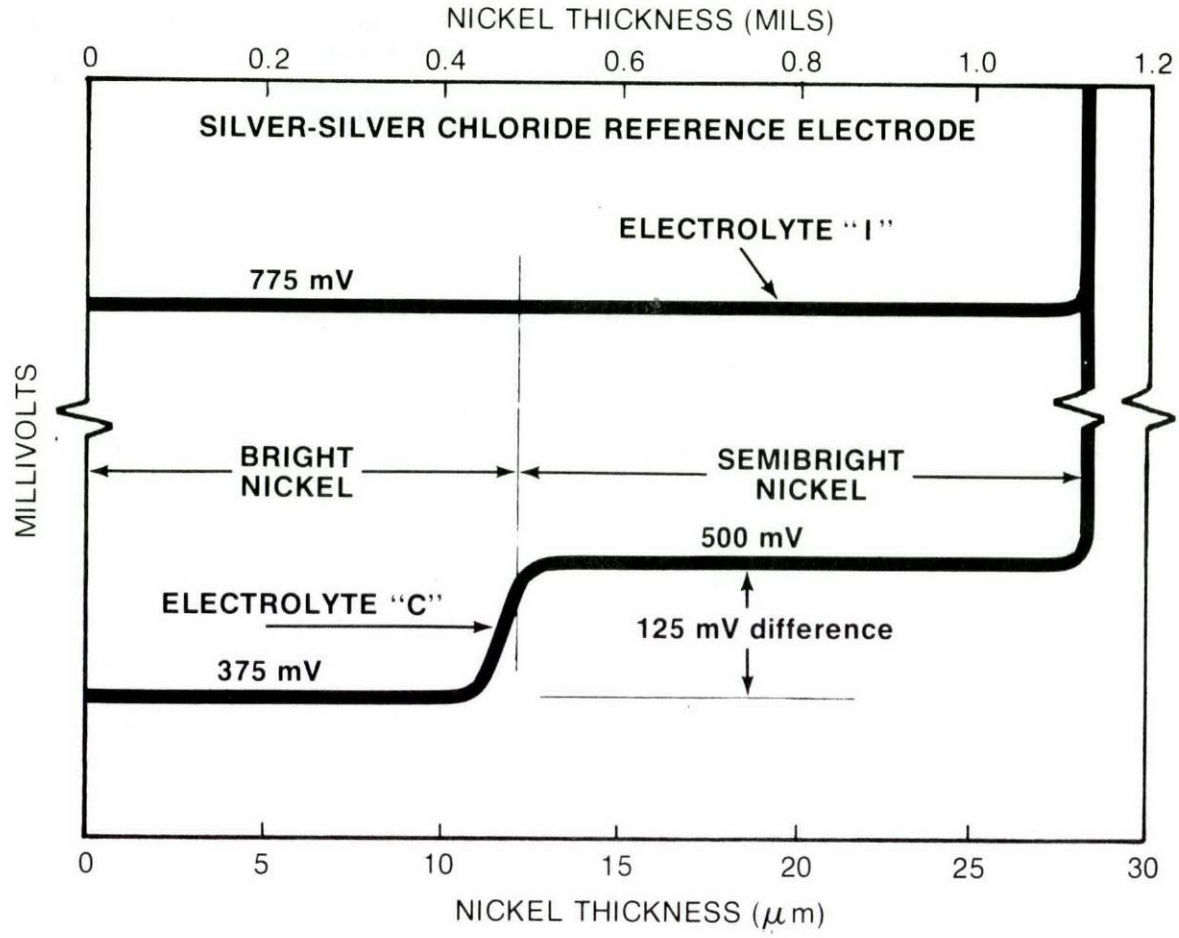

Fig. 8. Potential-thickness graphs of identical duplex nickel deposits showing the effect of NaSCN in the electrolyte.

Compounds like sodium thiosulfate, that can solubilize silver chloride or other compounds that can adversely react with silver or silver chloride (e.g., nitric acid, cyanides, ammonium, etc.) should also be excluded from electrolytes used with silver-silver chloride reference electrodes. If the silver reference electrode does become chemically contaminated, it may be cleaned by scrubbing with silicon carbide powder or abrasive paper until the silver is bright. The silver chloride film can then be reformed through actual use as explained above.

The electrochemical potential difference between the layers in multilayer nickel deposits, as measured using the "STEP" test procedure, is a function of the particular electrolyte used for the test, the condition of the silver-silver chloride reference electrode and the anodic electrochemical activity of the nickel deposits being tested. If the same electrolyte formulation is used in all the tests, the electrolyte ceases to be a variable for comparative purposes. Likewise, proper maintenance of the reference electrode eliminates it as a variable. The only remaining cause for a potential difference between nickel layers then, is the anodic electrochemical activity of the nickel deposits.

The anodic electrochemical activity of nickel has been shown by DiBari[14] to be related to the sulfur content of the nickel. Inclusion of carbon, selenium, iron, cobalt, or some other elements and compounds can also affect the electrochemical activity of nickel deposits. However, all of the electrochemical potential deficiencies we have seen in duplex nickel deposits have been related to excessive sulfur concentrations in semibright nickel deposits. Therefore, only the effects of sulfur will be considered in this paper.

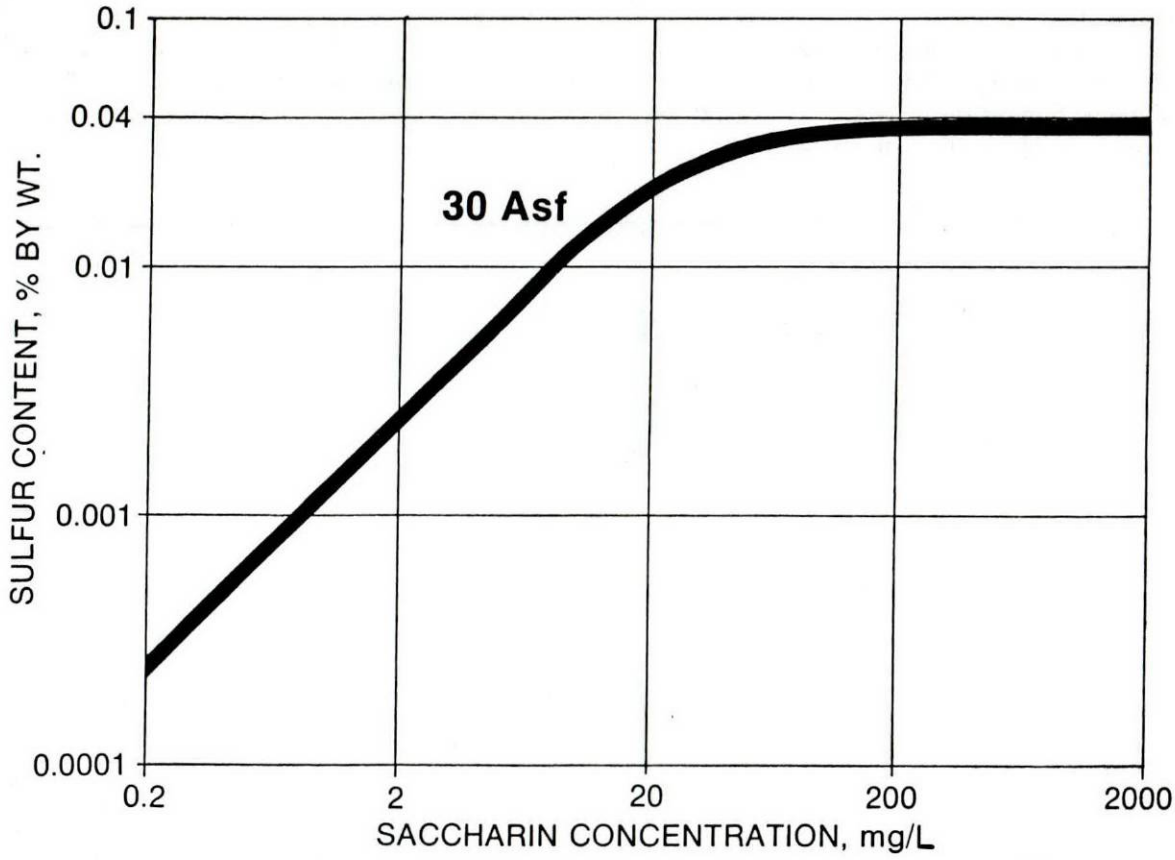

Fig. 9. Sulfur content in a nickel deposit as a function of saccharin concentration in a Watts nickel bath, 30 A/ft.^{2}

A graph adapted from Edwards[15], showing the relationship between the concentration of saccharin (a common bright nickel electroplating bath additive) in a Watts nickel bath and the percentage of sulfur included in the resulting nickel deposit is shown in Fig. 9. Other sulfo-oxygen (Class I) nickel additives behave similarly. Bright nickel plating baths typically contain at least one gram per liter of saccharin and/or other sulfo-oxygen brighteners and it is evident from Fig.9 that the sulfur content of a bright nickel deposit will be at least 0.04 percent. Addition of other normally used additives to a nickel plating bath can further increase the sulfur content of a bright nickel deposit to about 0.08 percent. Because of the relatively large reservoir of sulfur-contributing compounds present in bright nickel baths and the saturation effect evident in Fig. 9, the percentage of sulfur in a bright nickel deposit is quite constant unless unusual measures are taken to change it. Semibright nickel deposits are by definition sulfur-free, which is the reason that the electrochemical potential of semibright nickel deposits is more noble than that of a bright nickel deposit. At concentrations of less than about 200 milligrams per liter, as shown in Fig. 9, very small additions of saccharin to a nickel plating bath otherwise free of sulfur-contributing compounds, have a significant effect on the sulfur content of the deposit.

Fig. 10 shows how the potential difference varies between a bright nickel deposit having a constant sulfur content (and therefore a constant electrochemical potential) and a semibright nickel deposit plated from a bath to which small additions of saccharin are made.* When the semibright bath is free of sulfur-contributing compounds, the potential difference between the semibright and bright nickel is about 155 millivolts as

*These tests were carried out using an Oxy Metal Industries Corp. (Udylite), "66" bright nickel bath and "N2E" semibright nickel bath.

measured with the "STEP" test, a silver-silver chloride reference electrode and electrolyte C from Table I. Increasing the saccharin concentration to 6 ppm (6 mg per liter) in the semibright nickel bath results in a 100 millivolt potential difference while a 20 ppm sacharin concentration gives a difference of only about 25 millivolts! Similar results were observed using a semibright nickel bath containing 0.2 gram per liter of coumarin as the grain refining additive.

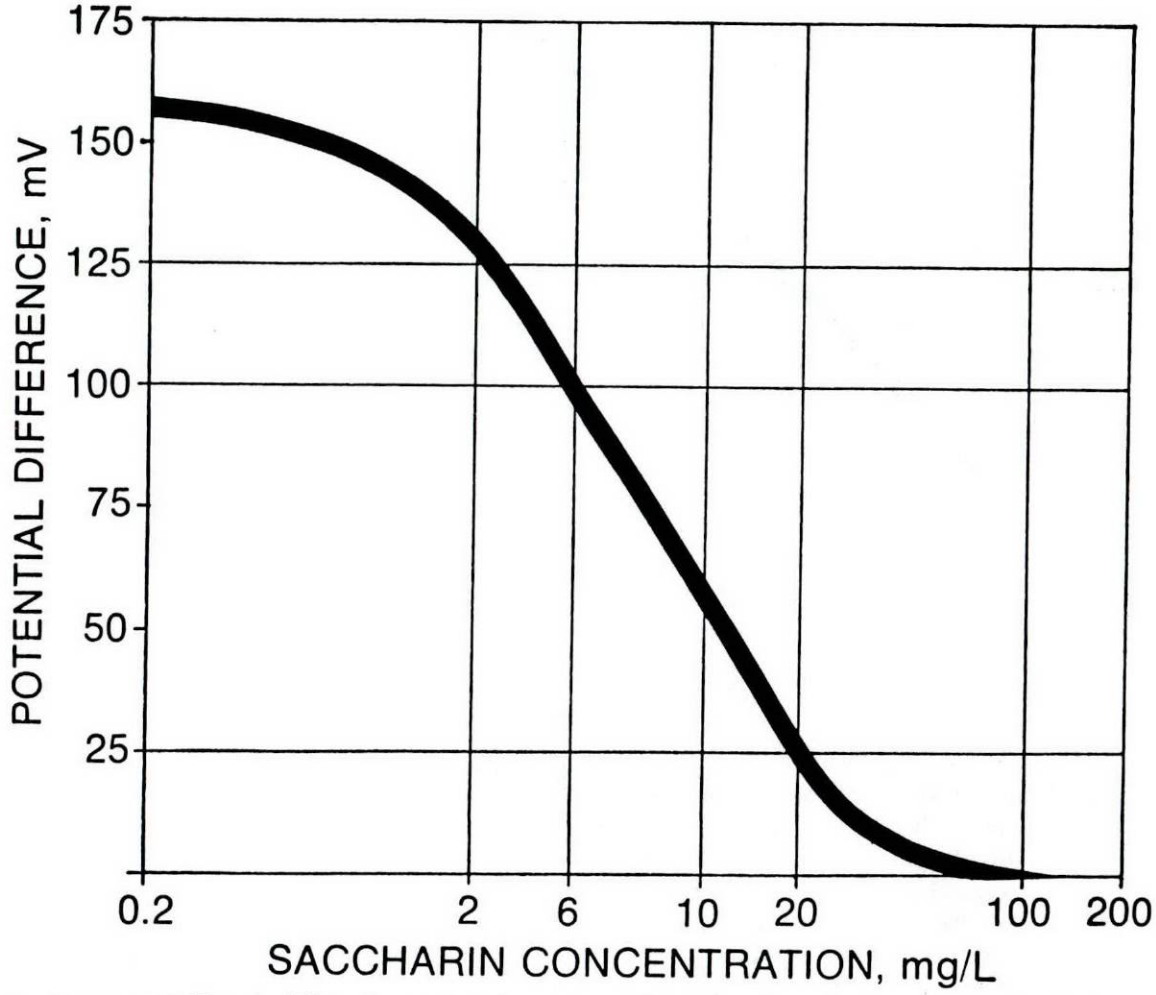

Fig. 10. Potential difference of duplex nickel deposit as a function of saccharin concentration in the semibright nickel bath, 30 A/ft.^{2}

The data from Figs. 9 and 10 was combined to show the relationship of the sulfur content in the semibright nickel to the potential difference between the semibright deposit and a bright nickel deposit of fixed sulfur content. The plating industry has long recognized that a semibright nickel deposit should have a maximum sulfur content of about 0.003 to 0.005 percent[16,17]. From Fig.11 it can be seen that a semibright nickel sulfur content of about 0.003 to 0.005 percent corresponds to a potential difference of about 125 to 100 millivolts. Our experience indicates that a minimum potential difference of about 125 millivolts between the bright and semibright nickel layers of a duplex deposit is required to prevent premature corrosion failure of the deposit. Interestingly enough, the potential difference between a sulfur-free Watts nickel deposit and a bright nickel is less than between the same bright nickel and a sulfur free semibright deposit.

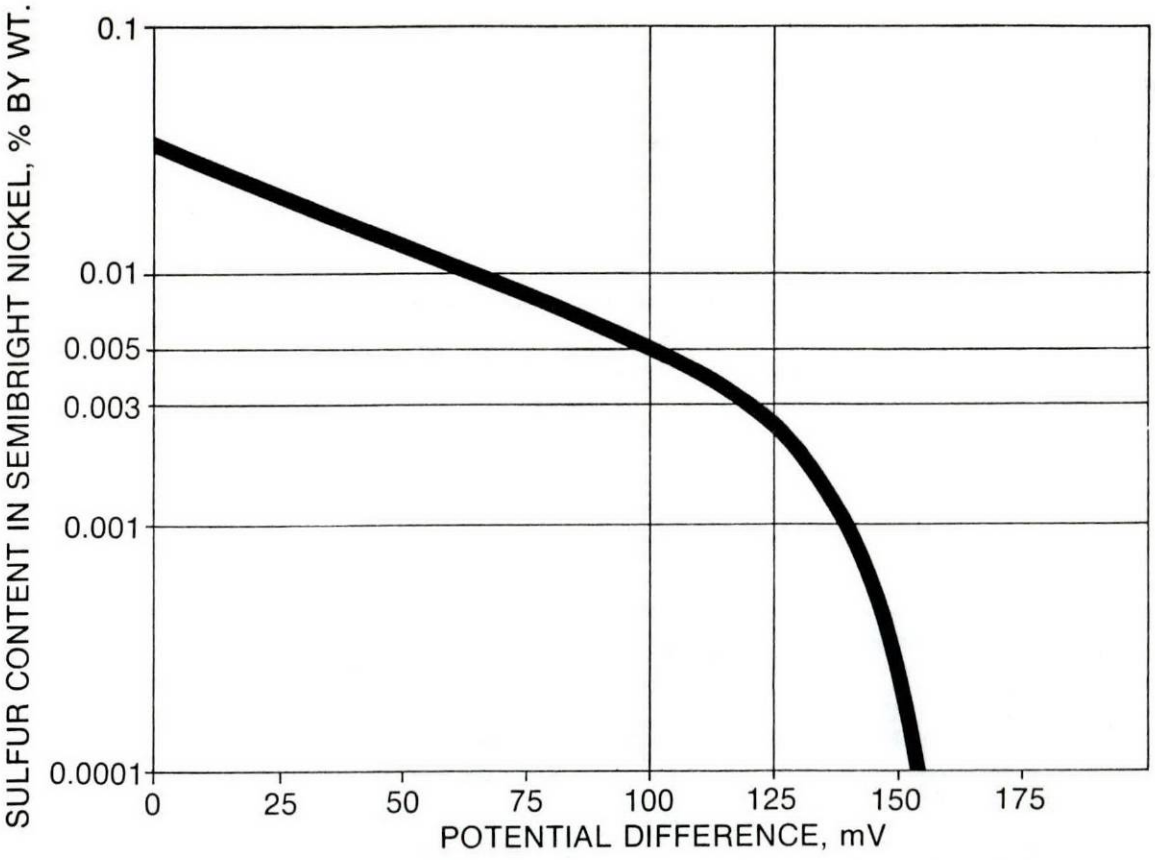

Fig. 11. Potential difference of duplex nickel deposit as a function of sulfur in the semibright nickel deposit, 30 A/ft.[2]

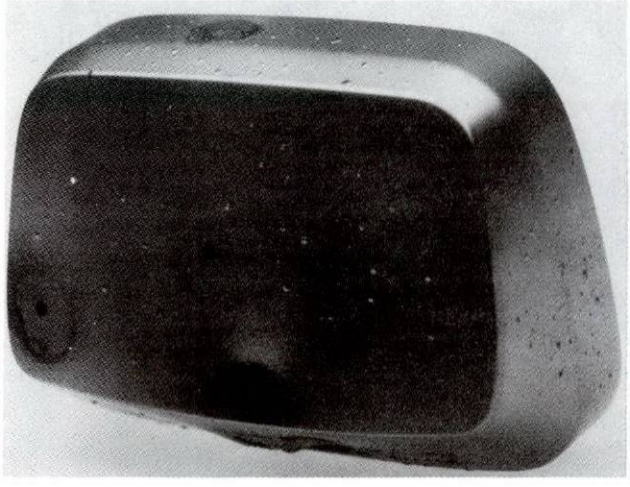

Fig. 12. Mirror removed from a 1973 model car driven 72,500 miles. Total nickel thickness 1.2 mil. "STEP" test potential difference of 65 millivolts

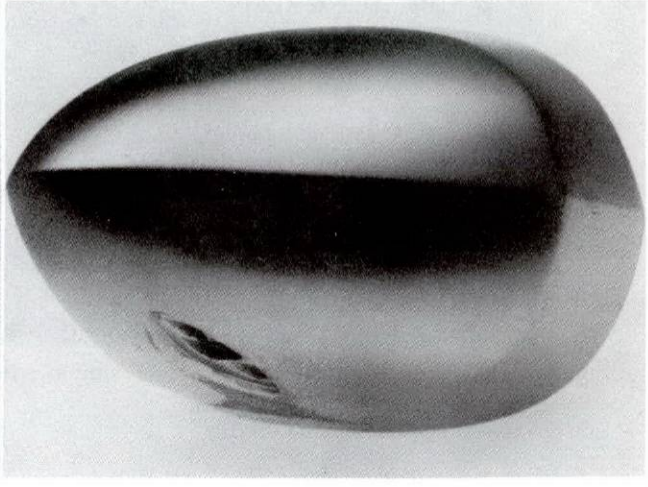

Fig. 13. Mirror removed from a 1972 model car driven 92,000 miles. Total nickel thickness 1.2 mil, "STEP" test potential difference of 145 millivolts

Photographs of two zinc base die cast outside rear view mirror shells are shown in Figs. 12 and 13. The mirror in Fig. 12 was removed in 1979 from a 1973 model car which had been driven 72,500 miles in the Detroit area. The total nickel thickness was about 0.0012 inch with a potential difference of 65 millivolts. The mirror in Fig. 13 was removed in 1979 from a 1972 model car which had been driven 92,000 miles in the Detroit area. Again, the total nickel thickness was about 0.0012 inch but the potential difference was 145 millivolts. As can be seen in the photographs, the mirror with the 65 millivolt potential difference was extensively pitted and blistered while the 145 millivolt difference mirror was free of basis metal corrosion, even though it had been in service longer.

Cross section photomicrographs of corrosion sites found in these two mirror shells are shown in Figs. 14 and 15. The corrosion pit in the deposit with a 145 millivolt potential difference (from the mirror in Fig. 13) was confined to the bright nickel layer as can be seen in Fig. 14. The much more noble semibright nickel layer showed no sign of corrosive attack indicating that the duplex mechanism was functioning properly. With only a 65 millivolt potential difference between layers, the semibright nickel shown in Fig. 15 (from the mirror in Fig. 12), was not sufficiently more noble than the bright nickel. As a result, even though corrosion proceeded laterally along the bright nickel layer, there was also attck of the semibright layer. In fact, it was difficult to find an example of this intermediate degree of corrosion because most corrosion sites had already penetrated the semibright layer.

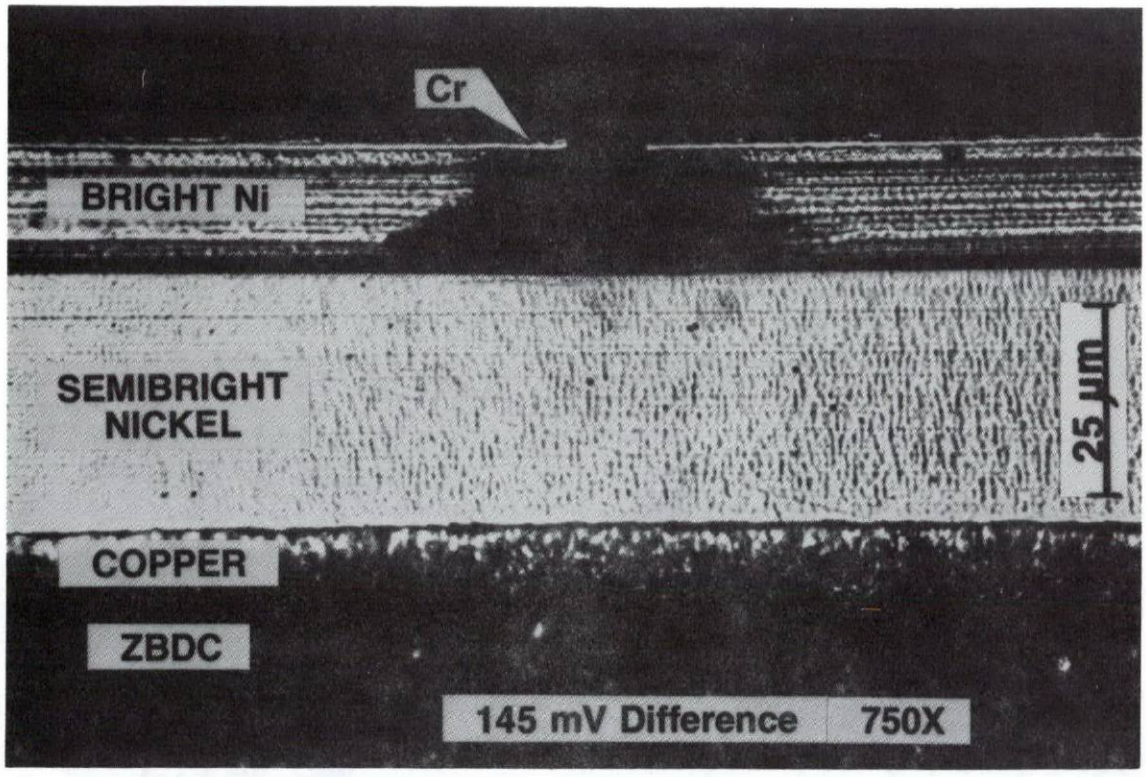

Fig. 14. Photomicrograph of nickel corrosion site in duplex nickel deposit with 145 millivolt "STEP" test potential difference, 750X.

The photomicrograph shown in Fig. 16 is a cross section of a duplex nickel deposit with only a 35 millivolt difference between nickel layers. In spite of a total nickel thickness presumed to be adequate (1.2 mils), the part failed one cycle of a Corrodkote accelerated corrosion test. The hemispherical corrosion pit extending

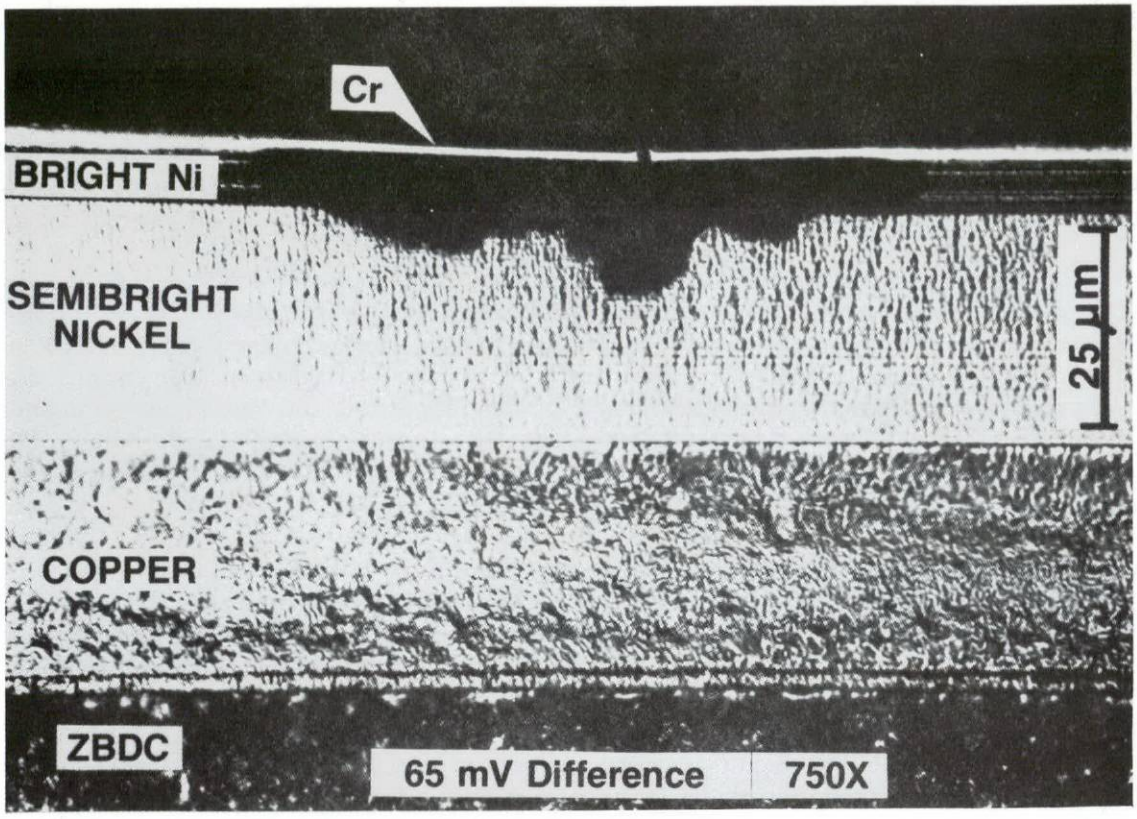

Fig. 15. Photomicrograph of nickel corrosion site in duplex nickel deposit with 65 millivolt "STEP" test potential difference, 750X.

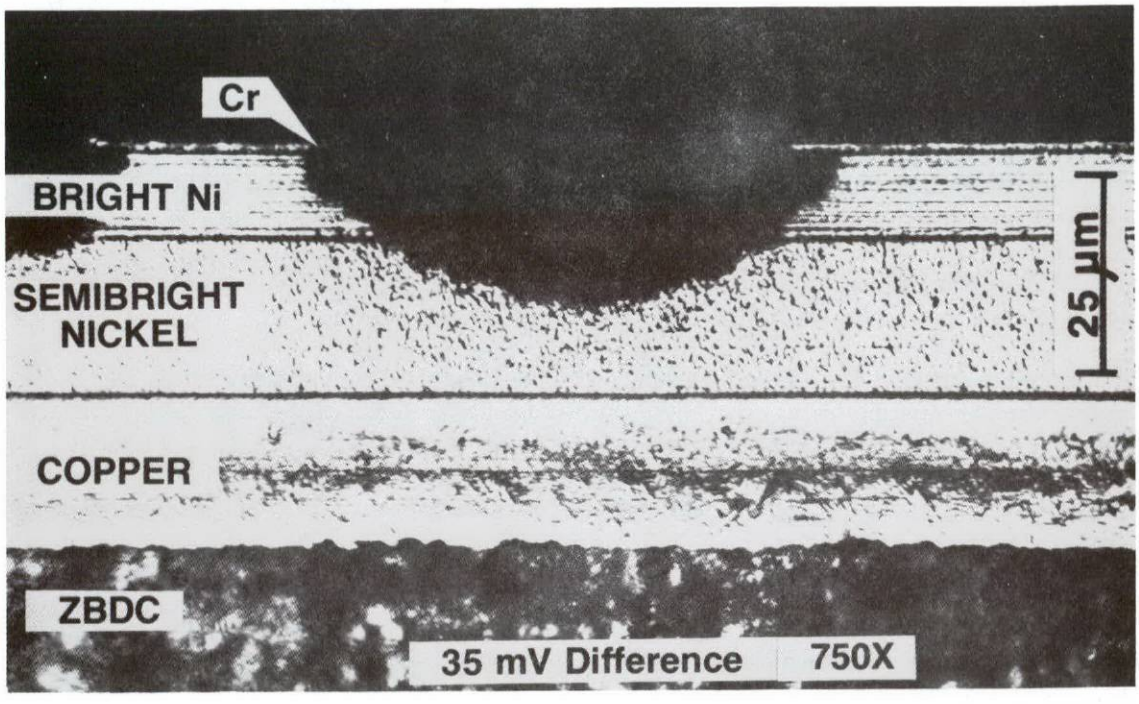

Fig. 16. Photomicrograph of nickel corrosion site in duplex nickel deposit with 35 millivolt "STEP" test potential difference, 750X.

through both nickel layers is typical of the kind of attack normally seen in single layer nickel deposits. It is evident from the photomicrograph that the semibright nickel layer corroded as readily as the bright nickel. Because of the inadequate electrochemical potential difference between nickel layers, the composite deposit acted like a single layer deposit for all practical purposes, even though two different nickel plating baths were used in its preparation. We have even seen double layer nickel deposits in which the semibright nickel was more active than the bright nickel by as much as 35 millivolts. Such an active "semibright" nickel does not fit the definition of a semibright nickel and once corrosion has progressed through the upper nickel layer corrosion may actually proceed at a faster rate in the underlying pseudo semibright layer.

"STEP" testing of many multilayer nickel plated parts from various domestic and foreign sources indicates that the potential difference between semibright and bright nickel layers can normally be expected to range from a high of about 185 millivolts (with the bright nickel more active than the semibright), to a low of about "minus"35 millivolts (i.e., the semibright nickel more active than the bright). It is not at all unusual to see well run plating plants consistently achieve at least a 140 millivolt potential difference between bright and semibright nickel layers. There is every reason to expect that duplex nickel deposits can be routinely produced in production plating plants that meet a minimum potential difference of 125 millivolts when everything is done correctly.

Duplex nickel deposits that we have observed with poor corrosion performance attributable to an inadequate potential difference all appear to have had problems in the semibright nickel rather than the bright nickel. Generally, the semibright bath was found to be contaminated with Class I, sulfo-oxygen, bright nickel plating additives, or else proper maintenance additions of semibright additives were not made. Contamination with Class I additives (usually saccharin) can result from deliberate addition of these materials in an attempt to overcome physical deficiencies in the semibright nickel (e.g., poor ductility, high tensile stress, grainy, dull or dark deposits, etc.), or may be due to accidental additions of bright nickel additives (e.g., poorly labeled containers, misinformed or improperly instructed workers, etc.). A less obvious source of contamination is through the use of treatment tanks and filters used for both bright and semibright baths which are not sufficiently cleaned after being used with a bright nickel plating bath. Addition of reclaimed nickel solutions to the semibright nickel bath can also cause problems because it is extremely difficult to reduce all the sulfur contributing compounds to low enough concentration levels necessary for semibright nickel bath replenishment.

A number of people*have suggested increasing the activity of the bright nickel layer to provide a greater potential difference between the semibright and bright layers. Such a procedure might be used to overcome the poor potential difference resulting from a faulty semibright nickel deposit, or to provide even greater corrosion protection to a good duplex nickel system. There is certainly an opportunity for research along these lines. However, DiBari[18] and Durbin[19] have suggested that an unusually active bright nickel deposit might corrode at an accelerated rate and possibly result in severe pit corrosion at the deposit surface. We have no evidence to confirm or deny such a possibility but offer it as a warning.

It is important to mention that duplex nickel deposits with exemplary potential differences may nevertheless fail prematurely if other problems exist. Highly stressed deposits that crack and expose basis metal, deposits with poor ductility that crack when bent, inclusion of foreign matter in the deposit, poor metal finishing or poor basis metal (porous castings, slivers and burrs), gas pits in the deposit and similar problems can all result in corrosion failure. Platers must be vigilant with respect to all aspects of plating if quality results are to be consistantly achieved.

*Practically everyone who has been shown the "STEP" test and stopped to consider the implications of the potential difference between nickel layers.

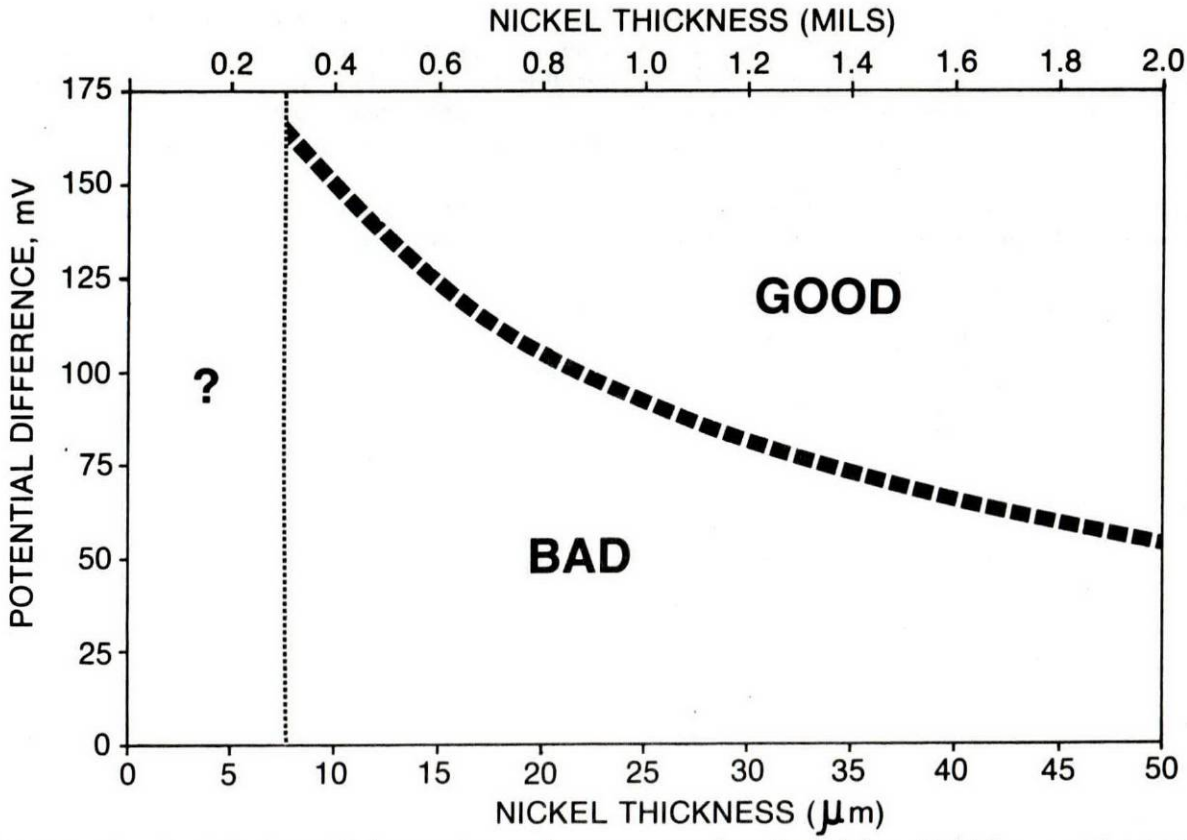

Fig. 17. Graph of duplex nickel corrosion performance as a function of deposit thickness and potential difference.

Based on the data accumulated to date, which admittedly is still incomplete, it is possible to construct a graph like the one shown in Fig. 17. This graph represents good and bad corrosion performance of duplex nickel deposits expressed in terms of total nickel thickness and potential difference between nickel layers. As a duplex nickel deposit increases in thickness, there is less need for a large potential difference to obtain adequate corrosion protection. In other words, a sufficiently thick single layer nickel deposit can provide as much corrosion protection as a thin duplex nickel deposit. However, when more realistic, cost effective, thinner duplex nickel deposits are specified, a satisfactory potential difference is essential. Absolute minimum deposit thickness is still a question mark because deposit porosity, leveling, brightness, low current density coverage and similiar characteristics become increasingly important and must be considered. Naturally, a "grey area" exists on either side of the curve in Fig. 17. Finally, the use of microdiscontinuous chromium and a very active nickel layer between the bright and semibright nickel deposits can provide significant additional corrosion protection. These two factors have not been completely explored in our work but should not be overlooked when the best possible corrosion protection with the least nickel thickness is required.

Conclusions

The recent development of the Chrysler "STEP" test has made it possible to easily and rapidly measure the thickness of the individual nickel layers in multilayer nickel deposits. More importantly, the electrochemical potential difference between the nickel layers can also be measured. Because the magnitude of the potential difference is related to the overall corrosion resistance of the deposit, the test results can give an indication of deposit quality. The test may also provide the best means for monitoring the effectiveness of very active nickel layers of the type sandwiched between the semibright and bright nickel.

If the test equipment is used correctly and properly maintained, few operational difficulties will be encountered. In some cases it may be necessary to match the electrolyte used in the test to the particular nickels being tested because it has been noticed that not all semibright nickel deposits are anodically stripped with equal ease. However, there is evidence to suggest that this phenomenon may be used to qualitatively identify semibright nickel deposits plated from coumarin and non-coumarin containing baths.

Tests and observations indicate that a minimum "STEP" test potential difference of 125 millivolts is required between the bright and semibright layers of a duplex nickel deposit if the superior corrosion resistance of duplex deposits is to be consistantly obtained. The reason for not achieving a potential difference of this magnitude or greater, ordinarily appears to result from contamination of the semibright nickel bath with Class I, sulfo-oxygen bright nickel bath additives. Part per million concentrations of such additives in a semibright nickel bath can convert the bath to a bright nickel bath from the standpoint of the electrochemical activity of the resulting deposits.

Acknowledgement

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C-1

LIGHT METALS FINISHING SESSION C

Recovery Systems for the Light Metals Finisher

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RECOVERY SYSTEMS FOR THE LIGHT METALS FINISHER

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ABSTRACT

A trend towards chemical recovery is emerging in light metals finishing. Utilizing cation and anion exchange as well as acid retardation principles, a new technique called Reciprocating Flow Ion Exchange has been applied to a wide variety of recovery applications in this field. Basic system design is discussed as well as ways in which such recovery systems have helped stabilize and improve finishing operations, abate pollution and reduce costs.

1. INTRODUCTION

Although recovery of spent process baths and rinsewaters has been widely practised in the electroplating industry over the past several years, the light metals industry has not practised chemical and water recovery to the same extent. This could be due to the lower value of the chemicals employed in finishing light metals or the lack of suitable techniques by which these chemicals can be effectively and economically recovered.

A trend towards recovery is now emerging in this industry, both in new and existing plants. There are a number of factors which have contributed to this development.

1. Increased water and chemical costs. Because of the relatively large tonnage of chemicals consumed in light metals finishing, a small increase in chemical costs can be translated into significant savings through recovery.

2. Commercialization of a number of new recovery processes, some of which were originally developed for the electroplating industry.

3. Increased environmental pressures. Recovery systems can save money and at the same time help abate pollution or improve the operation of a conventional waste treatment system.

4. Recognition of the fact that proper utilization of a recovery system can frequently stabilize and/or improve the finishing process itself, from both a cost and quality point or view.

One of the unit operations that has been extensively utilized for chemical recovery in the electroplating industry is ion exchange. The purpose of this paper is to discuss some ways that ion exchange can be utilized for chemical recovery in light metals finishing.

2. WATER AND CHEMICAL RECOVERY BY ION EXCHANGE

Until fairly recently the use of ion exchange for pollution abatement and recovery in the metal finishing industry has been limited. This was primarily due to the limitations of the conventional fixed bed technology that has evolved over the past twenty or thirty years in the water treatment industry. Generally speaking, this technology is not well suited to the treatment and/or production of the fairly concentrated solutions encountered in metal finishing.

The advent of continuous counter-current ion exchange systems improved the technical feasibility of the ion exchange process somewhat but the high capital cost and complexity of these systems has severely limited their applications. A patented[1,2] ion exchange technique called Reciprocating Flow Ion Exchange or "RECOFLO" has overcome many of these limitations and expanded the range of application of the ion exchange process in this industry.

3. RECOFLO ION EXCHANGE

While detailed discussion of RECOFLO fundamentals is beyond the scope of this paper, it can be simply characterized by a number of features that distinctly set it apart from conventional ion exchange technology. These include;

1. Fine resins
2. Short beds
3. Low exchanger loadings
4. Countercurrent regeneration and rinsing
5. Liquid stratification in the bed
6. High flow rate
7. Short cycles

These features combine to improve the feasibility of the ion exchange process in the following ways;

1. smaller equipment
2. lower capital costs
3. improved regeneration and uptake efficiencies
4. ability to treat and produce concentrated solutions with minimum intermixing or dilution
5. short offstream times for regeneration eliminate the need for standby equipment.

As a result it has been possible to utilize ion exchange for a number of chemical recovery applications which were previously not feasible by conventional ion exchange. The RECOFLO technique has been utilized in a number of chemical recovery applications in the electroplating industry since 1971.

4. RANGE OF APPLICATION

Cation and anion exchange can be utilized for chemical recovery in a number of ways. A lesser known process called "acid retardation" is also finding wide application. These processes can be utilized by themselves, or in combination.

4.1 Cation Exchange

Cation exchange is applied in two main areas;

1. Removal of metallic cations from dilute rinsewaters. Regeneration of the cation resin with sulphuric or hydrochloric acid usually yields a more concentrated solution of the metal which can often be recycled to the process bath.

2. Removal of metallic cation impurities from concentrated process baths. Application of this sort are restricted to baths which are not too acidic, since uptake of metals onto the resin is poor under highly acidic conditions.

The use of cation exchange for removal of aluminum impurities from process baths has been limited in the past. This is because of the nature of the aqueous aluminum ion. An excess of acid representing several times the stoichiometric or theoretical dosage is normally required in the regeneration of strong acid cation resins. This excess acid must normally be neutralized prior to recycle or discharge of the spent regenerant solution. This problem is particularly acute for aluminum since the resin dramatically prefers the trivalent aluminum cation over the monovalvent hydrogen cation. The low equivalent weight of aluminum (i.e. 8.9) results in very low resin capacities for aluminum. Moreover, the high resin preference for aluminum further reduces resin working capacities so that frequent regeneration of the resin is necessary.

RECOFLO techniques have proven beneficial in overcoming these difficulties to a very large degree allowing the use of low exchanger loadings and relatively low regeneration dosages.

A number of RECOFLO "decationizers" have been used for removal of Al^{3+}, Cr^{3+}, Fe^{3+}, and Cu^{3+} impurities from hard chrome plating baths with excellent results. Experienced gained in this area has proven applicable in light metal work.

4.2 Anion Exchange

The main application of anion exchange has been removal of anions from dilute rinsewaters.

Regeneration of the anion resin is normally accomplished with sodium hydroxide to yield a concentrated sodium salt solution of the original anion. This recovered salt can be subsequently converted to the acid form by cation exchange if desired.

4.3 Cation/Anion Exchange

By combining cation and anion exchangers it is possible to completely de-ionize an aqueous solution. Apart from de-ionization of tap water, the main application of this process is purification of rinse waters to allow recycle of the water.

4.4 Acid Retardation

Some time ago[3] it was observed that certain polymeric resins would 'sorb' (ie. absorb/adsorb) strong acids such as sulphuric, hydrochloric, and nitric but would not sorb metallic salts of these acids. Desorption of the acid is readily achieved with water. By utilizing RECOFLO techniques it is possible to elute a purified acid product from the resin with no dilution of the acid strength. This process, known as acid retardation, is not as well known as cation and anion exchange and was in fact not commercially exploited to a significant extent until RECOFLO techniques were applied to the process in 1976.

The process has been packaged into a standard, skid mounted piece of equipment called an Acid Purification Unit or "APU".

There are two basic steps in the APU process (see figure 1). In the "upstroke" acid feed solution containing a metallic salt impurity is metered into the bottom of the resin bed. The free acid is sorbed by the resin and the metallic salt byproduct solution flows from the top of the bed. In the "downstroke"

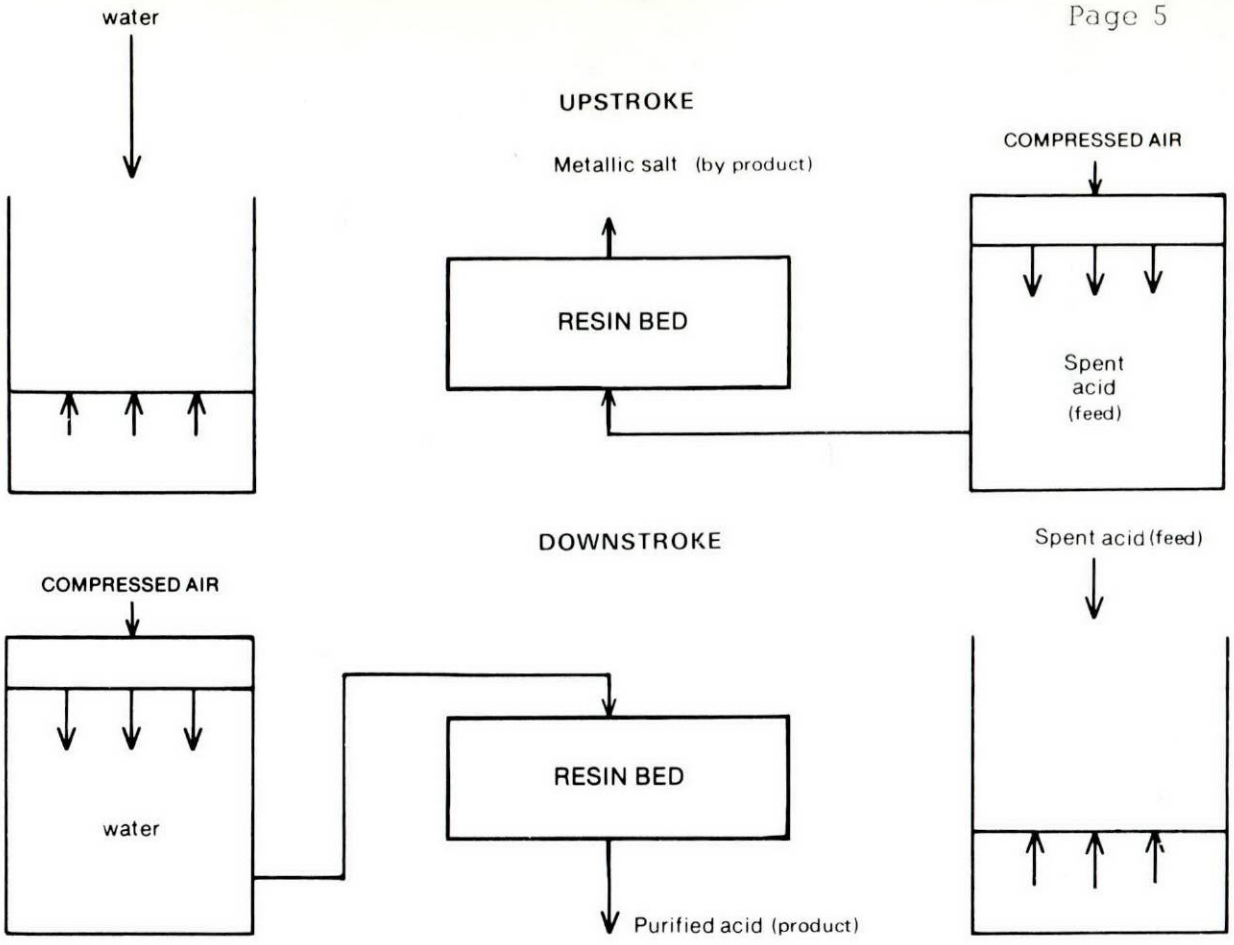


FIGURE I - APU Process

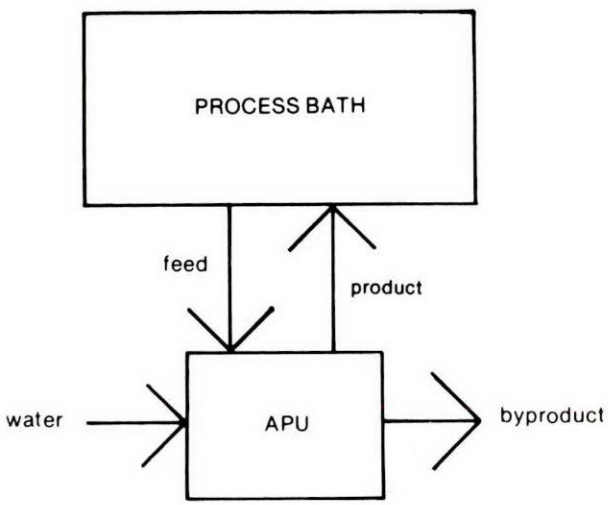


Figure 2 - APU Bath Purification

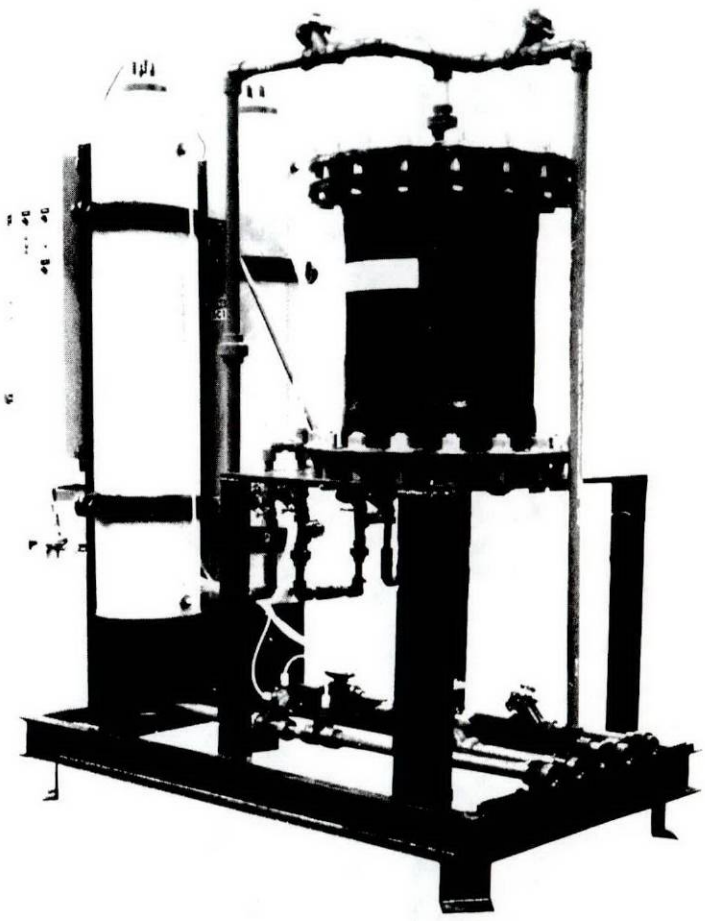


Figure 3 - AP16-24, Acid Purification Unit

DCU / APU BATH PURIFICATION

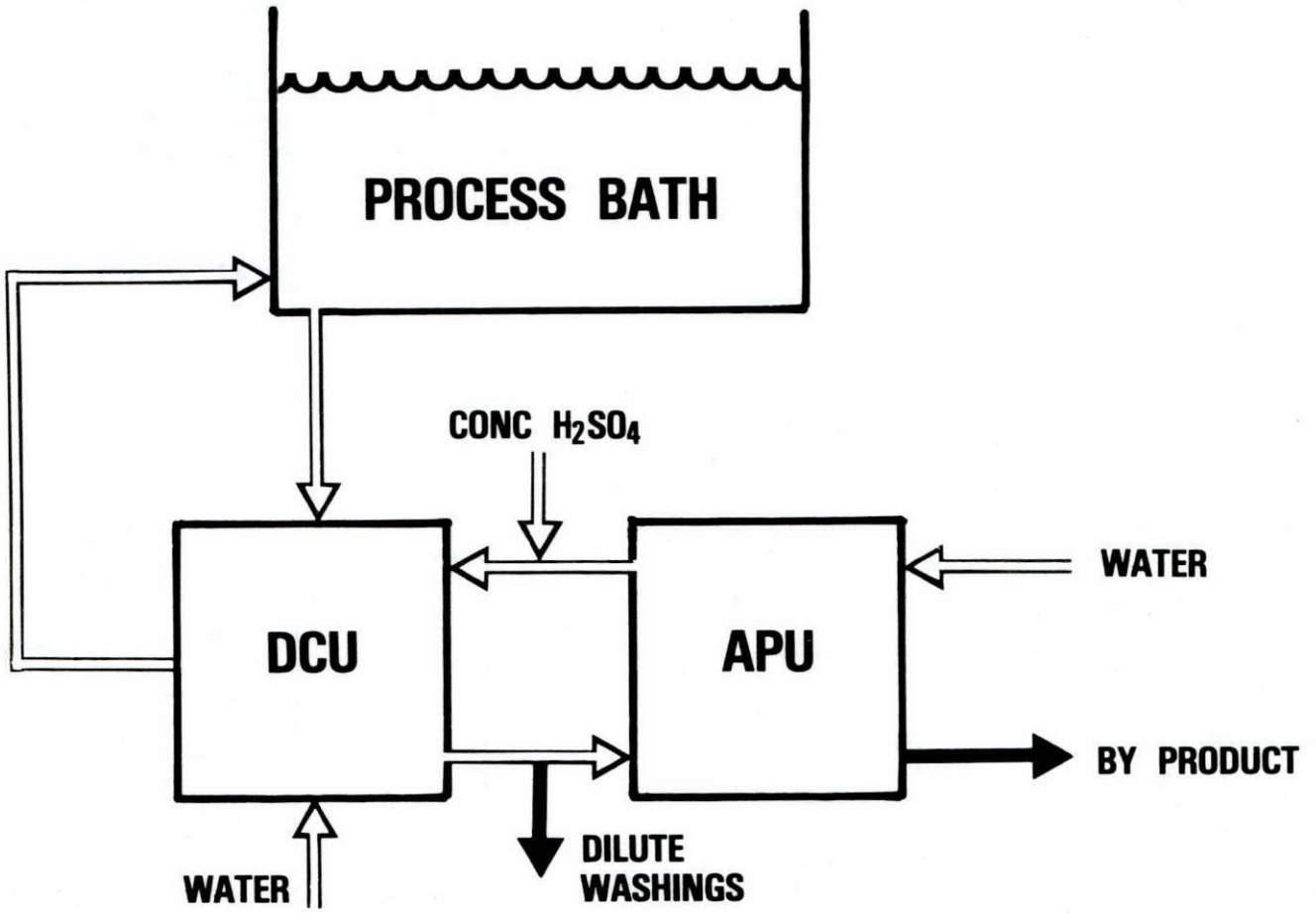


Figure 4

water de-sorbs the acid from the resin producing a purified acid product solution from the bottom of the bed.

The APU has seen application in two main areas:

1. Purification of strongly acidic process baths (see figure 2);

2. Recovery of excess acid from cation exchange regenerant solutions (see section 4.5);

The fact that only water is consumed in the process has made recovery of a number of relatively inexpensive acids feasible.

4.5 Cation Exchange/Acid Retardation

The APU provides an ideal means of recovering the excess acid from the cation exchange regenerant solution. The purified acid product from the APU can be re-fortified with a small amount of fresh concentrated acid and re-used for regeneration of the cation resin. The net result is that the regeneration can be accomplished with a dosage only marginally above the theoretical or stoichiometric amount. With the aid of an APU, cation exchange can be applied in areas which were previously not feasible.

Figure 4 shows the basic layout of a typical DCU/APU system. Contaminated process solution flows to the DCU and the purified process solution flows back to the bath. The DCU is periodically regenerated with acid and washed with water. The dilute washings flow to waste and the concentrated portion of the spent regenerant flows to the APU. The acid in the spent regenerant solution is retained by the APU and the impurities are rejected in the APU byproduct stream. Water elutes the acid from the APU which,after re-fortification with a small amount of fresh acid,can be reused by the DCU. The APU can be set up to remove 90% of the metallic impurities and recover about 90% of the free acid fed to it.

5. SULPHURIC ACID ANODIZING

Most anodizing is done in sulphuric acid electrolytes. In all of these baths dissolved aluminum tends to build up in proportion to the ampere hours of anodizing carried out. It has been estimated that, under normal anodizing conditions, 15 grams of aluminum are dissolved per square meter of work processed per hour of anodizing time[8]. Eventually the aluminum reaches a level where it impairs the process and quality of the film. At this point all or part of the bath must be discarded and replaced with fresh solution.

Utilizing the acid retardation principle, the APU can be used to continuously remove aluminum sulphate impurities from the bath.[4] By this means bath life can be extended indefinitely.

In March 1977, the first APU (see figure 3) was started up to purify a sulphuric acid anodizing bath. Since that time a large number of similar units have been installed around the world. Users of these units have reported a number of benefits associated with use of the APU including the following;

1. removal of phosphate and miscellaneous metallic impurities as well as aluminum.
2. savings in labour formerly required to decant and makeup fresh baths.
3. reduced alkali requirements for waste treatment.
4. reduced sulphuric acid purchases.
5. more uniform film thicknesses and reduced seal times.
6. lower operating voltage with corresponding electrical energy savings.
7. reduced cooling requirements.

Sulphuric acid anodizing baths containing other minor components such as boric acid, glycerine, glycolic acid etc. can also be treated by this method.

Figure 3 shows an APU that will remove 1.8 kg/h of aluminum while holding the sulphuric acid anodizing bath at about Al = 10 g/L. Typical operating data are shown in table 1.

TABLE I TYPICAL APU RESULTS - H_2SO_4 ANODIZING RECOVERY

	Flow rate (L/h)	H_2SO_4 (g/L)	Al (g/L)
Feed (bath)	298	183.8	12.2
Product	296	175.0	4.2
Waste	175	13.0	12.0
Water	173	0	0

6. INTEGRAL COLOUR ANODIZING

A variety of organic acids are used in the integral colour anodizing of aluminum including sulphosalicylic, sulphophthallic, boric etc. These baths are more sensitive to dissolved aluminum impurity buildup than conventional sulphuric acid baths and the aluminum content has to be maintained at a much lower level and within much closer limits. The higher replacement valve of these baths necessitates some means of impurity removal.

Rates of aluminum buildup in these baths have been estimated as 27 grams per square meter of work per hour of anodizing time (at 2.58 amp/dm^2)[9].

The lower free acidity of these electrolytes allows the use of cation exchange for aluminum removal and indeed conventional cation exchange has already been used extensively for this application. The large amount of downtime for frequent regenerations and the high regeneration dosages normally required allow considerable room for improvement however and the APU/DCU system as shown in figure 4 can be shown to process significant advantages in these respects.

7. PHOSPHORIC ACID ANODIZING

Falling somewhere between sulphuric acid and the organic acids in terms of acid strength, phosphoric acid anodizing baths can be purified by either an APU or DCU. Taking into consideration the relatively high value of phosphoric acid and the role of the phosphate ion as a pollutant, the best approach appears to be the DCU/APU type system as shown in figure 4.

Solution is fed directly from the bath to the DCU. Some dilution of the phosphoric acid may occur during treatment by the DCU. In this case a simple atmospheric evaporator that operates directly for the bath may be necessary to remove this excess water (see figure 13).

8. NITRIC ACID DE-SMUTTING

The APU has been used in the electroplating industry for removal of metallic impurities from nitric acid rack stripping baths.

Nitric acid baths, 20-50% w/w in concentration, are frequently used for de-smutting aluminum. The actual amount of metal dissolved in the acid is so low that only rarely does the bath have to be dumped because of metallic contamination. Usually the problem is one of maintaining the strength of acid in the bath.

The bath is constantly being depleted in acid strength due to dragout of acid and drag-in of water. Because these baths operate at room temperature and there are no evaporation losses, the only way to maintain bath strength is by decanting part of the bath and topping it up with concentrated acid. This is undesirable from several points of view.

1. the toxic nitrate ion cannot be removed by simple neutralization
2. alkali requirements for neutralization are high
3. handling nitric acid is hazardous

The APU has been successfully used in the electroplating industry for purification of nitric acid rack stripping baths[5]. No major modifications were required for this application.
The operating conditions of an APU can be adjusted so that the product is slightly higher in nitric acid concentration and lower in flow than the feed solution from the bath. The APU can then be used to remove water from the bath to allow makeup of fresh concentrated acid. Assuming one wants to maintain an acid strength of 35% w/w HNO_3 (50% vol.) and the dragout/drag-in rate is 0.12 litre/m^2 (3 US gal/1000 ft^2) then one must remove approximately 0.06 litres of water from the bath for each square meter of work processed.

An APU has recently been installed to remove 25 L/h of water from a nitric acid desmut bath. It was found that special attention must be paid to filtration of fine suspended solids in the bath solution for successful operation of system.

9. NITRIC AND HYDROCHLORIC ACID ELECTROCHEMICAL ETCHING

Dilute nitric acid and hydrochloric acid solutions, often with additions of various organic acids and/or small amounts of other inorganic acids, are used for electrochemically etching aluminum foils. These baths of course become contaminated with dissolved aluminum and must be frequently dumped.

Because these baths are often fairly dilute they may lend themselves to purification by cation exchange better than acid retardation. It is necessary to utilize an APU in conjunction with the decationizer to improve chemical regeneration efficiency sufficiently to make recovery truly viable. A large system of this type was recently delivered to a manufacturer of lithographic plates for removal of aluminum from a hydrochloric acid based solution.

10. PHOSPHORIC ACID BRIGHT DIPPING

Concentrated phosphoric acid based baths usually with additions of nitric, sulphuric, acetic and/or chromic acid are used to polish aluminum. After brightening, the adhering bright dip solution, now contaminated with aluminum, must be immediately rinsed from the metal with water. Typically 5-10 grams of aluminum are etched for each square meter of work processed. Due to the high acid concentration (ie. 70-80% H_3PO_4) and high viscosity, dragout losses are appreciable, typically 0.3-0.4 L/m^2 compared to about 0.12 L/m^2 for a "water-like" process solution.

The rinsewater can be reconcentrated to bath strength by evaporation but the aluminum contamination must be first removed before recycling to avoid fouling the bath. Most previous purification systems based upon cation exchange or acid retardation have failed, mainly because the cost of treating the final waste stream and disposing of the resulting sludge generated by the system was excessive. The DCU/APU system has greatly alleviated this problem.

A typical phosphoric acid recovery system is shown in figure 5. Concentrated rinsewater flows to the DCU where it is purified and then to the evaporator where it is concentrated to bath strength and recycled. The DCU is regenerated in conjunction with the APU as discussed in section 4.5.

The aluminum sulphate waste or byproduct produced by the system can be neutralized in the plant waste treatment system or concentrated by evaporation and sold as liquid alum.

Table 2 shows projected results when this approach is applied to recovery of dragout from a typical phosphoric/nitric bright dip operation.

Figure 6 and 7 shows a Decationizer and Acid Purification Unit respectively that will be employed in conjunction with an evaporator in a Japanese anodizing plant for recovery of a phosphoric/sulphuric acid bright dip solution.

The large recovery potential from processes of this type make recovery an extremely attractive proposition. When total operating costs of 4.3¢/lb are subtracted from a value of 20¢ per lb. for 80% phosphoric acid, an installation consuming 500 tons per yearsave up to $140,000 per year based upon a typical recovery efficiency of 90%.

PHOSPHORIC ACID RECOVERY SYSTEM

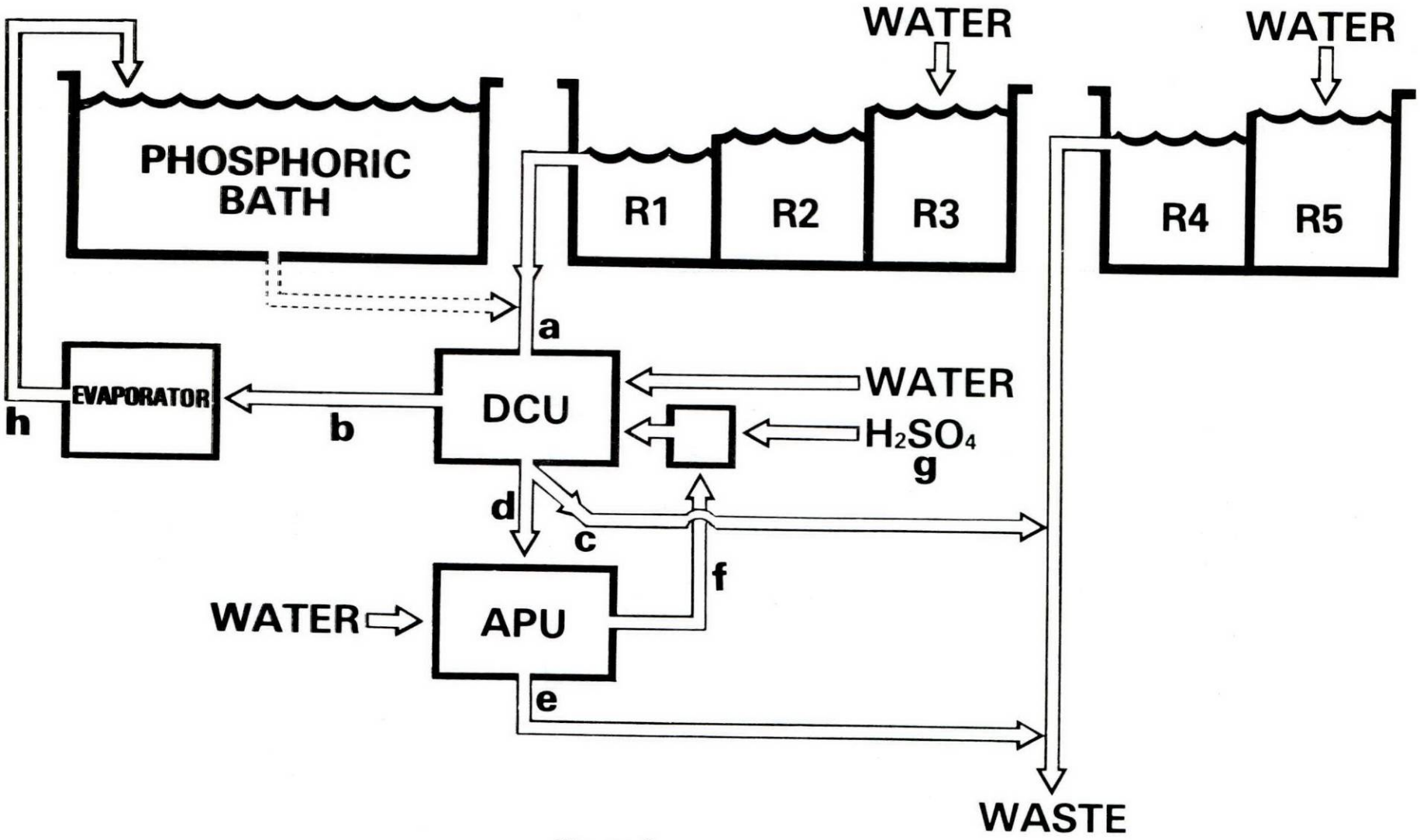


Figure 5

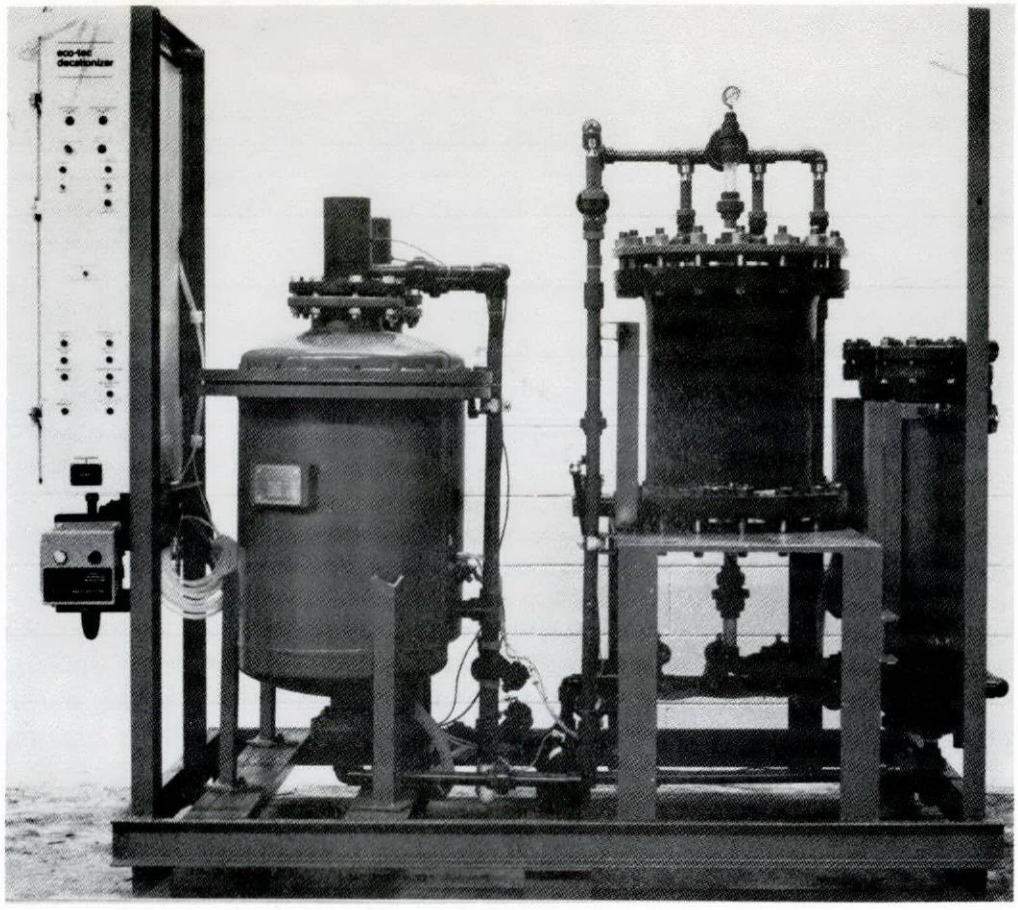


Figure 6 - DC16-D Decationizer for Phosphoric Acid Purification

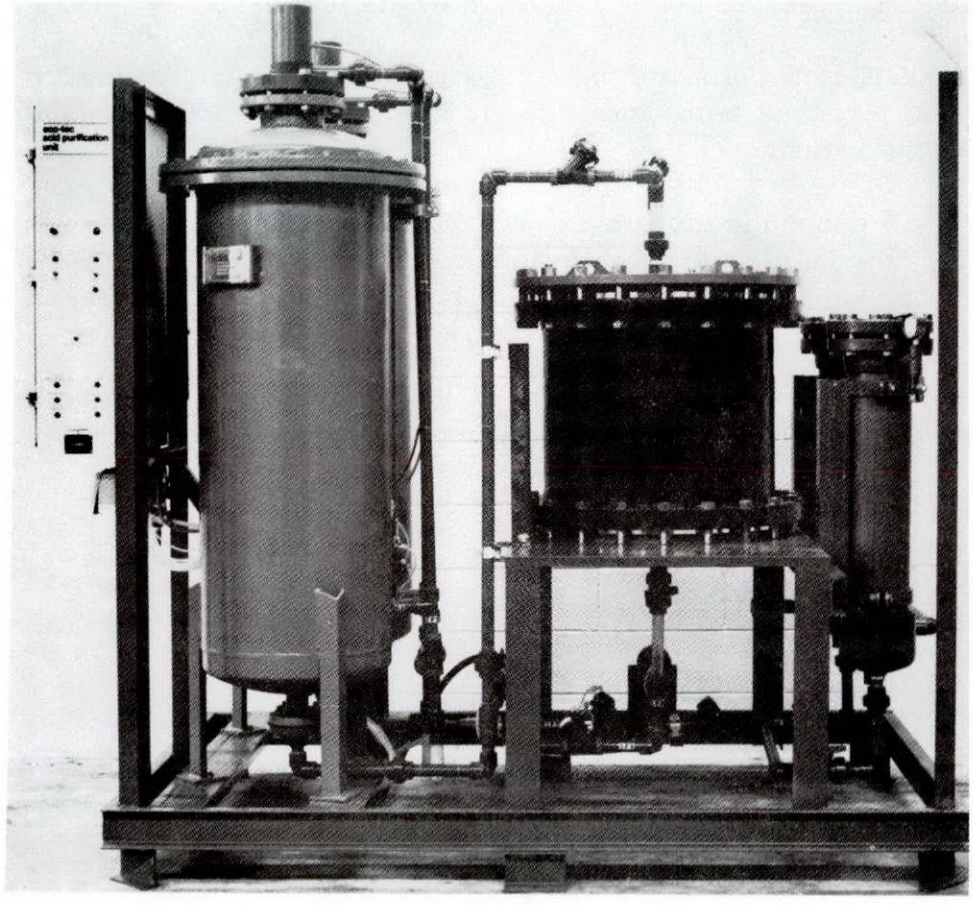


Figure 7 - AP24-24 for H_2SO_4 Regenerant Recovery

TABLE 2 - TYPICAL RESULTS - PHOSPHORIC/NITRIC BRIGHT DIP RECOVERY

	lb/lb 80% H_3PO_4	$lb. 80% H_3PO_4
66^0 Be sulphuric acid	0.229	$0.0069
lime	0.202	$0.0061
steam	5.65	$0.0226
sludge disposal	1.11	$0.0083
	TOTAL OPERATING COSTS	$0.043

11. CHROMATE PROCESSES

Chromate, either as chromic acid or the potassium (or sodium) salt is used in several aluminum finishing processes including chromic acid anodizing, conversion coating, de-smutting and dichromate sealing (see table 3). To avoid pollution hazards there has been a recent trend away from chrome based processes even though these baths are often better understood, easier to control, superior in performance and less expensive to operate than the chrome-free baths. The availability of viable chrome recovery systems suggest that a re-evaluation of any moves in this direction should be considered. Recovery of hexavalent chrome from plant wastewater not only reduces costs but make waste treatment easier and less costly thereby tipping the scale back in favour of the chromate process.

Pollution results from chromate processes in two ways; 1. dragout to rinsewater; and 2. process bath dumps due to contamination with aluminum and/or trivalent chromium.

Since 1970 ion exchange units using RECOFLO techniques have been used in over fifty chrome plating installations for recovery of purified chromic acid from rinsewaters and purification of hard chrome plating baths. This technology has been recently successfully applied to other chrome processes with excellent results.

TABLE 3 - CHROME BASED PROCESS FORMULATIONS

Anodizing

CrO_3 = 30-110 g/L

Conversion Coating

CrO_3 = 6-20 g/L
H_3PO_4 = 20-100 g/L
F^- = 2-6 g/L

De-smutting

CrO_3 = 35 g/L
H_2SO_4 = 185 g/L

Sealing

$K_2Cr_2O_7$ = 15-100 g/L
Na_2CO_3 = 4-18 g/L

11.1 Rinsewaters

The cation/anion exchange process is used for chromate recovery from rinsewaters. Actually, for chromic acid recovery a three bed cation/anion/cation process is often employed (see figure 8).

Rinsewater is first pumped through a cation "pretreater" bed which removes cationic metallic impurities such as aluminum and trivalent chrome and then through an anion bed which removes the chromate ion. The resulting deionized water is recycled back to the rinse tanks. The pretreater is regenerated with acid, discharging the contaminants to waste. Regeneration of the anion bed with sodium hydroxide yields sodium chromate, which when passed through the other cation bed is converted to chromic acid at a concentration of 7-10% which can be recycled back to the process bath. Figure 9 shows such a three bed chrome recovery unit.

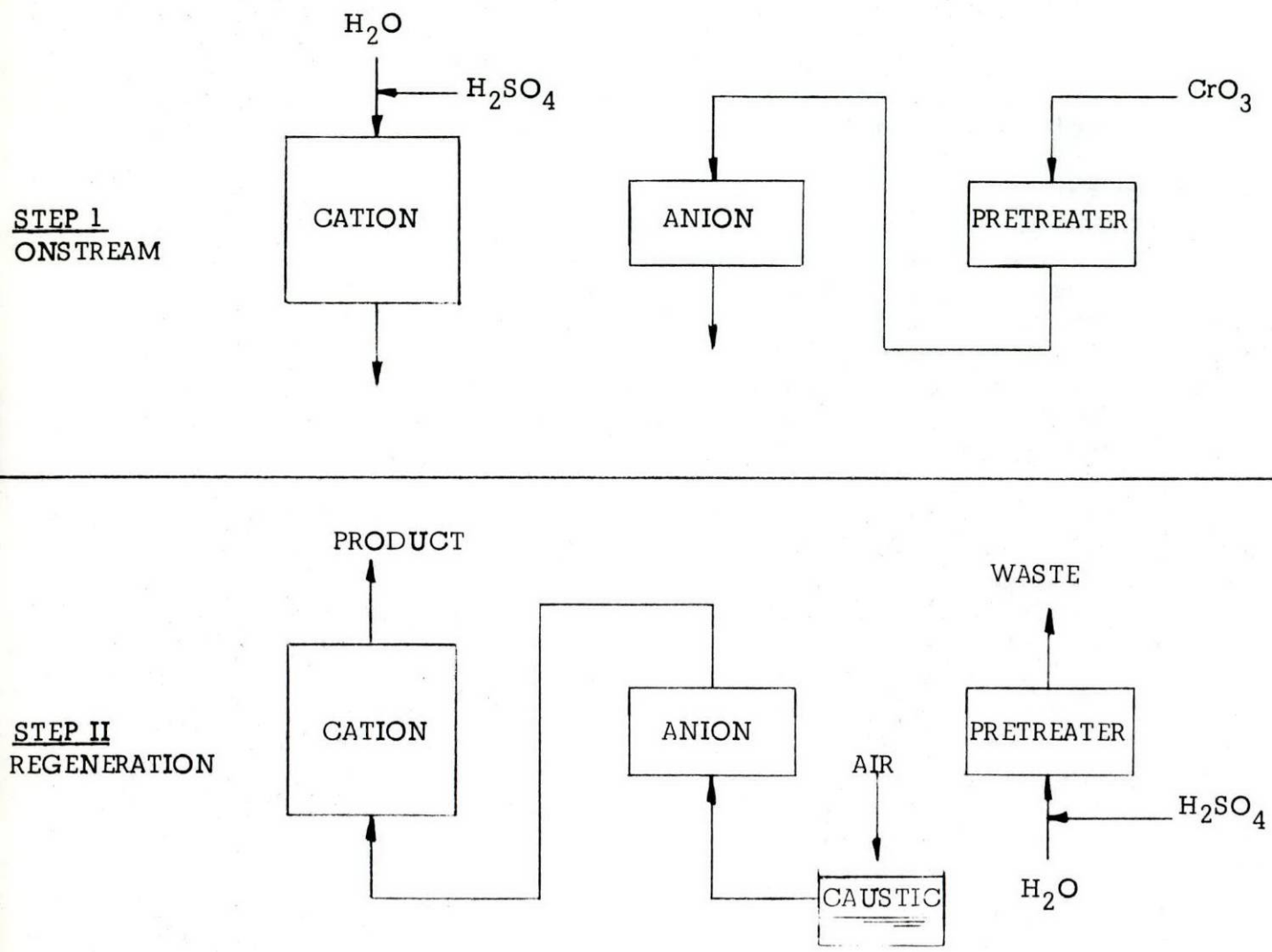
In cases such as the conversion coating and de-smutting baths shown in table 3, the chromate constitutes a minor portion of the bath's chemical inventory. For these processes it may not be desirable or economical to recover all of the constituents since the chromate not only represents the largest value but also the major pollution hazard. It is possible to selectively recover the chromate ion as a purified concentrate and allow the remaining components to flow to waste. In this manner both capital and operating costs can be reduced. This is possible since the dichromate ion is vastly preferred on the anion exchange resin to sulphate, phosphate, fluoride, nitrate or most of the other anions that may be present.

11.2 Process Baths

Chromic acid anodizing and conversion coating baths must be periodically dumped because of aluminum and/or trivalent chromium contamination. A Decationizer or DCU/APU type system can be used to continuously remove contaminants from the bath and extend bath life indefinitely.

It has been found that the presence of fluoride ion in conversion coating baths hinders the uptake of aluminum and trivalent chrome impurities on the cation resin. As a result, low exchanger loadings and high regenerant dosages must be employed. This problem is handled quite effectively by the methods discussed here.

FIGURE 8: CHROME RINSE RECOVERY



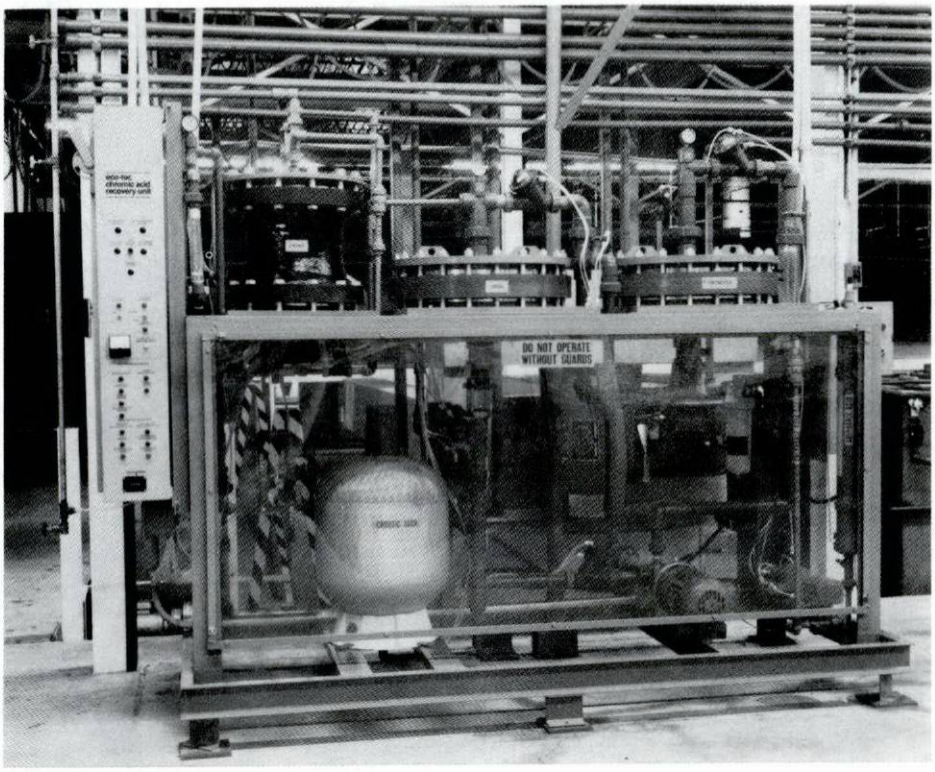


Figure 9 - Chromic Acid Recovery Units

12. ELECTROLYTIC COLOURING

A prime area where the possibility of reclaiming valuable metallic salts presents itself is in electrolytic colouring operations. Electrolytes based upon nickel, copper, cobalt or tin, frequently in conjunction with boric acid, magnesium sulphate, aluminum sulphate or various organic acids are used to electrolytically impart colour to the anodized surface.

Recovery of these metals from rinsewater is advantageous for two reasons. First of all, salts of cobalt and tin and to a lesser extent nickel and copper represent significant value. Secondly, plants discharging to a sanitary sewer are frequently allowed to discharge aluminum hydroxide but the presence of hydroxides of these heavier metals would preclude this practice and in any case make ultimate sludge disposal more difficult.

Numerous systems recovering copper and nickel sulphate from electroplating rinsewaters[7] have demonstrated that cation exchange systems can effectively recover metallic salts from rinsewaters. Only minor modifications were required for this application.

Careful sulphuric acid regeneration of a cation resin loaded with these metals yields a concentrated metallic sulphate solution at a pH of approximately 1-1.5. In the case of baths buffered to higher pH's, a modified APU (or "de-acidification unit (DAU)") can be used to raise the pH of the recovered product to bath operating levels.

Most of these baths operate near room temperature so that evaporation losses are negligible. Atmospheric evaporators that artificially increase bath evaporation at low operating temperatures must be used to allow recycle of the recovered metallic salt solution to the colouring bath.

Figure 10 shows a typical recovery system layout for an electrolytic colouring operation

Rinse flows from the first rinse tank through the decationizer (DCU) which removes the metals and discharges the purified rinsewater to waste. Deionized water is used to feed the rinses. Sulphuric acid regeneration of the DCU yields metal sulphate product which after de-acidification is collected and periodically recycled back to the colour bath. Bath solution is continuously recirculated through the atmospheric evaporator to remove water from the bath.

Figures 11, 12, and 13 show a decationizer, de-acidification unit and atmospheric evaporator used for recovery of a valuable metal salt from an electrolytic colouring system.

ELECTROLYTIC COLOUR BATH RECOVERY

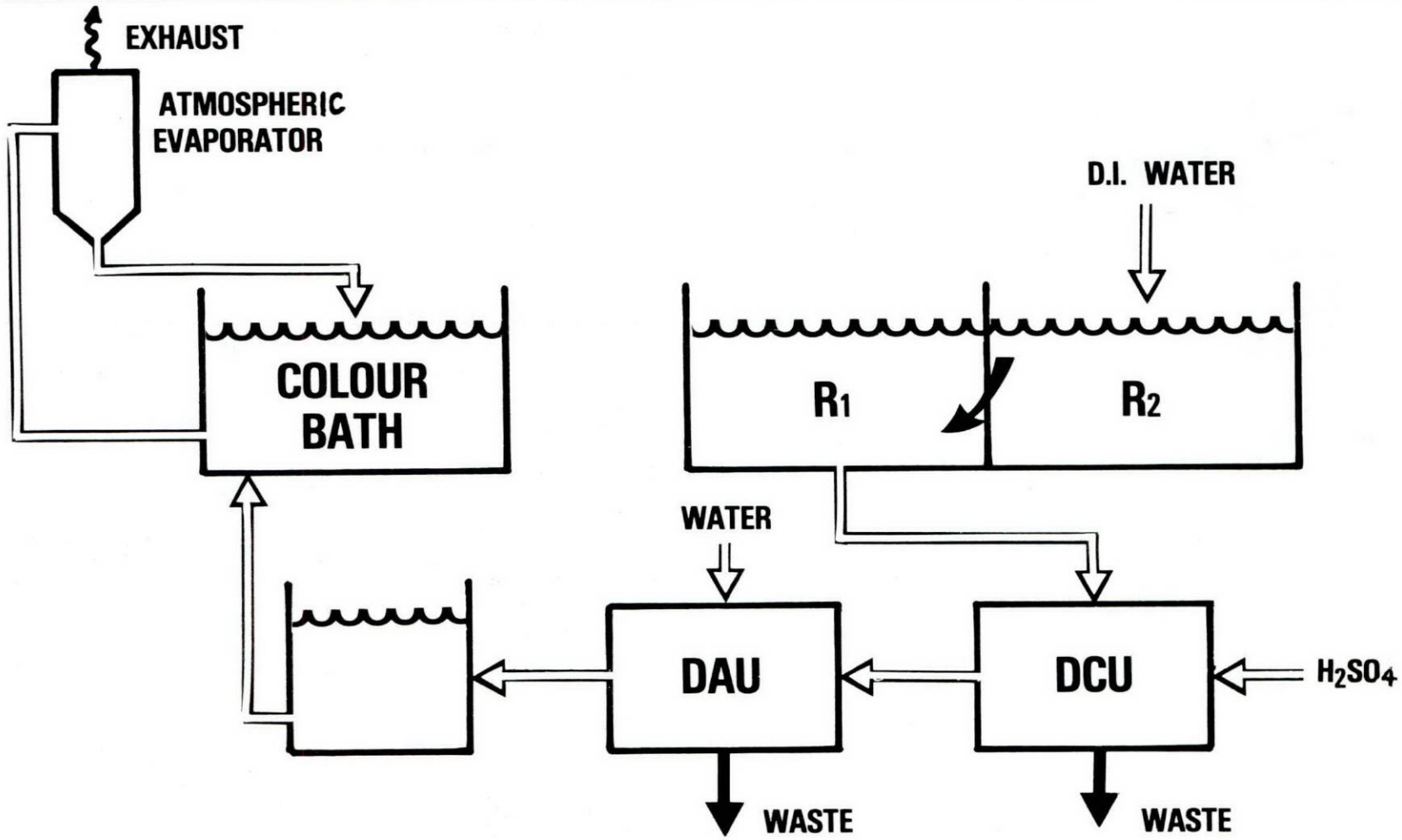


Figure 10

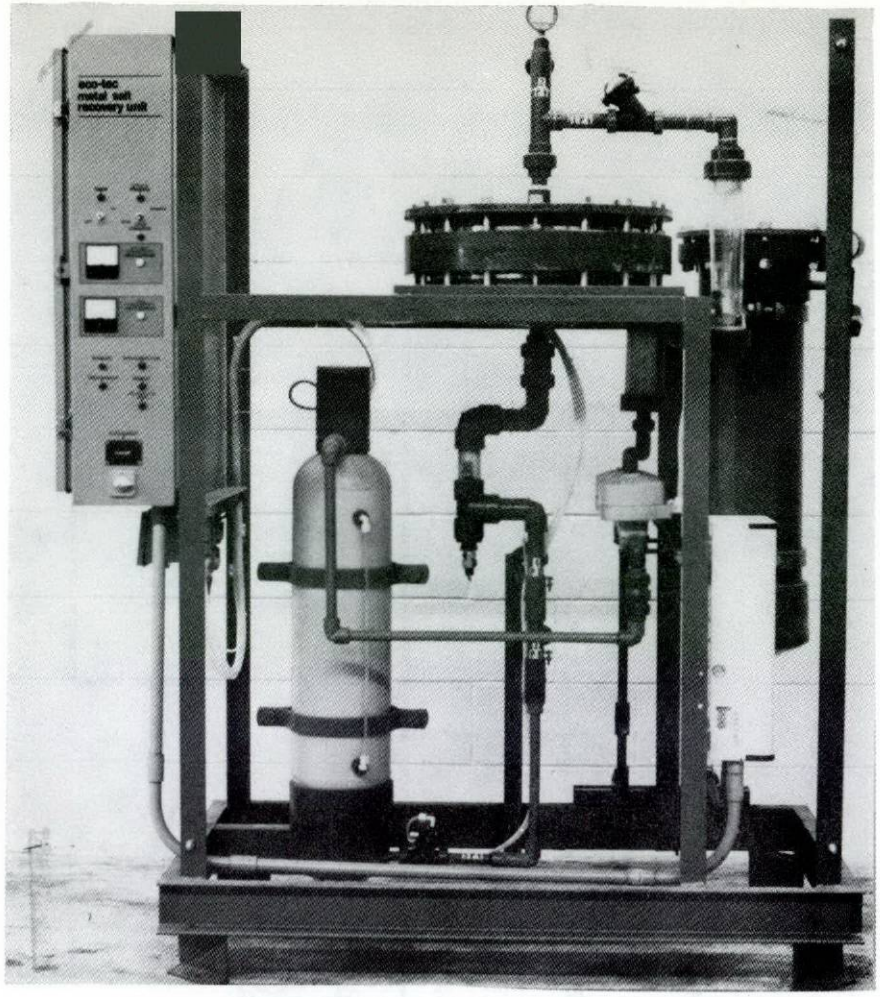


Figure 11 - Metal Salt Recovery Decationizer

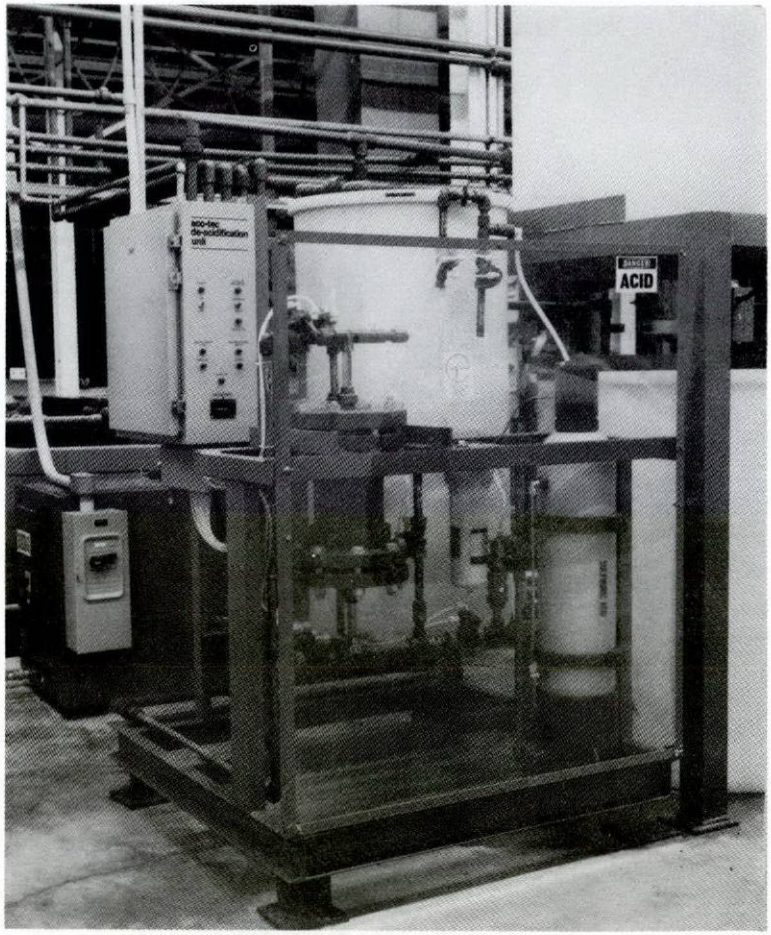


Figure 12 - De-Acidification Unit

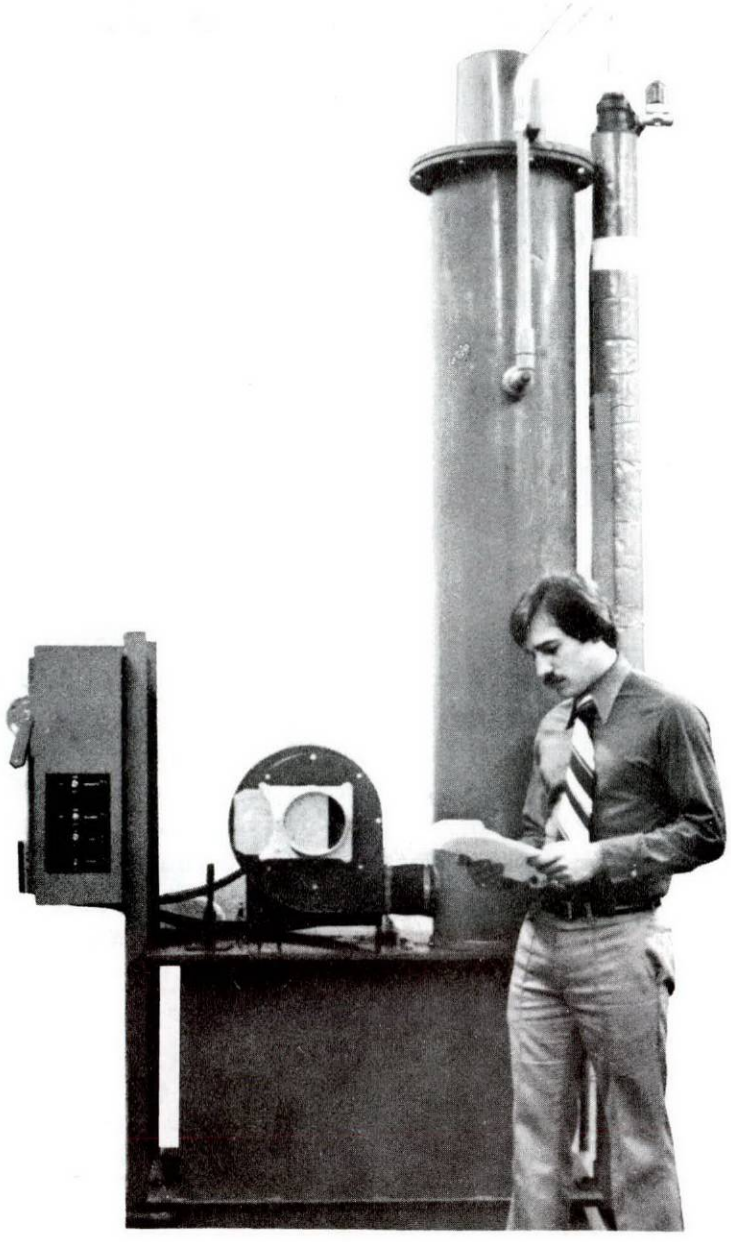


Figure 13 - Atmospheric Evaporator

13. WATER RECYCLE

Large quantities of water are consumed in rinsing work after each process bath. Most of the water can be easily de-ionized by cation/anion exchange and re-used. Indeed since de-ionized water is required for several rinses and makeup of many baths, the same unit can serve both purposes.

Recovery of rinsewaters in this manner simplifies waste treatment because it is much easier and cheaper to treat a concentrated, low volume stream than a dilute, high volume stream. Reaction tanks, reagent pumps and clarifiers are all reduced in size. Moreover, the character of sludge precipitated from a concentrated wastewater is generally superior to that produced from a dilute solution.

The nature of the rinsing process is such that typically only 10 per cent of the water is used to rinse 90 per cent of the chemicals from the work. Conversely 90 per cent of the water is consumed in actually rinsing only 10 per cent of the chemicals. Operating costs in ion exchange are mainly related to chemical loadings and only to hydraulic flows to a very minor degree. These two principles can be used to great advantage in designing a viable rinsewater recovery system.

The system shown in figure 14 illustrates this point. Although only one process step is shown, several processes would of course be tied in together in a similar manner. Conductivity controllers (CC) mounted in rinse tanks R1 and R2 control additions of water to the tanks. The first rinse R1 is maintained at about one tenth of bath strength through additions of a very small amount of water equivalent to about ten times the rate of dragout. Overflow from R1 flows directly to the waste treatment unit (WTU).

Desired final rinsewater purity in R2 is maintained through additions of large amounts of recovered water. The overflow from R2 flows to a de-ionizer or water recycle unit (WRU) where it is purified and recycled.

To facilitate monitoring and maintainance, the various conductivity controllers are best located in one central panel such as the one which is shown in Figure 15. (The other unit to the right is a central monitor panel indicating the status of the various recovery systems in the plant).

Automatic regeneration of the WRU may occur once or twice each hour for a period of only about 5 minutes if RECOFLO techniques are used, eliminating the need for a duplicate standby unit. Regeneration yields a low volume, concentrated liquid that flows to the waste treatment unit (WTU).

RINSEWATER RECYCLE

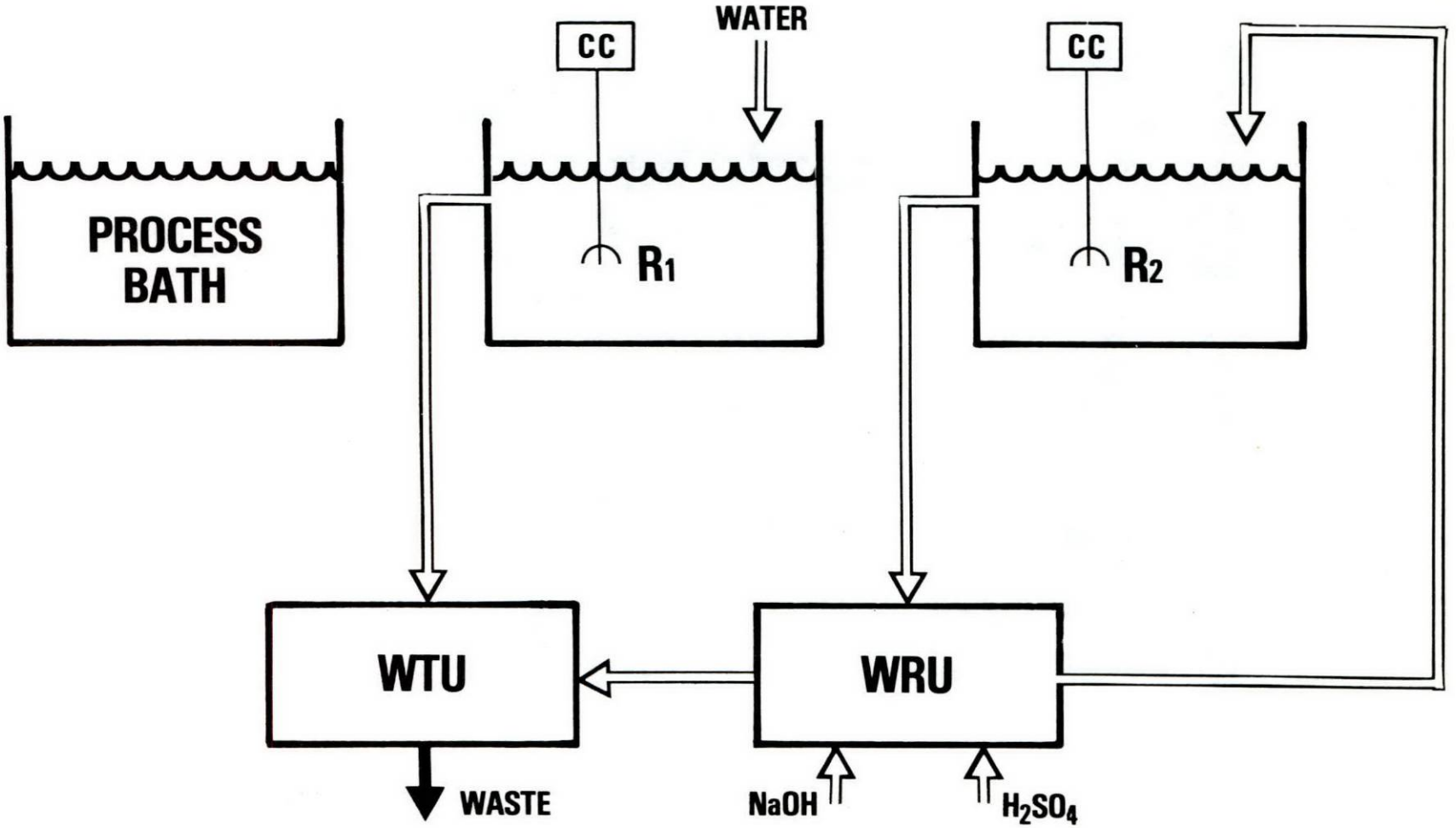


Figure 14

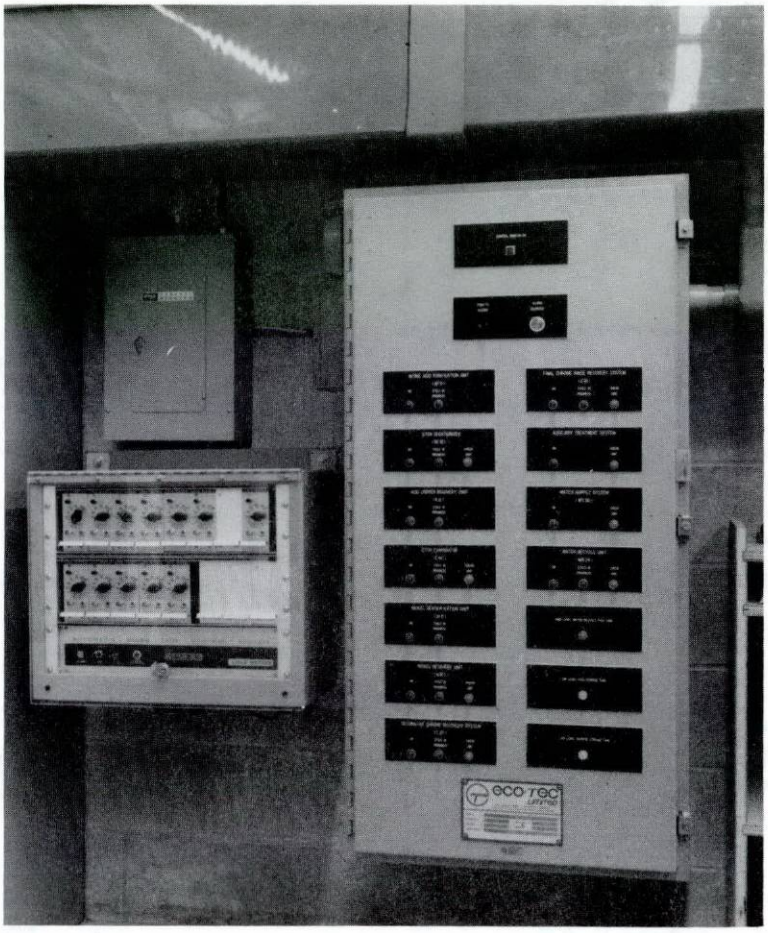


Figure 15 - Central Rinsewater Control Unit (left)

14. CONCLUSION

Technology for recovery of chemicals and water used in the finishing of light metals is now emerging and finding wide acceptance. In particular, a wide variety of recovery processes based upon ion exchange technology are now available.

Recovery of even inexpensive process baths such as sulphuric acid anodizing can be shown to be worthwhile when side benefits such as pollution control and process stabilization and improvement are considered along with direct economic savings. The benefits of recovery of more expensive and/or toxic chemicals such as chromic acid are even more pronounced.

Any existing or proposed new light metals finishing facility should seriously investigate chemical and water recovery as a means of abating pollution, reducing costs and improving their processes.

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C-2

LIGHT METALS FINISHING SESSION C

High-Performance Clear Coating

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HIGH PERFORMANCE CLEAR COATING

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ABSTRACT

A new technology has been developed to protect bright finished aluminum surfaces from corrosion. This technology involves a hybrid silicone/silica material which can be applied as a clear coating. The material combines the ease of handling and application of conventional paints with superior performance properties. The coating will maintain the bright appearance of the substrate aluminum against a wide variety of degrading environments including salt spray, humidity, and prolonged exposure to light.

Introduction

A new technology has been developed to protect bright aluminum surfaces from corrosion. This technology involves utilizing a new silicone/silica hybrid material as a clear protective coating.

This clear coating should be considered a very high performance coating in that it exhibits resistance to a wide variety of stresses; e.g., chemicals, humidity, heat, sunlight, etc., for extended periods of time. This coating allows bright finished aluminum alloys to be used in applications where they were not considered before because of their relatively quick appearance degradation, inability to be clear anodized or for lack of adequate clear coatings.

The Material

This new clear coating is comprised of a hybrid silicone/silica material carried in a solvent mixture. The solids/carrier concept corresponds to traditional paint technology. This allows the coating to be handled and applied like an ordinary paint while the material forms a clear coating with exceptional protective properties. The uniqueness of the technology lies in the nature of the hybrid material combined with the ease of handling and application.

The silicone/silica hybrid is formed by chemically bonding extremely small silica particles into a silicone resin matrix. The silicone portion imparts the traditional thermal and chemical stability of silicones. The silica part provides additional coating hardness and improves adhesion to aluminum. The excellent adhesion of the cured coating to aluminum is believed to derive mainly from the strong secondary bonding forces between the siloxanes and

silanols in the coating and the aluminum oxide present on virtually all aluminum surfaces.

The silicone portion of the hybrid does not act as a release agent. There is no danger of contamination of other surfaces by this material as there might be with silicone fluid species.

The carrier system is comprised of a mixture of organic solvents and some water. However, the water is there as a by-product. This is not a water based coating. The solvents act as both an application vehicle and in a stability role for the hybrid solids. The coating has a flash point exceeding 100°F which makes it non-red label for shipping and storage purposes. The coatings solids content may be varied from approximately 40% downward by the addition of more solvent. A 30% solids composition, based on weight, has been found to give the best combination of storage stability and application ease. The material is stable at this solids content in excess of six months at ambient temperature.

The solids/solvent nature of this coating allows it to be handled and applied by conventional paint techniques. Once manufactured, the material needs no further additions of any other components. It can be applied "straight from the can". Traditional mechanical application techniques such as air spraying, dipping, flowcoating, and even brushing can be utilized. Electrostatic spraying of this material has been shown to be an excellent way to maximize application efficiency. The coating cannot, however, be electrodeposited due to its incompatibility with the water necessitated by this method. Conventional equipment, methods and safety precautions can be used. No unusual corrosive or toxicological properties to this material are known to exist.

Primers, conversion coatings or special surface preparations are not needed for this coating. Best performance has been found when the material has been applied to clean, dry aluminum surfaces. Chromate conversion coatings, needed to provide adequate adhesion and corrosion resistance when organic finishes are used, will degrade the performance of the coating. This may be due to an insulating effect on the secondary bonding forces between the coating and the aluminum.

The coating must be thermally cured to attain its high performance characteristics. The cycle required is time and temperature dependent. The higher the temperature, the shorter the time required. The heat energy serves to crosslink or "set" the resin matrix. A cured coating has few residual locations for further chemical reaction. This yields a stable coating which does not "age". A typical cure cycle would be 30 minutes at 300°F metal surface temperature. This is in the range of high performance organic paints.

When this material is properly applied and cured, it forms a thin, clear, hard coating on the substrate aluminum. The cured coating may vary in thickness from less than .0001 inch to no more than .0008 inch. There is little apparent relationship between thickness and corrosion resistance although abrasion resistance is directly proportional to thickness. Cured

films of greater than .0008 inch in cross section form a great deal of internal stress which leads to film crazing and premature adhesion failure. The optimal cured coating thickness appears to be approximately .0002 inch. This is considerably less than the ∿.001 inch typical of organic coatings. A thinner film results in less distortion and dulling of the bright substrate surface. The coating is also exceptionally clear. Polished aluminum surfaces coated with this material show less than a 5% drop in total reflectance when compared to the original.

The coating material is hard, but, because of the thinness of application, the hardness of the substrate will have an effect on the hardness measurement. The coating on 3H pencil hardness aluminum will register a 3 or 4H pencil hardness. On 8H pencil hardness alloy, it will register 8 or 9H. In general, the perceived hardness of the coating will equal or exceed that of the substrate material. The coating is not very flexible and elongation of cured films is limited to ∿5%. This precludes all but the most mild post forming operations; thus, the coating is intended as a final process finishing step.

Coating Performance

Aluminum surfaces coated with this material can maintain this appearance through a wide range of corrosive environmental exposure. Laboratory tests of various types have been accepted by industry as quick methods to predict the performance of coatings in actual use for extended periods of time. Coated surfaces have performed exceptionally well in these sorts of tests. However, laboratory tests cannot always duplicate accurately all the degrading forces found in actual use. Objects coated with this material have also shown excellent results when subjected to actual use in their intended environments. Long term commercial usage of the coating is the final test of value. This has recently begun and will be reported on later in this paper.

Corrosion Resistance

The main reason for a protective clear coating on aluminum surfaces is to maintain the bright appearance of that surface during exposure to environments that otherwise would degrade it. The bulk properties of the aluminum are much less affected by corrosive exposure. This coating material does an exceptional job of maintaining the surface appearance of polished aluminum.

Test panels coated with this material have withstood over 1,000 hours of salt spray with no appreciable degradation. Panels and assorted objects such as wheels and bumper sections have withstood 44 hours of exposure to Copper Accelerated Acetic Acid Salt Spray (C.A.S.S., ASTM B368) with virtually no change. Test panels coated with this material have been subjected to Corrodokote testing (ASTM B380) with insignificant corrosion resulting. Coated panels exposed in Midwestern industrial environment for almost one year show only very slight corrosion.

An automotive manufacturer ran extruded aluminum bumper sections: one, a production anodized piece; the other, a buffed piece coated with this material, side by side in C.A.S.S. testing. Their specification at that time called for six hours of exposure with no more than six 1/8" spots of

corrosion evident. The coated bumper ran 96 hours before it exceeded this limit while the anodized bumper failed close to the specified six hour time. Another major Detroit automaker subjected a coated cast aluminum wheel to a 30,000 mile test track corrosion test. Thecoated wheel maintained the original appearance of the wheel much better than wheels coated with the current production organic clear coating.

Breaks in the coating, scribe marks or holidays allow corrosion to occur. However, it has been demonstrated that the corrosion does not spread preferentially along the coating/substrate interface as often occurs with conventional organic coatings. The corrosion remains localized at the site of the break in the coating. This can be attributed to the excellent adhesion of the material to thesurrounding aluminum surface.

Chemical Resistance

The highly inorganic nature of the cured coating would indicate a theoretically high degree of resistance to chemical attack. This conclusion is supported by test data. The coating shows virtually no affect from exposure to a wide variety of common organic solvents and chemicals. It possesses good resistance to a wide pH range of acidic and basic materials. However, strong acids or bases will eventually attack the coating.

Panels coated with this material have been immersed in a variety of common chemicals with no deleterious affect. Immersion for up to two months in gasoline, ethanol, methylene chloride, toluene, acetone, heptane, and 5% NaCl has had no effect.

Coated substrates have been exposed to a number (>>100) of wash cycles in an automatic dishwasher during home use with no deterioration. Coated panels have been boiled for eight hours in heptane, 5% aqueous acetic acid, 10% aqueous ethanol, and over 30 hours in water with no effect.

Moisture Resistance

Coatings derived from this new material exhibit excellent resistance to moisture which can frequently cause film failures in many coatings. Bubbling, swelling, hazing, loss of adhesion, and other detrimental effects caused by exposure to water or water vapor do not occur. The coating remains adherent and clear during extended exposures. Coated aluminum panels have withstood over 5,000 hours of exposure in a Cleveland Humidity Cabinet with no loss of adhesion or clarity. Panels have been boiled in water for more than 30 hours with no deterioration. Surfaces coated with this material have been immersed in 100°F water for more than 100 hours with no effect.

Resistance to Weathering

Both the material itself and aluminum surfaces coated with it have shown excellent resistance to deterioration from light. Coated panels have withstood over 1,000 hours' exposure in a QUV cabinet with no loss of adhesion, loss of clarity or other deterioration. Exposures in Atlas Weatherometer for well over 1,000 hours have given similar results. Buffed panels exposed

to concentrated sunlight in Arizona testing have shown less than 3% loss of reflectance after two million Langley's (cal/cm^2), equivalent to 8-12 years of exposure in a Midwestern climate. Coated panels exposed to an industrial environment, angled at 45° south, show no signs of chalking, checking, yellowing, or loss of adhesion after a year of exposure.

The highly inorganic nature of the cured film leaves little opportunity for photochemical degradation. The organic chemical species which are the potential sites for light initiated reactions, and thus film breakdown, are not significantly present in this material. The coating will not yellow as many organic clear coatings do.

Resistance to Thermal Degradation

The inorganic nature of the cured film allows the coating to withstand high temperatures without "burning". The ability of the silicon-oxygen-silicon bond found in silicones, to "absorb" temperature variations, coupled with the exceptional coating adhesion to aluminum allows the coating to suffer severe thermal shocks without deteriorating.

Coated panels have withstood cycling from $-70^{\circ}F$ dry ice/isopropyl alcohol to boiling water repeatedly with no loss of adhesion, crazing, hazing or other film failure. Scribed panels were immersed in the dry ice/isopropyl alcohol bath and, immediately upon withdrawal, subjected to 90 psig steam blasting with no rollback, hazing or loss of adhesion.

Aluminum cookware coated with this material has been in actual use for over six months on both electric and gas appliances. It has shown no degradation, browning or loss of adhesion even with direct contact on the electric range heat elements or gas flames.

Aluminum panels coated with the new hybrid material have been heat aged at $250^{\circ}C$ ($482^{\circ}F$) for more than two months with no coating degradation.

Resistance to Mechanical Degradation

The cured coating is highly crosslinked. This, coupled with the presence of the silica particles, makes the coating hard and abrasion resistant as compared to more elastomeric organic coatings. The degree of abrasion resistance relative to organic clear coating depends on the test method used on measurement criteria. Hard coatings perform better in some abrasion tests and softer elastomeric coatings perform better in others. The coating is not as hard or abrasion resistant as an equivalent thickness anodic film.

Coated panels subjected to SAE J400 Gravelometer testing have shown a loss of adhesion at the point of impact of the projected gravel. However, even after these panels were subjected to C.A.S.S. (ASTM B368) corrosion testing there was no creeping loss of adhesion or corrosion in places other than the original breaks in the coating.

Actual Use Testing

Two major areas where a clear protective coating for aluminum may be of commercial interest are housewares and automotive parts. These have received the greatest amount of attention in terms of performance evaluation although other areas are being investigated. Some large scale actual use tests have been initiated utilizing representative products in these areas.

In the houseware area, more than a dozen sets of cooking utensils, i.e., pots and pans, coated on the exterior with this material have been in use for from six months to over a year. The coated pieces have been exposed to both electric and gas heating, dishwashers and hand washing. The coating has remained clear and adherent. The coated polished aluminum areas show no signs of the appearance degradation that would normally be expected of bare aluminum utensils used in the same circumstances. A large scale consumer use test involving 100 coated fry pans is currently underway. This coating is not approved for food contact so the testing is restricted to exterior surfaces only.

Aluminum wheels are probably as harsh a testing substrate for a coating as can be found in the automotive area. Wheels are subjected to a large amount of road salt, mud, water and general abuse. If a coating can protect an aluminum wheel from degradation during actual use, then it should be more than adequate to protect bright aluminum used on other areas of an automobile such as bumpers and trim.

An actual use test involving coated, highly polished, cast and forged aluminum wheels has been in progress since January, 1979. These wheels have been mounted on taxis, salesmen's cars and trucks in several different locations in the Midwestern region. The test has accumulated over 3,000 vehicle days and over 200,000 total miles. The coating has performed very well; protecting the wheels from degradation caused by road salts, car washes, etc. The wheels still appear as shiny as when they were originally mounted. Uncoated control surfaces (aftermarket wheels are sold without a coating) are heavily corroded. This test will continue indefinitely.

A major Detroit automaker is currently testing coated wheels on its corrosion test track. Another earlier test involved a comparison between a wheel coated with this material and a wheel finished with the current production organic coating. These were run on the corrosion test track for 20,000 plus miles and resulted in the hybrid coated wheel maintaining a better appearance than the production organic coated wheel.

Another automaker is running an extensive test track and fleet use evaluation of aluminum bumpers coated with this material. Preliminary results indicate that the clear coating performs at least as well, if not better, than anodized bumpers while providing some improvement in initial appearance.

Initial Commercial Usage

This new material has been available on the market for a short time. Many firms are involved in evaluating the coatings for use as a substitute for currently used clear organic coatings or anodic finishing in applications where the organic coatings may give inadequate protection or the anodic finish may give more than is actually warranted. Many other firms are involved in reevaluating product concepts where this new coating could allow them to utilize a less expensive aluminum alloy (no need for a high purity alloy to facilitate clear anodizing) or to substitute one manufacturing process for another (polished, coated castings for anodized or coated sheetwork).

For example, a manufacturer of ovens for recreational vehicles had developed a new lightweight aluminum oven. The interior polished aluminum surfaces of the oven would badly discolor and stain during use. Utilizing this new coating, the maker was able to protect the aluminum interior and thus maintain the bright appearance of the oven interior while marketing a lightweight item ideally suited for the weight-conscious RV industry.

A West Coast manufacturer of automotive accessories is selling a motorcycle luggage rack utilizing this coating. Instead of anodizing the aluminum extrusion, it is polished and then clear coated at a cost savings.

Aftermarket aluminum pickup and van bumpers are being coated by a manufacturer in the Midwest. These were previously clear coated with an organic or anodized. This new, clear coating gives increased corrosion resistance with better appearance than the organic coating at less cost than the anodizing.

A major cookware manufacturer has a specialty egg cooking appliance which utilizes this new coating. On it, both the heating and the heated surfaces are coated. This protects the aluminum from the discoloration caused by cleaners while allowing a brighter finish on the metal itself for eye appeal.

Another product poised for entry into the marketplace is polished brass beds finished with the coating. A manufacturer has completed evaluation with very satisfactory results. The appearance of brass coated with this material is superior to that coated with organic clears. The material also withstands all the common household chemicals that it may come in contact with; such as soda pop, hair spray, and nail polish remover and because of its thermal stability, resists degradation from cigarettes accidentally left on its surface.

You can see that this new hybrid material opens up new opportunities for aluminum and aluminum finishers. The unique combination of ease of handling and application, similar to conventional paints, coupled with its extraordinary protective properties allows aluminum to be utilized in applications not readily accessible to it before. Polished cast aluminum may be used in corrosive environments where before, because of its inability to be clear anodized, it could not. Coated bright aluminum sheet and extrusions can be used to replace chrome plating in some applications because the bright appearance can now be maintained.

The material gives an alternative finish method for aluminum. It enables different and more cost-efficient alloys to be used because they do not necessarily have to be clear anodized. It also provides an alternative finish to anodizing when corrosion protection is important and organic clears are inadequate. This material is a new technology which opens up new opportunities for the aluminum industry and aluminum finishing.

C-3

LIGHT METALS FINISHING SESSION C

Formation of Barrier-Layer Anodic Oxide in Simulated Electrodeposition Primer Electrolyte

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Abstract

Anodic aluminum oxide films were formed on 1199, 3105, 3004 and 5182 in electrolytes containing succinic, acrylic and malonic acids neutralized to pH 7 and 9 with 2(dimethylamino)ethanol to simulate the anodic reactions thought to occur on anodic deposition of organic primer film.

Current efficiencies for anodic film formation were determined as a function of metal pretreatment. Current efficiencies were low for 3004 and 3105 and were lowered slightly by chromium(III) and chromium(VI) pretreatments. The pretreatment films were largely unaffected by the anodizing.

The film and aluminum consumption weights as a function of weight gain on anodizing showed the films in all cases to be non-porous, close to Al_2O_3 in composition, with a small, nearly constant hydrated oxide layer near the outermost surface.

Introduction

Electrodeposition of organic resin primers are becoming increasingly important in commercial practice. Films may be deposited both anodically and cathodically. The film deposition itself is a secondary reaction resulting from surface pH change brought about by the primary electrode reaction.

An anodic electrodeposition primer solution/dispersion contains a resin which may typically be an acrylic polymer containing carboxylate groups in the polymer chain. The baths typically are operated at an alkaline pH. Deposition of primer films occur when the carboxylate anionic groups are acidified on encountering hydrogen ions generated by the primary electrode reaction which may be either formation of anodic aluminum oxide or oxidation of water, each of which produce one equivalent of hydrogen ion per faraday of charge.

The mechanisms of film formation have been studied extensively (ref. 1-4). Most of the work has been reported for steel substrates, however, and little attention has been given to an examination of the primary electrode reaction or to the formation of films on aluminum. In this paper we describe experiments designed to study the primary electrochemical reactions occurring

during the anodic polarizations of aluminum under electrolyte conditions comparable to those in an anodic electrodeposition of organic resin.

Experimental

Alloys investigated were those important in the coil coating industry, 3004, 3105 and 5182, in addition to 99.99% aluminum (1199) used as a comparison standard.

The electrolyte was designed to simulate a commercial electrodeposition primer electrolyte as closely as possible except that it contained no resin. The electrolyte function of the resin was replaced by a low molecular weight carboxylic acid. Acrylic, malonic and succinic acids were investigated. All gave essentially the same results and most of the work reported here was with solutions containing succinic acid. Four liter aqueous baths were used containing 1% n-butanol, 0.5% butylcellosolve, 0.04 eq/l carboxylic acid and 2(dimethylamino)ethanol to raise the pH to 7 or 9. The bath temperature was 25 or 45°C in most experiments.

The bath contained two stainless steel cathodes positioned about 1.3 cm on either side of the anode. The cathode to anode area ratio was about 4.5. Minimal stirring was used only to maintain a uniform bath temperature.

The anodes were foil or thin sheet flag-shaped electrodes approximately 30 cm^2 total area. The electrodes were immersed to a point just above the main electrode body on the flagpole. Precise areas were measured with a micrometer after anodizing. No adverse solution-air interface effects were observed.

Currents and voltages were recorded with time on a recorder having a time response of 0.5 sec. full scale. The charge was obtained by numerical integration of the current-time curves.

Each run consisted of 10 to 14 specimens anodized at about 0.5 sec. intervals. The pre-set maximum voltage was 90-100 volts. At first the voltage rises linearly at constant current to the maximum value, then the current decays to a low value at constant voltage. The specimens were anodized at intervals chosen so that most of them would be at constant current, but several were anodized longer, well into the current decay period.

The specimens were cleaned in inhibited alkaline cleaner, immersed for two min. in 50% nitric acid, pretreated, rinsed in distilled water, then in methanol, and air dried. They were weighed to ±2μg in this state (W_1), after anodizing (W_2), and after film removal (W_3) in a solution containing 35 g/l CrO_3 and 20 ml/l H_3PO_4 at 85°C.

The pretreatments studied were two-minute immersion in the CrO_3-H_3PO_4 solution at 85°C; five-minute caustic etch (50 g/l NaOH at 57°C) followed by two minutes immersion in 50% HNO_3; 5, 10 and 15-second immersion in an amorphous chromium phosphate conversion coating bath (designated the chromium(III) bath); and a 10-second immersion in an accelerated chromate conversion coating bath (designated the chromium(VI) bath).

In one series, specimens were cut for examination by transmission electron microscopy. Specimen weights were corrected for this small tab. Ultramicrotome slices of cross sections were examined at a magnification of 100,000X. A number of slices from each specimen were examined. The cleanest slice from each specimen was used for thickness measurement and an average of eight thickness measurements was taken for each photograph.

In one series with 1199, films were formed in a 5% solution of ammonium pentaborate in ethylene glycol. This electrolyte is known to form films at 100% current efficiency, and this experiment served to verify the experimental technique.

Results

Figures 1 and 2 show the film and aluminum consumption weights versus total charge and the film weight versus aluminum consumption on 1199 in succinate solution at 25°C with an initial current density of 13.9 ma/cm^2 and a maximum cell voltage of 100 volts. This experiment used the CrO_3-H_3PO_4 pretreatment which generally gave the most clean and reproducible surface. The solid lines of figures 1 and 2 are the theoretical values. In this experiment the current efficiency was very close to 100% for both aluminum consumption and film weight and the film is very close to Al_2O_3 in composition.

Figures 3 and 4 show the same experiment but at 40°C. The numbers by each point on figure 3 are the total anodizing time in seconds. About 8 seconds were required to reach maximum voltage in this experiment so the last three points represent specimens anodized into the current decay period. For up to about 11 seconds the results conform very closely to theoretical 100% current efficiency and to a film of composition, Al_2O_3 with no porosity. Beyond 11 seconds the film formation current efficiency falls below 100% and the ratio of film to aluminum consumption falls below the theoretical 1.89. This can only be interpreted as the beginning of pore formation.

The current decay curves were analyzed according to the theory of Dignam (ref. 5). Dignam showed that non-steady state conditions of current decay can be used to obtain steady state kinetic parameters for film growth. The current decay rate is given by

$$(1) \quad i_o/i = BVi_o ft/D^2 + 1$$

where i_0 is the initial current density, B is the inverse Tafel slope, V is voltage drop across the film, D is film thickness, t is the time from the beginning of current decay and f is a constant given by $f = M/ZF\rho$ where M/Z is the equivalent weight of the film, F is the faraday constant and ρ is film density. We assume M/Z = 17 and ρ = 3.2 g/cm^2 so that f = 5.5 x 10^{-5} cm^3/amp-sec. In Dignam's theory, B is an inverse function of the field, E = V/D so that the term in BV/D^2 in equation 1 is approximately constant. This permits evaluation of B from the slope of plots of i_0/i versus t. The parameter, B, is given by

$$(2) \quad B = -2u_s{}^2E/C\emptyset kT + u_s/kt$$

where u_s is an ion jump distance, C$\emptyset$ is an activation energy at zero field, k is the Boltzman constant and T is absolute temperature.

Figures 5 and 6 are plots of i_0/i versus t for the ammonium borate electrolyte and the succinate electrolyte at various values of the initial current density. Values of V_{film} were estimated by extrapolating the linear voltage rise vs t curves to zero time to obtain the solution voltage drop. Values of film thickness were obtained coulometrically from the relation,

$$(3) \quad D = fQ/A$$

where Q is the total charge and A is specimen area. The validity of this treatment is shown by a comparison of TEM and coulometric values for one series in figure 7. From the slope of i_0/i versus t plots B values were calculated for each point on the decay curves. These are plotted versus the field as shown in figure 8 from which the kinetic parameters, u_s and C$\emptyset$ may be obtained. Values for the ammonium borate and succinate electrolytes are tabulated in Table 1. Agreement with those obtained by Dignam is satisfactory for the borate electrolyte, and for the succinate electrolyte at the lower pH.

Table 1

Electrolyte	u_s (eÅ)	C$\emptyset$ (ev)	Reference
ammonium borate	25.0	7.08	5
ammonium borate	28.3	7.7	this work
succinate, pH 9, 25°C	17.7	4.3	this work
succinate, pH 7, 45°C	24.2	5.6	this work

The effect of temperature on the rate of current decay is shown in figure 9. These results suggest that porosity begins to form, as expected, much earlier in the current decay period at higher temperature.

The formation of anodic films on the alloys is typified by the curves of figures 10 and 11, for 3105 alloy with a CrO_3-H_3PO_4 pretreatment. Here the solid lines represent a linear regression fit to the linear portions of the data. Three additional features are apparent when compared with 1199, 1) the intercepts are not zero, 2) the slopes in figure 10 are less than theoretical, 3) deviations from linearity occur in the plots of film weight, aluminum consumption and weight gain on anodizing. The points close to linearity are all during the constant current portion of the program and the deviations occur during the current decay portion. The plot of film weight versus aluminum consumption is linear over the whole range of data, however, and the slope is close to the theoretical 1.89. This suggests that the reduction in coulombic efficiency in this case is due to oxygen evolution at the expense of film formation, and not to a film porosity. The reduced slope of the coulombic plots suggests that oxygen evolution occurs concurrently with film formation over the entire range of the experiment and that when film formation current decays, oxygen evolution becomes predominant. Also, the non-zero intercept suggests an initial film which subsequently is removed along with the anodic oxide on stripping.

It is also useful to plot the film weight and the aluminum consumption as a function of the weight gain on anodizing. This is shown in figure 12. The intercept at $t = 0$ should give the initial foreign film weight. The value is $3\mu g/cm^2$ compared to values of 6 and 5 for the intercepts of film weight and aluminum weights versus Q in figure 10.

Caustic etch pretreatments on the 3000 series alloys magnify the decreased anodic oxide coulombic efficiency as shown in figure 13. Here the break in the curve occurs during the constant current part of the program and coincides with a decrease in the rate of voltage rise. A plot of film weight versus aluminum consumption for this experiment (not shown) was linear over the entire range, again with a slope close to theoretical indicating a film close to Al_2O_3 with no porosity.

Examination of the surface of an etched 3105 specimen by scanning electron microscopy showed that etching exposes large constituent $MnAl_6$ particles which protrude several hundreds of angstrom units above the surface and evidently serve as oxygen evolution sites; however, they do not become active as such until the anodic oxide has grown to about 400-500Å thick.

The effect of reduced coulombic efficiency for oxide formation is shown also by the rates of current decay for 3004 alloy shown in figure 14 for various pretreatments. The effect is shown both by the reduced rates of current decay and by the higher current at the end of the experiment. The coulombic

efficiency for film formation can also be estimated by comparing the coulombs flowing at constant current for a given system to that for 1199 metal with a CrO_3-H_3PO_4 pretreatment for which the efficiency is 100%. The efficiency is given by Q(1199)/Q(alloy).

The results of all experiments are given in Tables 2-5. Tables 2 and 3 are the results of plots of film weight, aluminum consumption and weight gain versus coulomb and Tables 4 and 5 are the results of plotting film weight and aluminum consumption versus weight gain and film weight versus aluminum consumption.

Discussion

Examination of Tables 2 and 3 permits the following generalizations. 1) The current efficiency for 1199 was close to 100% with all pretreatments. 2) The experimental error to the 95% confidence limit is lowest in almost all experiments with the CrO_3-H_3PO_4 pretreatment. 3) The current efficiency for 3004 and 3105 is low for all pretreatments (40-70%). 4) The current efficiency for 5182 is intermediate between the 3000 alloys and 1199 (60-90%). 5) The Cr(III) pretreatments have a slightly greater effect on lowering the current efficiency than Cr(VI) pretreatments. 6) The current efficiencies for anodizing at pH 9 are slightly lower than for pH 7. 7) Etching of 3004 and 3105 reduces the current efficiency drastically because of exposure of oxygen evolution sites. Judging from the current-voltage-time curves the Cr(III) pretreatment results in a similar but smaller effect.

The weight relationships can be analyzed in the following way.

1) $W_1 = A_1 + S$

2) $W_2 = A_2 + F + S$

3) $W_3 = A_2$

4 a. $\dfrac{F}{A_1 - A_2} = 1.89$

b. $\dfrac{F}{W_2 - W_1} = 102/48 = 2.125$

c. $\dfrac{W_1 - W_3 - S}{W_2 - W_1} = 54/58 - 1.125$

where: S = pretreatment film weight

A_1 = initial true weight of aluminum specimen

A_2 = final true weight of aluminum specimen

F = true Al_2O_3 film weight

W_1 = initial experimental weight

W_2 = anodized experimental weight

W_3 = stripped experimental weight

All weights are expressed in $\mu g/cm^2$. The apparent values of film weight, aluminum consumption and weight gain on anodizing are $W_2 - W_3$, $W_1 - W_3$ and $W_2 - W_1$, respectively.

Equation 1 states that the initial weight measures the initial aluminum plus the pretreatment film. On anodizing the experimental weight consists of a smaller aluminum weight (A_2) plus the anodic film plus the pretreatment film assumed to be unchanged by anodizing (equation 2). The final weight is just the stripped aluminum, A_2 (equation 3). Equations 4 a, b, and c, express the three ways of writing the formula weight ratios of Al_2O_3. Solving 1, 2, 3, and 4 a, b, or c to eliminate A_1, A_2 and F gives

5 a) $W_2 - W_3 = 1.89(W_1 - W_3) - 0.89S$

b) $W_2 - W_3 = 2.125(W_2 - W_1) + S$

c) $W_1 - W_3 = 1.125(W_2 - W_1) + S$

The relations in Tables 4 and 5 represent these slopes and intercepts, and in most cases the fit is satisfactory.

The weight-coulomb relationships can be obtained in a similar way. They are

6 a) $W_2 - W_3 = 176.3\ Q + S$

b) $W_1 - W_3 = 93.3\ Q + S$

c) $W_2 - W_1 = 82.9\ Q$

These equations imply that the intercept values, b_{FQ}, b_{AQ}, b_{FG} and b_{AG} should all have the same value, S. They do not. The values are always in the order $b_{FQ} > b_{AQ} > b_{FG} = b_{AG}$. The simplest postulate to account for this discrepancy is a slight degree of hydration. We must assume that in any one series of films the absolute water content of the films is a constant. This would be the case if the water were contained in a constant layer at the outermost surface of the film and perhaps can be regarded as a sealing effect, a reaction of the normally anhydrous oxide at the outermost surface with water. This postulate is supported by the data of figure 1. In this experiment at room temperature there is no intercept anomaly but at the higher temperature of the other experiments (45°C) the extent of such a hydration would be expected to increase.

To incorporate this effect into the weight relationships

the following modifications must be made, letting H = weight of incorporated water (in $\mu g/cm^2$)

1) $W_1 = A_1 + S$ (no change)

2) $W_2 = A_2 + F + S + H$

3) $W_3 = A_2$ (no change)

4 a) $\frac{F}{A_1 - A_2} = 1.89$ (no change)

b) $\frac{F}{W_2 - W_1 - H} = 2.125$

c) $\frac{A - A}{W_2 - W_1 - H} = 1.125$

The results are

7 a) $W_2 - W_3 = 1.89\ (W_1 - W_3) - 0.89S + H$

b) $W_2 - W_3 = 2.125\ (W_2 - W_1) + S - 1.125H$

c) $W_1 - W_3 = 1.125\ (W_2 - W_1) + S - 1.125H$

and

8 a) $W_2 - W_3 = 176.3Q + S + H$

b) $W_1 - W_3 = 93.3Q + S$

c) $W_1 - W_3 = 82.9Q + H$

The values of the intercepts thus are

$b_{FQ} = S + H$

$b_{AQ} = S$

$b_{GQ} = H$

$b_{FG} = S - 1.125H$

$b_{AG} = S - 1.125H$

which are consistent with the observed values.

The pretreatment film weight can be obtained directly from the intercept b_{AQ} (equation 8b). This intercept is to be compared with the values of pretreatment weight determined by nitric acid stripping shown in Tables 2 and 3, are in reasonably good agreement with the intercept values which suggests, to a first approximation, that anodizing over a conversion coating has little effect on the conversion coating.

The next phase of this research will be to carry out similar experiments with electrolytes containing the resin.

Among the several questions to be answered are: To what extent does the anodic film growth control the current decay rate and the amount of resin deposited? Also, can this be modified by pretreatment in a way to give a higher efficiency for resin film formation? Finally, how are the primary electrode reactions responsible for either a good or poor application of resin film and can the primary electrode reaction be controlled to minimize formation of defects?

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Table 2

Weight-Coulomb Relations in pH 7 Succinate at 45°C

Metal	Pre-Treatment	Slopes			Intercepts			Current Efficiency (%)			Pre-Treatment Weight ($\mu g/cm^2$) [1]	Q(1199)/Q(Alloy)
		a_{FQ}	a_{AQ}	a_{GQ}	b_{FQ}	b_{AQ}	b_{GQ}	F	A	G		
Theory		176.3	93.3	82.9	0	0	0	100	100	100	-	1.00
1199	CrO_3-H_3PO_4	175.5	88.8	86.6	5.0	2.9	2.1	99.5	95.2	104.5	-	1.00
3105	"	131.4	65.0	65.4	7.5	4.5	3.1	74.5	69.7	78.9	-	.61
3004	"	145.4	75.5	70.1	6.6	4.4	2.2	82.5	80.9	84.6	-	.66
5182	"	168.4	85.4	82.6	6.1	4.1	1.9	95.5	91.5	99.9	-	.74
1199	Cr(III)	160.8	78.4	82.2	29.5	28.8	0.7	91.2	84.0	99.2	23.6	1.08
3105	"	91.8	47.2	48.6	49.7	48.5	0.7	52.1	50.6	58.6	48.9	.53
3004	"	91.3	47.6	43.6	42.4	39.0	3.5	51.8	51.0	52.6	47.3	.52
5182	"	165.0	82.6	78.8	22.1	23.2	1.3	93.6	92.4	95.1	21.7	.74
1199	Cr(VI)	150.4	74.8	76.1	26.1	24.8	1.3	85.3	80.2	91.8	18.0	1.02
3105	"	122.0	67.7	53.7	22.3	22.2	0.2	69.2	72.6	64.8	28.4	.60
3004	"	132.9	73.7	59.6	19.7	18.8	1.6	75.4	78.7	71.9	14.8	.54
5182	"	133.7	67/4	66.4	16.1	14.5	1.6	75.8	72.2	80.0	11.5	.78

(1) Pretreatment weight obtained by stripping 3 pretreated-only specimens in 50% HNO_3

Table 3

Weight-Coulomb Relations in pH 9 Succinate at 45°C

Metal	Pre-Treatment	Slopes			Intercepts			Current Efficiency			Pretreatment Weight ($\mu g/cm^2$)	$\frac{Q(1199)}{Q(Alloy)}$
		a_{FQ}	a_{AQ}	a_{GQ}	b_{FQ}	b_{AQ}	b_{GQ}	F	A (%)	G		
1199	CrO_3-H_3PO_4	176.4	89.1	84.2	13.9	12.1	0.8	98.4	95.5	101.6	-	.97
3105	"	127.7	66.4	61.5	7.1	5.9	1.2	72.4	71.2	74.2	-	.51
3004	"	102.3	52.9	49.3	11.0	7.9	3.1	57.9	56.7	59.5	-	.55
5182	"	145.7	78.0	68.7	8.5	5.0	3.4	82.6	83.6	82.9	-	.79
1199	Cr(III)	175.4	91.5	83.9	30.6	28.8	1.8	99.5	98.1	101.2	32.3	.97
3105	"	78.4	42.2	38.5	36.2	33.1	2.7	44.5	45.2	46.4	37.1	.51
3004	"	98.6	50.6	47.4	41.7	38.9	2.2	55.9	54.2	57.2	43.2	.41
5182	"	111.6	52.6	59.1	51.0	48.4	2.7	63.3	56.3	71.3	53.4	.67
1199	Cr(VI)	181.2	90.8	89.6	23.2	22.2	1.2	102.8	97.3	108.0	17.4	.96
3105	"	116.2	62.4	51.6	29.7	26.9	2.9	65.9	66.9	62.2	28.3	.59
3004	"	91.5	44.5	47.3	23.8	21.2	2.5	51.9	47.7	57.0	20.7	.49
5182	"	133.9	68.0	66.4	14.8	13.0	1.7	76.0	72.9	80.0	8.0	.75
3105	Etch	137 →45	96 →23	24	-	-	-	78 →26	100 →25	29	-	.41
3004	Etch	133 →45	79 →26	65 →20	-	-	-	76 →26	85 →28	65 →20	-	.35
5182	Etch	148.0	71.0	63.3	6.3	7.8	0.5	84.3	76.1	76.4	-	.82

Table 4

Film and Aluminum Consumption Versus Anodizing Weight Gain
and Film Weight Versus Aluminum Consumption
in pH 7 Succinate at 45°C

Metal	Pretreatment	Slopes			Intercepts			Slope 95% Confidence Limit		
		a_{FG}	a_{AG}	a_{FA}	b_{FG}	b_{AG}	b_{FA}	a_{FG}	a_{AG}	a_{FA}
Theory		2.125	1.125	1.89	0	0	0			
1199	CrO_3-H_3PO_4	2.02	1.02	1.97	0.8	0.8	- 0.6	.06	.06	.05
3105	"	2.04	1.04	1.96	1.1	1.1	- 1.1	.16	.15	-
3004	"	2.05	1.05	1.95	2.2	2.2	- 2.1	.08	.10	-
5182	"	1.99	1.00	2.00	2.5	2.4	- 2.3	.04	.04	-
1199	Cr(III)	1.99	.98	2.03	27.6	27.8	-28.9	.22	.21	-
3105	"	2.07	1.08	1.92	47.1	46.9	-42.8	.14	.12	-
3004	"	2.11	1.11	1.90	42.4	39.0	3.5	.22	.22	-
5182	"	2.21	1.21	1.83	20.9	20.4	-17.1	.46	.45	-
1199	Cr(VI)	2.00	0.99	2.02	23.8	23.5	-23.7	.40	.32	-
3105	"	2.11	1.11	1.90	23.0	23.0	-20.7	.23	.23	-
3004	"	2.18	1.18	1.85	16.5	16.5	-14.0	.21	.21	-
5182	"	1.92	0.92	2.09	13.6	13.5	-14.8	.08	.09	-

Table 5

Film and Aluminum Consumption Versus Anodizing Weight Gain and Film Weight Versus Aluminum Consumption in pH 9 Succinate at 45°C

Metal	Pretreatment	Slopes			Intercepts			Slope 95% Confidence Limit		
		a_{FG}	a_{AG}	a_{FA}	b_{FG}	b_{AG}	b_{FA}	FG	AG	FA
1199	CrO_3-H_3PO_4	2.06	1.05	1.95	12.3	12.4	-11.7	.09	.09	.07
3105	"	2.09	1.13	1.86	4.5	4.2	- 3.3	.12	.13	-
3004	"	2.10	1.10	1.90	4.3	4.3	- 3.8	.08	.07	.05
5182	"	2.12	1.13	1.88	1.3	1.2	- 1.0	.07	.07	.05
1199	Cr(III)	2.07	1.07	1.89	27.1	27.1	-23.6	.05	.07	.04
3105	"	1.74	0.78	2.23	32.9	32.4	-39.4	.20	.19	-
3004	"	2.00	0.99	2.02	36.5	36.5	-37.4	.20	.20	-
5182	"	1.79	0.80	2.23	46.9	46.8	-57.8	.15	.15	-
1199	Cr(VI)	1.99	0.99	1.91	21.2	21.3	-18.1	.26	.26	.24
3105	"	2.17	1.17	1.85	23.7	23.7	-20.3	.19	.19	-
3004	"	2.01	1.01	1.99	18.3	18.3	-18.1	.20	.20	-
5182	"	2.00	1.00	2.00	11.5	11.5	-11.5	.08	.08	-
3105	Etch	2.11	1.11	1.87	3.9	3.8	- 2.5	.15	.15	.09
3004	"	1.98	0.96	1.97	4.7	4.9	- 3.9	.13	.20	.13
5182	"	2.19	1.20	1.76	7.0	6.9	- 4.0	.32	.25	.16

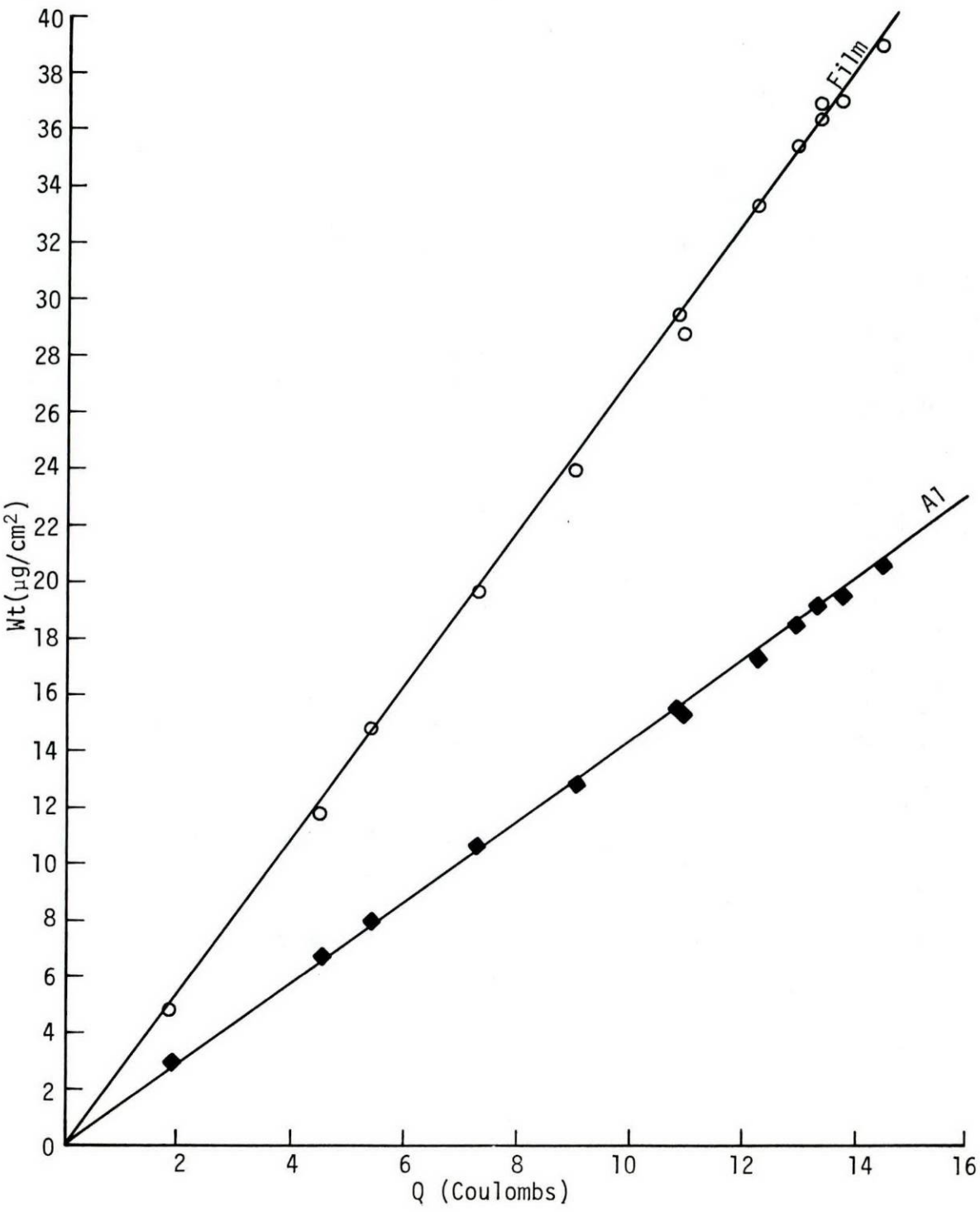

Figure 1. Weight vs Coulomb Relations in Succinate Solution 91 V, 25°C, 13.9 ma/cm^2 initial current density, 64.2 cm^2 specimens.

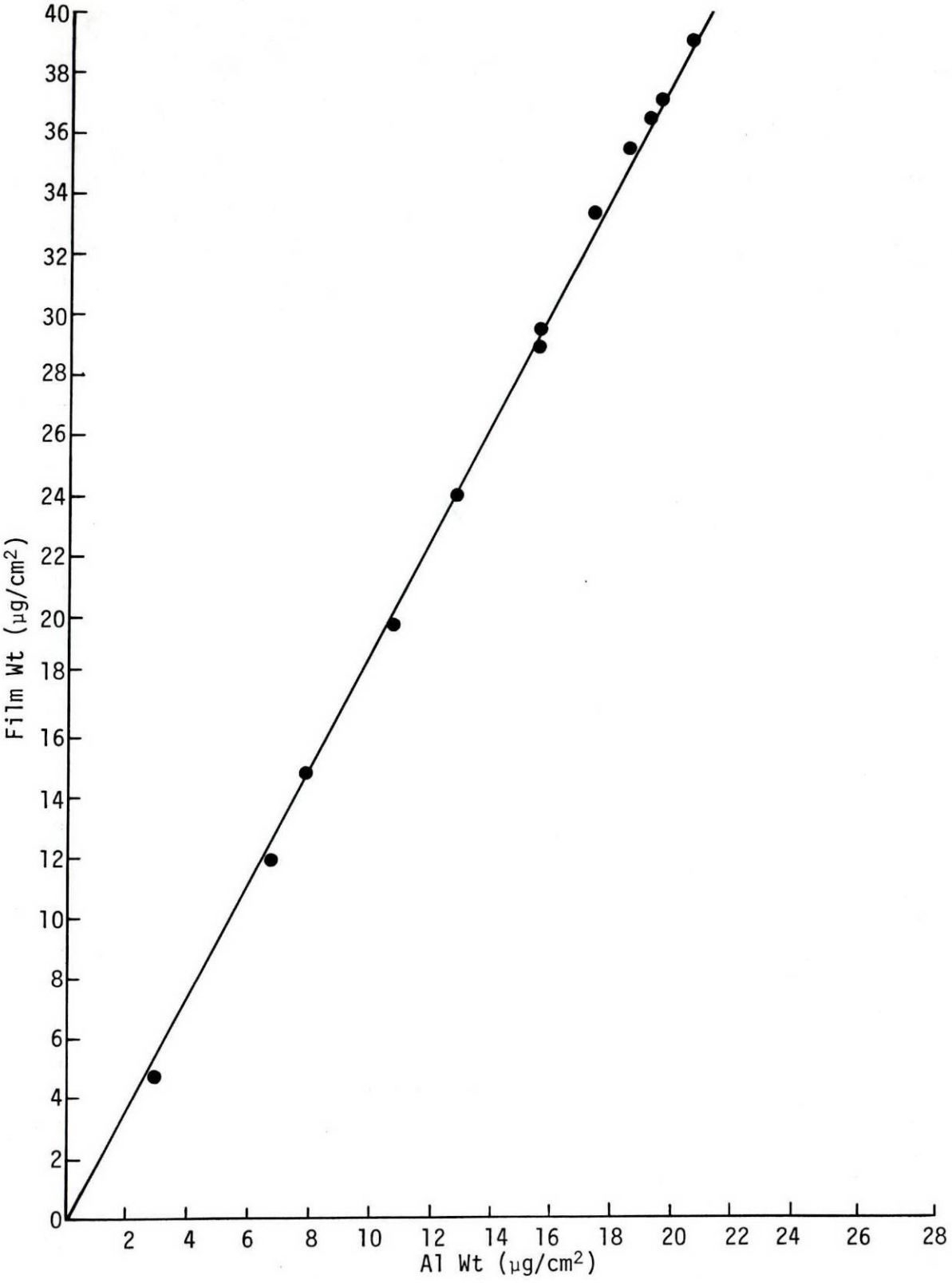

Figure 2. Film Weight vs Aluminum Weight in Succinate Solution 91 V, 25°C, 13.9 ma/cm^2 initial current density, 64.2 cm^2 specimens.

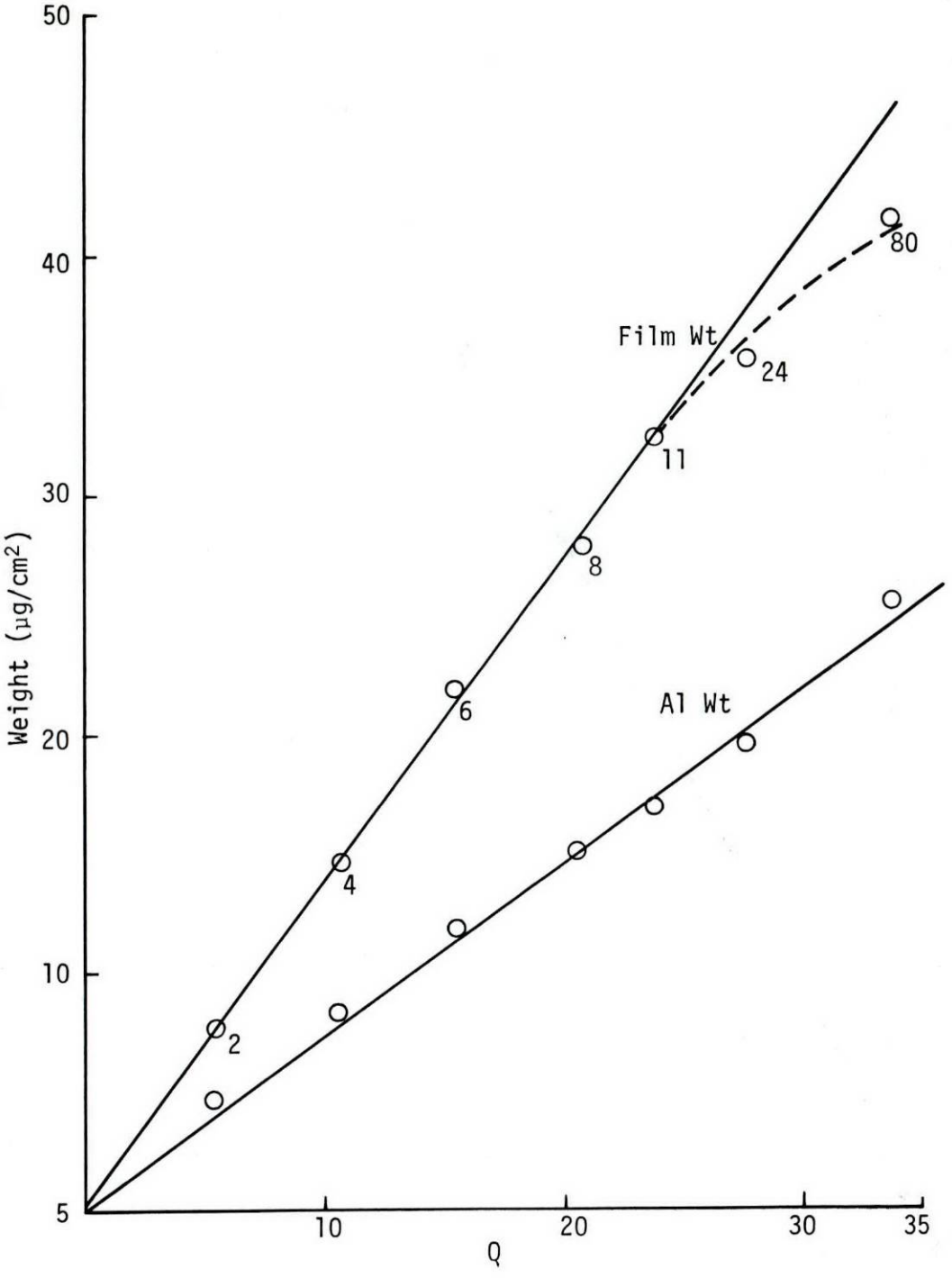

Figure 3. Weight vs Coulomb Relationships in Succinate Solution

40°C, 82 V, 20 ma/cm^2 initial current density. Numbers refer to total anodizing time.

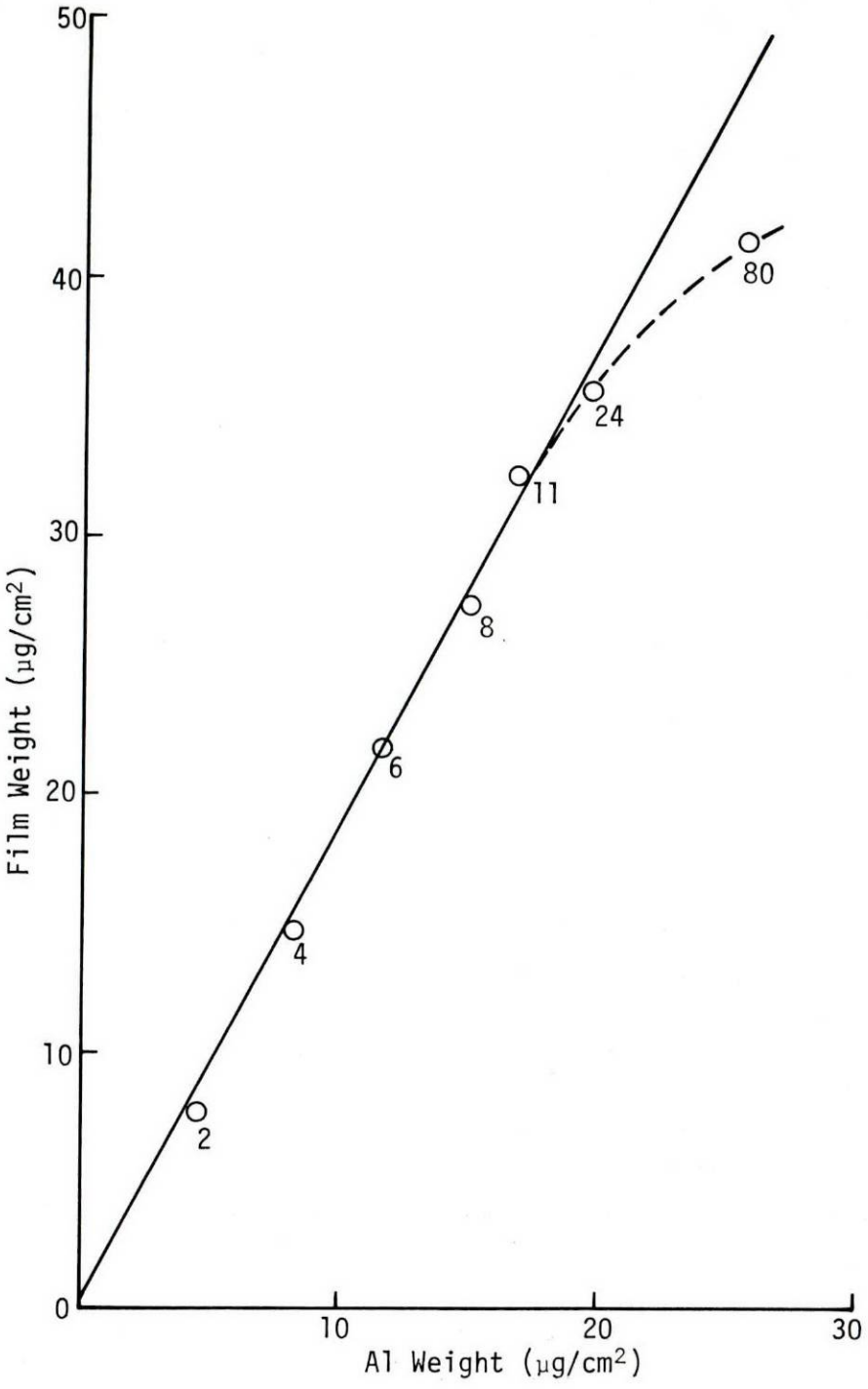

Figure 4. Film Weight vs Aluminum Weight in Succinate Solution

40°C, 82 V, 20 ma/cm^2 initial current density. Numbers refer to total anodizing time.

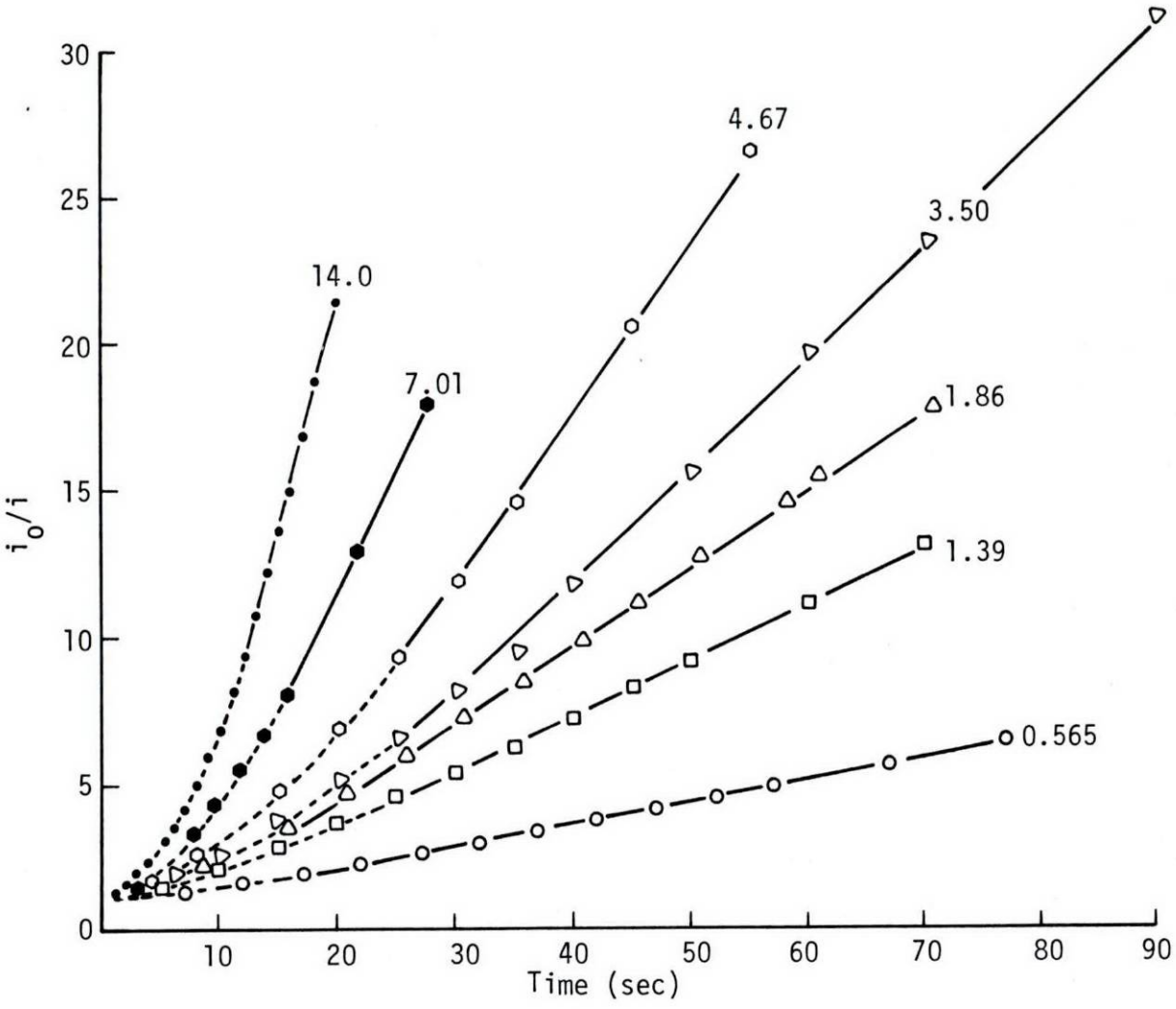

Figure 5. Current-Time Relations in Ammonium Borate-Ethylene Glycol Electrolyte i_o in ma/cm^2 is Shown on Each Curve

85 V, 25°C

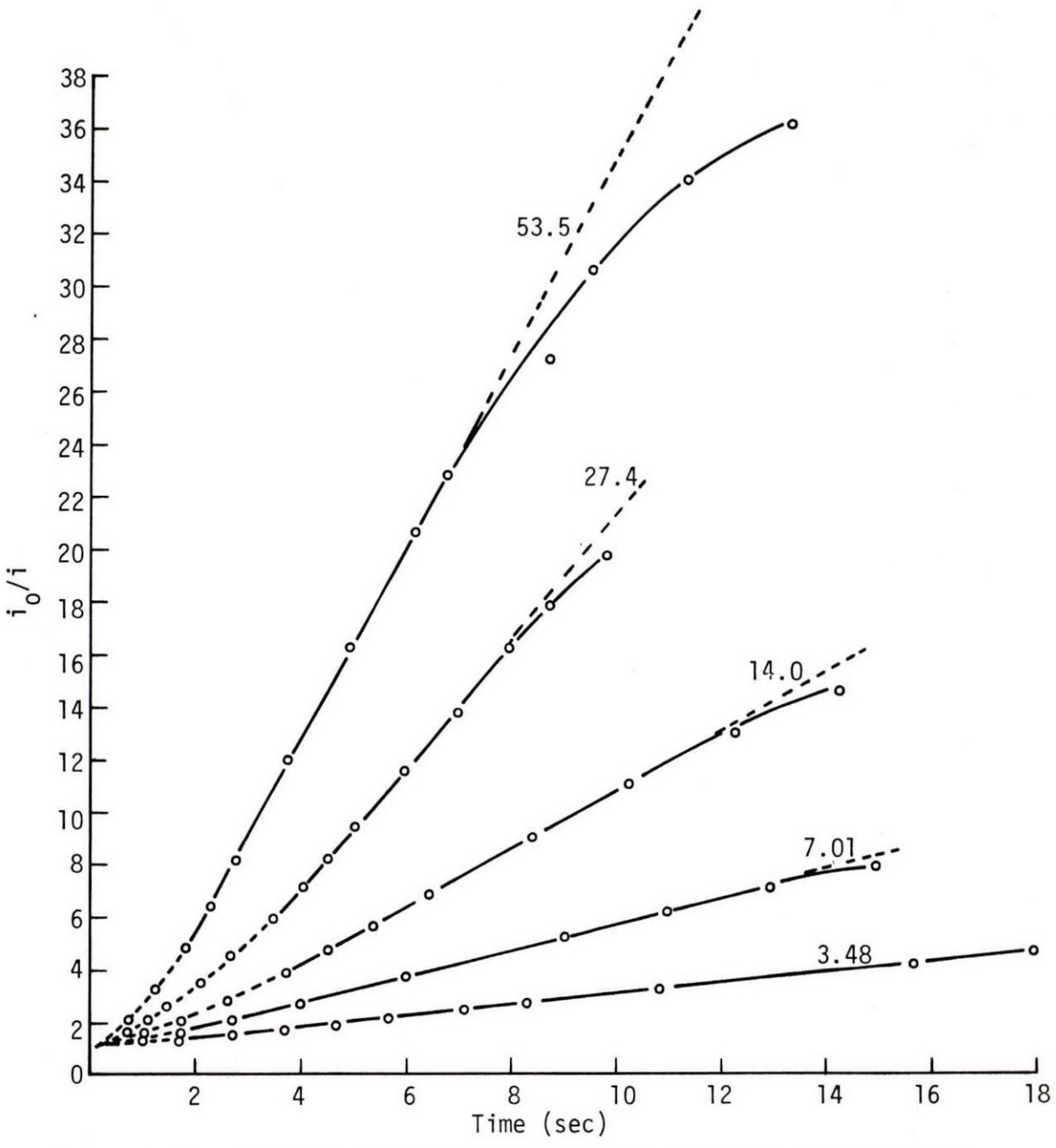

Figure 6. Effect of Initial Current Density on Current-Time Relation in Succinate Solution i_o in ma/cm^2 is Shown on Each Curve

80-95 V, 25°C constant absolute current with variable specimen area.

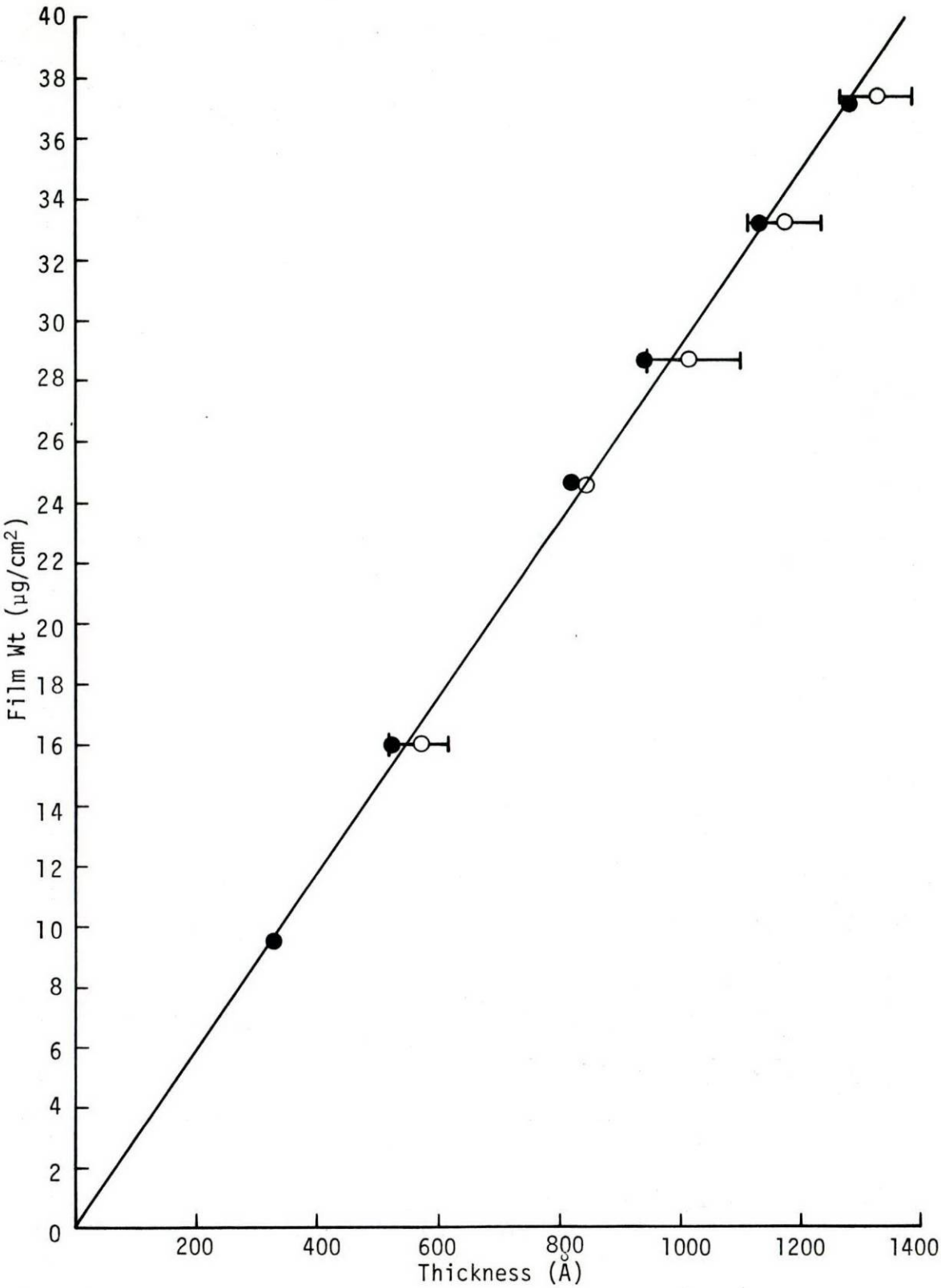

Figure 7 . Film Weight vs Film Thickness in Acrylate Solution

45°C, 14 ma/cm^2 initial current density. Fully formed films at final voltages varying from 20 to 77 V. Closed figures--thickness calculated from coulombic relationship; open figures with error bars--TEM values.

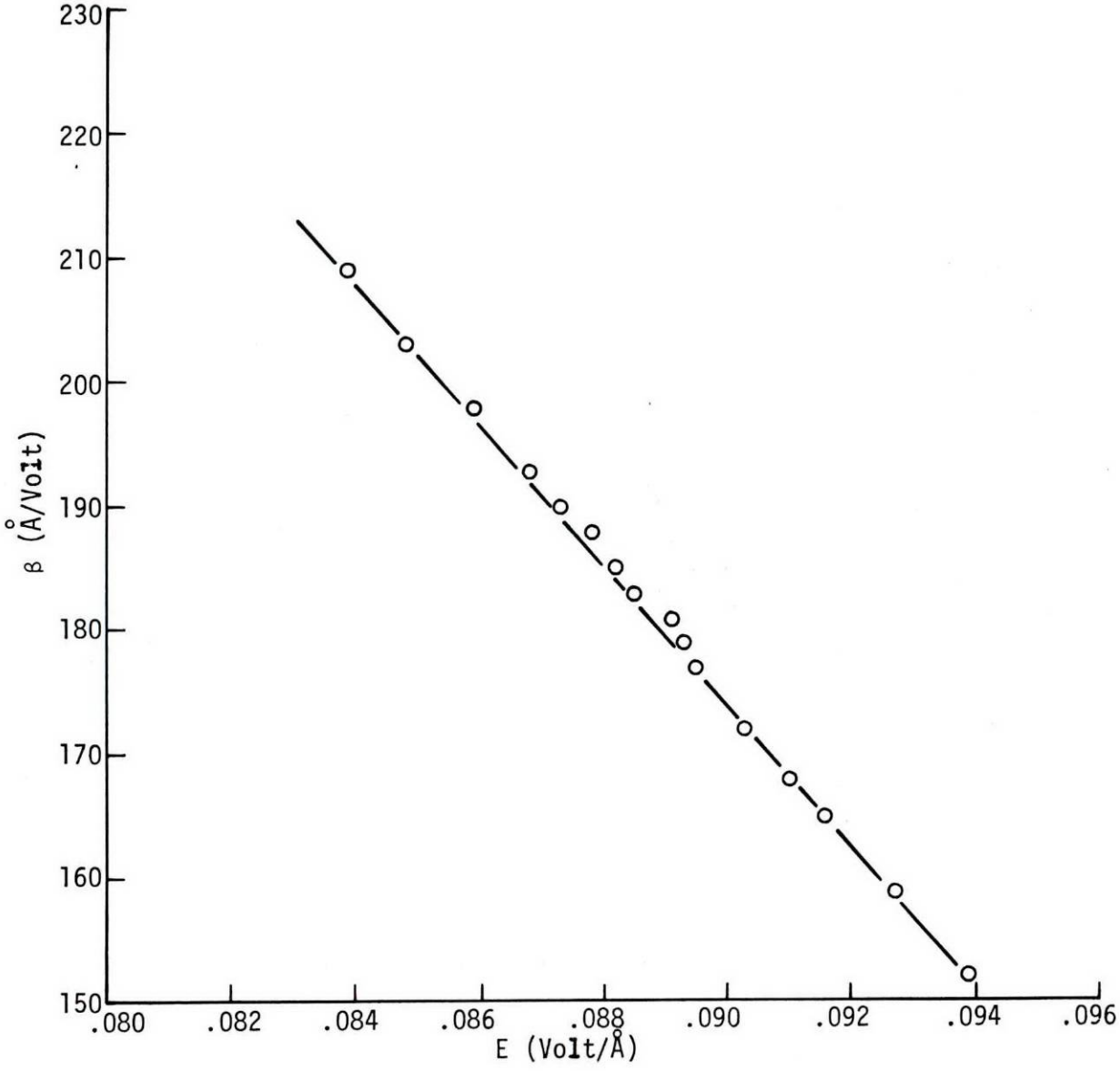

Figure 8. Reciprocal Tafel Slope vs Electric Field for Oxide Formed in Succinate Solution

91 V, 25°C, 13.9 ma/cm^2 initial current density, 64.2 cm^2 specimen.

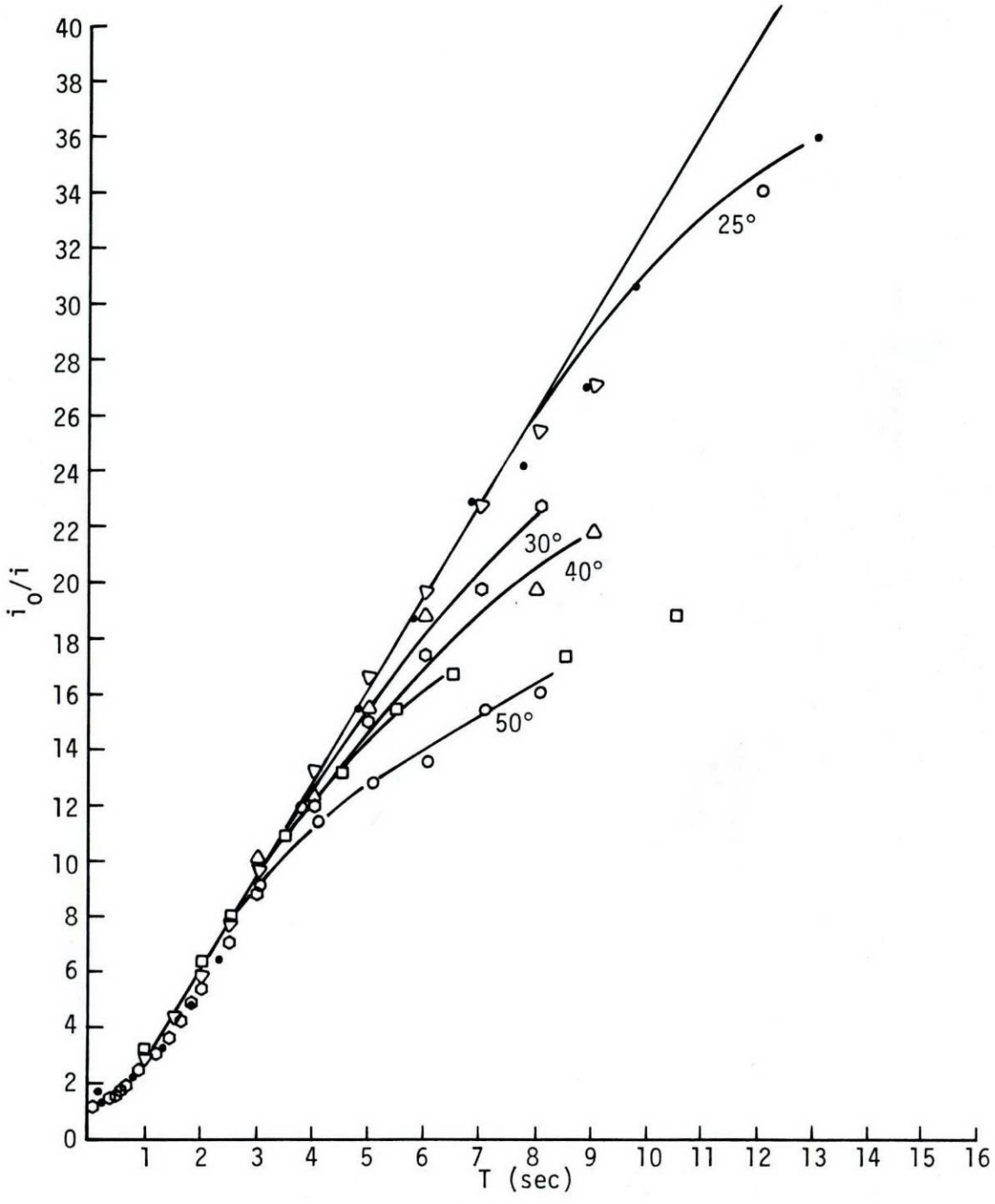

Figure 9. Effect of Temperature on Current-Time Relation in Succinate Solution

95-100 V, 53.7 ma/cm^2 initial current density.

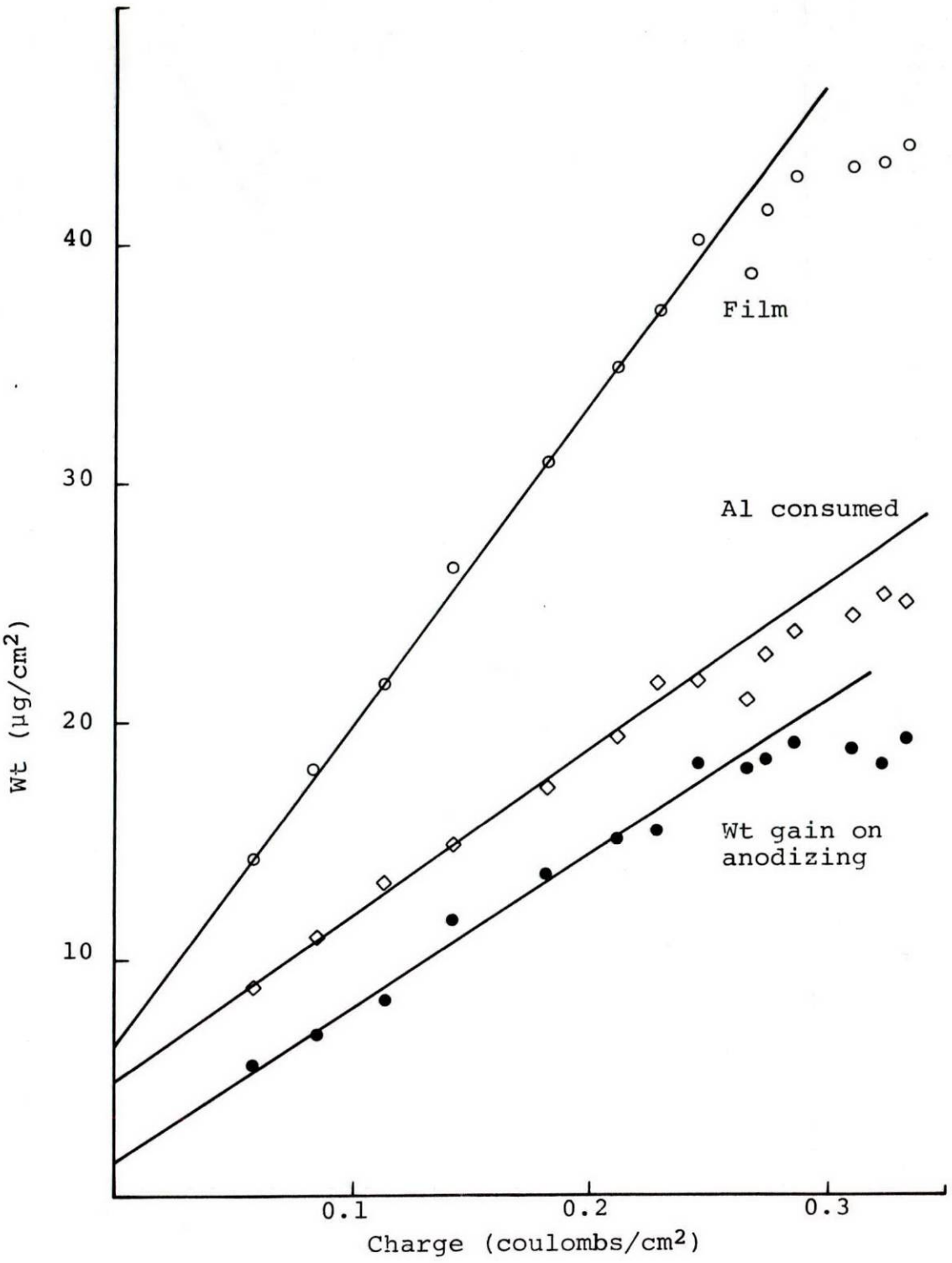

Figure 10. Weight-Coulomb Relations in 45°C Succinate 3105 alloy with CrO_3-H_3PO_4 Pretreatment 82v, 30 ma/cm^2 initial current density

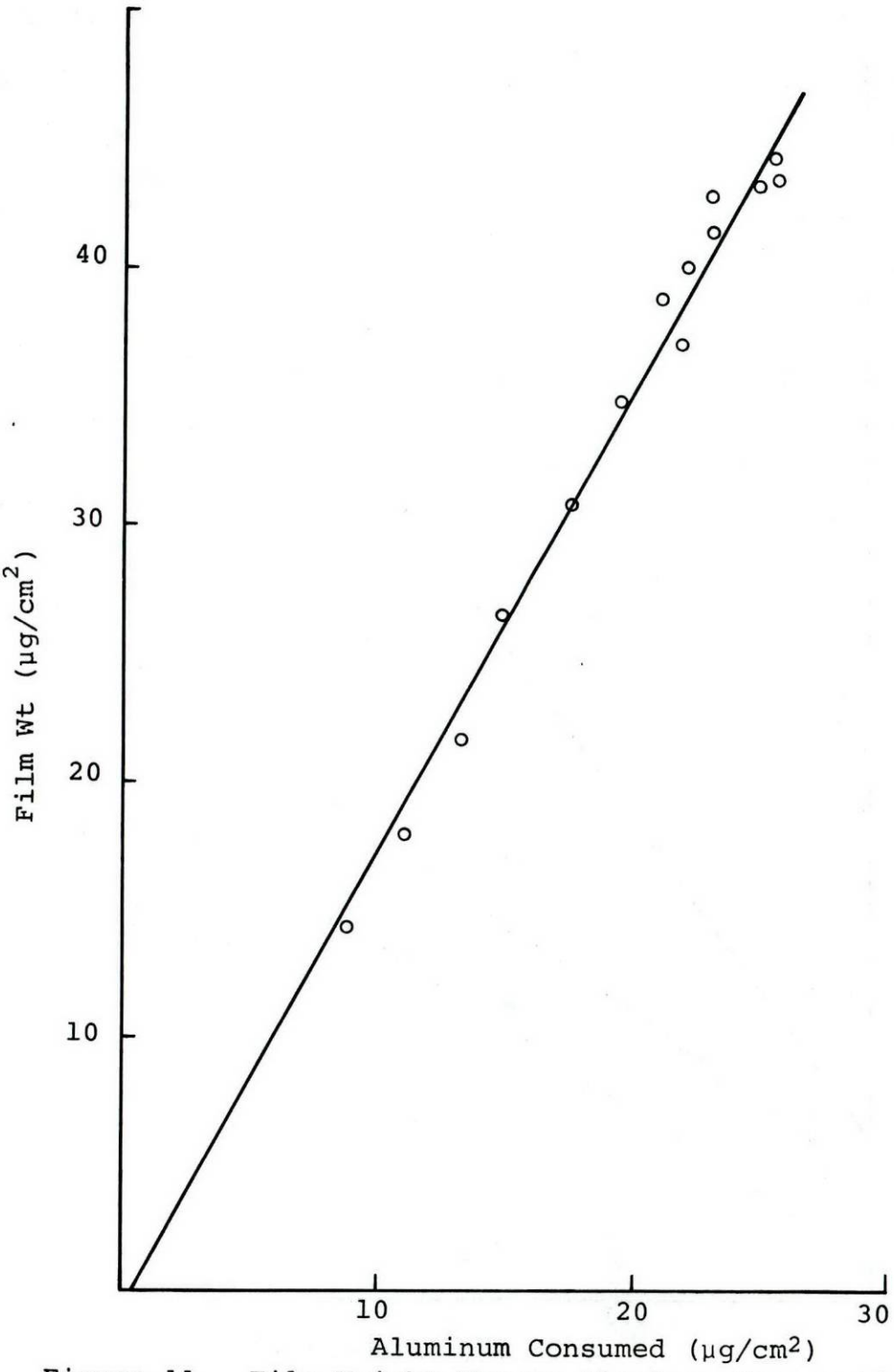

Figure 11. Film Weight Versus Aluminum Consumption 3105 Alloy With CrO_3-H_3PO_4 Pretreatment 45°C Succinate, 82v, 30 ma/cm2 Initial Current Density

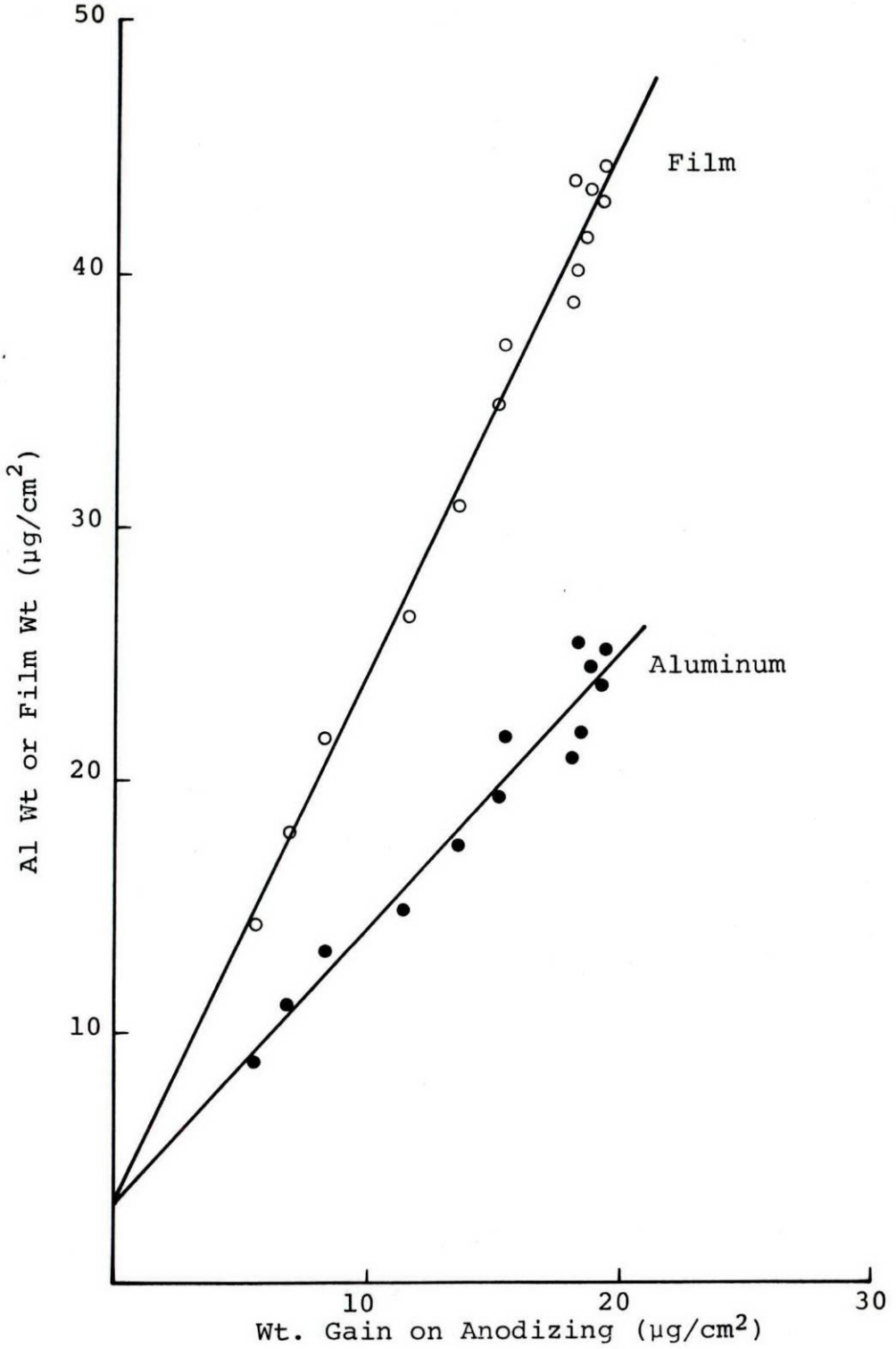

Figure 12. Aluminum Consumption and Film Weight as a Function of Anodizing Weight Gain 3105 Alloy with CrO_3-H_3PO_4 Pretreatment 45°C Succinate, 82v, 30 ma/cm² Initial Current Density

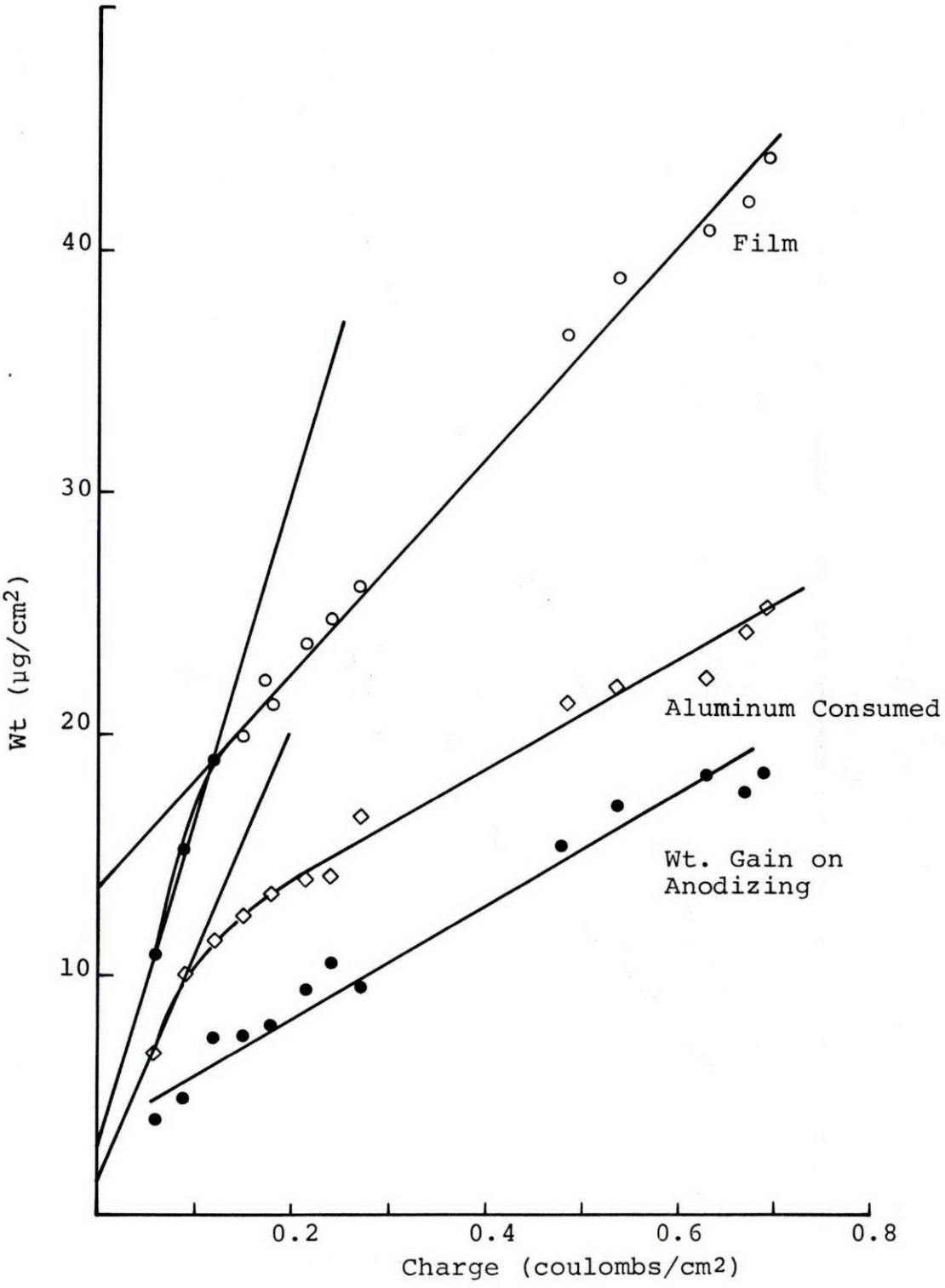

Figure 13. Weight-Coulomb Relations

3105 alloy with caustic etch pretreatment
45°C Succinate, 82v, 30 ma/cm^2 initial
current

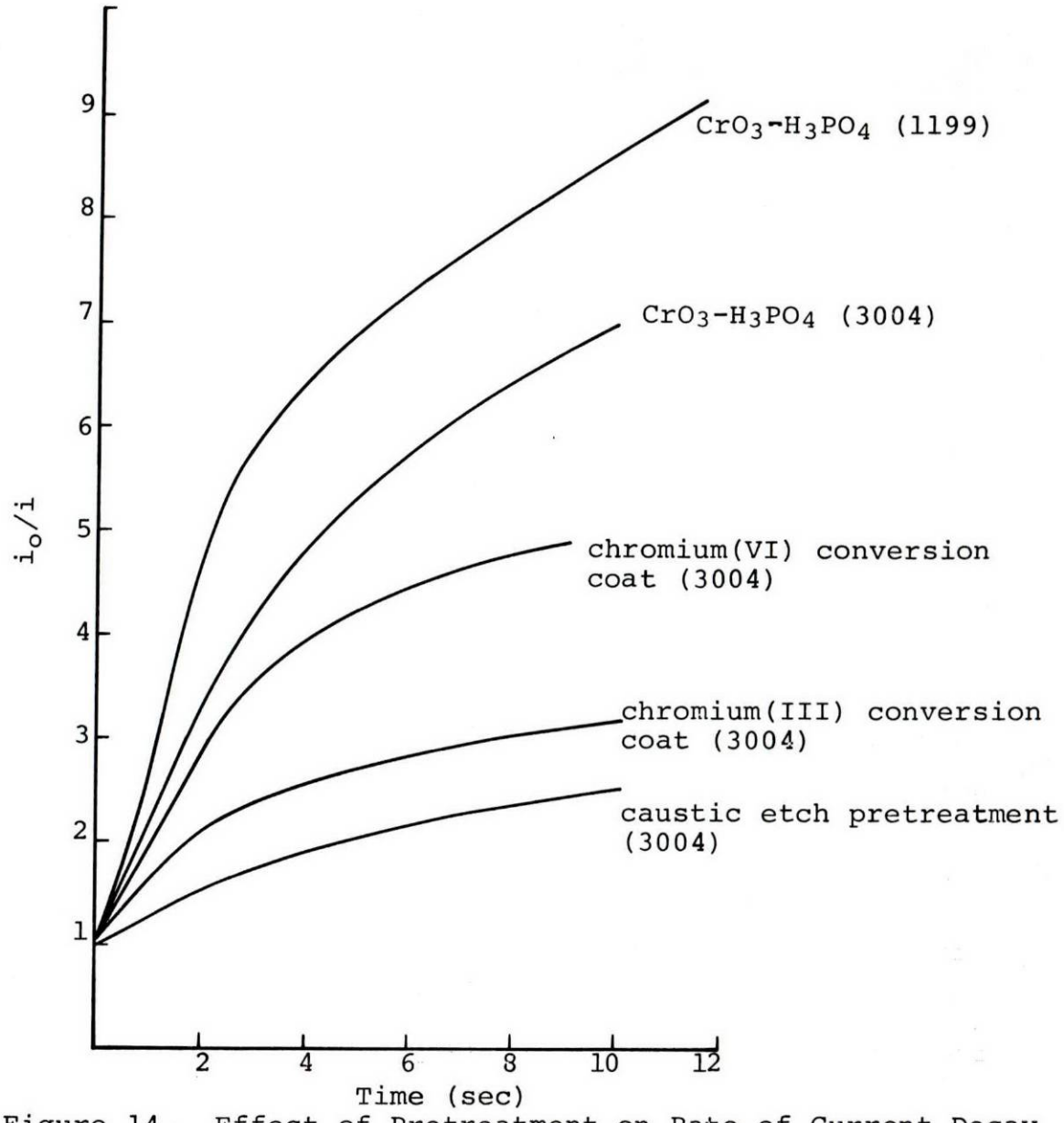

Figure 14. Effect of Pretreatment on Rate of Current Decay 45°C Succinate, 82v, 30 ma/cm² initial current

C-4

LIGHT METALS FINISHING SESSION C

Adhesion of Electrodeposited Coatings to Aluminum

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ADHESION OF ELECTRODEPOSITED COATINGS TO ALUMINUM

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I. Introduction:

Whenever two clean metals are placed in intimate contact, as was shown by Buckley (1), strong adhesive bonding occurs. A theory discussing this formation of metallic bonds was presented by Ferrante and Smith (2). Though the theory of Ferrante and Smith was based on first principles, neither the effect of interfacial dislocations nor the effect of stored strain energy was included in their calculations. A number of mechanistic theories are available in the literature, among them include the weak boundary layer theory of Bickerman (3) and a Griffith-Irwin type theory presented by Good (4) and others (5-9). The understanding of the forces responsible for bonding are important not only for electrodeposited coatings, but also for the fields of friction, wear, and fracture. The development of new coatings for hard to plate materials, such as aluminum, in which adhesion is usually a problem, requires an understanding of at least the general mechanism by which metallic coatings adhere to metals. The subject of adhesion to an anodic oxide will be treated in another paper.

II. The Effect of Surface Energy:

As has long been known, the adhesion between two metallic surfaces in contact is related to the surface energies of each of the two metals. This relationship can be found by considering the total system energy of the metals in contact and comparing it to the total system energy when the metals are separated. The energy difference between the two cases is the adhesive energy per unit area given by,

$$E_{ad} = \gamma_1 + \gamma_2 - \gamma_i \qquad [1]$$

If two identical metals, of the same orientation, are considered, then $\gamma_1 = \gamma_2$ and

$$E_{ad} = 2\gamma - \gamma_i \qquad [2]$$

therefore, in the case of perfect autoepitaxy ($\gamma_i = 0$) equation [2] becomes

$$E_{ad} = 2\gamma \qquad [3]$$

The relationship given by equation [3] would have to hold no matter where the interface was located, and, therefore, represents the cohesive energy of the material. In the case of aluminum, for example, E_{ad} = 1680 ergs/cm^2. This is only an approximate number because the surface energy varies with the orientation and accurate experimental values are

difficult to obtain. If two dissimilar metals are used and γ_i is small, then the adhesive energy would appear to always exceed the cohesive energy of the material with the lower surface energy. Therefore, if a normal force were applied to the coated substrate, fracture would occur in the material with the lower surface energy. If the assumption of a small interfacial energy were correct, then destructive measurements of adhesion, such as peel tests, would only be measurements of the cohesive energies of the lower of the two surface energy materials, and would not be measurement of true adhesion.

However, as will be discussed below, the interfacial energy in general can not be neglected; and, in any case, coatings are often non-continuous, so that adhesion measurements can often be related to the area fraction of the substrate coated. Heating the coated substrate will in general improve adhesion by (a) promoting chemical bonding, and by (b) promoting diffusion. Therefore, heating a coated substrate will not test adhesion, as is often thought. Only in the worst case when a gas is trapped under a large blister in a very poorly adherent coating, or perhaps when the coefficient of thermal expansion is great, will heating reveal a problem.

In practice, the interfacial energy is not a small number, and so calculations of adhesive energy must first determine the interfacial energy, which depends on the crystal structure of the material and the coating, the misfit between these two structures and the stored elastic strain energy in both the coatings and the substrate. The following development is based in part on the theory of interfacial energy proposed by Jesser and Kuhlman-Wilsdorf (10) and calculations on the zinc-aluminum interfacial shear modules and given in Appendix I are based on data in a paper by Rudman and Averbach (11). In addition to the above effects on adhesive energies, a discussion of the effect of a pre-existing crack in the interface on adhesion is presented.

III. The Effect of Structure:

It is assumed that the potential energy variation experienced by an atom of the coating material moving along the substrate is given by a Peierls-Narbaro function as,

$$V = {}_xV_o \left[1 - \cos \frac{2\pi x}{{}_xa_s} \right] + {}_yV_o \left[1 - \cos \frac{2\pi y}{{}_ya_s} \right] + C \qquad [4]$$

where V_o represents the potential energy amplitude, a_s the lattice constant of the substrate and C the potential energy/atom of a coating atom when sitting in the bottom of the potential trough. Under these conditions, as was assumed by Van der Merwe (12), the adhesive energy is proportional to an average potential amplitude, $V_o = 1/2({}_xV_o + {}_yV_o)$, and for N number of atoms,

$$E_{ad} = 2\ KNV_o \qquad [5]$$

where for fcc materials K = 3. The potential V_o is related to the shear modulus of the interface G_o as was again shown by Van der Merwe by

$$V_o = \frac{G_o a_2}{2\pi N d} \qquad [6]$$

The subscripts denoting the x and y dependence have been left off for clarity, d is the verticle separation between the coating and the substract. By using this expression for the average potential amplitude (6) in equation [5], the adhesive energy per unit area can be written as

$$E_{ad} = \frac{K G_o a_s^2}{2\pi^2 d} \quad . \qquad [7]$$

Numerical values for the adhesive energies are obtained by assuming a symmetrical x and y potential distribution and a close packed configuration with the substrate. The lattice parameter in the interface is approximated by

$$a = \frac{2a_c a_s}{a_c + a_s} \quad , \qquad [8]$$

and the interfacial shear modulus is calculated based on an assumption of a linear correlation of shear modului and bonding energy (13) and by using the data of Rudman and Averbach (11). Thus, through the lattice parameters of the coating and substrate, a_c and a_s, the effect of structure has been introduced into the calculations of adhesive energy. For epitaxial deposits of zinc on aluminum (14), the adhesive energies from equation [7] are given by:

$$Al(111)//Zn(0001): E_{ad} = 1531 \text{ ergs/cm}^2$$
$$Al(011)//Zn(0001): E_{ad} = 1283 \text{ ergs/cm}^2$$
$$Al(100)//Zn(0001): E_{ad} = 928 \text{ ergs/cm}^2$$

Since the cohesive energy of zinc is in the neighborhood of 1480 ergs/cm^2, it is seen that even on the $(\overline{100})$ plane of aluminum that failure of zinc coated aluminum will occur within the interface on (011) and (100) aluminum planes. This calculation is only a first approximation and more exact calculations have to take into account both the existence of interfacial dislocations and their effect on bonding, as well as, the amount of interfacial energy stored in the lattice in the form of elastic strain energy. In the latter case, the dislocation density should be reduced.

IV. The Effect of Misfit Dislocations on Bonding Energy:

If a significant misfit between the crystal structure of the coating and the substrate exists, a series of interfacial dislocations will form in such a way as to minimize the resultant strain energy. The interfacial energy can now be written as

$$\gamma_i = {}_xE_d + {}_yE_d + CN \qquad [9]$$

where C, represents, as previously discussed, the potential energy of an atom sitting in a potential trough. The number of atoms is given by N and the energy of an array of dislocations by Ed. (Note: $CN = \gamma_1 + \gamma_2 - 2KNV_o$.) The adhesive energy can now be written as,

$$E_{ad} = 2KNV_o - ({}_xE_d + {}_yE_d). \qquad [10]$$

The dislocation energy per unit area was shown by Van der Merwe to be given, leaving out the x and y substrates, as,

$$E_d = \frac{Gb}{4\pi^2}\left\{1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln\left[2\beta(1 + \beta^2)^{1/2} - 2\beta^2\right]\right\} \qquad [11]$$

where $\beta = \dfrac{2\pi Gb}{P(1 - \nu)(1 + \frac{G_1}{G_2})G}$, P is the vernier period

$\dfrac{a_s a_c}{a_c - a_s}$, and b is the Burgers vector in the interface. By introducing the effect of dislocations into the interface, it is seen that the presence of interfacial dislocation will serve to reduce the adhesive energy over the dislocation free model. The results of calculations for our special case of epitaxial coatings of zinc on aluminum are shown below.

$Al(111)//Zn(0001): E_{ad} = 1331$

$Al(011)//Zn(0001): E_{ad} = 1198$

$Al(001)//Zn(0001): E_{ad} = 841$

V. The Effect of Strain Energy on Adhesion:

As a result of misfit between the substrate and the coating, strains will be induced in both the substrate and coating lattices, the density of misfit dislocations, if they exist, will be reduced and the adhesive bonding affected in a complex manner. In the way proposed by Jesser and Kuhlman-Wilsdorf, the new strained lattice parameters at a strain, e, are given by,

$$a_c' = a_c + a_c e_c \text{ and } a_s' = a_s - a_s e_s \quad , \qquad [12]$$

Therefore, the total adhesive energy is given by

$$E_{ad} = 2KNV_o - {}_xE_d + {}_yE_d - E_s \quad . \qquad [13]$$

It was shown by Jesser and Kuhlman-Wilsdorf (10) that the strain energy, E_s, can be expressed as

$$E_s = G_c h_c \cdot \frac{x e_c^2 + y e_c^2 + 2\nu x e_c}{1 - \nu_c} + G_s h_s \cdot \frac{x e_s^2 + y e_s^2 + 2\ x e_s\ y e_s}{1 - \nu_s} \qquad [14]$$

where ν is poisson ratio and h represents thickness. The strain e is given by

$$e_c = \frac{-b a_1 \ln\left[2\beta' \quad 1 + \beta^2 \quad ^{1/2} - 2\beta^{12}\right]}{\left(1 + \frac{G_1}{G_2}\right)\left(a_2 + a_1\right)\left(2\pi hc\right)\left(1 + \nu\right)} \qquad [15]$$

For a thick substrate, $e_s = 0$. As a result of strain, however, the dislocation contribution to the interfacial energy will be reduced. A new value (Eq. 11) can be calculated by using equation [12] to calculate new values for the misfit. For example, under consideration, the new values of the adhesive energy, given below.

Al(111)//Zn(0001) = 1301 ergs/cm^2
Al(110)//Zn(0001) = 1168 ergs/cm^2
Al(001)//Zn(0001) = 811 ergs/cm^2

A comparison between values calculated from the above theory and calculations and measurements of other investigators is shown in Table I.

VI. The Effect of a Pre-Existing Crack in the Interface on Adhesion:

A pre-existing crack in the interface can result in adhesive failure by reducing the stress necessary in order to cause failure. Such a crack can be a result of poor cleaning, blistering, pores, patches of oxide or other causes. So that stress resulting from say, a difference in the thermal expansion coefficient between the coating and the substrate or from the substrate flexing, will cause a crack to propagate parallel to the surface. The model considered in this calculation is shown in Figure 1 and consists of a crack of length 2c and unit depth, located in the interface between a substrate of surface energy γ, and a coating of surface energy γ_2.

The total surface energy of the crack is then given by

$$E_s = 2c\gamma_1 + 2c\gamma_2 = 2c(\gamma_1 + \gamma_2) \qquad [16]$$

In order to find the stress, σ, at which the crack will just start to propagate, the energy is equated with the stored strain energy as

$$E_{surface} = 2c(\gamma_1 + \gamma_2) = E_{strain} = \left(\frac{\sigma^2}{E_1} + \frac{\sigma^2}{E_2}\right)\frac{\pi c^2}{2} \qquad [17]$$

where E represents Young's modulus. Under equilibrium

$$\frac{\partial \left(E_{surface} - E_{strain} \right)}{\partial c} = 0 \qquad [18]$$

so that

$$\sigma_{critical} = \sqrt{\frac{2 \left(\gamma_1 + \gamma_2 \right)}{\pi c \left(\frac{1}{E_1} + \frac{1}{E_2} \right)}} \qquad [19]$$

In the case of aluminum and zinc, the results of equation [19] are plotted as a function of the crack half length in Figure 2. For cracks that are less than one micron, the stress to cause delamination exceeds 2×10^9 dynes/cm^2 (30,000 psi). °For cracks in aluminum only, the stress (Griffith Criteria) is 1.95×10^9 dynes/cm (28,300 psi) and for one micron cracks in zinc 2.2×10^9 dynes/cm^2 (28,300 psi). Note that once a crack has started, it may run along the interface, go into the coating or move into the substrate. A more detailed discussion of crack propagation along an interface was given by Good (4). In any case, once a crack has started to grow, the stress necessary to make it continue to grow drops off very rapidly, so that under conditions of constant stress (and constant crack radius) the coating will delaminate. In the more ductile coatings, the crack radius at the tip can enlarge and the crack be effectively blunted.

VII. Discussion and Conclusions:

Both the existance of interfacial dislocations and the stored elastic strain energy contribute in a significant way to the adhesion of metallic coatings onto crystalline aluminum substrates. For non-crystalline substrates, aluminum or otherwise, the adhesive energy for metallic coatings (both crystalline and amorphous), would be relatively higher than for the comparable crystalline material.

Calculations have only been presented for the case of zinc coatings on aluminum substrates; however, a basis now exists for future calculations of the relative adhesion between nickel, iron, copper, tin and various alloy coatings to aluminum, and results for these materials will be reported in the future. It was shown above that the greatest adhesive energy occurs when coatings are deposited on (111) aluminum compared to the other principle planes. Moreover from equation [7], it is predicted that the higher index planes (greater surface energy planes) would exhibit greater adhesion than the principle planes. If this turns out indeed to be the case, then extruded alloys would exhibit greater adhesion than their sheet counterparts. Since extruded parts can be made in thicker cross section than the comparable rolled sheet, the incentive of improved adhesion may make a change to extrusions desireable.

In Table I a comparison between the adhesive energy determined by a number of different techniques is presented. The definition of adhesive energy used by Ferrante and Smith differs from the definition used in this paper by exactly a factor of two. When allowance is made even for this discrepancy, the adhesive energies are still below these calculations

by a factor of about twenty percent. It should be noted that Ferrante and Smith did not take into account the lattice mismatch between zinc and aluminum, nor did they take into account the stored strain energy. These factors would have reduced their values even further.

The surface energy of alloys is in general greater than the surface energy of pure aluminum and is proportional to the ultimate tensile strength. It would then seem that adhesion on alloys would be proportionally greater than on pure aluminum. This does not seem to be the case, however. One therefore draws the conclusion that this discrepancy is the result of either incomplete coverage of the surface due to incomplete oxide removal or is the result of of defects in the zinc layer resulting in the existence of a crack in the interface.

It is important to note that these calculations represent the minimum energy to cause adhesive failure and do not take into account the work required to cause elastic and plastic deformation in either the coating or the substrate. Moreover, the strain energy released during the propagation of a crack in the interface, equation [14], should be included in equation [15], as in some cases this significantly affects the stress required to propagate a preexisting crack.

ACKNOWLEDGEMENTS:

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APPENDIX I: The Zinc Aluminum Binding Energy-Sheer Modulus of Aluminum-Zinc Interface

1. From Rudman and Averbach (11)

ΔH 800 cal. Z = number of nearest neighbor of type + No. = 6.023×10^{23}

.5

X_{Zn}

$\Delta Hm = x_A x_B \Omega$

where $\Omega = ZN_o \; H_{AB} - 1/2 \; (H_{AA} + H_{BB})$ represents the deviation from normality. [R. A. Swalin. Thermodynamics of Solids, J. Wiley & Sons.]

Note for an ideal solution

$H_{AB} = 1/2(H_{AA} + H_{BB})$

2. Let $Z = 1$, $x_A = x_B = 1/2$

$\frac{\Omega}{ZN_o} = H_{AB} - 1/2(H_{AA} + H_{BB})$ in the molar value

$\Delta Hm = (1/2)(1/2)\Omega = 800$

$\Omega = 3200$ cal. = 3.2 K cal.

$H_{AB} = 3.2 + 1/2(H_{AA} + H_{BB}) = 3.2 + 1/2[36.7 \text{ (Al-Al)} + 7(\text{Zn-Zn})] =$ 21.9 K cal. mole

3. $G_{Zn} = 3.8 \times 10^{11}$ $H_{Zn} = 7$ K cal./mole $H_{Al-Zn} = 21.9$ K cal./mole

$G_{Al} = 2.49 \times 10^{11}$ $H_{Al} = 36.7$

$$\frac{H_{Al} - H_{Al-Zn}}{H_{Al} - H_{Zn}} = \frac{14.8}{29.7} = .49$$

$\Delta G = 1.31$

$G_o = G_{Al} + .5\Delta G = 2.49 + .65 = 3.14 \times 10^{11}$ dynes/cm^2.

TABLE I: ADHESIVE ENERGY (ergs/cm^2) - THEORIES VS. EXPERIMENT

		Theory					Experiment
Substrate	Coating	Surface Energy $\gamma_s + \gamma_c$	+ Structure $2KNV_o$	+ Misfit Dislocations	+ Strain Energy	Ferrante & * Smith	Rabinowicz †
Al	Al	1680				405 (810)	900
$Al_{(100)}$	Zn	1580	928	841	811	360 (720)	900
$Al_{(100)}$	Zn		1283	1198	1168		900
$Al_{(111)}$	Zn		1531	1331	1301		900
Al	Sn						
	Ni	2590					
	Cu	1940					
	Mg	1390				320 (640)	
Al_2O_3	Ni						480
	Cu						475
	Fe						695
	Stainless Steel						1440 ††
Ni	Ni	3500					1750
Cu	Cu	2200				320 (640)	2333
Zn	Zn	1480					5700
Sn	Sn						

*J. Ferrante & J. R. Smith, Sur. Sci., 38, 77 (1973).
†Rabinowicz, J. Appl. Phys., 32, 1440 (1961).
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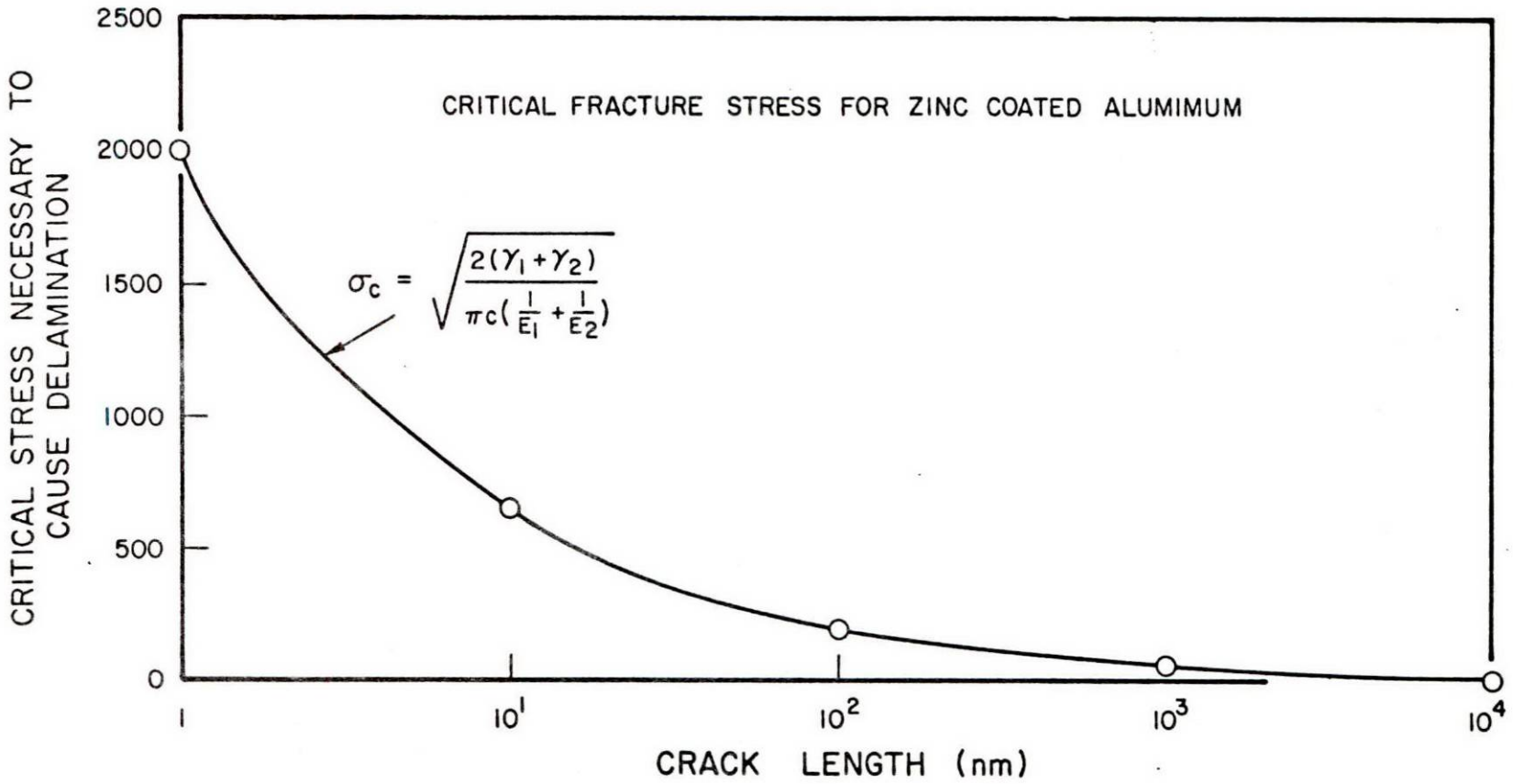

Figure 2: Critical fracture stress plotted as a function of crack half length

D

WORKSHOP ON REDUCTION OF PRECIOUS METALS USED IN ELECTRONICS

SESSION D

(No papers formally presented at this session)

E-1

LIGHT METALS FINISHING SESSION E

Hard-Anodizing of Aluminum by Low Voltage

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HARD-ANODIZING OF ALUMINUM BY LOW VOLTAGE

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James H. Morse
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ABSTRACT

A new low voltage hard anodizing process employs DC voltage up to 20V with superimposed AC voltage, and provides up to 6-7 mil coatings with high abrasion resistance. The breadkown voltage of the coatings may reach 4-5 kV DC. The coatings are uniform, pit free and develop significantly less than usual edge-defect.

INTRODUCTION

Anodizing of aluminum is a process of coating the metal with an oxide film which is formed through a combination of oxygen with aluminum. Anodizing processes differ in the sources of oxygen and in the means by which the oxygen is transported to the aluminum. Oxygen may be supplied from air, or plasma, or electrolyte, or some other source, with the help of diffusion, or heating or an electric field (for more details see [1,2,3]).

The anodizing process which is most extensively used in industry is the electro-chemical anodizing in an electrolyte. The process is carried out by having the current flow through the aluminum which is immersed in an oxygen containing electrolyte with the aluminum connected anodically. The properties of the anodic coating can change dramatically depending upon the composition of the electrolyte, its temperature, the waveform of the applied voltage, and the program under which the voltage is varied. Porous oxide films having sapphire hardness and with a thickness in the order of one or several mils (1 mil = 25.4μm) are produced by an electrochemical process which is called the "hard-anodizing process". The process was discovered in this country about three decades ago and is distinguished essentially a) by using an electrolyte, which contains a rather high concentration of a strong acid, (like sulphuric acid), b) by maintaining the electrolyte at a temperature which is well below room temperature (at 0°C, for instance), and c) by application of a gradually increasing voltage to keep the current from dropping below a reasonable level.

It became clear very early that it was not simple to create a "universal" hard-anodizing process which would be equally successful in providing hard-coating of any thickness of any aluminum alloy. A long effort to obtain this goal started and a number of different hard-anodizing processes were developed. These processes are known under different proprietary names such as the Martin Process, Sanford Process, Alumilite Process, etc. Each process has its own range of aluminum alloys and coating thickness at which the process is most efficient. We will discuss here the next step towards development of a "universal" hard-anodizing process. This step is primarily distinguished by implementation of a low DC voltage during the anodizing process.

LOW-VOLTAGE HARD-ANODIZING PROCESS

It was recently discovered that with the aid of a special power supply, which superimposes AC voltage over DC voltage, it is possible to economically produce hard coatings on aluminum at a low anodizing voltage. This process we will further refer to as the "LV"-process versus high-voltage ("HV") processes ordinarily in use. The LV-process includes the raising of the DC voltage component to a maximum value, which is less than 20V (predominantly 18V) after which the voltage does not change substantially during the rest of the anodizing cycle (see Fig. 1).

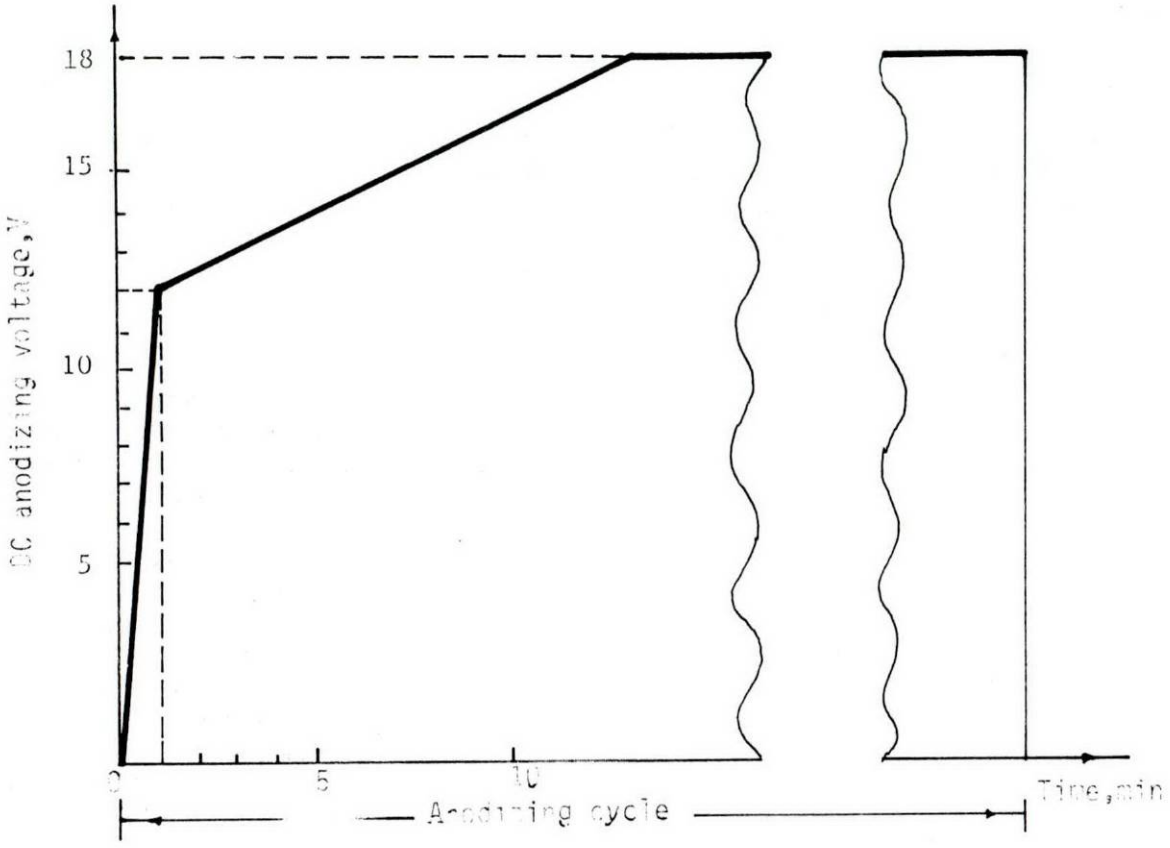


Fig. 1 Voltage-time relationship for the LV-process

The power supply may be with a single or three-phase input and it has a two-terminal output which provides DC voltage with a superimposed AC voltage (see Fig. 2). The AC component may be sinusoidal or non-sinusoidal and the ratio of the amplitude of a sinusoidal component to the DC component may vary. Preferably this ratio should be close to 100% (see Fig. 2c). Some properties of hard-coatings produces by the LV-process are illustrated on Fig. 3 and 4.

The 4 x 4 inch samples of aluminum alloys 2024, 6061, and 7075 were anodized in a water solution of sulphuric acid (200 g/l) with a weak acid additive according to [6] (1/3 of the sulphuric acid content). The temperature of the

electrolyte varied from 40°F to 50°F and is indicated in figure captions.

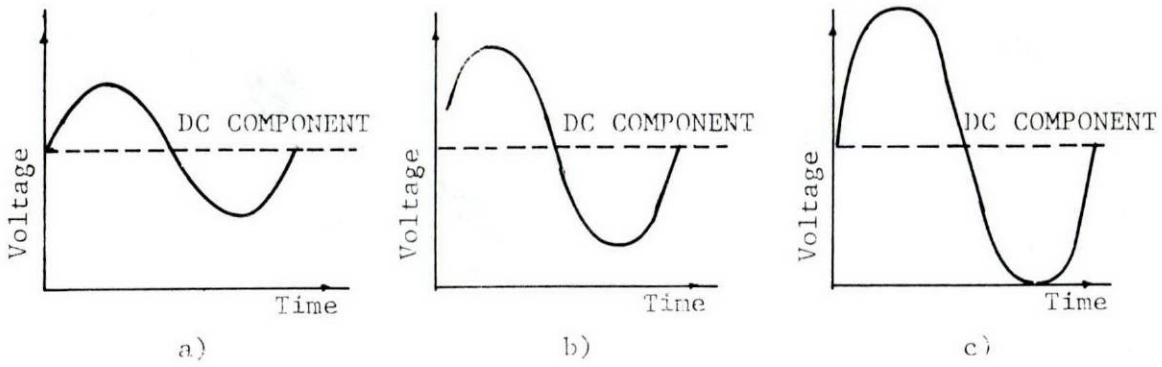


Fig. 2. Voltage waveforms provided by power source 5.
a) 50% AC component; b) 75% component; c) 100% component

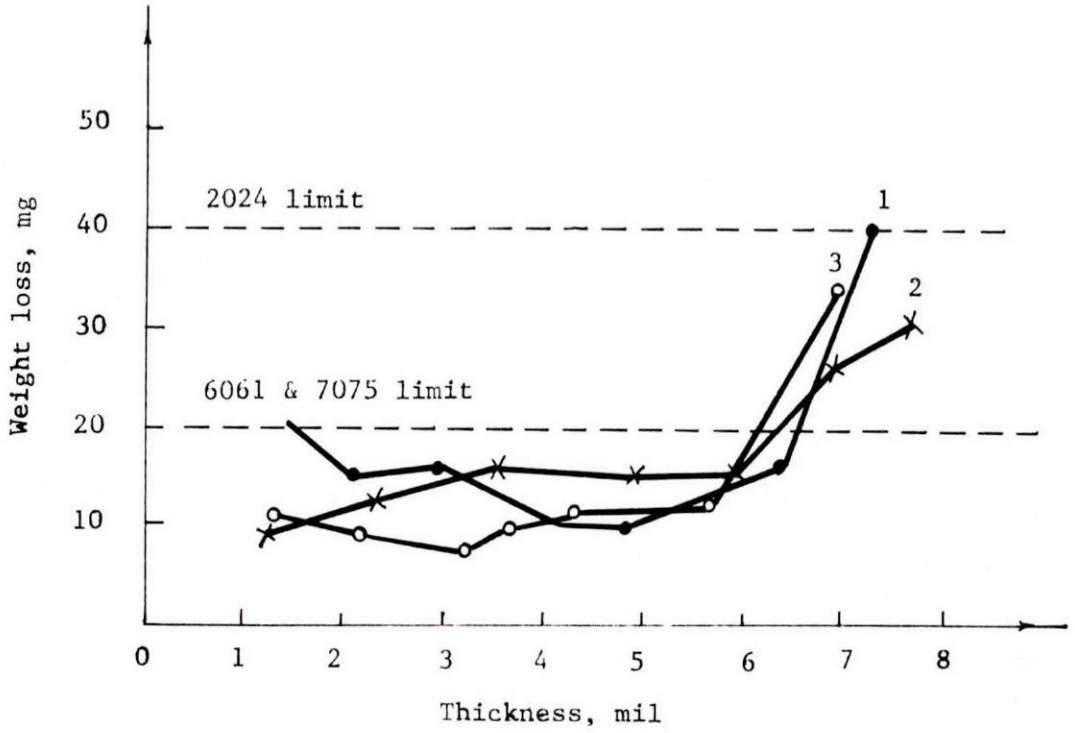


Fig. 3 Weight loss versus coating thickness for the LV-process. 1-2024 alloy, electrolyte temperature 40°F, 2-6061 alloy, 45°F, 3-7075 alloy, 40°F.

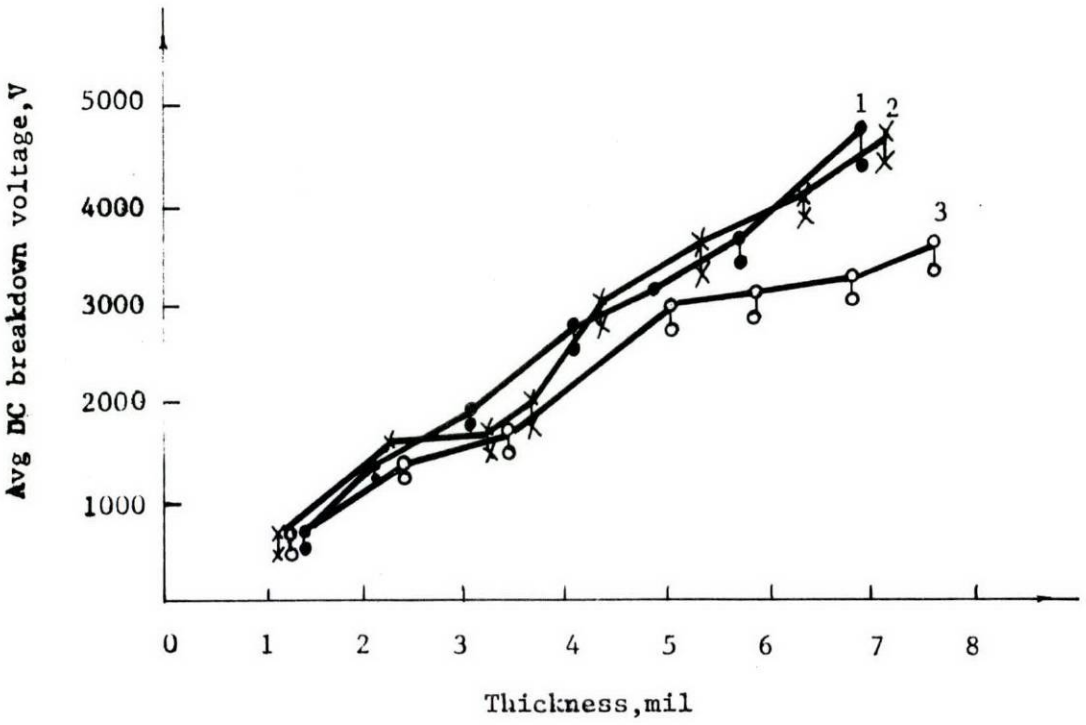


Fig. 4. DC breakdown voltage versus coating thickness for the LV-process. 1-2024 alloy, electrolyte temperature 40°F, 2-6061, 45°F, 3-7075, 40°F.

The LV-process was carried out at a voltage, the negative peak of which would be about the same magnitude as the DC component. The DC component was increased according to the pattern of Fig. 1. The Abrasion Resistance data presented on Fig. 3 were obtained with the help of a Taber Abraser according to method 6192 in Fed. Test Method Std. No. 141a. According to the test, the abrasion resistance is evaluated by the weight loss observed after 10,000 revolutions of the abrasive wheels under a load of 1 kg. A lesser weight loss means a higher abrasion resistance. The horrizontal broken lines represent the admissible level of abrasion resistance according to Military Specification MIL-A8625 C "Anodic coatings for aluminum and aluminum alloys". The possible fluctuations of the abrasion test results described in [7] are taken into consideration. The breakdown voltage data for different alloys are presented on Fig. 4 and were obtained at an average of 12 readings at 12 different spots on the anodized sample. The anodized aluminum was negative during the test. The positive electrode is made of copper with a hemispherical contact area having a 5mm radius. Besides the average data connected on the graph by a solid line, the magnitude of standard deviation is also indicated for each average data being located always below the corresponding average voltage.

The photograph on Fig. 5 illustrates the edges of the two anodized samples of 7075 alloy hard-coated by the LV-process (sample 1) and the HV-process (sample 2). The HV process was a Classic Sanford Process where a convention-

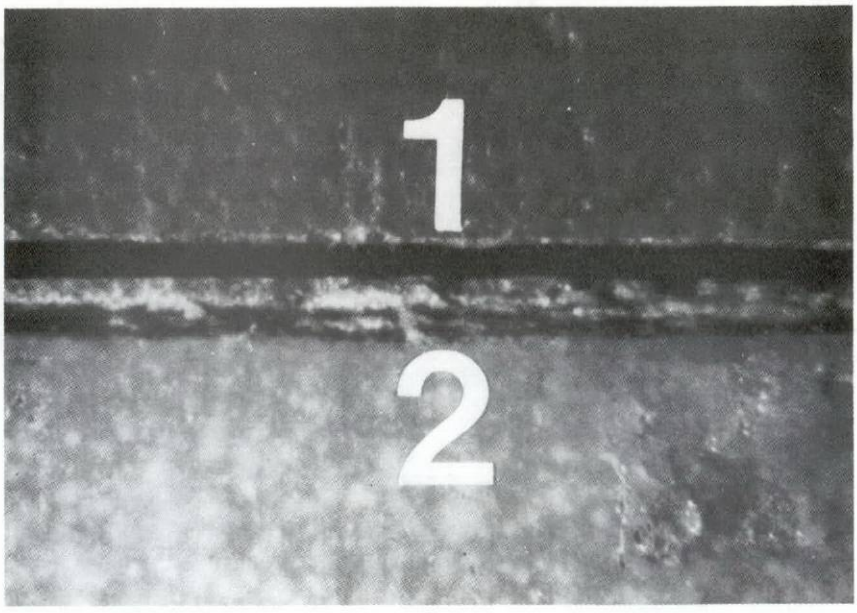
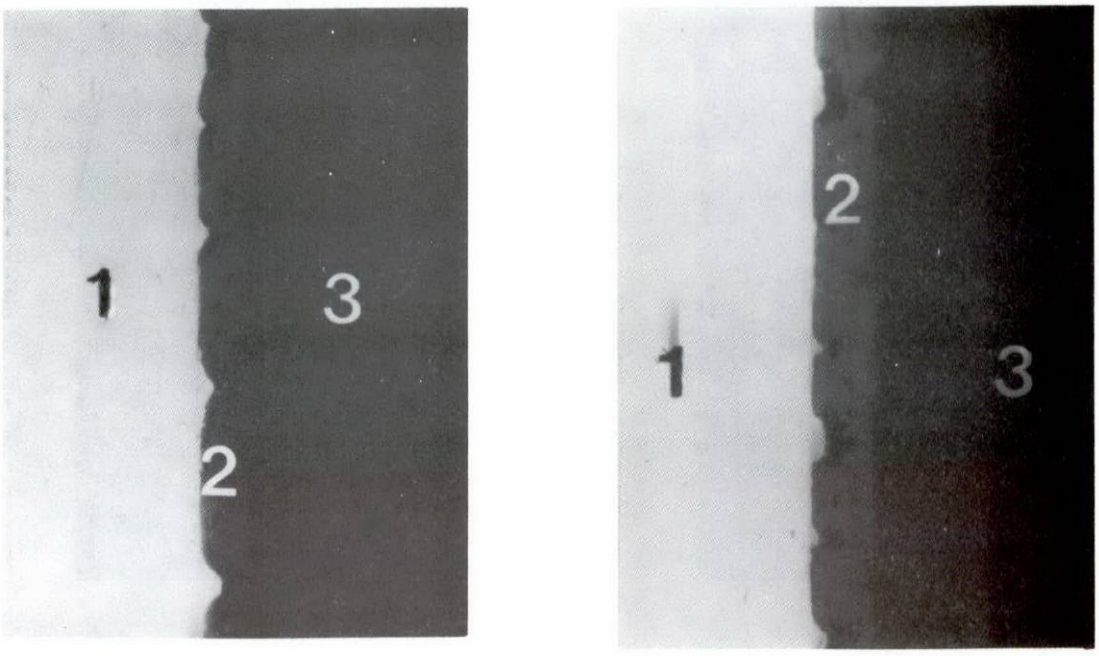


Fig. 5. Edges of two 7075 alloy samples with the same coating thickness. 1-anodized by the LV-process, 2-anodized by the HV-process.



a) b)

Fig. 6 Cross section of an oxide film formed by the HV-process at 29°F: a) 2024 alloy, 2.7 mil, b) 7075 alloy, 3.5 mil. 1 - aluminum, 2- oxide film, 3- plastic medium.

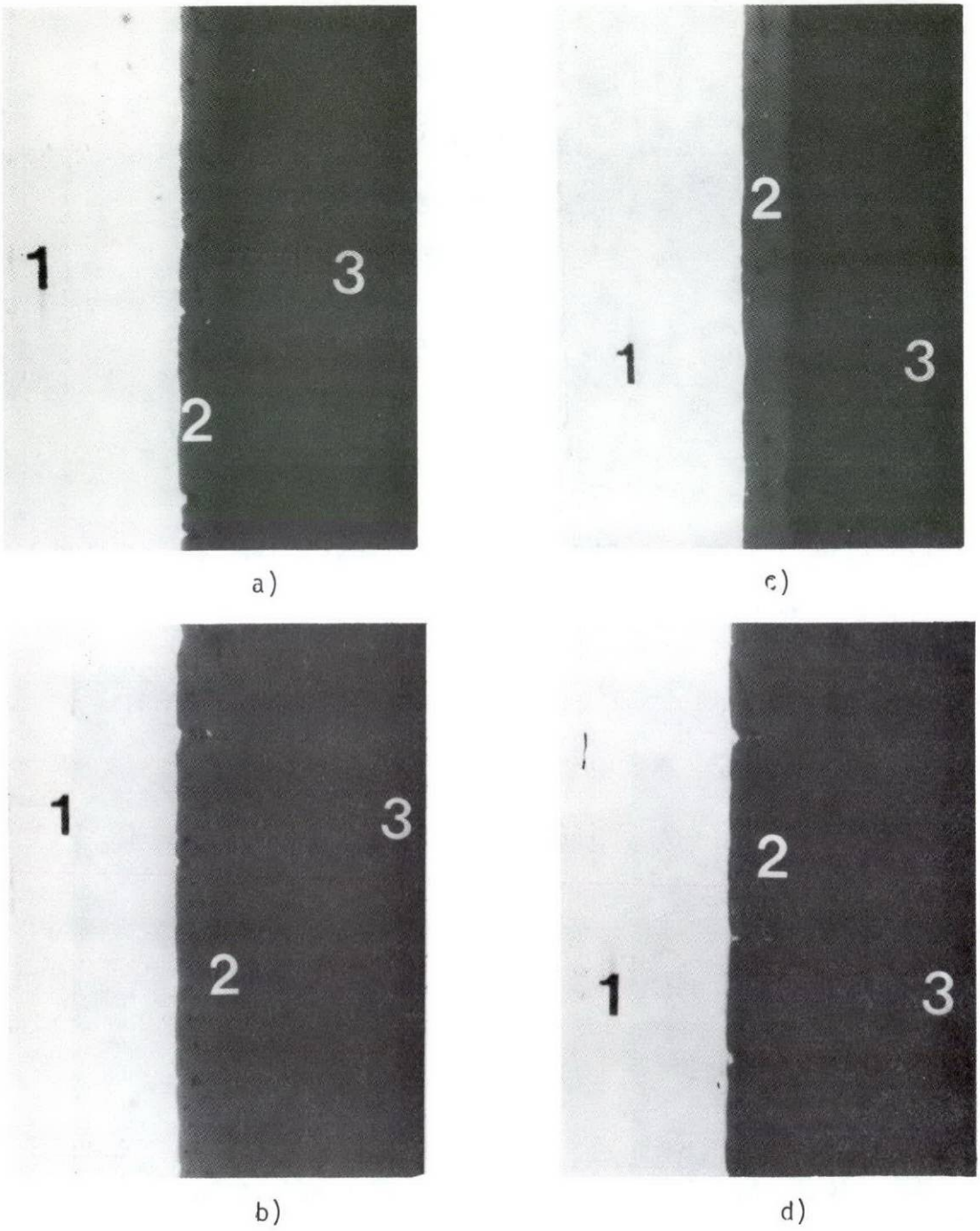


Fig. 7 Cross section of the oxide film formed by the LV-process: a) 2024 alloy, 2.6 mil thick, 40°F, b) 2024, 5.7 mil, 50°F, c) 7075, 3.1 mil, 40°F, d) 7075, 5.6 mil 40°F.

al electrolyte was used (320 g/l of sulphuric acid plus a weak acid additive according to [6]) at a temperature of 32°F. The DC voltage was raised to 18V during the first minute and then about 1V per 2 minutes. The thickness of the coatings on each of the samples was the same - 3 mils.

Photographs in Fig. 6 and 7 illustrate the uniformity of the LV-coatings compared to the HV-coatings (Fig. 6) produced by the Sanford Process described above. Regardless of being hard and meeting the Military Specifications as to Abrasion Resistance requirements, hard oxide films on heavily alloyed aluminum often have internal cavities called pits. A pit exposes itself whenever the oxide film is honed or ground to remove the outer surface.

In spite of conducting the process at a low anodizing voltage the current density during the LV-process is rather high going up to 70-80 A/ft^2 on alloy. That is why the time of anodizing is relatively short, which is illustrated by the dependance of the anodizing time upon coating thickness at Fig. 8.

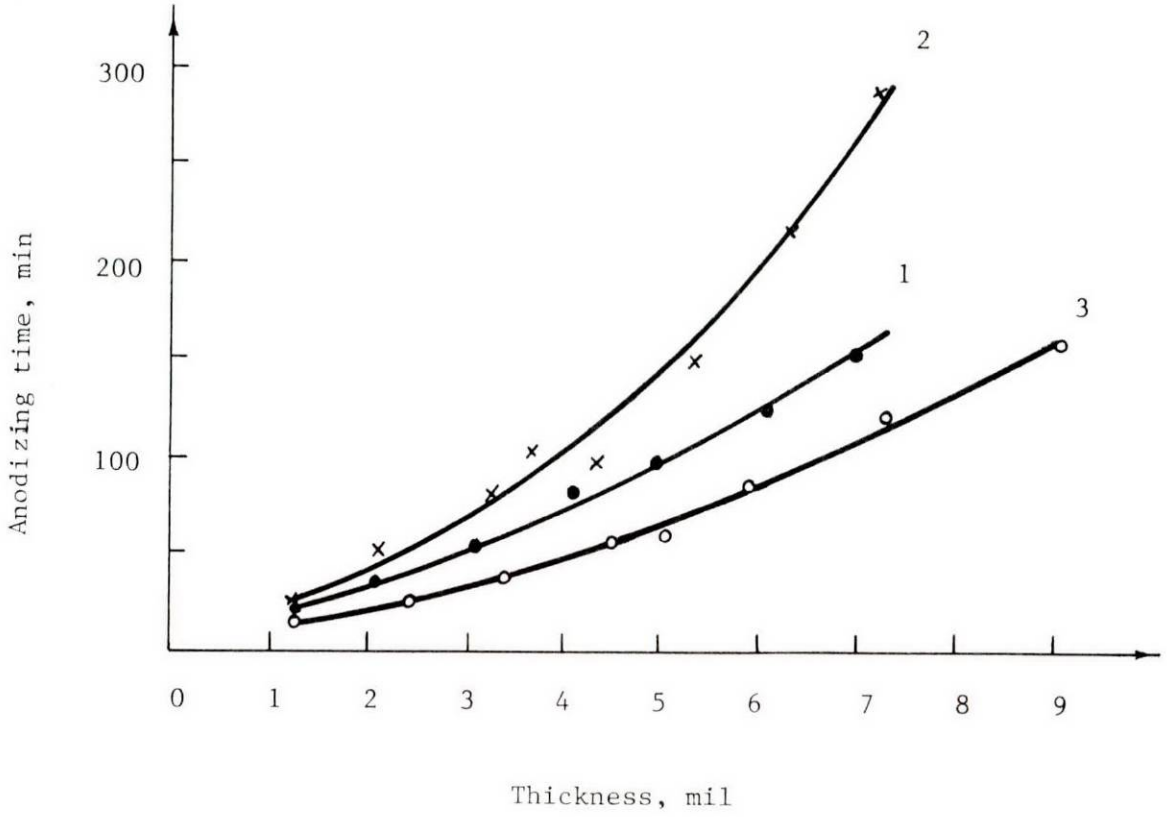


Fig. 8 Anodizing time versus coating thickness for the LV-process. Electrolyte temperature 45°F, 1-2024 alloy 2-6061, 3-7075

DISCUSSION

The analysis of the abrasion resistance of LV-hard-coatings, as it follows from Fig. 3, shows that these coatings at thicknesses up to 6-6.5 mils remain very hard, meeting the Military Specification requirements with a good reserve. It is remarkable that the 2024 alloy, which in HV-processes yields an oxide film of considerably poorer quality than other alloys as to abrasion resistance, produces a hardcoat of about the same high quality as for other alloys when it is formed by the LV-process.

The data of Fig. 4 show approximately linear increase of the DC breakdown voltage versus thickness for 2024 and 6061 alloy. For a thickness of 6-7 mils the breakdown voltage may exceed 4000V DC. The examination of the photograph on Fig. 5 shows that the sample 1 which was anodized by the LV-process has a clean edge as compared to the edge of the sample 2 anodized by the HV-process. The two samples are shown on the photograph separated by a dark gap. The oxide film at the edge of the sample 2 is formed in a strikingly different manner as compared to sample 1. The sample 2 has a very pronounced "edge-defect".

The analysis of Fig. 6 and 7 demonstrates the dramatic deminishing of the number of pits on 2024 and 7075 alloys when the LV-process is used. The LV-process provides comparatively pit-free coatings not only at 3 mils, but also at 6 mil thicknesses as well.

We believe that the remarkable properties of LV-coatings ensue primarily from the fact that the LV-oxide films are more uniform and ductile. Uniformity is sequential from the anodizing voltage being kept unchanged through a considerable portion of the anodizing cycle. As has been known[8], the distance between the pores in an oxide film is proportional to the applied voltage. This means that the higher the anodizing voltage, the fewer pores per unit of surface area will be formed. In the LV-process, the maximum V_{max} is reached during a short period (run-in period) and then the voltage stays unvariable (dwell period). At Fig. 9 the run-in period is schematically represented only by two voltage steps, V_1 and V_2, before the maximum voltage V_{max} is reached. At each step, the formed oxide has a porosity corresponding to the voltage of the step. So, when the maximum voltage was reached two different layers, 1 and 2, with different porosity had been formed. The major part of the coating, layer 3, is formed during the rest of the anodizing cycle (dwell period) when the voltage remained maximum. That is why the coating, except the very external layer, (See Fig. 9) has homogeneous porosity.

On the other hand, since the maximum DC voltage is much lower than in the case of a HV-process the oxide film is much more porous. As a consequence the oxide film is more ductile and less susceptible to cracking, ensuring a neat and clean edge at a thickness where HV-process will cause a considerable edge-defect. Higher porosity also causes savings of Coulomb electricity. According to Faraday's law, a definite amount of electricity Q (in Coulombs) is needed to produce a definite mass M of coating via an electro-chemical

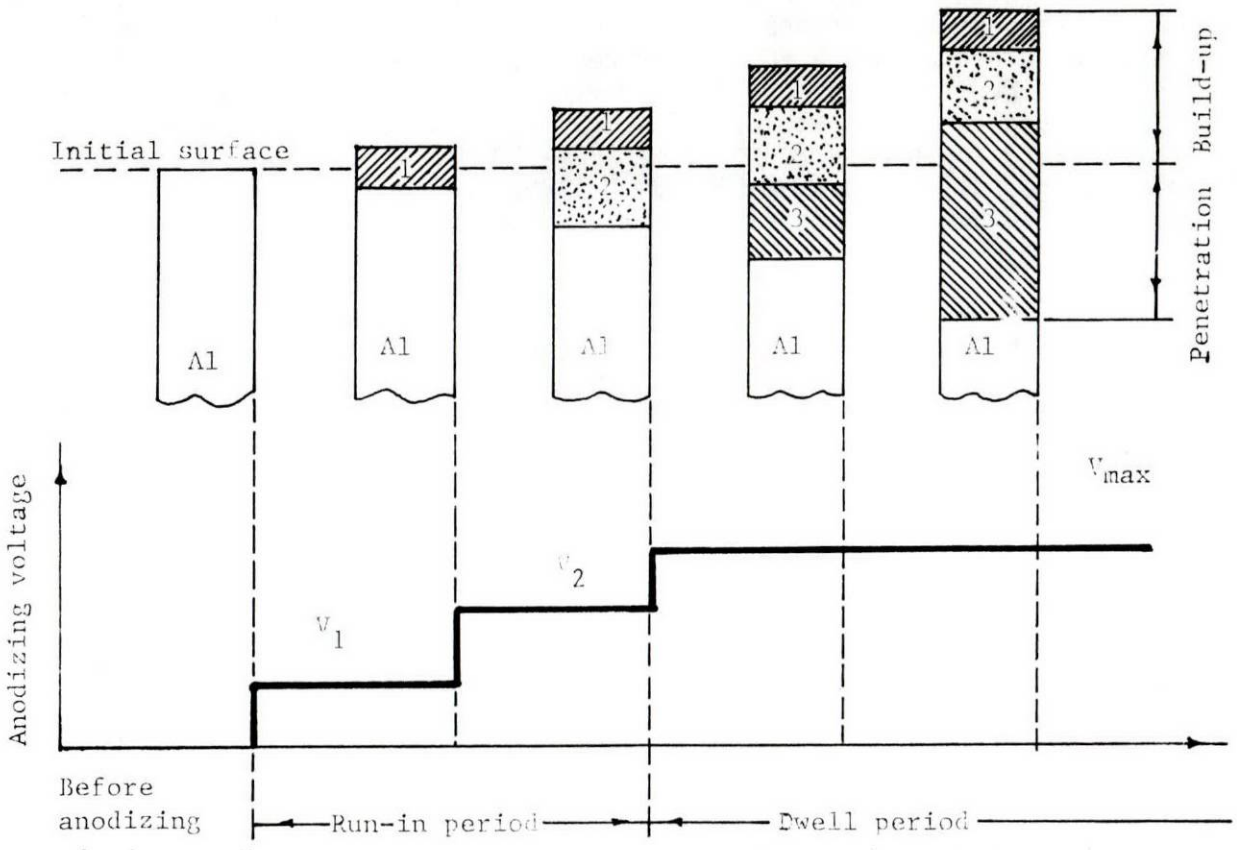


Fig. 9. Schematic diagram for oxide film growth during the LV-process. 1,2-oxide film formed during the run-in period, 3-oxide film formed during the dwell period.

process:

$$Q = K\,M \tag{1}$$

where k is Faraday constant.

Mass is related to coating surface S, thickness d and density D by equation

$$M = d.SD \tag{2}$$

Consequently from (1) and (2) we deduce

$$Q = k.Sd.D$$

From this equation if follows, that if density D of the oxide film diminishes, which happens when anodizing is conducted at a lower voltage, then the amount of electricity which is needed to produce a coating of the same thickness d on the same surface S also diminishes. The HV-process, like Sanford Process, needs 12 ampere-hours to cover 1 square foot (929 cm^2) with one mil (25.4) thickness. The LV-process needs only 10.6 A.h/ft^2/mil, which gives about 15% savings of electricity.

Examination of the anodizing time data, presented at Fig. 8, shows that the 7075 alloy needs the shortest period to form an oxide film of the same thickness as on other alloys. 2024 alloy needs about 30% more time, and 6061 alloy about 2.5 times more. It is remarkable that with the help of the LV-process 6 and even 7 mil-thick-films may be anodized on 6061 alloy temper T6 after a reasonable period of time (200-250 min - see Fig. 8) and these coatings are still hard (see Fig. 3). It is ordinarily difficult to obtain more than 3-3.5 mils on this alloy if a HV-process is used.

CONCLUSIONS

Low voltage hard anodizing process, (the LV-process) permits the manufacture of oxide films which are superior to the coatings anodized by the HV-process. The new coatings produced by the LV-process are more uniform, have higher abrasion resistance, less pronounced edge-defect, higher breakdown voltage, and are more porous and ductile. The new process is simple to operate and it saves energy.

ACKNOWLEDGEMENTS

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E-2

LIGHT METALS FINISHING SESSION E

Continuous Coil Anodizing—A Technical Update

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CONTINUOUS COIL ANODIZING - A TECHNICAL UP-DATE

Howard A. Fromson

The current annual consumption of pre-anodized coil in the United States is estimated at more than 100,000,000 pounds. During its early market development preanodized coil was used primarily as a substitute for batch-anodized aluminum in transportation (truck siding, trailer roof panels, etc.), consumer durables (appliance panels, welded furniture tubing) building components (lighting reflectors, ceiling panels, kitchen tiles). Its relative flexibility permitted post-anodizing fabrication such as bending and punching without any significant damage to the anodic coating, particularly in applications for interior use.

The costs were substantially less than batch anodizing, in some cases 1/4 the cost, and where exposed edges or slight crazing could be tolerated, many millions of dollars were saved.

These existing markets for traditional pre-anodized products have continued to expand, but at a much slower rate. Organic coatings, high temperature resistant, corrosion resistant, and esthetically attractive, have provided strong competition.

But other markets, primarily technical in nature, have provided new opportunities for continuous coil anodizing.

The single largest non-decorative market for pre-anodized aluminum coil is in lithography. Approximately 400,000,000 square feet of anodized aluminum coil are consumed for lithographic purposes in the United States alone.

Millions of pounds of aluminum are also pre-anodized to form the separator on the double and triple glazed window and door sections so much in demand in these days of high-energy costs. Pre-anodized aluminum coil is even used in such sophisticated applications as the phosphorescent luminescent panels now becoming so popular in automotive and aeronautical instrument panels.

Most of these new technical applications for pre-anodized coil demand high-speed operations to minimize unit costs. The thickness or gauge of the coil in these new markets is generally under .020", and in some cases is as thin as .002"

The limiting parameter in continuous coil anodizing for technical use, particularly for light gauges has been the ability to introduce current into the web at high rates without burning the web. As most of you are aware, in continuous coil anodizing the web is used as its own conductor. The ultimate constraint is the current-carrying capacity of the web, which in turn is a function of its cross-sectional area.

Various methods have been proposed to increase productivity or the rate at which current can be introduced into the web without burning. They divide themselves into four techniques:

A. Baffled Entry, a process for limiting electrical current flow at the moment of critical entry into the electrolyte to guarantee formation of a completely sound barrier layer before high current anodizing begins.[1]

B. One Side Anodizing, a process to minimize the amount of total current required by limiting the anodizing process to one side of the web.[2]

C. Stepped Current Introduction, a process to maximize the amount of total current carrying capacity at higher voltages by a gradual step-wise increase in a multi-cathode, multi-rectifier tank, the increase in cathode area being controlled with respect to the current per unit cross section, so as to prevent premature return of current to the rectifier.[3]

D. Turbulent Pressurized Cooling, a process to increase the current carrying capacity of the web/conductor by high turbulent flow of a continuously recirculating electrolyte around the web within the confines of an enclosed elongated vessel containing both the positive and negative electrodes.[4]

In the early 1970's, our company, Ano-coil Corporation of Rockville, Connecticut began to experiment in new ways of introducing current into continuous anodizing lines, which eventually resulted in a series of patents. We chose to remain with our basic contact cell technology: our goal was to increase our productivity without substantially altering our physical and electrolytic plant. Ten years of experience of operating our lines had taught us how critical very minor changes in cathode configuration, pump velocities, temperature of electrolyte, as well as simple line tension could be when introducing current into continuous webs. We elected, therefore, to stay with our basic line concept of highly visible webs and easily accessible rolls in open-faced tanks.

The process was based on the unique valve characteristics of anodized oxides, similar to that of semi-conductors. When aluminum is made the anode in a standard polyvalent acid such as sulfuric acid, the barrier oxide is formed at somewhere around 12v. With the same electrolyte, and the same amperage used to originally anodize the surface, but reversing the polarity on the already anodized aluminum surface to make it the cathode, the voltage dropped from 12 to 2 volts. In other words, the voltage required to form the anodic oxide is approximately 12 volts, but the voltage required to carry the current through the oxide cathodically is only 2 volts.[5]

With this insight, we designed an anodizing cell where the current was introduced into the web through an already existent oxide film. Let me explain!

A typical coil anodizing line would use a contact drum or a liquid contact cell. The liquid contact cell permits the introduction of somewhat larger currents into the moving web, but the cross section of the web is still

the limiting factor. In order to understand the theory of our process, let me first describe how the conventional liquid contact works. Figure 1 shows a schematic diagram of a coil line where the web enters the liquid contact cell A. Current is fed from the positive side of the rectifier to lead

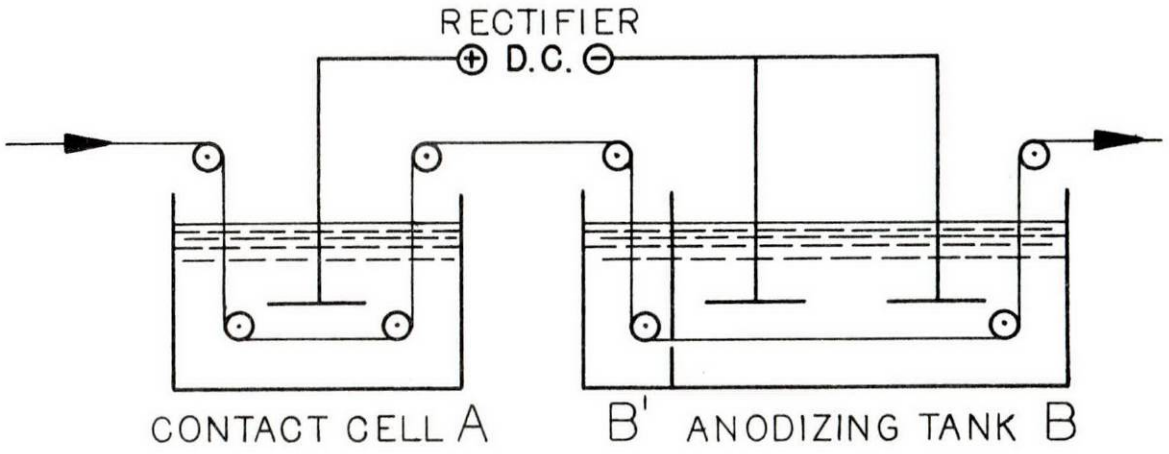

FIG. 1

anodes, and flows through the electrolyte to the web which is negative relative to the anode. The negative side of the rectifier is connected to lead cathodes in the anodizing tank B. The current travels through the web, which enters the baffle area B^1 as it passes through the anodizing tank. In this tank, the web becomes the anode, and an anodic coating is formed on both surfaces of the web. The web then passes through rinses, a dye bath if required, and a seal bath.

Our process adds another anodizing tank located upstream from the liquid contact cell as shown in Figure 2. Furthermore, we add one more rectifier. We now have anodizing tank A, followed by liquid contact cell B, followed by anodizing tank C. (We call this the ABC process). The positive side of Rectifier 1 is connected to one of the lead anodes in the liquid contact cell and the negative side is connected to lead cathodes in tank A, the first anodizing cell. The positive side of Rectifier 2 is connected to the second lead anode in the same liquid contact cell, and the negative side is connected to the lead cathodes in the second anodizing tank B. The current from Rectifier 1 now forms a loop through the web in Tank A and back to the Rectifier. The moving web, which now has an anodic coating, passes through liquid contact cell B. The current from Rectifier 2 passes through the oxide coating to the web into tank C where the anodizing continues as the current completes the loop back to Rectifier 2.

Having made it possible to introduce current into an aluminum web

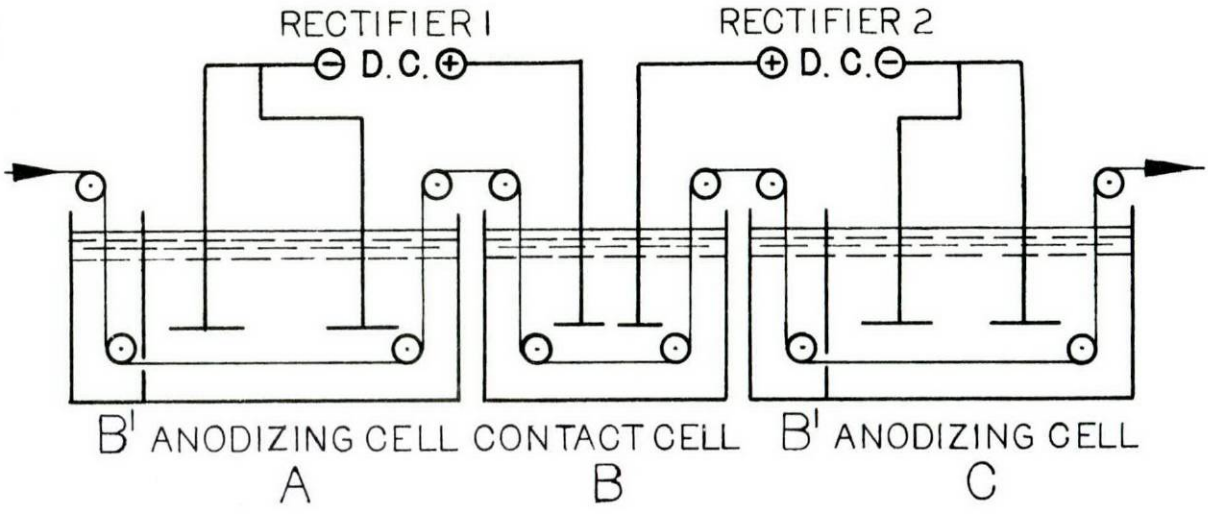

FIG. 2

through the oxide itself, at a cost of only 2 volts of resistance, it now became possible to design a series of cells, such that substantially all the current is pumped into the web at a multiplicity of points, each cell functioning with its own anodizing circuit, so current can be introduced into the web through a multiplicity of cross-sections.

Having determined that current can be introduced intc an aluminum web through the oxide at a cost of only 2 volts, a completely new design concept is now possible. Since the ABC process eliminates the need to carry the total anodizing current through one cross-sectional area of the web, it is possible to double or even quadruple the amount of energy in the web by simply introducing additional current at one or more sections of the web. viz. Figure 3

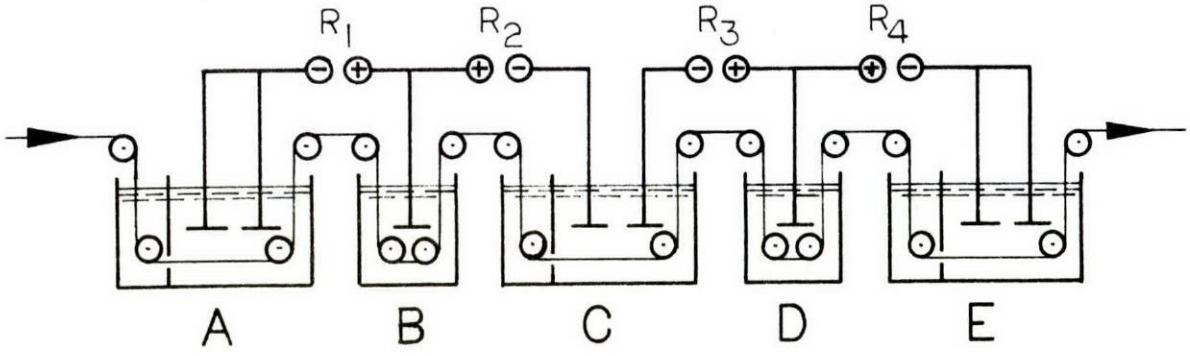

FIG 3

It will be apparent also that it is possible and desirable to use different voltages at succeeding locations as the anodic oxide becomes thicker.

Since the electrolyte dissolves a portion of the newly formed anodic coating, close control of the temperatures in all tanks, particularly the liquid contact cell, is critical. A correction must be made for the slight loss of anodic oxide which occurs, but this has been found to be constant for any given set of conditions.

We at Ano-coil have been using the ABC process for more than six years. During this period we have anodized webs as thin as .002 x 48" and we have increased the productive capacity of our equipment by more than 100% without additional lines. We presently have licensees who, without the ABC process would not have been able to produce an anodic film at a competitive price.

The unique features of our process make it possible to utilize the anodized web for many other subsequent treatments. With ABC it is now possible to simultaneously anodize, and often times with the same current, electro-plate, electro-paint, and/or electrolytically dye a continuous web or wire of aluminum at high speeds.[6] We have successfully deposited nickel, copper, and chrome in and on anodized substrates by utilizing the negatively charged web in the contact cell with suitable electrolytes as the plating substrate. And if there were sufficiently large markets ABC lends itself to the continuous production of coiled sheet or wire self-dyed by the Kalcolor ™ or Duranodic™ processes of Kaiser Aluminum and Alcoa.

To sum up, the Ano-coil ABC process results in the following advantages for coil anodizing:

A. A more than 100% increase in productivity.

B. A substantial slash in capital cost per unit capacity.

C. The opportunity to continuously anodize in electrolytes that require stepped increases in voltage.

D. The possibility to continuously electro-deposit metallic and organic coatings and inorganic dyes in and on porous anodic oxides.

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5. H.A. Fromson, U.S. Patent Re. 29,754, 1978

6. H.A. Fromson, U.S. Patent 3,929,594, 1975
   H.A. Fromson, U.S. Patent 4,021,592, 1977

L-3

LIGHT METALS FINISHING SESSION E

The Coloration of Anodized Aluminum Architectural Components by the Overdyeing of Integral Color or Two-Stage Electrolytically Colored Oxide Films

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The Coloration of Anodized Aluminum Architectural Components by the "Overdyeing" of Integral Color or Two-Stage Electrolytically Colored Oxide Films.

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Abstract

The range of colors available from the currently used architectural anodizing processes leaves much to be desired for the architect who wishes to make full use of color as a design element. The overdyeing of either integral color or two-stage electrolytically colored anodic oxides with selected organic dyes enables the architect to offer new shades which were previously unavailable. The suggested processing conditions and control procedures to assure consistantly high quality are discussed in detail. The results of laboratory tests and preliminary exterior exposures are also presented.

In the presentation today, we will describe new methods for producing a wide range of colors heretofore unattainable. These colors are produced by combining current available technology; that is to say we will 'over-dye' either an integrally colored or a 2-stage electrolytically colored oxide film with selected organic dyes to obtain a colored film having the characteristics of both methods for coloration.

We will discuss the basic integral color process, the basic two stage electrolytic coloring process and the combined process, with emphasis on the controls required in the dyeing steps, since these procedures may not be familiar to you.

We will also present some data concerning the lightfastness of the combined process, the amount of dye actually in the coating, and the location of the various colorants within the oxide film.

During the past twenty years the continued improvements in old methods and new developments in processing technology for the production of colored architectural components, have been responsible for the increasing use of color as well as form as a part of the structural component.

At present there are basically two methods for producing colored aluminum architectural components: (Slide 1)

COLORED ORGANIC COATINGS --- PAINTS

ANODIC COATINGS ------

INTEGRAL COLOR
TWO-STAGE ELECTROLYTIC
ADSORBTIVE DYEING

Slide 1

METHODS FOR COLORING ARCHITECTURAL COMPONENTS

COLORED ORGANIC COATINGS — PAINTS

ANODIC COATINGS— —

- INTEGRAL COLOR
- TWO-STAGE ELECTROLYTIC
- ADSORBTIVE DYEING

Using paints it is possible to obtain an almost unlimited range of colors, including pastels and even white. In spite of this obvious advantage, the method is not without drawbacks - the possible loss of adhesion of the coating, scratching or abrasion of the film, and most importantly, the hiding of the metallic characteristics of the aluminum substrate.

With those methods based on anodizing, we are able to preserve the metallic appearance of the substrate, due to the relative transparency of the oxide film.

Let us now discuss the ways of producing architecturally "useful" colored oxide films.

The next slide shows the basic integral color process. (Slide 2)

INTEGRAL COLOR PROCESS

Basic Electrolyte	"SULFO" acid with low sulfuric acid content
Current Density	2.5-3.7 amps/sq.dm 24-36 ASF
Voltage	65-80 final voltage
Temperature	21-30°C (70-78°F)
Colors	Limited range - BRONZE GREY BLACK

In the next slide we show the basic two-stage electrolytic process. (Slide 3)

TWO - STAGE ELECTROLYTIC COLOR PROCESS

Conventional Sulfuric Anodize -- Followed by
Electrolytic Color Deposition
AC Treatment in electrolyte containing
NICKEL, COBALT, COPPER or TIN salts

Two Separate Processes

Oxide thickness determined by function, NOT COLOR
Easier color control - NOT alloy or temper dependent
Lower voltage & current needed - AC rather than DC
Color independent of thickness

The two-stage processes seem to be gradually replacing the integral color processes, in spite of requiring additional tanks and equipment. They do not need the high DC voltages or refrigeration needed in the integral color process. Also in the two-stage electrolytic process the color is not dependent on the

Slide 2

INTEGRAL COLOR PROCESS

Basic Electrolyte	"SULFO" acid with low sulfuric acid content
Current Density	2.5-3.7 Amps/sq.dm (24-36 ASF)
Voltage	65-80 V — Final
Temperature	21-30°C (70-78°F)
Colors	Limited range — BRONZE GREY BLACK

TWO — STAGE ELECTROLYTIC COLORING PROCESS

Conventional Sulfuric Anodize — — Followed by

Electrolytic Color Deposition
AC Treatment in electrolyte containing NICKEL, COBALT, COPPER or TIN salts

- Two Separate Processes

Oxide thickness determined by function, NOT COLOR
Easier color control-NOT alloy or temper dependent,
Lower voltage & current needed — AC rather than DC
Color independent of thickness
Limited color range

oxide film thickness, the alloy, temper or some of the other variables as in the integral color processes.

With regard to the over dyeing of these colored oxides, any of the colors which can be produced are suitable, but the bronze shades offer the most interesting range of new colors.

It is not possible to do the dyeing step before the electrolytic coloring, since in some cases the presence of the dye will interfere with the deposition of the inorganic colorant. Also, the treatment of the dyed film in a highly acidic media, such as that required in electrolytic coloring even without the current, generally causes bleeding out of the dye, resulting in non-uniform color and inherent lightfastness problems.

It should also be pointed out that the RINSING between the various processing steps MUST be of the highest quality, preferably a cascade, counter-current station with a total dwell time of about 10 minutes followed by a standing distilled or DI water rinse of 2-3 minutes duration. This will ensure that there will be minimal drag-in of either the electrolytic coloring bath or the sulfuric acid into the dyebath.

For the dyeing step, we find that the same high standards which are required for the dyeing of clear architectural work must be adhered to. These are shown in the next slide. (Slide 4)

DYEING CONDITIONS

	content g/l*	pH + 0.5	Shade
Yellow 3GL	3.0	5.5	Lemon Yellow
Red B3LW	5.0	5.5	Garnet Red
Blue G	5.0	5.5	Dark Blue (navy)
Turquoise PLW	12.0	5.0	Turquoise
Black GL Paste	30.0	5.0	Black (Graphite)
Deep Black MLW	10.0	4.5	Jet Black (Telephone)
Gold 4N	10.0	4.5	Gold Shades**

*"Effective Dye Content ---- 75-80% of nominal
Dye Time 20-30 Minutes except Golds
Dye Temperature 60°C ± 5 (140°F. ± 9 except Golds)

**Gold --- Bath Temperature 50°C. (120°F.)

Immersion Time	
2 minutes	Champagne
4 minutes	Pale Gold
6 minutes	Medium Gold
10 minutes	Dark Gold

DYEING CONDITIONS

	Nominal Content g/l*	pH ±0.5	Shade
Yellow 3GL	3	5.5	Lemon Yellow
Red B3LW	5	5.5	Garnet Red
Blue G	5	5.5	Dark Blue (Navy)
Turquoise PLW	12	5.0	Turquoise
Black GL Paste	30	5.0	Black-Graphite
Deep Black MLW	10	4.5	Jet Black
Gold 4N	10	4.5	Gold Shades**

*"Effective" Dye Content — 75 - 80% of NOMINAL

Dye Time 20 - 30 Mins — Except Gold
Dye Temperature 60°C + 5 (140°F + 9) — Except Gold

GOLD	Bath Temp.	49°C —	120°F
	Immersion Time	2 Mins.	Champagne
		4 Mins.	Pale
		6 Mins.	Medium
		10 Mins.	Dark

The controls needed are shown in the next slide. (Slide 5)

DYEING CONTROLS

Constantly Monitor	Temperature of Dyebath Immersion Time
Each Shift or Daily	pH of the dye solution
Daily	Dye Concentration
Weekly	"Effective" Dye Concen=tration

As for the Sealing operation, we suggest the conditions which are shown in the next slide. (Slide 6)

SEALING CONDITIONS

Nickel Acetate	3-5 g/l Nickel
pH	5.5-6.0
Temperature	97°C (207°F) Minimum
Time	45 Minutes

In the control of the dyeing operation, the techniques required for measuring the dye content (both nominal and effective) are NOT widely practiced. I will briefly outline them for you. For the nominal, we optically compare (using a spectrophotometer or colorimeter) the absorbtion, at a fixed wavelength in the visible region, of a freshly prepared solution of the proper dye content with the absorbtion, at the same wavelength, of a sample of the tank solution. Naturally both solutions must be at the same dilution, pH, etc. By calculation we can arrive at the ratio of the strength of the working tank.

In order to determine the "effective" strength of the dye tank, and by "effective" dye content, I mean that portion of the total dye content present which is actually effective in the coloration of the oxide. To measure this "effectiveness", we must do the following: Using two pieces of anodized aluminum of the same convenient size, (area known) we dye one in a fresh solution of the proper dye content (100% activity) and the other in the working solution. We then strip the coating and dyestuff using inhibited sodium hydroxide, (to prevent destruction of the dye), and measure the absorbance of these two solutions. From this we can calculate the "effective" dye content.

Knowing the effective dye content, we can make additions to the tank to bring it up to the correct dye strength. It has been

Slide 5

CONTROLS FOR DYEING

Constantly —	**Temperature**
	Immersion Time
Each Shift — or Daily	**Dye Bath pH**
Daily —	**Dye Concentration**
Weekly —	**"Effective" Dye Content — Gold**

SEALING CONDITIONS

Nickel Acetate	3 - 5 g/l Nickel
pH	5.5 - 6.0
Temperature	97° C (207° F) Minimum
Time	45 Minutes

found in practice that, when the effective strength falls to 75-80% of the nominal content, it is NOT practical to reinforce the bath because the level of contamination is too high. The things that decrease the effective content are mainly sulfate and aluminum ions, both of which combine with the dye molecule and render it ineffective in coloring the oxide film. Good rinsing, therefore, is essential to keep sulfates and aluminum out of the dyebath.

Having discussed the individual processing steps in some detail, we shall now present some test data which was obtained from specimens prepared as follows. (Slide 7)

SAMPLE PREPARATION

Degrease and Matte Etch	
Anodize to 25 Micron (1.0 Mil)	16% Sulfuric Acid 60 minutes 14-15 Volts DC 1.3 amps/Sq. dm. (12 ASF) 21°C (70°F)
Electrolytically Color	AC Treatment in either 1. Nickel Bath 2. Tin Bath
Dye	GOLD 4N YELLOW 3GL RED B3LW BLUE G TURQUOISE PLW
Seal	Nickel Acetate Based

The next slide shows admittance data for a number of samples prepared in a nickel bath. (Slide 8)

SAMPLE PREPARATION

Degrease and Matte Etch	
Anodize to 25 Micron (1.0 Mil)	16% Sulfuric Acid 60 minutes 14-15 Volts DC 1.3 amps/Sq. dm. (12 ASF) 21 °C (70 °F)
Electrolytically Color	AC Treatment in either 1. Nickel Bath 2. Tin Bath
Dye	Gold 4N Yellow 3GL Red B3LW Blue G Turquoise PLW
Seal	Nickel Acetate Based

Slide 8

ADMITTANCE VALUES
Micro Siemens

	ELECTROLYTIC BRONZE NICKEL SALT			
	CLEAR	LIGHT	MEDIUM	DARK
CLEAR	12	12	12	13
Red B3LW	12	12	12	12
Yellow 3GL	13	13	13	13
Turquoise PLW	14	14	14	14
Blue G	50	50	50	50

ADMITTANCE - MICRO SIEMENS

ELECTROLYTIC BRONZE

NICKEL SALT

	CLEAR	LIGHT	MEDIUM	DARK
CLEAR	12	12	12	13
RED B3LW	12	12	12	12
YELLOW 3GL	13	13	13	13
TURQUOISE PLW	14	14	14	14
BLUE G	50	50	50	50

The admittance data is as anticipated and is similar to the values found on clear dyed films. The high values found for the blue were also found in our earlier work.

The results of both standard salt spray and the Kasternich tests are the same as those of either the electrolytic or dyeing process alone. Thus the corrosion resistance of the combined process is anticipated to be the same as that of either process alone.

In the accelerated corrosion tests, no differences were noted between dyed and undyed specimens prepared as we have discussed. Acid dissolution tests show no effects of degradation of the oxide film by either the dye or the dyeing operation with the exception of Sanodal Blue G, which seems to cause a loss in corrosion resistance as measured by this test. This does not show up in either CASS or the Salt Spray results, however.

The admittance values for electrolytic films colored in tin salts (not shown) are all higher, due no doubt to the low pH of the tin bath attacking the unsealed oxide.

The results of weight-loss tests are all in the range of 2-8 mg/dm^2 - well within the permissible limits.

The loss of colorant intensity after 3200 hours of Fade-O-Meter exposure is shown in the next slide. (Slide 9)

Slide 9

LOSS OF COLOR INTENSITY

Fade-O-Meter 3200 Hours

	ELECTROLYTIC BRONZE			
	CLEAR	LIGHT	MEDIUM	DARK
CLEAR	0	0	0	0
Gold 4N	5	5	5	5
Red B3LW	0	0	0	0
Yellow 3GL	0	0	0	0
Turquoise PLW	10	10	10	10
Blue G	0	0	0	0

LOSS OF COLOR INTENSITY 3200 Hours FADE-O-METER

ELECTROLYTIC BRONZE

	CLEAR	LIGHT	MEDIUM	DARK
CLEAR	0	0	0	0
GOLD 4N	5	5	5	5
RED B3LW	0	0	0	0
YELLOW 3GL	0	0	0	0
TURQUOISE PLW	10	10	10	10
BLUE G	0	0	0	0

The behavior exhibited by the gold and turquoise are the same as was seen in previous work, and we also see that the presence of the electrolytically deposited colorant has no adverse effect on the light fastness of the organic dye. The exposure corresponds to about 5 years of natural weathering. The preliminary results of long term exterior exposures confirm the laboratory findings - these tests are continuing.

It is possible to measure the quantity of organic dye in an anodic coating by dissolving the oxide and then measuring the amount of colorant using spectrophotometric methods. The extinction values shown are dimensionsless and are a measure of the amount of dye present in the film. (Slide 10)

EXTINCTION VALUES

ELECTROLYTIC BRONZE

	CLEAR	MEDIUM	DARK
RED B3LW	0.66	0.58	0.64
YELLOW 3GL	0.43	0.36	0.36
TURQUOISE PLW	0.84	0.83	0.84
BLUE G	0.70	0.78	0.78

From this data we see that the amount of organic dye absorbed is not materially affected by the presence of the inorganic colorant.

By means of X-ray fluorescence, one can also determine the amount of the colorant in the oxide film. The impulse counts

Slide 10

EXTINCTION VALUES

		ELECTROLYTIC BRONZE	
	CLEAR	MEDIUM	DARK
Red B3LW	0.66	0.58	0.64
Yellow 3GL	0.43	0.36	0.64
Turquoise PLW	0.84	0.83	0.84
Blue G	0.70	0.78	0.78

found using Tin in the case of the electrolytic colored film, and Copper for the dyes (since they are copper complexes) are shown. (Slide 11)

X-RAY FLUORESCENCE
TIN - COUNTS IN 100's PER SECOND

	ELECTROLYTIC BRONZE			
	CLEAR	LIGHT	MEDIUM	DARK
CLEAR	0	20	26	34
RED B3LW	0	21	26	34
TURQUOISE PLW	0	19	26	34

From this data we see that as the color of the electrolytic bronze becomes darker, the amount of tin present in the film increases. We also note that overdyeing does not change the amount of tin present.

In the next slide data for the organic dye is shown. (Slide 12)

X-RAY FLUORESCENCE
COPPER - COUNTS IN 100's PER SECOND

	ELECTROLYTIC BRONZE			
	CLEAR	LIGHT	MEDIUM	DARK
RED B3LW	17	17	19	19
TURQUOISE PLW	10	10	12	10

From this data we see that the amount of organic dye absorbed is independent of the electrolytic pre-coloring and, in fact, is the same as we would find on clear oxides.

This data shows that the two methods of coloring do not interfere with each other, and hence we would expect that the properties of each will not be adversely affected by the other.

The distribution or location of the colorants within the anodic oxide was investigated using an Electron microprobe. In the slides which follow, we show plots of the elements characteristics for each of the various treatments. Tin for the electrolytic coloring, Copper for the Red and Turquoise dyes, Chromium for the Black and Nickel for sealing.

Slide 11

X-RAY FLOURESENCE

TIN

COUNTS IN 100's PER SECOND

	ELECTROLYTIC BRONZE			
	CLEAR	LIGHT	MEDIUM	DARK
CLEAR	0	20	26	34
Red B3LW	0	21	26	34
Turquoise PLW	0	19	26	34

Slide 12

X-RAY FLOURESENCE

COPPER

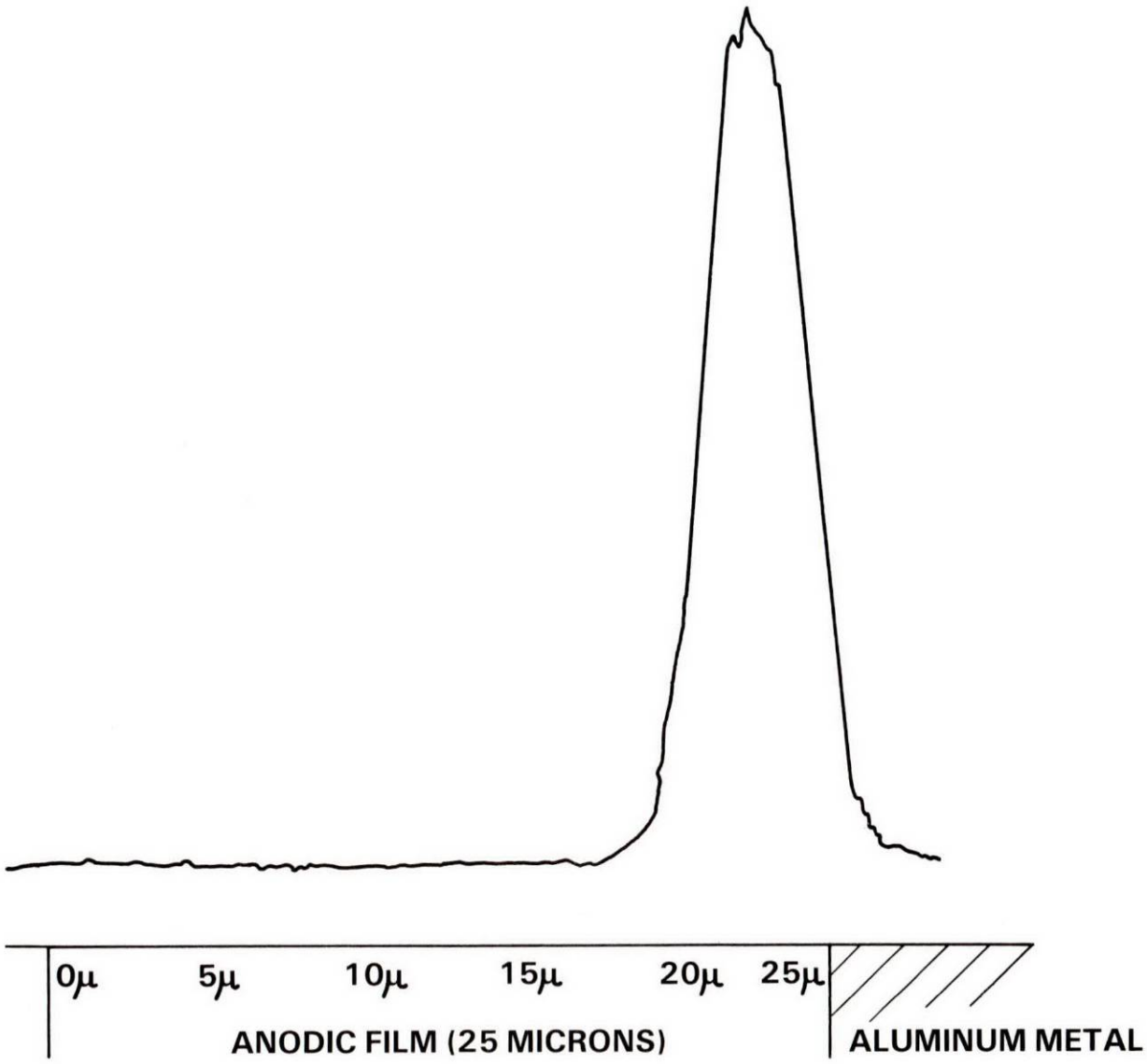
COUNTS IN 100's PER SECOND

	ELECTROLYTIC BRONZE			
	CLEAR	LIGHT	MEDIUM	DARK
Red B3LW	17	17	19	19
Turquoise PLW	10	10	12	10

The first slide shows a medium bronze tin film. (Slide 13)

Slide 13

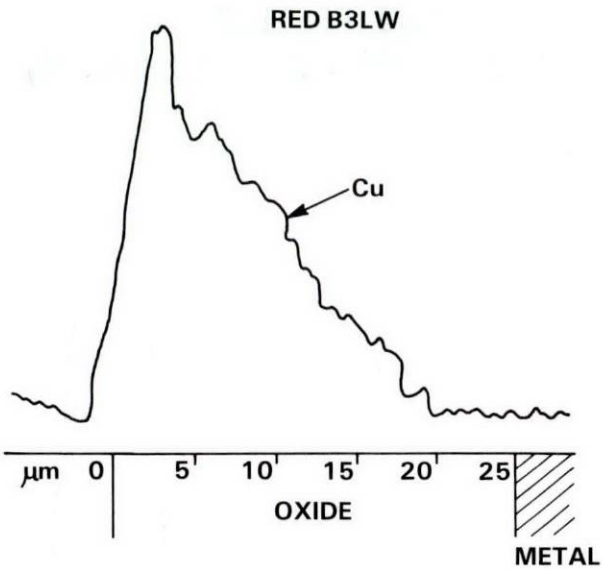
ELECTRON MICRO-PROBE
TIN TRACE
MEDIUM BRONZE — TIN BATH



In the next slides data for the organic dyes are shown. (Slides 14, 15, 16)

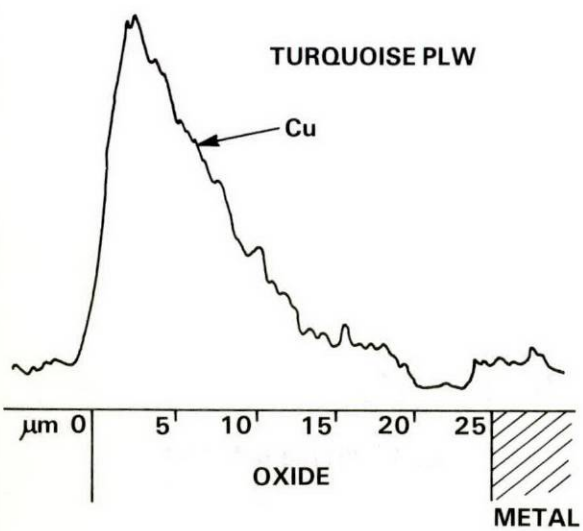
Slide 14

ELECTRO MICRO-PROBE
DYED CLEAR FILM
COPPER TRACE



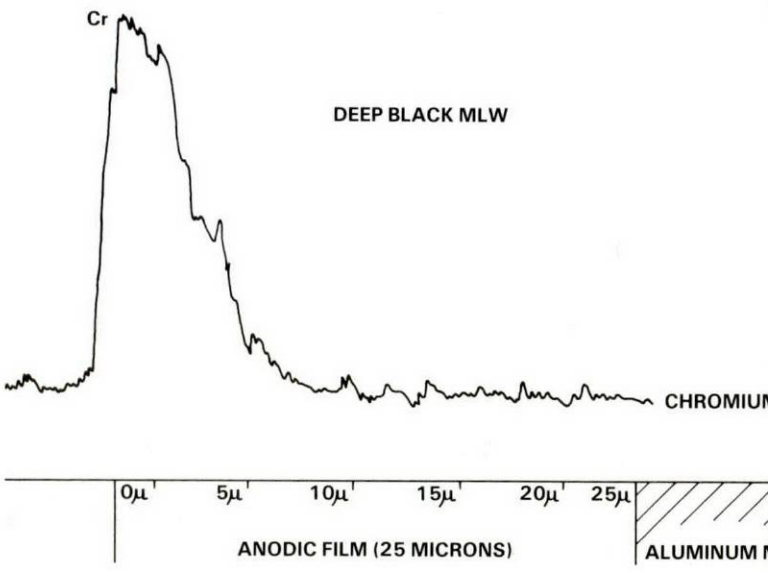
Slide 15

ELECTRON MICRO-PROBE
DYED CLEAR FILM
COPPER TRACE



Slide 16

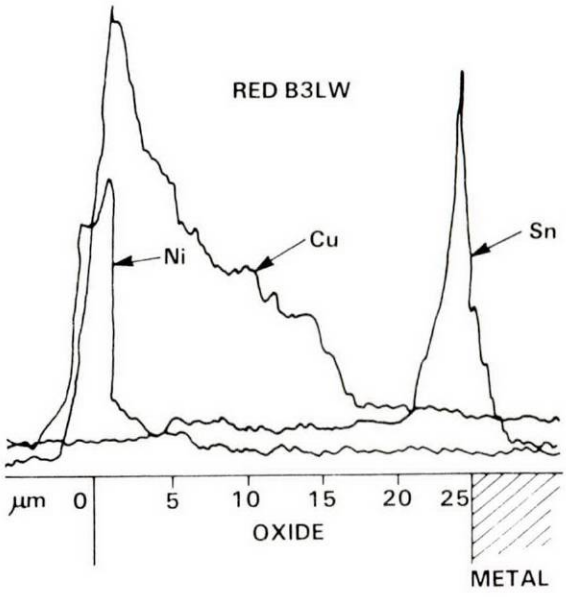
ELECTRO MICRO-PROBE
DYED CLEAR FILM
CHROMIUM TRACE



The next slides show a medium bronze electrolytic film, over dyed with either the Red and the Turquoise dye then nickel acetate sealed. We see the location of the 2 colorants is the same as in the individual process alone. (Slides 17, 18)

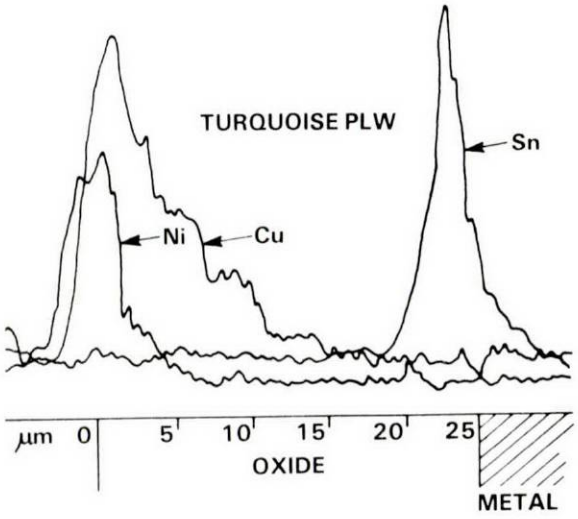
Slide 17

ELECTRON MICRO-PROBE
ELECTROLYTIC BRONZE (TIN)
DYED (COPPER)
NICKEL SEAL (NICKEL)
METAL TRACES



Slide 18

ELECTRON MICRO-PROBE
ELECTROLYTIC BRONZE (TIN)
DYED (COPPER)
NICKEL SEAL (NICKEL)
METAL TRACES



In all cases, we see that the electrolytically applied colorant is found deep within the oxide near the metal-oxide interface - roughly 23 microns. The dye is predominantly in the first 10 microns from the air-oxide interface and that the nickel from the sealant penetrates only 2 or 3 microns.

This data indicates that the lightfastness of the over dyed electrolyte films will be of the same order as that of a similarly dyed clear film of the same thickness, which previously have been shown to be suitable for the potential use.

In the presentation today we have discussed some methods for the production of an interesting new range of colors suitable for use in architectural applications. This entails the 'overdyeing' of either an integral color or a two-stage electrolytically colored anodic oxide film.

We have discussed, in some detail, the processing controls that are necessary and also presented data concerning the sealing quality, lightfastness and corrosion resistance of these films.

We have also presented some data dealing with the location and distribution of the various colorant materials within the anodic coating.

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2. Integral Color Process
3. Two-Stage Electrolytic Coloring Process
4. Dyeing Conditions
5. Controls for Dyeing
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8. Admittance Values
9. Loss of Color Intensity 3200 Hours Fade-O-Meter
10. Extinction Values
11. X-Ray Fluorescence Tin Content Electrolytic Bronze
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13. Electron Micro-probe Tin Trace Electrolytic Bronze
14. Electron Micro-probe Copper Trace Red B3LW Dyed Film
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E-4

LIGHT METALS FINISHING SESSION E

Self-Regulating High-Temperature Anodizing Process with Full Utilization of Alkaline and Anodizing Wastes

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Tokyo

SELF-REGULATING HIGH TEMPERATURE ANODIZING PROCESS WITH FULL UTILIZATION OF ALKALINE AND ANODIZING WASTES

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Tokyo

ABSTRACT

The anodizing electrolyte consists of sulfuric acid-ammonium sulfate which permits operation up to 30-40°C and as anodizing proceeds, alum is continuously precipitated, keeping Al content in the electrolyte at optimum concentration. Caustic etching solution with gluconic acid is recovered by adding Na_2SiO_3 to spent solution, precipitating zeolite, and alkali and gluconic acid are recovered for re-use. Both precipitates and that from rinse water are utilized for adsorbent, molecular sieve, substitute for tri-polyphosphate etc. and raw materials for artificial gems, watch glass etc. The process is successfully operated at a big architectural plant both for as-anodized and for further electro-colored, windows, curtain walls etc.

Introduction

Some years ago, at the laboratory of the University, the research was made to develop an anodizing process by which the properties of the produced films are comparable or superior to those of normal sulfuric acid anodizing process, at operation temperatures up to 40°C. The process should be used, of course, at normal temperature (18-22°C) and also for so-called "hard anodizing". The idea was independently conceived by one of the authors (S.Tajima) in order to train young freshmen for aluminum surface finishing by a contract with a certain company. We found that the sulfuric acid bath containing mainly alkali sulfate was to this purpose by which alum is continuously precipitated, keeping Al^{3+} content at optimum[1,2]. Later, one of the authors (Y.Umehara) in collaboration with a certain pharmaceutical company, developed a process of recovering alkali etching solution including gluconic acid , a chelating agent and by this existence, Al sludges are usually difficult to be removed during alkaline pretreatment of aluminum and aluminum alloys (mainly 6063). These two processes were combined by Y.Umehara and brought into practical use at the Tokorozawa plant of the Showa Koki Co., Tokyo, one of the leading architectural aluminum producers in Japan. Thus, the self-regulating, high temperature continuous anodizing process with full utilization of caustic and anodizing wastes for adsorbent, molecular sieve etc. on the one hand and for producing α-alumina (artificial gems), color-intensifier of vegetable pickles are successfully operated together with collected waste solution treatment and

ever-improved up to now. The anodic films produced by this process is comparable with or even superior to normal sulfuric acid anodizing films and they can also be subjected to succeeding electro-coloring operation. The paper describes the principles underlying the processes and outlines the practical processes being operated at the Showa Koki Co., Tokorozawa factory, Japan.

Principles of Self-Regulating High Temperature Anodizing

The normal surfuric acid anodizing is performed at about 20°C and above this temperature, the film dissolution loss is larger and also the quality deteriorates. In order to avoid temperature rise, it is usual to cool by refrigerators. As a means of securing the same film forming efficiency and quality at higher temperature, an idea of adding common anion-containing soluble salts to suppress the film dissolution occurred to the author and it was found that ammonium sulfate and/or potassium sulfate addition was particularly effective and profitable.[1)]
By this process, electrolysis below 40°C is possible and some of the merits are as follows;
1) Refrigeration is not always required. Natural cooling or cooling by air or water or only occasional use of refrigerator is enough according to the climate conditions.
2) The anodized film obtained at or above 20°C is usually harder and of excellent qualities.
3) Rapid anodizing is possible. For rapid anodizing, high current densities than normal 1-1.5 A/dm^2 must be used, which naturally lead to the elevation of the bath temperature, which in turn, lowers the film forming efficiency and degenerate the quality of the film. Therefore, the possibility of rapid anodizing means roughly high temperature anodizing.
4) Further, the important merit of this process is that Al^{3+} ion which is formed by anodic dissolution (i.e. which does not contribute to the film formation) gradually precipitates as alum of lower solubility, thus the concentration of Al^{3+} ion in the solution is automatically maintained at about 0.5% in the above-mentioned temperature range, which is considered to be an optimum Al^{3+} concentration for surfuric acid anodizing. Thus by only recovering the by-product (alum), the continuous operation without waste became possible. When the process was developed, the author called it as SRHT process (Self-regulating, high temperature process).
5) The films thus formed can be further electro-colored by presently popular two step electro-coloring processes by which Sn, Ni, etc. are electrodeposited in the pores by AC or DC in respective salt solutions. At the Showa Koki Co., this electro-coloring process is practiced. The hitherto known electro-coloring processes by V.Caboni (Italy, 1936),[3)] G.Elssner (Germany 1940), Asada (Japan 1966), Eurocolor 800 (Pechney) etc., specify electro-coloring on normal sulfuric, or chromic, or oxalic acid films, while the present films, can also be subjected to electro-coloring process.

To express the film forming efficiency, Mason[5] of ALCOA defined in early 1940s', the term "coating ratio" which is still used very often.

$$\text{Coating ratio (C.R.)} = \frac{\text{weight of formed oxide}}{\text{weight loss of substrate Al}}$$

Although the theoretical value is $Al_2O_3/2Al=1.89$, in normal sulfuric acid anodizing, C.R. is said to be about 1.35-1.40. The data obtained in one of the authors' (S.Tajima) laboratory are shown in Fig.1, which indicates that the efficiency lowers steeply with the temperature rise.

According to Tajima & Shimura,[6,7] the statistical calculation of the thickness of anodic films in 15vol% H_2SO_4 at 1A/dm^2 for 99.99% Al is as follows:

$$d\ (m\mu)=0.347t-10^{0.025T-2.078}t^{1.34}$$

for example, the time t needed for d=0 at T=48°C is 16.5 min, and for T=48°C, the film grows at first but after passing through maximum thickness, d=0 in 16.5 min, where only thin barrier film remains.

In contrast, when ammonium or potassium sulfate is added to sulfuric acid electrolyte, the C.R.-Bath voltage relations are shown at 35°C in Fig.2.

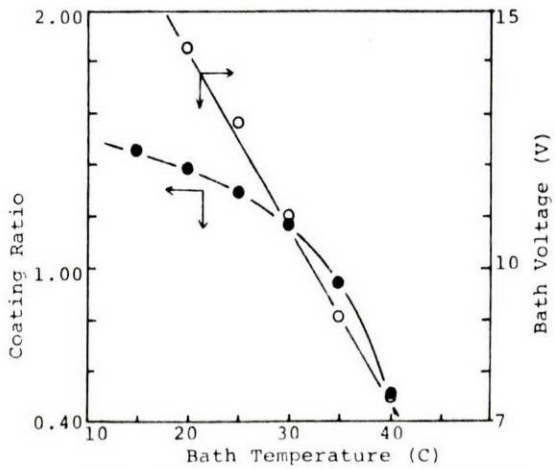

Fig.1 Relation between Temperature, C.R. and Bath Voltage. (15wt.%H_2SO_4, 1A/dm^2)

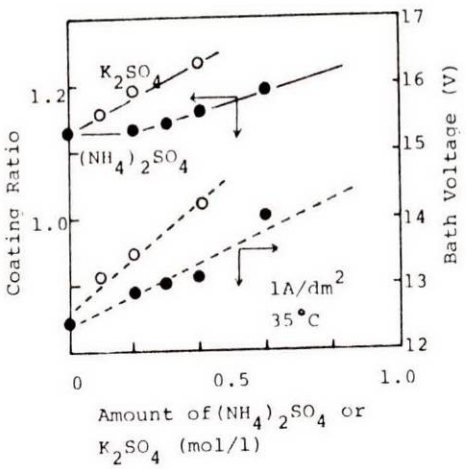

Fig.2 Relation between $(NH_4)_2SO_4$, K_2SO_4 addition, C.R. and Bath Voltage.

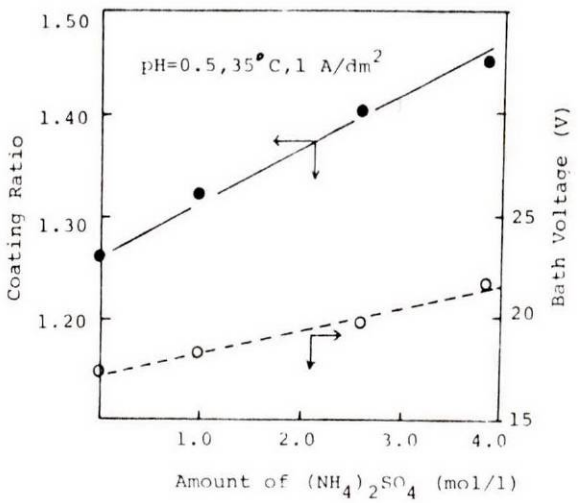

Fig.3 Relation between $(NH_4)_2SO_4$ addition, C.R. and Bath Voltage (pH-const.)

About 0.4-0.6 mol addition of salts to sulfuric acid is comparable to straight 15vol% sulfuric acid at 20°C.
Fig.3 shows the relation between C.R. and bath voltage at 35°C when ammonium sulfate is added to sulfuric acid, by keeping pH of the solution at 0.5. By addition of 4.0 mol of ammonium sulfate, the C.R. surprisingly attains 1.45. When 0.4 mol/l of K_2SO_4, $(NH_4)_2SO_4$ or Na_2SO_4 is added to 1 mol H_2SO_4 (about 10wt%), the coating ratio is in the order K_2SO_4 (1.21), Na_2SO_4 (1.16) and $(NH_4)_2SO_4$ (1.16). From these data, it is clear that sulfuric acid-soluble alkaline sulfate bath is fitted for high temperature anodizing, as well as at normal or lower temperatures
For reference, the authors will show the solubilities of aluminum sulfate and alum in Table 1, as a basis for self-regulating, continuous operative anodizing bath with gradual precipitation of alum.

Table 1
Solubilities of aluminum sulfate and alums in water at 0, 20 and 40°C.

	molecular wt/temp	0°C	20°C	40°C
$Al_2(SO_4)_3.18\ H_2O$	666.45	60.7	70.7	89.2
$AlK(SO_4)_2.12H_2O$	474.40	5.43	11.0	25.0
$AlNH_4(SO_4)_2\cdot 12H_2O$	453.34	4.97	12.6	23.61
$AlNa(SO_4)_2.12H_2O$	458.30	70.7	75.1	83.6

It is clear that the solutions of ammonium and potassium alum in water is particularly smaller. The Al^{3+} ion concentration in these saturated alum solution is calculated as 7.5 & 14 g/l at 20 & 4
This Al^{3+} concentration is optimal for anodizing in sulfuric acid. In normal sulfuric acid anodizing, it is usual that the electrolyte must be discarded when Al^{3+} content in the solution becomes 12-20 g/l, while in these alum anodizing electrolyte, Al^{3+} ion concentration is automatically controlled by gradual precipitation of alum which can be recovered and used as by-product. Thus the H_2SO_4-alkaline sulfate electrolyte is automatically controlled and continuously used only by occasional addition of ammonium sulfate, or ammonia and sulfuric acid.
The film available by this process at 35°C is comparable or superior to normal sulfuric acid films in appearance, thickness, abrasion resistance, Vickers' hardness, dye adsorption and in corrosion resistance.
Further, the additions of aliphatic carboxylic acid such as oxalic, malonic. lactic or formic acid to the bath gives superior films to the normal sulfuric acid films without losing self-regulating characteristics.[2]

Principles of recirculation of caustic etching solution and utilization of its waste[7]

The Showa Koki Co., where one of the authors (Y.Umehara) is active as chief engineer, with cooperation of a certain pharmaceutical company, developed a process of recirculating caustic etching solution which includes 0.5% or more of gluconic acid to make possible uniform etching of the architectural aluminum panels without any flow marks which may happen during withdrawal of the panels from the etching solution, and gives products a refined beauty.(Photo 1) Further the addition of gluconic acid which is rather popular, prevents aluminate deposition at the bottom of the tank, the insides of piping and transfer pumps.

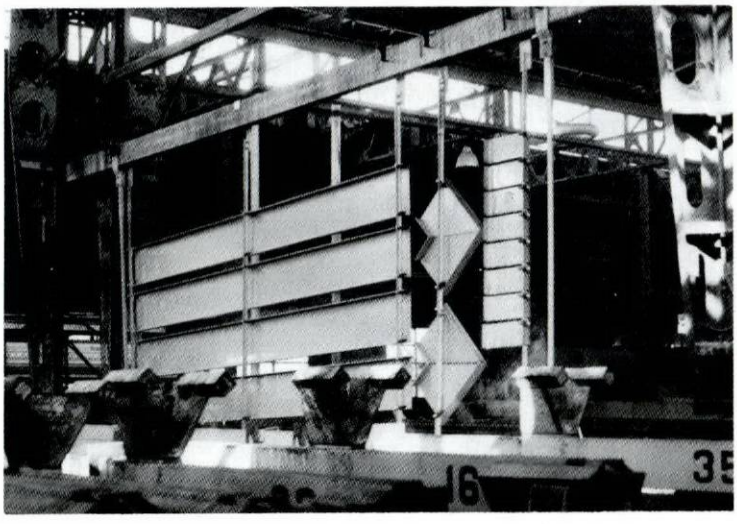

Photo 1
Withdrawal of panels from alkali etching tank
(Showa Koki Co., Tokorozawa Factory, Japan)

This merit is, at the same time, a demerit since 0.1% or more of gluconic acid addition makes difficult the "crystallization of aluminum hydroxide", which is a basis of the so called "Bayer" waste recovery process.
To overcome the demerit of the use of gluconic acid, one of the authors (Y.Umehara) developed a process of regenerating alkali and gluconic acid from waste alkali. Na_2SiO_3 reacts just as calculated within a few hours, at rather high temperature. Sodium alumino silicate, the so-called "synthetic zeolite" precipitates in large crystals and is readily filtered off and separated.

$$6 \cdot NaAl(OH)_4 + 2 \cdot Na_2O(SiO_2)_3 \xrightarrow{*} 3 \cdot Na_2O : Al_2O_3(SiO)_2)_2 + 4NaOH_2O$$

One typical practical example is shown in Table 2.

Table 2
Alkali Recovery Process
Waste Caustic Soda

Volume	NaOH	Na-gluconate	Al in g/l
20 m^3	130 g/l	8.5 g/l	45.0

*JIS spec. NO. 3

Recovered Caustic Soda

Recovered Volume	Free NaOH	Yield	Na-gluconate	Yield	Zeolite
20 m^3	84.4 g/l	53.84%	6.8 g/l	80.0%	6 tons

By good conditioning of the reaction, the products can be separated, one as synthetic zeolite and the other as pure sodium hydroxide. The recovered caustic soda contains virtually no Al, which makes the control of the etchant components easier.
Thus, both caustic soda and sodium gluconate are recovered in ca. 80% yields without discarding even a single drop* of the waste alkali solution and the zeolite produced is 6.0 tons.
It is possible to maintain the amount of Al dissolved in the etchant at a minimum (2% or less) during the run. Accordingly, the drag-out loss of Al from the etching solution is minimized and the amount of hydroxide formed during adjustment of the pH of waste water is reduced to less than half of the popular value.
The filtration of aluminum hydroxide becomes easier and the amount of suspended solids in waste water solution, a factor contributing to water pollution, can be made virtually nil.
The flow sheet of alkali recycling process is shown in Fig.4.

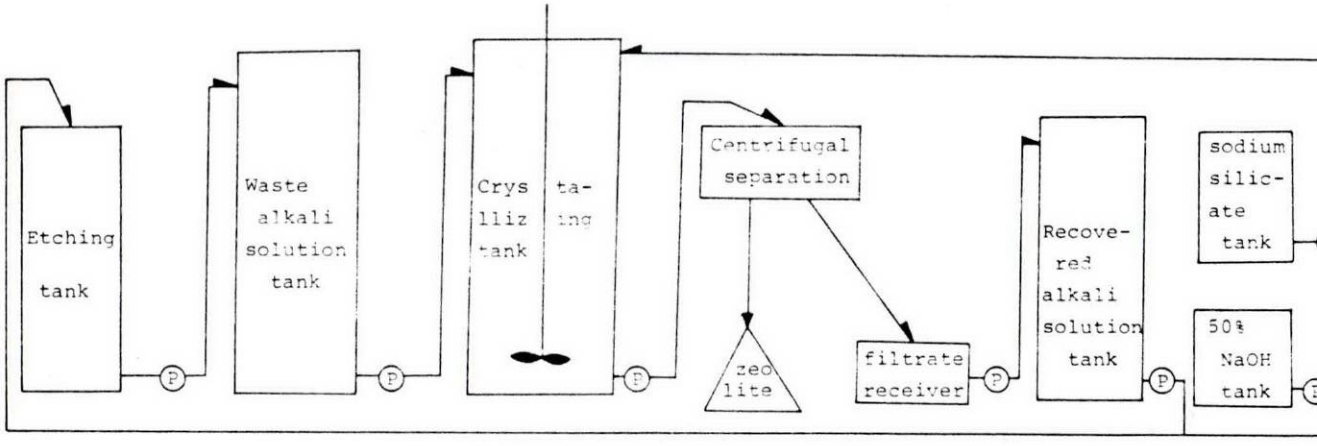

Fig.4

Properties of the by-product zeolite
1) The examination of by-product zeolite can be deemed as the same as that of zeolite 4A of US make from X-ray diffractograph.
2) The chemical composition is, for example, shown in Table 3.

Table 3
Composition of by-product zeolite

Al_2O_3	Na_2O	SiO_2	Fe_2O_3	H_2O	Cr	Cu	Mn	Ni	As
24.0	15.9	32.5	0.0056	rest	7	4	4	8	0.1
					(%)				

Mg	Pb	Cd
0.001	0.4	0.01 (ppm)

* see next page.

*
This zeolite still includes caustic soda and is discharged from the centrifugal separator with recovery of 20% of caustic soda solution.

3) Ion exchange capacity 4.5 meqv/g
4) Gas absorption H_2O (in Rh 30%) 24%; SO_2, NO_x NH_4^+ gas 22-24%

5) Particle size distribution is shown in Table 4.

Table 4
Particle size diameter dispersion

Specimen	5	6	7	8	9	10	15	20	25	30mμ
Crude	<16	6.6	12	10	10	10	22	5.1	3.1	1.7
Washed in water	<23	29	19	8.4	3.5	2.2	7.8	3.1	1.0	1.2

6) Morphology of zeolite is shown in Photo 2. (20 mm in the Photo corresponds to 5 mμ)

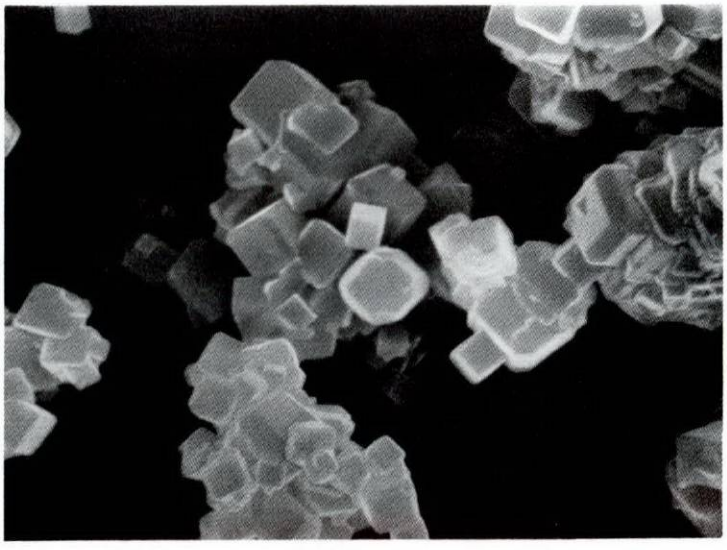

Photo 2
Morphology of zeolite

7) Economical consideration of recovery of caustic soda from waste etching solution

The balance data per one recovering operation of 20 m^3 caustic soda solution as of Nov.1979 is shown in Table 5 (where US$ 1.00 =Japanese ¥230)

8) New use of zeolite

In Japan, the total demand of zeolite 4A as molecular sieve, moisture remover, ion-exchanger etc. was not over 80 tons per year, while since 1968, a new use of builder instead of sodium tri-polyphosphate has been developed. It is expected that total

demand of zeolite 4A as builder will be over 50.000 tons per year and the half of anodizing plants in Japan, if the process is adopted, is expected to easily supply above demand at a reduced price.

Table 5
The balance data

	¥	$
Expenditure		
1. Labor cost	12.000	52.17
2. Fuel cost	15.500	67.39
3. Electric power cost	10.000	43.47
4. Sodium silicate	185.000	804.34
5. Cost of materials consumed	20.000	86.95
6. Repay of construction & equip.	100.000	434.78
Total	342.500	1489.13
Income		
1. Recovered NaOH as 7%, 20m^3	91.000	39.56
2. Recovered Na-gluconate	83.200	36.17
3. By-product zeolite (unit price of crude zeolite ¥35,000/ton)	210.000	91.30
Total	382.000	166.08

Balance + ¥39.500 (US$ 171.73)/charge

Practice of self-regulating anodizing process using H_2SO_4-ammonium sulfate

By the order-made window and curtain wall manufacturers excepting USA, many of their products are now surface-treated with two-step electro-coloring process[3,4] which was originally developed by V.Caboni in Italy, 1936 and practically applied by Asada in Japan in 1965 or with similar process mainly in Japan and in Europe. However, they are subjected to a strict inspection of color matching, corrosion resistance, hardness and alkali-resistance to satisfy the requirement for higher class buildings. To keep high quality of color-anodized films, severe control of the electrolyte as well as caustic soda etching solution are needed. During anodizing, unnegligible amount of aluminum dissolves into the electrolyte resulting in the reduction of coating ratio as shown in Fig.1 and in the loss of Al. According to our experience, ca. 20g of Al is lost in the conventional 15% sulfuric acid anodizing when we intend to get 12 μm oxide film on 1 m^2. Thus we must control the Al^{3+} concentration at optimum, say, between 5-10g/l to secure good quality of the film. Excess Al ion is needed to be removed by a simple operation.
For this purpose, one of the authors (Y.Umehara) has applied the self-regulating H_2SO_4-ammonium sulfate bath developed by Tajima (co-author) and by his co-workers referred to above.[1]

The practical details now being applied at the Showa Koki Co., Saitama Factory is as follows:
1) Electrolyte; 15wt.% sulfuric acid, 0.5% NH_4 ion, 1% Al ion. Under these conditions, ammonium alum and accordingly Al ion is automatically precipitated to keep the anodizing electrolyte at optimum conditions.
2) Recycle and recovery treatment from waste electrolyte to fresh electrolyte is shown in Fig.5.

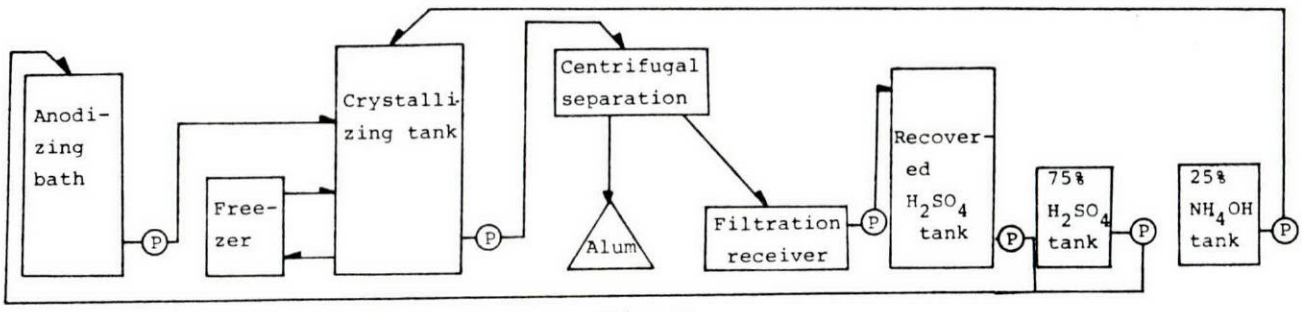

Fig.5

The electrolyte with excess Al ion content (over 1%), is pumped up to the crystallizing tank together with equivalent ammonium. Dissolved Al ions immediately combine with ammonium sulphate $(NH_4)_2SO_4$ to precipitate as fine crystals of ammonium alum, by rapid cooling of the solution by moderate freezer outside the anodizing bath (note:the process can be operated up to 40°C, but presently at Showa Koki, moderate cooling of the solution is done from the view point of efficiency and required quality of the film). The electrolyte containing alum is transferred to the centrifugal separator. Separated alum is scratched down and the filtrated sulfuric acid is fed back through the recovery acid tank to the anodizing tank. The compositions of waste electrolyte and the recovered one are shown in Table 6.

Table 6

Waste Electrolyte (average value from 5 lots)

Volume	Total H_2SO_4	Al ion	Added 25% NH_4OH
$15.9m^3$	16.9%	1%	296 litre

Recovered Electrolyte

Recovered Vol.	Free H_2SO_4	Al ion	By-produced alum	Yield
$15.2m^3$	13.4 %	0.54%	1212Kg	76.2%

3) Properties of the film anodized with recovered electrolyte
Recovered electrolyte which contains a small amount of Al^{3+} gives better result then non-Al^{3+} containing bath. Moreover, the films obtained from this bath are better electro-colored. The comparison of the films obtained from our bath and from

normal sulfuric acid bath shows that the present film is superior, by 10 um thickness, particularly in corrosion resistance in NaOH and in abrasion resistance (according to the Japan Industrial Standard tests). The original patent of this process states that the electrolyte containing moderate ammonium ion in sulfuric acid can be used up to 40°C, but aluminum for order-made architectural products can better be anodized at room temperature to get harder and better alkali-resistant properties.

4) The purity of by-product ammonium alum

The by-produced crude alum still contains a small amount of recovered electrolyte. However, other impurities are very small as shown in Table 6.

Table 6

Cr	Cu	Fe	Mg	Mn	Ni	As	Hg	Cd	
1.5	0.7	36.3	9.8	0.9	0.4	9.0	0.3	0.6	(ppm)

5) The use of by-product alum

1. Addition agent to foods; It is effective to keep clear color of salted vegetables. Ammonium alum is used after calcination.
2. Raw material for artificial jewellies; We can make nearly 100% purity α-alumina from pure alum subjected to 3 times recrystallization. The use of this artificial gems are extending not only to decorative accessories but also to watch glass and to lens for deep-see use, etc. at remarkably reduced cost, which are shown in Photo 3.

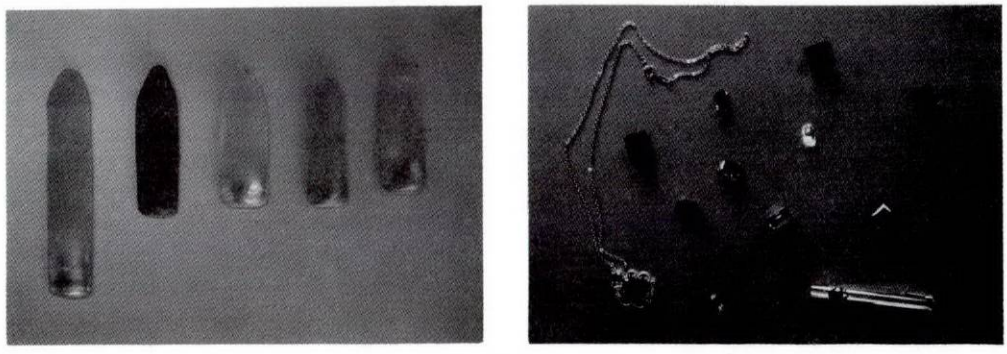

Photo 3. Roh materials(α-alumina) and artificial gems

6) Economic consideration of H_2SO_4-ammonium sulfate process

The balance data per one recovery operation of 16m^3 waste electrolyte is shown in Table 7.

Table 7

1. Expenditure		¥	$
Cost of 25% ammonium solution	¥32/litre x 300=9	6.00	41.74
Electric power	¥20/KWH x 50=1	.000	4.35
Labor cost	2/3man, ¥12000/day x 2/3=8	.000	34.78
Repayment for construction/batch		9.500	41.30
Total		28.100	122.17

2. Income

		¥	$
Price of recovered sulfuric acid		54.315	236.15
By-product alum	¥20/Kg x 1212=	24.240	105.39
Total		78.555	341.52
Balance		+50.455	219.37

Pollution treatment of collected waste rinse water and evaluation of by-product aluminum oxide grains

In anodizing operation, a lot of waste rinse water that over-flows from each rinse tank is discharged after oil removal, etching, neutralizing and anodizing. The discharged waste water which contains more or less Al^{3+} ion, alkali and/or acid must be neutralized to produce a large amount of aluminum hydroxide, so called suspending solid (SS). To comply with the national regulation of waste water pollution that is specified as SS below 90 ppm and pH 5.8 to 8.5, the following treatment is done as shown in Fig.6.

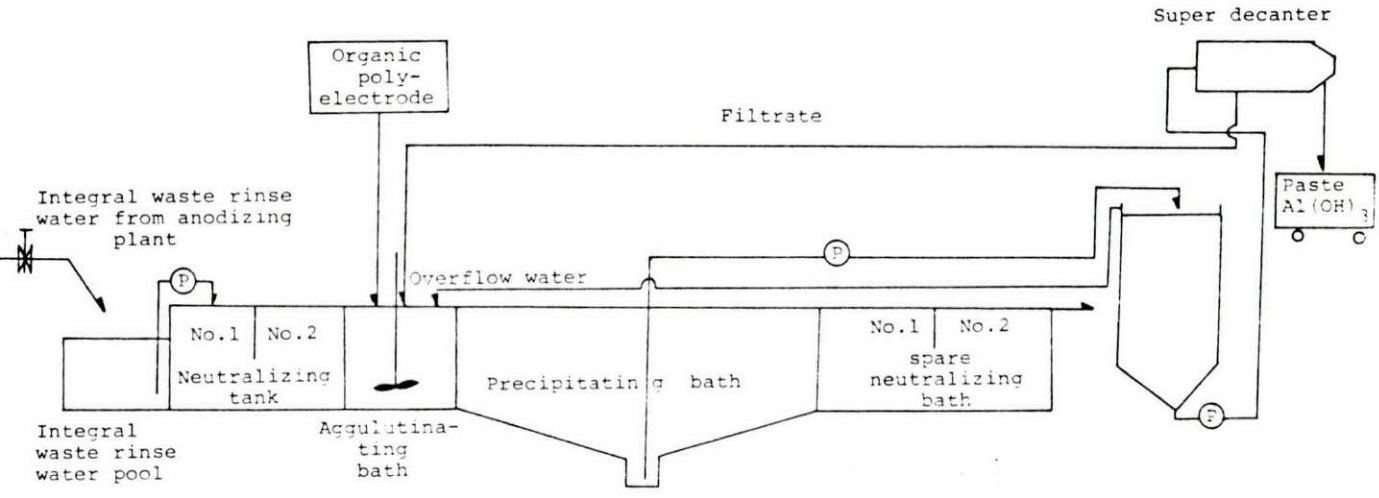

Fig.6

1) Collected waste rinse water treatment plant
Waste water is pumped up to the next bath to neutralize automatically with waste caustic soda solution, and the suspending aluminum hydroxide (SS) is agglutinated with organic poly-electrolyte in the next mixing tank and after aggulutination it is lead to precipitation bath where flocks (diameter 10mm) of aggulutinated SS precipitates on the bottom in the course of flowing down slowly (1 m/min) to the end of the bath and the cleaned water over-flows to the next bath where cleaning is confirmed. Precipitated SS flocks are separated with superdecanter to aluminum hydroxide paste and filtrate solution.

Hydroxide paste is dried and ignited in rotary furnace to become porous grain.

2) Explanation of rotary dryer and ignition furnace

Discharged paste from the super-decanter is put into the paste accumulator (ca. 1.5 m^3 capacity). The paste is pushed onto the rotary furnace and delivered down a little by little by 1 RPM with an inclination of 1/10. During the run, the charged paste is treated with direct high temperature flame that is shot from waste oil burner, and thus produced alumina is discharged from the end of the furnace, which is immediately blown into the cyclone through steel pipe.(Fig.7)

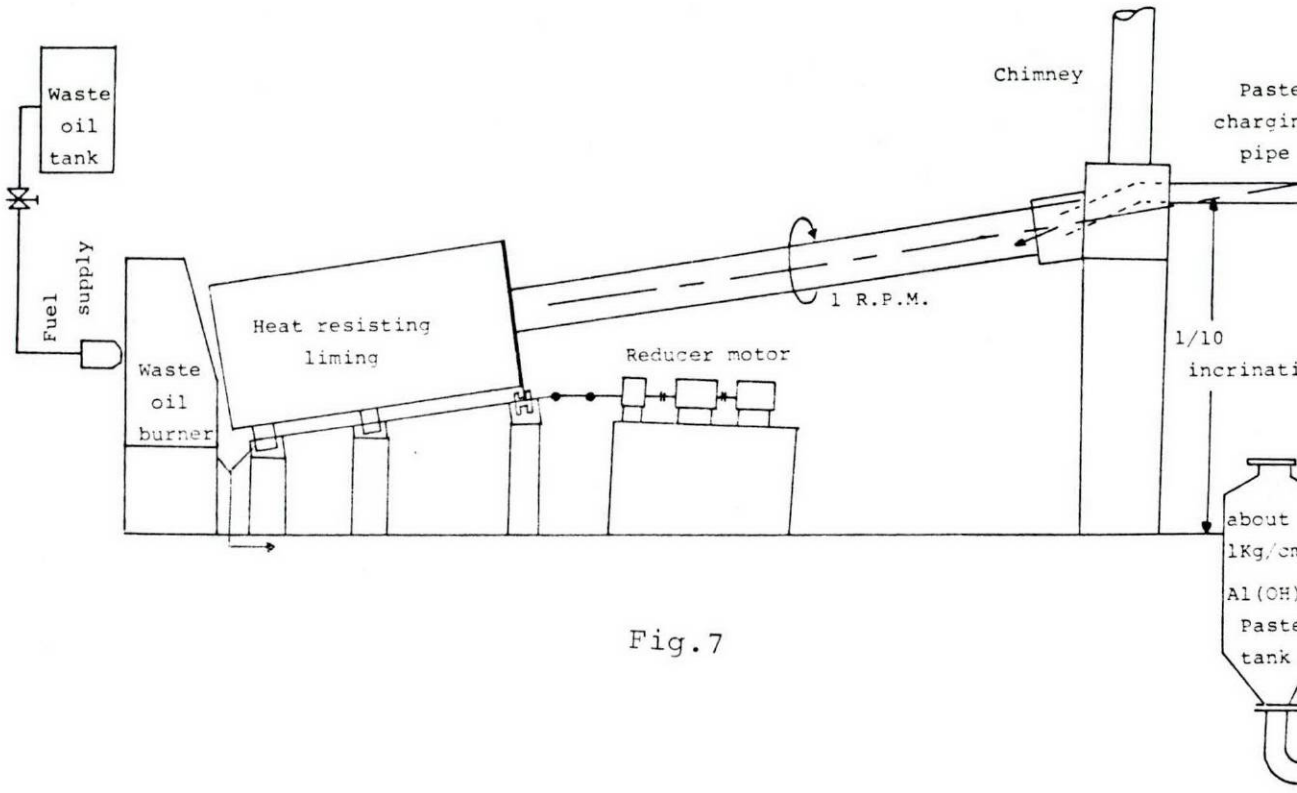

Fig.7

3) Chemical composition of ignited grains are shown in Table 7.

Table 7
Chemical composition of ignited grains (ppm)

Fe_2O_3	SnO_2	Pb_2O_3	MnO_2	Cr_2O_3	As_2O_3	CdO	HgO	Al_2O_3
0.69	0.67	0.04	0.03	0.007	7.6	2.5	0.05	rest

4) The use of ignited grains

1. Oil removers; Scattered oil on the road due to, for example traffic accident, can be removed easily by covering with a small amount of this grains and by sweeping them off.
2. Filler for sand box of pets; As a filler of sand box for

removing various kinds of disagreable smell and their urin.

5) Econ0mic Assessment of the operation of dry and ignition furnaces

From 2 tons of paste, 300Kg of ignited grains are produced with ca. 180 litre of waste oil and 1/3 working labor/day.

Table 8

		¥	$
1. Expenditure			
Cost of waste oil as fuel	¥35/l x 180	=6300	27.39
Cost of labor	¥12.000/day x 1/3	=4000	17.39
Repayment of construction/batch	$\frac{¥3.000.000 \times 25\%}{12 \text{ months} \times 22 \text{ working days}}$	=2840	12.35
Total		13.140	57.13
2. Income			
Price of ignited grains	¥10/Kg x 300	=3000	13.40
The saving of money to be paid to the contract tender of aggulugated aluminum hydroxide	¥13.000/ton x 2	=24.000	104.35
Total		27.000	117.39
Balance		+13.860	60.26

ACKNOWLEDGMENT

Thanks are due to President K. Aoyama, Showa Koki Co. for permission of publication and to Dr. S. Matsuzawa for preparing the paper.

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ELECTRONICS
SESSION F

Selective Gold Electroplating Electronic Multilead-Headers

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SELECTIVE GOLD ELECTROPLATING ELECTRONIC MULTILEAD HEADERS

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ABSTRACT

Eliminating or reducing the use of gold is of primary importance. This manuscript compares the standard barrel process with the automatic endless belt apparatus that selectively deposits gold on the tops of inverted multilead headers. Also the preparation of parts and plating solution parameters are discussed. Studies of the effect of peak, pulse and base currents on the deposit topology using the Scanning Electron Microscope and Auger are given.

Introduction

As gold spirals upward in price, various approaches by users in the electronics industry are being considered to reduce electroplating costs. These approaches include:

1. Reducing the thickness to the minimum functional amount.

2. Place the gold selectively by applying only where needed.

3. Replace the gold with a less expensive metal either completely or partially.

For the semiconductor header under study it was found that no metal performed as well as gold, however it appears that some metals can be substituted with a minimal of sacrifice depending on the application.

For example electroless nickel, electrolytic nickel, silver, tin, tin-lead, electroless nickel-born, electroless nickel ternary alloys and palladium exhibited merit and are used in place of gold when carefully evaluated as to the intended function of the coating.

In the case of an 8 pin integrated circuit header, where gold is needed for eutectic die bond and ultrasonic wire bond, it is evident that plating on the header post tops and eyelet areas is all that is necessary. (See Fig. 1) Solderability of the external leads can be accomplished after complete assembly by tin plating or tin-lead dipping the leads of the devices. From this approach originated the unique idea of the selective continuous belt feed plater.[a] (See Fig. 2) This equipment selective electroplates gold onto the wire bond post tops and eyelet of the 8 pin T05 header at the rate of approximately 6500 units per hour. The units are subsequently eutectic die bonded and ultrasonically wire bonded. The gold savings, (see process in Table I and II) is $216.39 per thousand headers at $600 per troy ounce gold when compared with conventional barrel plated headers.

(a) Developed by Auric Corp., Newark, N.J. (U.S. Patents 3951772 and 4048043)

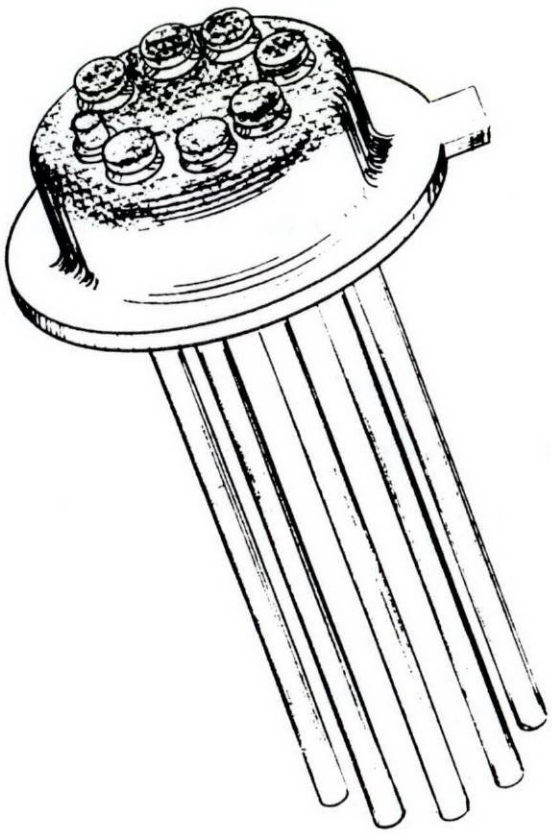

Fig. 1 Selective Plated Header

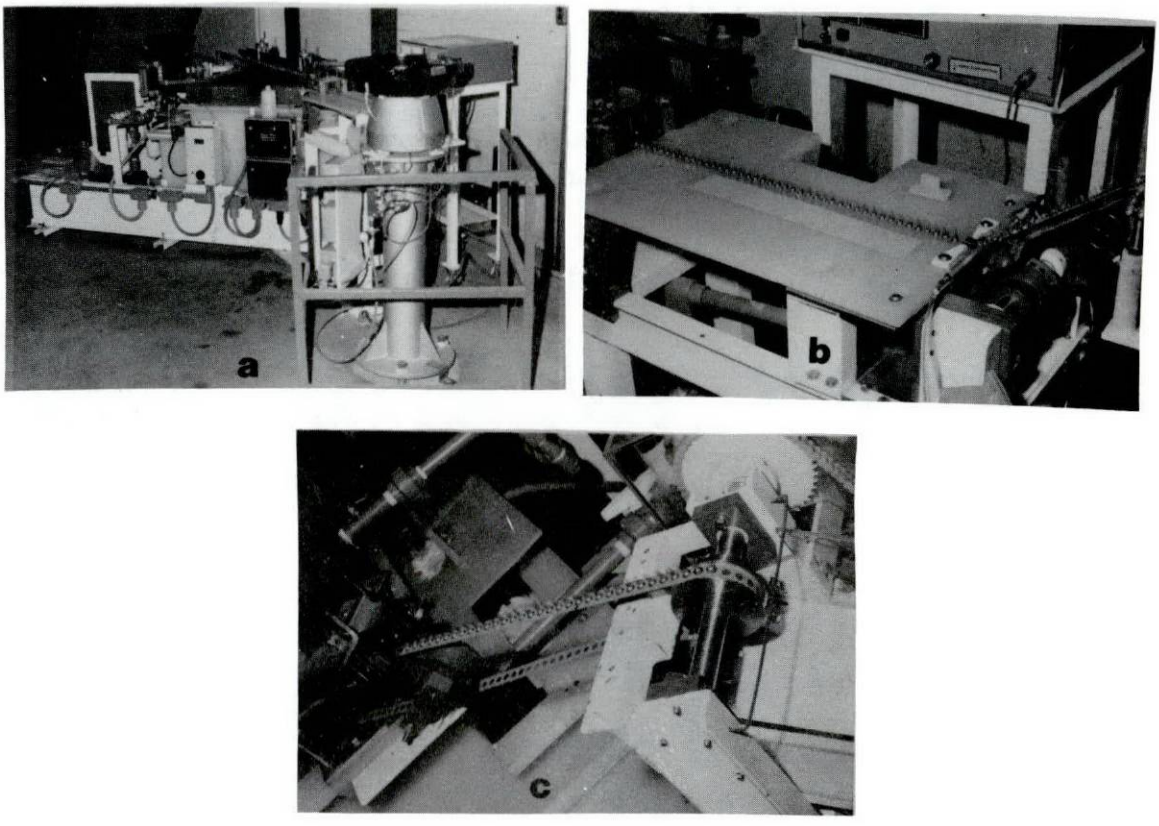

Fig. 2 Selective Continuous Belt Feed Plater

(a) Overall view of equipment

(b) Inverted headers being fed onto solution carpet

(c) Plated headers coming from machine

Table I

Standard Barrel Plating Process

Pickle, Cut and Bright Dip and Rinse

Load Barrel 7,500 units and 5 Beakers of 5mm Ballast

Alkaline Clean

Acid Pickle and Rinse

Cyanide Activator and Rinse

Gold Strike

Gold Save Dip and Rinse

Gold Plate

Gold Save Dip and Rinse

Unload

Hot DI Water Rinse

Centrifuge Dry

Package

Gold Standard per 1000 headers

0.41185 Tr. Oz./Thousand

Table II

Selective Continuous Belt Plater Process

Pickle Cut and Bright Dip and Rinse

Acid Pickle

Rinse

Hot DI Rinse

Centrifuge Dry

Load Automatic Feeder (6500 per hour)

Gold Plate

Gold Save Dip

Rinse

Acid Rinse

Rinse

Hot DI Rinse

Package

Gold Standard per 1000 headers

0.05119 Tr. Oz./Thousand

Testing Procedures

The following post plating quality tests are performed to insure that the headers are functional during die and wire bond assembly operations:

A. Bake Test

This test is done to simulate die and wire bonding temperature excursions. The test is made in air at 500°C for 3 minutes. The headers are then examined under 10 power magnification for

1. Blisters

2. Discoloration

3. Missing Plating

B. Gold Thickness

The gold is measured in the center of the header eyelet by Beta back-scatter equipment.

C. Die and Wire Bond

Destructive line tests are made on the devices where the proper wetting (75% coverage or more) of the silicon die is examined. The wire bond is tested by measuring the grams of force experienced to make the wire break or pull loose. The Motorola requirement for this test is a minimum of 4 grams. The wire bond is made ultrasonically with one millimeter aluminum wire.

Discussion

The continuous belt plater is especially suited for selective plating of transistors and integrated circuit headers and is somewhat similar to continuous brush plating techniques. The headers are fed continuously across a belt or carpet saturated with gold solution. The post tops and eyelets are in the down position and move across the solution belt at an angle to the direction of movement of the belt. (See Fig. 3) Cathode contact to the lead and eyelets of the headers is made by means of a brass brush rail positioned over the solution belt, while a platinum anode is positioned beneath the solution belt to complete the plating circuit.

A pulse rectifier equipped with the capability of superinposing a standard D.C. ("base") current together with a square wave D.C. pulse is supplied with the plating hardware. The total list of process variables to be optimized are listed in Table III. After establishing a distance of the header post tops from the solution belt (Fig. 4) which would not interfere with plated grain structure effects of the rectifier variables on grain topology was investigated.

Fig. 5 clearly shows an increase in grain size with increased magnitudes of

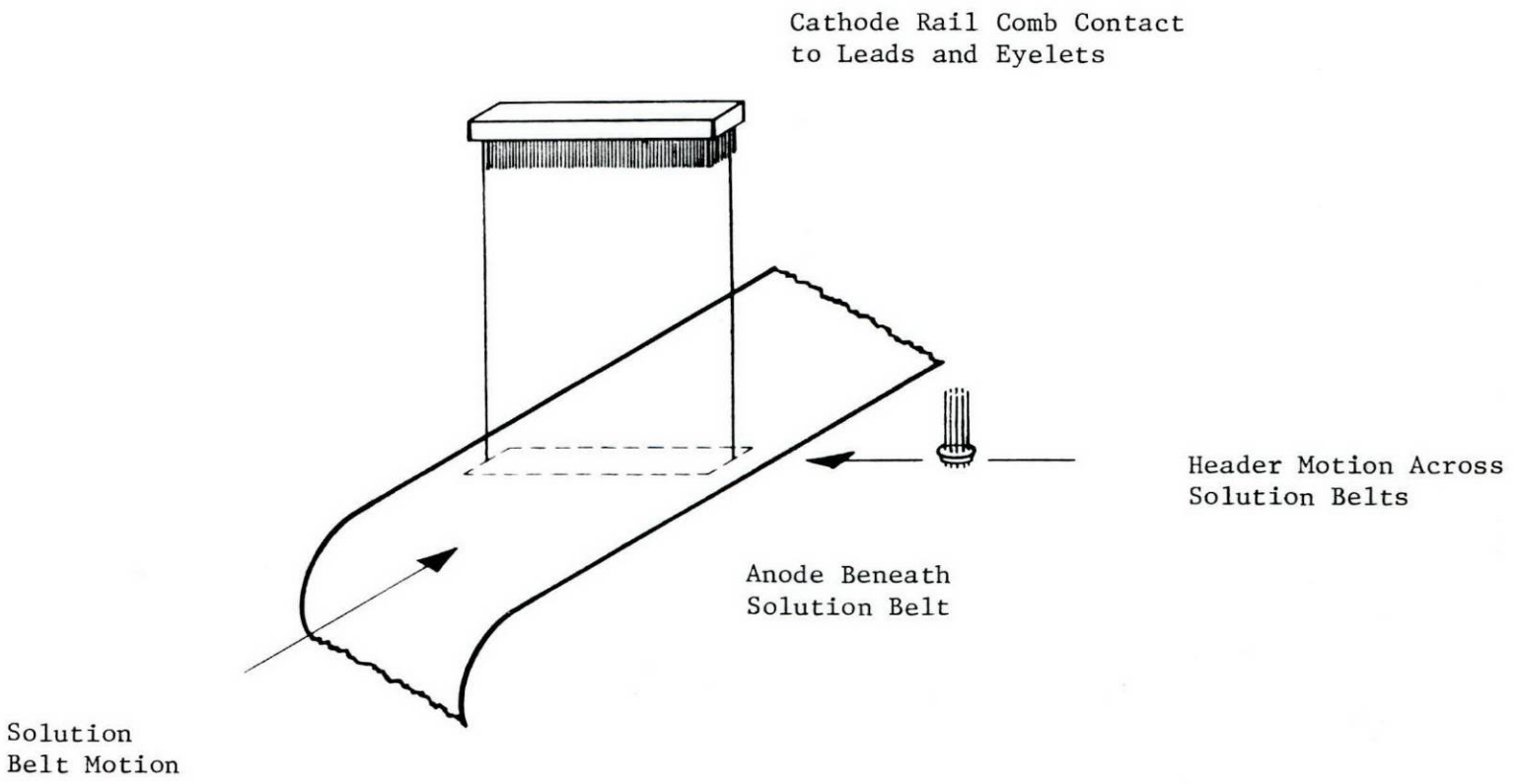

Fig. 3 Schematic Drawing of Relative Movement of Headers and Solution Belt

Table III

Process Varibles

I. Rectifier

1. Pulse Duration

a) ON 0-1.0 milisecond

b) OFF 0-10.0 milisecond

2. Base Current - 0-6 amps.

3. Peak Pulse Current 0-30 amps.

II. Solution Belt

1. Belt speed 0 - 202 cm/sec.

2. Solution Flow onto Belt 0-11.4 liters/min.

III. Rail Guide for Headers

1. Angle between rail and solution belt - must be especially optimized for header type.

2. Rail height from solution belt - 0.03 cm.

IV. Carrier Belt for Headers

1. Speed - 0 - 12,000 units/hr.

V. Solution Control

1. Temperature 50-66°C

2. Specific Gravity - 16-20°Be'

3. pH 5.8 - 6.2

4. Gold concentration 15-30 gm./liter

VI. Current Density

1. 50 amperes per square decimeter.

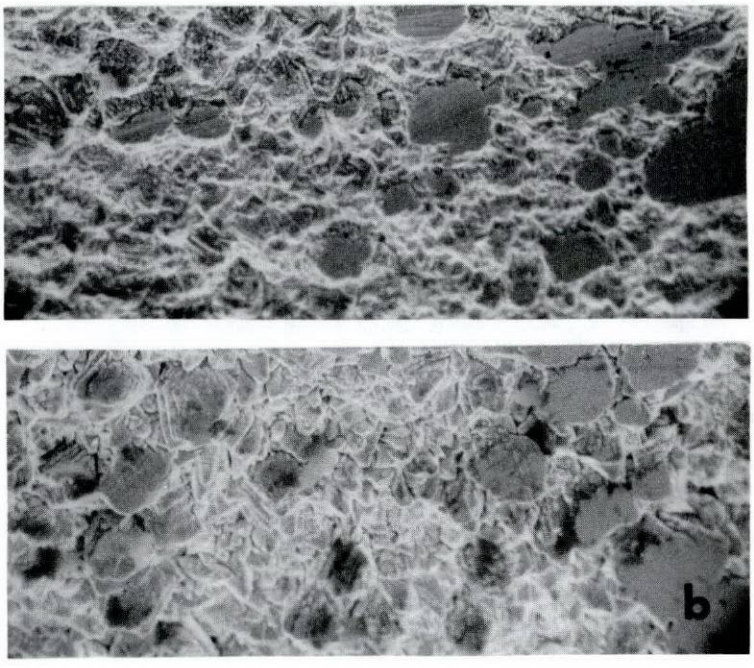

Fig. 4 - Effect of Post Top Distance from Solution Belt on Deposit Topology. 3000X

(a) Rail at lowest setting. Note smears due to rail setting.

(b) Rail at 0.003 inches above lowest setting

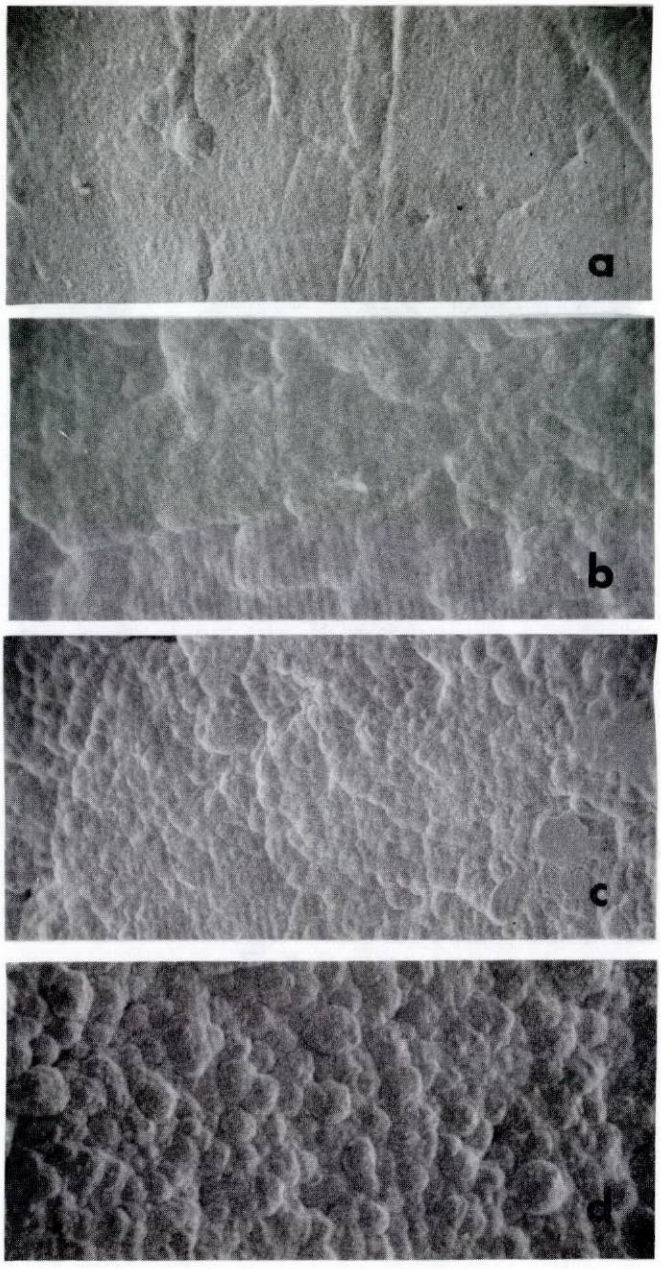

Fig. 5 - Grain Topology Variations with Variations in DC Base Current. 3000X

(a) 0 Amperes
(b) 1 Ampere
(c) 2 Amperes
(d) 5 Amperes

Machine Settings
Peak Current 20 Amperes
Pulse Current On 1.0 Ampere; Off 5.0 Amperes

superinposed base current and Fig. 6 is a matrix of peak pulse current magnitudes and its effect on grain topology. From these and other test matrices, a base current of 1-2 amperes and a peak current of 15-20 amperes was chosen to achieve eyelet deposit thicknesses of 50 microinches which is the internal Motorola specification requirement for this header.

The gold solution chosen for the test matrix is a proprietary one supplied by the equipment manufacture. It can be classed as a "neutral" type formulation utilizing potassium gold cyanide and citrate-phosphate compounds as the conductivity salts. The specifications for the solution and equipment settings are outlined in Table IV.

Utilizing this information the ratio of pulse current durations in miliseconds was studied as to its effect on topology (Fig. 7) and as to wire bond functionality. Pulse ratios of 16.7% - 25% gave satisfactory wire bonding while a ratio of 16.7% (On 1, Off 5) produced the most consistant and stronger pull strengths. (See Table V) This conclusion is also supported by the Auger surface analysis shown in Table VI in that at this pulse ratio the least amount of base metal diffusion occurs at the surface of the gold after simulating the temperature excursion at which the header is subjected to during die bonding.

Conclusions

The Selective Belt Plater is a viable technique for reducing gold useage on electronic headers. In the case represented in this report the reduction is approximately 87% when compared to conventional barrel plated units.

The base current, peak pulse current, and pulse duty cycle are important parameters to control to insure deposits which will wire bond after die bond temperature excursions. On the device studied a duty cycle of 16.7% produces the deposit characteristics desired.

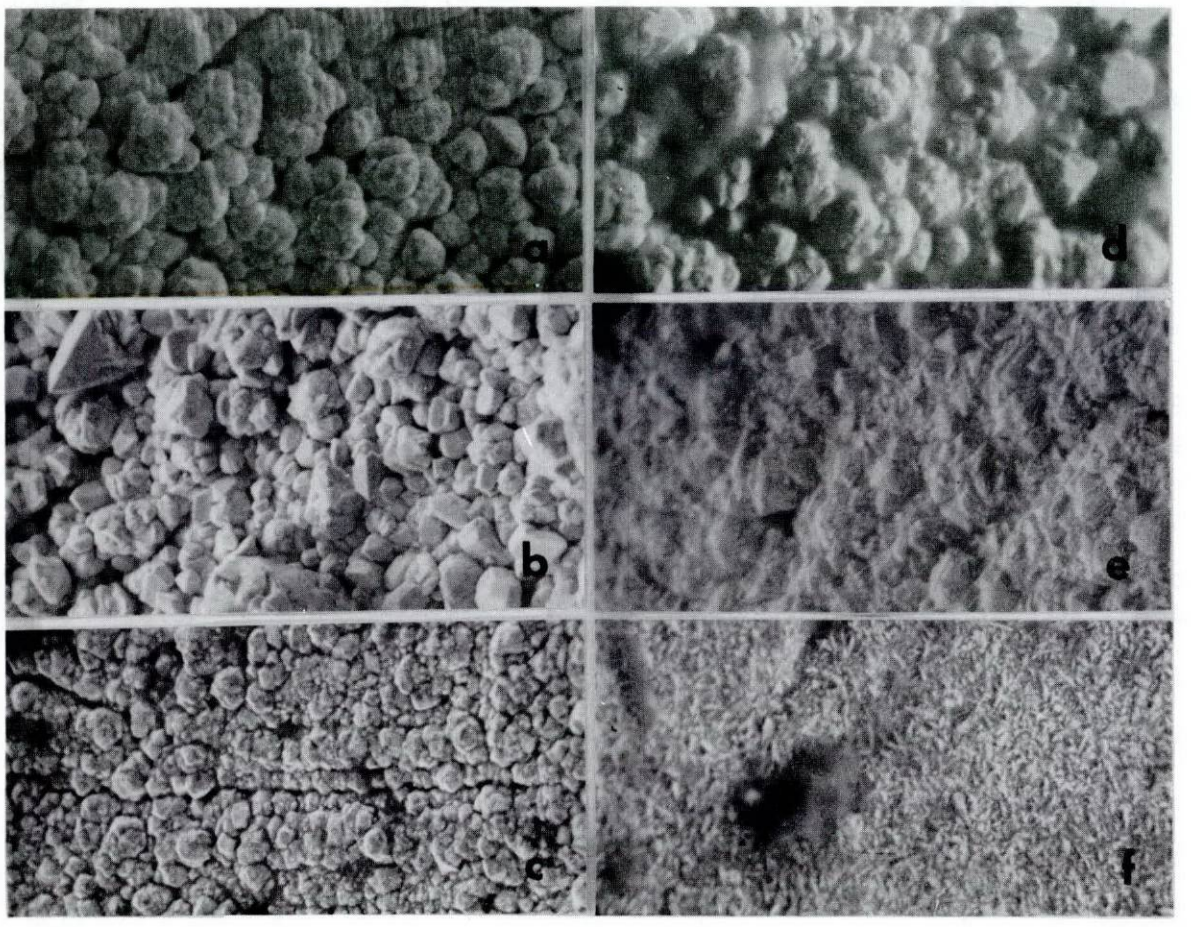

Fig. 6 - Effect of Peak Pulse Current Magnitude on Grain Topology. 3000X

Machine Setting:

Base Current 4 Amperes
Pulse Current On 1.0 Ampere; Off 5.0 Amperes

(a) 30 Amperes (b) 25 Amperes (c) 20 Amperes
(d) 15 Amperes (e) 10 Amperes (f) 5 Amperes

Table IV

Specifications for Carpet Plater

1. Solution - Proprietary Gold Solution
   a) Gold Concentration 22-24 gm/liter
   b) Specific Gravity 16-18°Be
   c) pH 5.8 - 6.0
   d) Operating Temperature 60-63°F
   e) Solution Flow on Belt (8.7-9.5 1/min. on flow meter)
   f) Solution belt speed set at 0.92 cm/sec.
2. Part Carrier Belt
   a) Speed 6.5K/hr.
3. Rectifier
   a) Total peak current 15-20 Amps.
   b) Continuous base current 1.0 Amp.

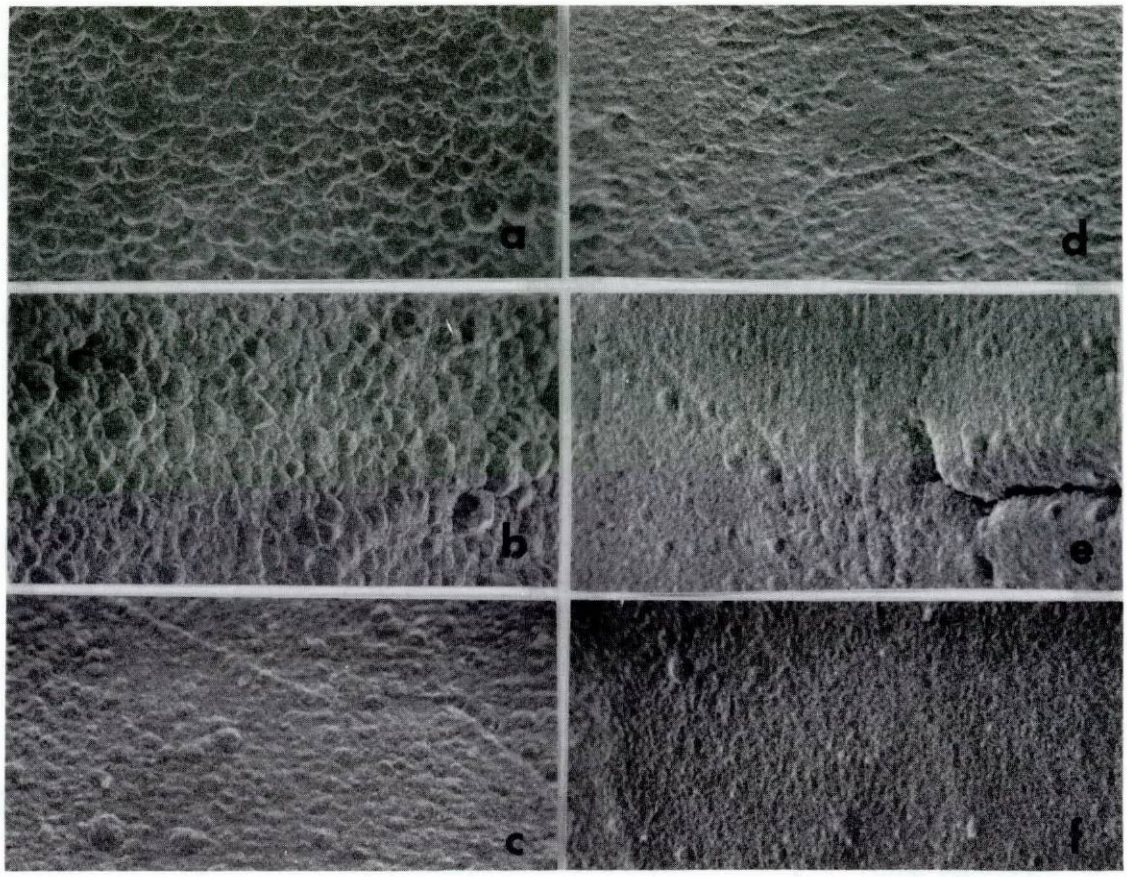

Fig. 7 - Effect of Pulse Current Magnitude on Grain Topology. 3000X

Machine Settings:

Base Current 1.0 Amper
Peak Current 2.0 Amperes
Rate 6.5K per hour
Solution Flow 2.5 gpm.

(a) On 1.0 Ampere; Off 2.0 Amperes
(b) On 1.0 Ampere; Off 3.0 Amperes
(c) On 1.0 Ampere; Off 4.0 Amperes
(d) On 1.0 Ampere; Off 5.0 Amperes
(e) On 1.0 Ampere; Off 7.0 Amperes
(f) On 0.5 Ampere; Off 5.0 Amperes

Table V

Effect of Pulse Ratio on Wire Pull

On/Off Ratio (Milisec/Milisec)	% On	Average Wire Bond (gm. Force)	Wire Pull Range (gm)
1.0/2.0	33.3	6.8	0 -10.9
1.0/3.0	25.0	8.2	5.2-11.5
1.0/4.0	20.0	8.7	6.1-11.8
1.0/5.0	16.7	8.4	6.5-10.5
1.0/7.0	12.5	8.1	0 -11.9
0.5/5.0	9.1	7.1	1.9- 9.8

Table VI

Auger Surface Analysis After
500°C for 3 Minutes in Air

On/Off Ratio (Milisec/Milisec)	% On	Average Auger On Wire Bond Area At % Ni	At % Fe
1.0/2.0	33.3	7.3	2.6
1.0/3.0	25.0	7.9	5.1
1.0/4.0	20.0	6.9	5.7
1.0/5.0	16.7	4.6	2.4
1.0/7.0	12.5	6.3	3.7
0.5/5.0	9.1	6.6	3.0

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F-2

ELECTRONICS
SESSION F

Continuous Selective Precious Metal Plating: Some Practical Observations

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CONTINUOUS SELECTIVE PRECIOUS METAL PLATING
SOME PRACTICAL OBSERVATIONS

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ABSTRACT

Reel to reel plating for the electronic industry is a relatively new application of plating technology.

This paper gives a summary of equipment available for continuous strip plating, particularly for selective precious metal reel to reel plating. An attempt has been made to analyse what we aim at with this technology and how this target can be obtained. Particular emphasis has been given to some practical aspects, such as helpful formulas, rinsing and effluent problems.

Introduction

Although continuous plating of strip and wire is known for many years, the typical use of reel to reel plating for electronics has been practised for only just over one decade. This in itself is logical, because of the tremendous growth of the electronic industry in the past 10-20 years and the parallel strong increased demand for plated components.

Characteristic in plating for electronics, is the requirement for precious metals. The sheer costs of these metals combined with the vast numbers of components required, automatically created a desire for functional or selective plating, e.g. plating in those areas only where the deposit is essential for the performance of the component.

A further demand was to have components interconnected or bandoliered to allow automatic assembly, another necessity created by the large volumes required. When these wishes of the electronic industry are combined with the tight specifications, high accuracy and reproducibility, which are common in this type of industry, it is clear that specialised reel to reel selective plating was the only answer for a number of components for the demands of the electronic industry (Fig. 1).

The author's company, which is engaged in supply of equipment as well as in subcontracting, has recognised the necessity of automatic selective plating in an early stage and has developed specialised equipment, which now has been in use for more than 10 years.

Why reel to reel plating ?

Before looking in more detail to systems available for selective reel to reel plating, it is worthwhile to summarise the reasons for, or the advantages of, using this technology, particularly for the electronic industry.

1. Volumes required are very large. Quantities per part may vary from below one million to several hundred millions per year.

2. Many components require precious metal on a functional area. Selective reel to reel plating, enables production of large numbers of parts with accurate selective plating. On a typical TO-92 transistor-frame, the amount of gold required for all-over plating to 1,3 micrometer is 2,3 mg, whereas with selective plating only 0,30 mg is used. On one billion parts the difference is 2 tons of gold and many billions of such parts are produced worldwide per year (Fig. 2).

3. Automatic assembly requires presentation of parts in a Rythmic configuration. Although other methods can be used, the simplest system is to present parts interconnected or bandoliered.

4. Automatic plating enables precise control of all plating parameters and therefore can meet the high specifications and reproducibility required in the electronic industry.

5. Reel to reel plating is automatic, and requires little labor. Although capital investment is high, outputs are also high and production costs per unit low.

The basic principle of reel to reel plating seems simple enough, just the mere transport of a chain of components or strip material through a number of process stations. In practise however, it is not as simple as that, there is a large variety in;

a) Geometry
b) Specifications
c) Base Metals

a) Geometry

Not only is there a large variety of prestamped parts with different shapes and sizes, but even plain stock strip material may vary so much, that problems can be entirely different with one strip compared with another. In Fig. 3, two solid stock materials are shown, both plated with gold. The wide strip is nickel silver 0,4 x 72 mm, plated with two 3 mm wide stripes of gold, 3 micrometer over 2 micrometer nickel. The narrow strip is stainless steel 0,024 x 0,38 mm also plated with 3 micrometer gold. The difference in mechanical handling, process cycle and method of direct current supply will be obvious.

b) Specifications

There is a large variety in specifications. Although a rough separation can be made between specifications for

Semiconductor applications and
Connector applications

each of these groups, or even individual users, may have dramatic differences in their specifications, usually caused by different technologies in further

assembly (Semiconductors) or in different applications (Connectors). One connector system may be subject to heavy wear, whereas another system may require low constant contact resistance at low contact pressures at elevated temperatures.

Seperately from specifications for top coatings, intermediate or barrier coatings may vary greatly depending on type of base metal, assembly method or application.

c) Base metals

There are no common base metals for reel to reel plating, not even for a group of applications. Semiconductor frames may be fabricated from brass, copper iron alloy, electrolytic copper, nickel, nickel iron alloys or nickel cobalt iron alloy.
Depending on the final coating, gold or silver, different barriers can be specified, such as copper, nickel, cobalt. Base metals used for contacts are phosphor bronze, beryllium copper, nickel-silver, brass, nickel-bronze, stainless steel etc.

It would indeed be a unique machine, which could handle the various base metals, the different geometries and plate various types of precious metals in different selective areas, over a choice of barrier coatings. To my knowledge such a machine has never been built and if it has been, it would probably never operate because of its immense complications.

How can reel to reel plating be done.

Since reel to reel selective plating is an apparent necessity, it is interesting to see what types of equipment or systems are marketed.

Without claiming to be complete and without much comment, presently available systems could be summarised as follows;

1. Simple controlled immersion plating.

Simple, suitable for pin type products; plates both sides of one end of strip or bandolier. Turning parts over 180° enables application of coating, same or different (dual tone) on other end of strip or bandolier in one pass-through. Disadvantage is low precision and low plating speed, due to low degree of agitation.

2. Controlled immersion plating with technical improvements.

Several arrangements are used to improve either accuracy or speed of deposition, or both, such as

2.1 Shielding
2.2 Water fall type agitation
2.3 Air masking

In Fig. 4, simplified sketches of these improvements are shown.

3. Controlled immersion using 3 level systems.

Such systems utilise a heavy organic non conducting fluid (gravity higher than gravity of electrolyte), which is not mixeable with aqueous electrolytes.

On top of this fluid floats the electrolyte. This system enables selective plating of middle sections of strips or bandoliered components (Fig. 5).

4. Fixed masks for one time use only.

Masking materials can be tapes, screen or photo resists. They are usually very accurate, but somewhat sensitive to heavy cleaning. Also they must be removed again, making the process less competitive.

5. Fixed masks for continous use.

Such masking devices could be;

5.1 Sliding type. Usefull for producing stripes on stock by simple passing strips over a slotted rigid mask. [2]

5.2 Tool type masks. In great use for producing spot selective plating on semiconductor frames. When tool is open, a section of product is inserted after which tool closes. One side of tool is solid, the other side has holes corresponding with the spots on the strip. When tool is closed, electrolyte is jetted on exposed areas. [3]

6. Brush type selective plating.

In Fig. 6, a schematic set-up is given. Parts are conducted whilst travelling allong a rotating drum which is covered with cloth soaked in electrolyte. The drum acts also as anode. Neat arrangement for particular jobs. [4]

7. Travelling masks.

These are re-usable masks which travel with strip or bandolier through the plating station. They normally are re-inforced rubber belts, which are by mechanical means pressed against those portions of the product, which do not require plating. Travelling masks can be

7.1 Straight. Masking belts are pushed mechanically against product.

7.2 Wheeltype. Masking belts are automatically pushed against product by regulating belt tension. As a matter of fact our company prefers the latter system, because it is universal, accurate and simple to adjust for a large variety of parts or strips. [5]

7.3 Slotted wheel type. In this case, the wheel has a slot in its circumference and the electrolyte is jetted from the inside on that portion of the strip or bandolier, which is exposed over the slot. In case of solid stock, no belts are required. In case of bandoliered parts, a cover belt is necessary. This type of wheel can be used for spot plating if circumference has holes instead of a slot (Fig. 7). [6]

8. Various systems.

Fig. 8 shows a special anode jet arrangement, which is claimed to give quite accurate spots. 7)

Wave type semi selective arrangement whereby a strip passes horizontal over an overflowing slot. 8)

It is not the intention to go more in detail on all these possibilities (and there are probably several more).

The jobplaters point of view.

In general problems associated with reel to reel selective plating in a captive shop, are limited, because the variety in geometry and plating specifications are usually not very large. For that reason it seems interesting to try and summarise what a jobshop would look for in reel to reel plating.

1. High travel speed
2. Easy to operate.
3. Optimum accuracy of selective plating
4. High reliability
5. Easy to adapt for a certain variety of products

1. High travel speed

Main factor in each reel to reel plating installation is that all process stations should be designed for high speed operation and not the plating processes only. Reduced time for cleaning can be obtained by using mechanical cleaning, Ultrasonics or high CD electrocleaning. Rinse times can be reduced by jet rinsing or air-agitation of rinse water. Nevertheless the main factor which determines eventually the speed of a machine remains the deposition speed of the plating solutions. Nickel with 25-40 micron per minute and gold and silver up to 60 micron per minute, are common to-day, and even faster processes are available.

Many future or present users of reel to reel plating, overlook however a phenomenon which is called the CCC or Current Carrying Capacity. Independant of how fast a plating solution can operate, the product or strip must be capable of transporting the required current.

In Fig. 9, a stamped part is shown, which is half of a push-button contact. These parts require silver plating all-over. The maximum current which can be pushed through this .002 (0,05 mm) thick brass bandolier without excessive heating-up, is 11 Amp., which limits plating speed for a single strand, single silver tank, reel to reel installation to appr. 1,5 Mtr per minute for a 3 micron silver all-over. Unless complications of multiple silver stations, or other interruptions for additional contacting are accepted, the maximum speed is determined only by the CCC of the bandolier. This limitation of speed by the CCC of the product is often encountered by bandoliered or pre-stamped parts which require all-over plating. In Fig. 10, a schematic set-up is shown to determine the CCC of a strip or bandolier.

In the practical case mentioned before, a 2m25 long silver plating station was available resulting in a dwell time of 1,5 minute. To obtain the desired 3 micron, a CD of 3,2 A/Dm^2 was necessary, however, the electrolyte permitted CD's of over 10 A/Dm^2. Hence the speed could have been 3 times faster if only the CCC had permitted it.

****

Once the CCC of a product is known, it is relatively simple to calculate the permissable speed of that product in reel to reel plating by using the following formulae;

$$V = 0,1 \times \frac{A \times R}{O \times S \times M} \quad \text{----------} \quad 1$$

In which;
V = Velocity in Mtr per minute
A = Amperage permissable on plating section (usually 2 x CCC with double contacts)
R = Efficiency of electrolyte in Mgr/Amp min.
O = Surface area of product to be plated in Dm^2 per Mtr strip lengt
S = Gravity of metal to be plated
M = Thickness desired in microns

Of course it is possible to change this formulae into feet, square inch and microinches. It does not look quite so logical then;

$$V = 61,027 \frac{A \times R}{O \times S \times M} \quad \text{----------} \quad 2$$

Now V = Ft/min
A = Total amperage
R = Mgr per Amp min.
O = Surface area in sq inches per foot of product
S = Gravity
M = Thickness in microinch

Another way to use the formulae as given in 1. is:

$$A = \frac{V \times O \times S \times M}{0,1 R} \quad \text{----------} \quad 3$$

At a predetermined speed, the required total current can be calculated in this way for obtaining a certain thickness.

Once a speed has been calculated for the apparent "bottle neck" station in the process sequence, the required amperage for all other stations can be quickly calculated using formulae 3.

****

2. Easy to operate

Machines which are easy to operate, are usually not developed, they gradually grow. The combination of designer and user of equipment creates an ideal situation to develop machines which are practical and indeed easy to operate.

The simplicity of operation begins with decoiling. Particularly at higher travel speeds, slack-towers and automatic connection of reel ends make operation easy. Separation of instruments into groups placed near to the relevant sections permits control at a glance.

Easy acces to guides, D.C.-contacts and all other parts, requiring adaptation or maintenance, is of utmost importance. Equally important is the use of selective systems which permit the use of soluble anodes. Insoluble anodes in many cases reduce quality of deposits, increase costs unnecessarily and increase necessity for accurate control of the relevant electrolyte.

3. Optimum accuracy of selective plating

All systems which have been mentioned before, have certain advantages, but also disadvantages. Stationary straight masks cannot absorb camber. Therefore allowance must be given for the presence of camber which reduces accuracy.

Solid masking for spotplating may result in different thicknesses for adjacent spots due to differences in anode activity or agitation.

It is therefore extremely important to use stationary anodes and agitation or jetting systems, and let the product travel at constant speed, in order to provide at least the same "history" to all products. The wheel type selective systems are ideal for this. They can moreover absorb a reasonable amount of camber by using a flexible coating on the wheel surface and they can be made very accurate.

Generally the larger the size of units or tools for selective plating, the lower the accuracy is that can be obtained.

For optimum accuracy in hard gold plating, where current efficiency is usually between 30-80%, control of the electrolyte is also very important. Accurate temperature regulation, automatic pH control and automatic dosage of gold salts and replenisher will all aid in keeping efficiency constant, so that tolerances for overplate can be kept minimum.

4. High reliability

Reliability of reel to reel selective plating machine, should be all-over: mechanical, electrical, chemical.

Mechanically a selective plating machine should also be able to handle delicate parts. Many systems nowadays use electronically controlled drive systems with digital read-out of speed and automatic and adjustable control of tension in strip or bandolier.

The guiding of the strip or bandolier in a selective plating machine, should be made in such a way as to present minimum friction; the same is valid for

entry and exit gates in treatment stations, when straight line type platers are used.

All parts and auxilliaries should be designed for round the clock operation. Guides or parts specific to a particular product would be easily interchangeable.

Electrically a selective plating machine can be made to look like a Christmas tree. For reliability of operation however, a certain amount of electric signalisation is required to enable operator to rectify situation before they deviate from standard too much. Of course these rectifications can be made automatically.

An important part of the electrical side of selective plating is safeguarding: motors against overload, rectifiers against short circuit, solution levels against being not there where they ought to be etc. As far as rectifiers are concerned, constant current rectifiers are recommended.

Chemically a selective plating machine should be adequate. In this case, adequacy means sufficient safeguards to enable perfect and reliable production even when some chemical parameters are not completely in the preferred ranges.

It really begins with pretreatment. An automatic selective plating machine can be your best friend, but make sure it has the tools to stay your friend. It is foolish to risk costly rejects by just having a marginal pretreatment or rinsing.

However, even with the best of precautions, surprises cannot be avoided. Quite often rejects of plating have their cause in conditions of the base metal. Inclusions may cause blistering or lifting of deposits, too much cold working may cause breaking off of corners with bendtest after plating, miniblisters may be formed due to cracks in base metal. In Fig. 11a and b, surface condition of a flat rolled brass 90 is shown. The cracks shown in a) have a maximum dimension 1 x w of appr. 10 x 2,5 microns. As can be seen in b), cracks have been overplated, but cause miniblisters after heattest. A simple Scanning Electron Microscope is a useful tool for the automatic selective electroplater.

Depending on the nature of strip or bandolier to be processed, a mechanical precleaning (Fiber or Scotch Brite brushes with alkaline cleaner) or an Ultrasonic precleaning is recommended. In both cases precleaning should be followed by at least one station, but preferably two of electrocleaning.

Prestamped parts may require electrolytic deburring. In that case a solvent or vapour precleaning presents parts clean and dry for deburring.

What is valid for pretreatment is also valid for all other chemistry. Leave nothing to chance.

Continuous low CD purification of nickel solutions, regular or continuous filtration of gold and nickel solutions over activated carbon etc. all help

to ensure continuous high quality plating.

Many of these facts are simple plating know-how, others are typical just for reel to reel plating.

Probably there is no other field in electroplating where sophisticated rinsing techniques can be used more succesfully than in reel to reel selective plating.

****

Rinsing in reel to reel plating machines deserves special attention, a different way of thinking. With comparitively cheap and simple provisions, reel to reel plating can be environmentally harmless, even when strong toxic or contaminating electrolytes are used. The following example is a typical illustration of this statement.

In Fig. 12a, b and c, a strip is shown travelling from a plating tank (possibly a nickel tank), into a rinse station on the right hand side. The strip is a .015 x 2.0 section, travelling at 17 ft per minute (5 mtr).

In a), the strip is introduced in the rinse water without precautions. Per hour 2,5 ltr of electrolyte is carried into the rinse water.

In b and c the strip passes through an air wipe (b) or a mechanical wipe (c). In both cases the amount of electrolyte carried into the cold water rinse is reduced to 0,25 - 0,4 ltr per hour. If the rinse tank on the right hand side of this drawing would have been a drag-out rinse and used to top-up evaporation losses of the previous nickel plating tank, the final equilibrium concentration in an average practical case would be 4-5 g/l Ni metal, compared with 80-100 g/l in the main plating tank. This value was obtained indeed in practical operation at a speed of 5 mtr per min. and a nickel bath temperature of 65°C. Backfeed of drag-out solution into the nickel plating tank and refill of drag-out with deionised water were automated.

In a next step, 2 more drag-out rinses were used with wipes. When the equilibrium was reached, the situation was:

Main nickel plating tank	80- 100	gr/ltr
First drag-out rinse	4-5,6	gr/ltr
Second drag-out rinse	0,2-0,4	gr/ltr
Third drag-out rinse	10-30	gr/ltr

With 24 hr per day production, 5 days a week, 50 weeks per year, a production of an average strip size of 2 inch wide

would bring a total amount of 36 grams of Ni-metal in the waste water system at 5 mtr per mintue production speed (based on drag-over of 0,2 ml/dm^2 and an average conc. of 20 mg/ltr Ni in third drag-out rinse in this machine).

The calculated loss when no wipes or drag-outs are used, would be appr. 36 grams in 10 minutes or 36.000 times more ! And this is the result of 4 simple air wipes and 3 simple drag-out rinses only !

The same is valid for gold of course, as it is for all hot solutions. And most electrolytes for reel to reel plating are hot, because we want high speed. In some cases when travel speeds are high and products more difficult to wipe, it may be necessary to use a fourth drag-out rinse in order to obtain the desired results.

When such low drag-out is obtained, a further step is not difficult to realise: A closed rinse system. In Fig. 13 a closed rinse system for use after Ni plating can be seen, comprising a transport pump, a mixed bed resin column and a carbon filter. These units can be small as the normal need for an effective rinse station in a reel to reel plater is only about 25-75 gallon per hour.

In Fig. 14 a similar system for rinsing after gold plating is shown. This sytem incorporates an additional gold ion exchange resin column.

****

Rinsing in reel to reel plating is, as in all other plating operations, important, but due to fairly high travel speeds, rinse times normally are quite short. A 6 inch long rinse section with a 15 ft per minute travel speed offers only a 2 seconds rinse time. For that reason, effective agitation of rinse water by air, jetting or forced circulation is necessary.

Agitation is equally important for final deionised water rinses. In one case rejects due to spotting-out of silver during a bake test were reduced from an appr. 10-12 % to virtually 0 % by introducing ultrasonic agitation in the final deionised water rinse.

The ideal situation for final rinsing for gold or silver is indicated in Fig. 15.

After the plating operation, drag-out rinses and normal rinses, not indicated in this drawing, the sequence shoud be:

- Cold deionised rinse
- Hot deionised rinse (50°C = 120°F) with ultrasonic agitation.

- Cold freshly prepared deionised water carbon polished.

Introducing this type of post treatment usually eliminates the bulk of such problems as discoloration, bad wire bonding or die attach in semiconductor plating or problems as bad contact resistance or staining in connector plating.

5. Easy to adapt for a certain variety of products

Reel to reel selective plating machines should be capable of handling a certain variety of products or alternative process sequences. An explicit danger however, exists of wanting to incorporate too many alternatives resulting in one or more of the following problems:

- High reject percentage. The chosen sequence is a compromise and includes many risks. A very simple example is treating alternatively nickel or nickel iron base metals and copper based materials through same pretreatment. Acids will pick-up traces of copper, which may give invisible immersion deposits on the Ni based material, leading finally to bad adhesion on this material.

- Too much down time. Following the example given above, it is clear that the danger of bad adhesion could be eliminated by renewing the acid. This would however give additional down time. Changes necessary for geometric variations or for meeting different specifications are usually even much more cumbersome.

A practical solution offering no risk and very little down-time for adaptation was effected in a machine for the product of Fig. 9. The requirement here was to plate the parts alternatively with silver all-over or gold selective. A parallel arrangement was incorporated in this machine as indicated in Fig. 16. Time required to change from one finish to the other was less than 2 hours. This included time for trials to check for correct position of selective plating and thickness.

Conclusions.

Reel to reel selective precious metal plating for the electronic industry is not just so simple. Experience is the key to succes. When contemplating possible application, the following rules or guidelines should be observed;

1. Plan a reel to reel selective plater for a limited group of components and/or process variations.

2. Do not take any risk in process sequence lay-out, particularly in respect to pretreatment and rinsing.

3. A fast single strand machine is easier to operate than a slower multiple strand line.

4. Investigate the attractive possibilities which reel to reel plating machines offer to prevent loss of expensive electrolytes or to eliminate

the need of effluent treatment.

5. Use preferably systems with continuously moving product and stationary anodes and agitation.

6. Use preferably systems which permit the use of soluble anodes also for selective plating stations.

7. Ensure that equipment is suitable for round the clock operation.

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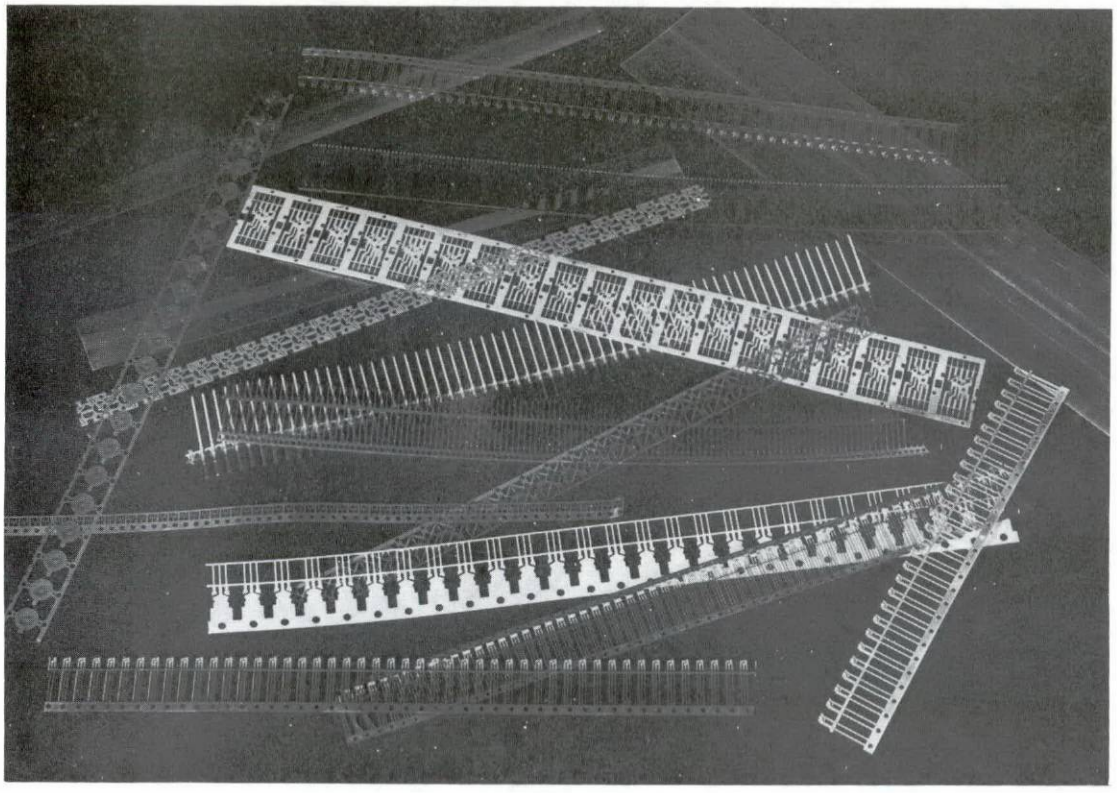
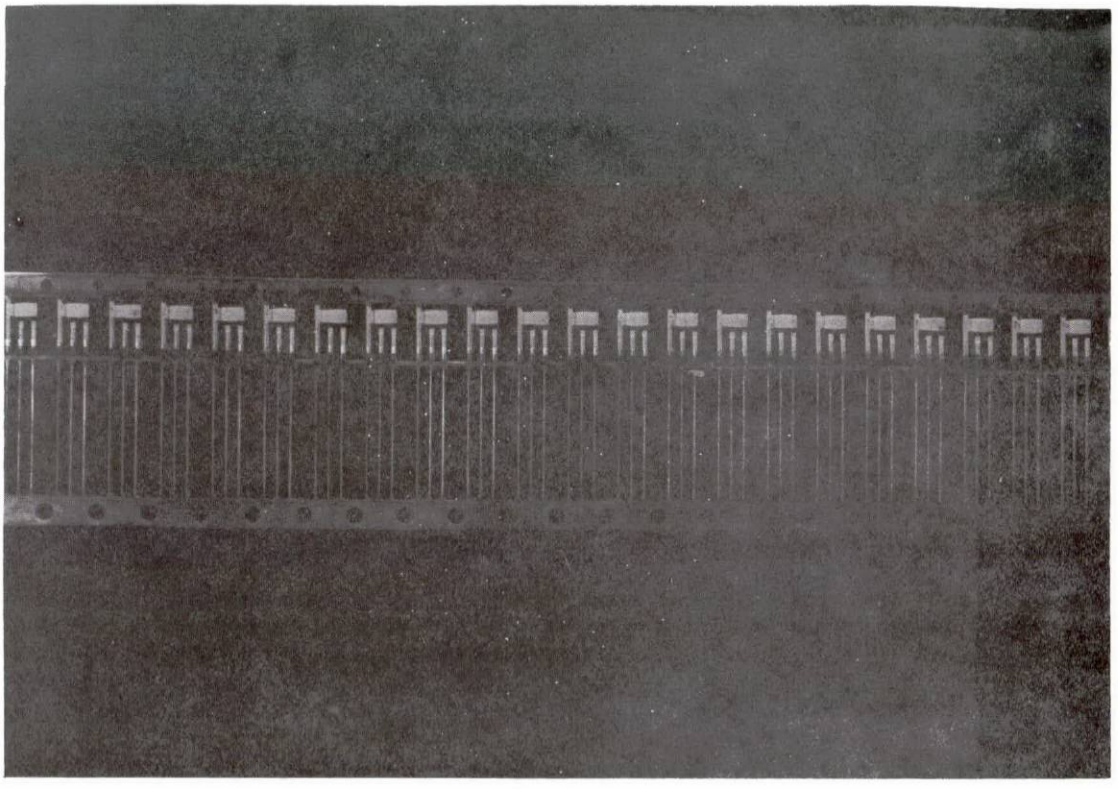


Fig. 1: Strips and bandoliered components, a typical mix of the variety.

Fig. 2: TO-92 frame. 2 tons of gold more required for all-over plating per billion products then with selective plating.



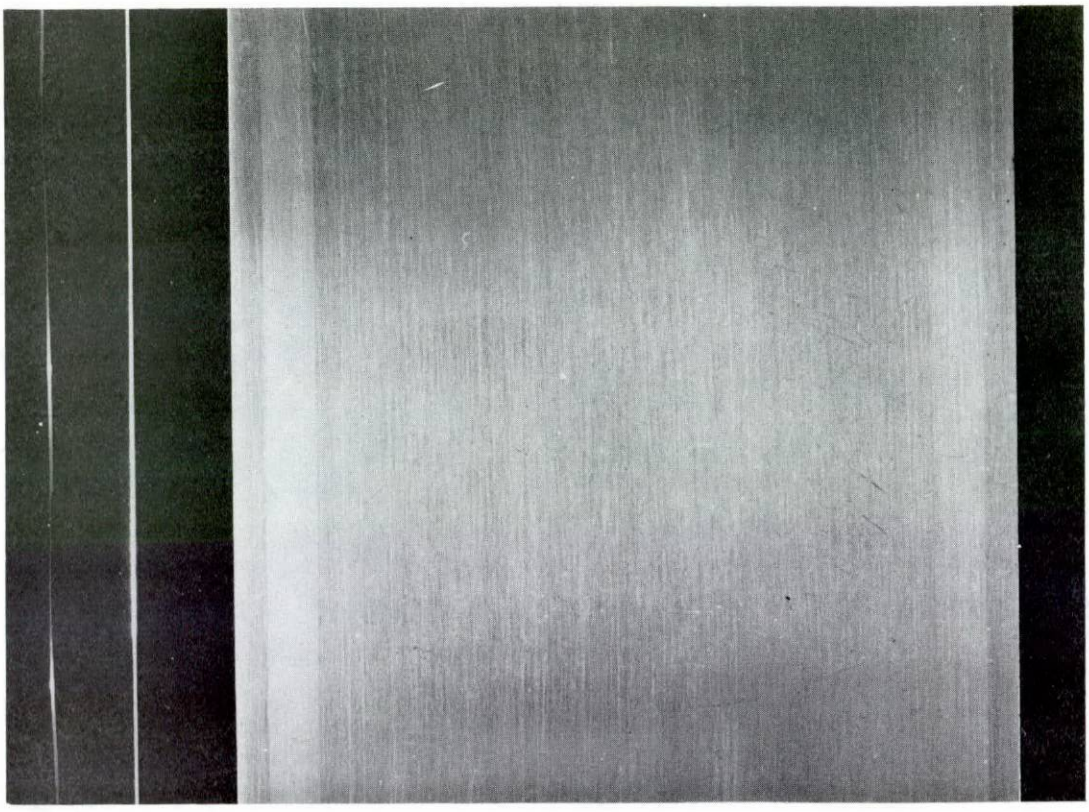


Fig. 3:
David and Goliath in strip plating. Large strip is 0,4 x 72 mm with 2 stripes of gold over Nickel on nickelsilver. Narrow ribbon is only 0,024 x 0,38 mm goldplated stainless steel.

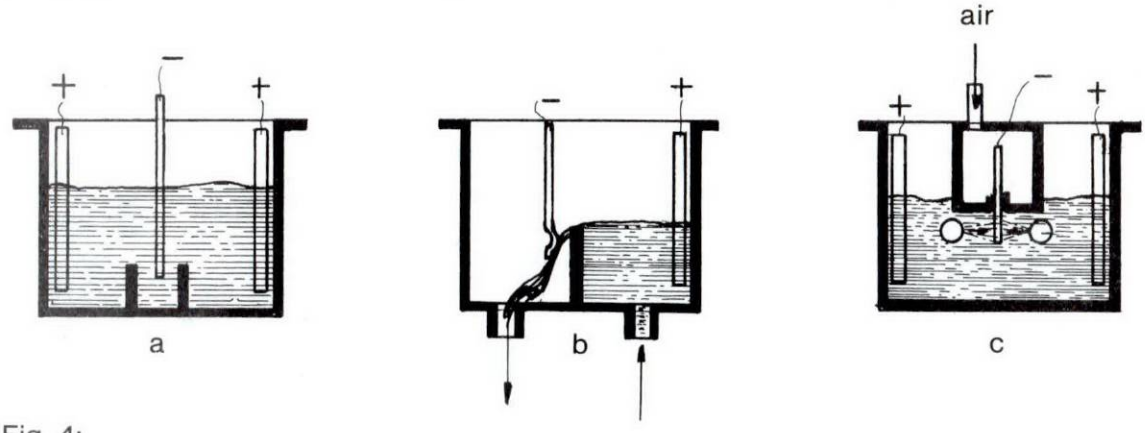


Fig. 4:

VARIETIES ON CONTROLLED DEPTH PLATING

a) simple shielding prevents excessive deposition at far end of strip

b) waterfall can be an effective system of agitation

c) box type guide, with pressurised air, provides more accurate solution level and enables stronger solution jetting.

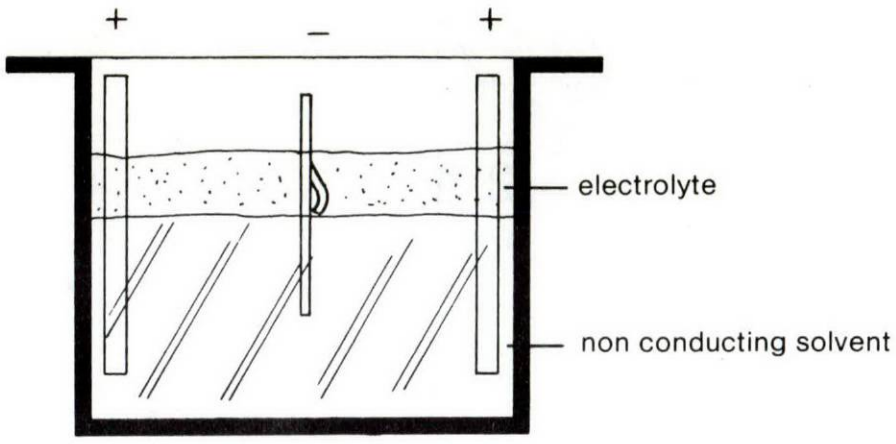


Fig. 5:

Multi level system;

lower liquid is non conductive solvent, with electrolyte floating on top.
Method for plating accurately a middle section of a bandoliered strip.

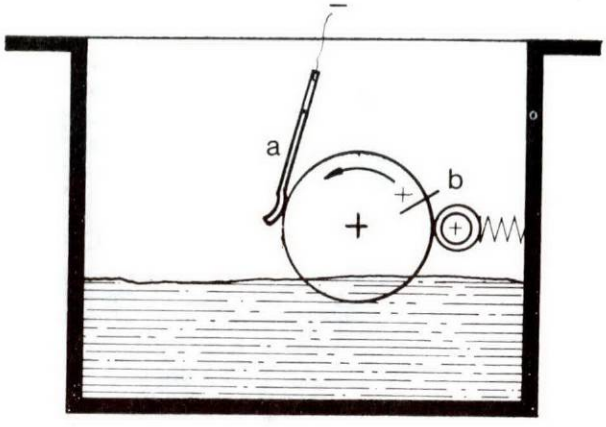


Fig. 6:

Brush type, drum shaped, selective plating set-up;

a) is bandoliered component,
b) is rotating drum type, brush/anode.

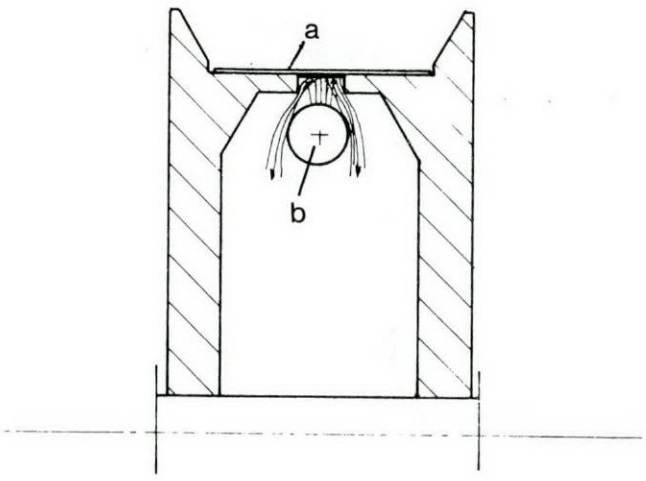


Fig. 7:

Schematic view of slotted wheel type selective plating system;

a) is strip to be plated,

b) is stationary anode/solution sparger.

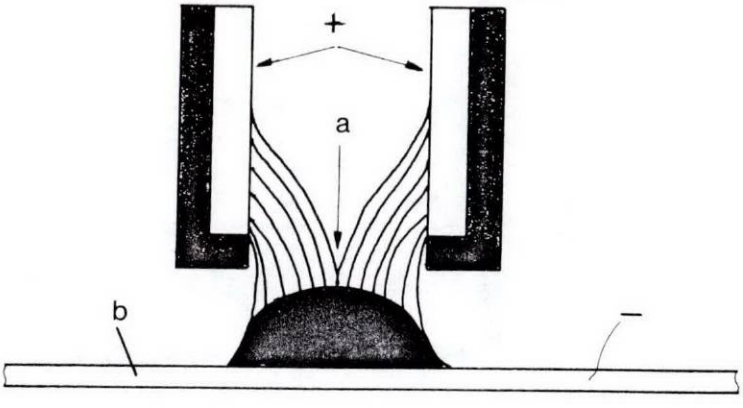


Fig. 8:

Electrolyte jetted as indicated with arrow a),
through jet-pipe with internal anode,
deposits spots on substrate b).

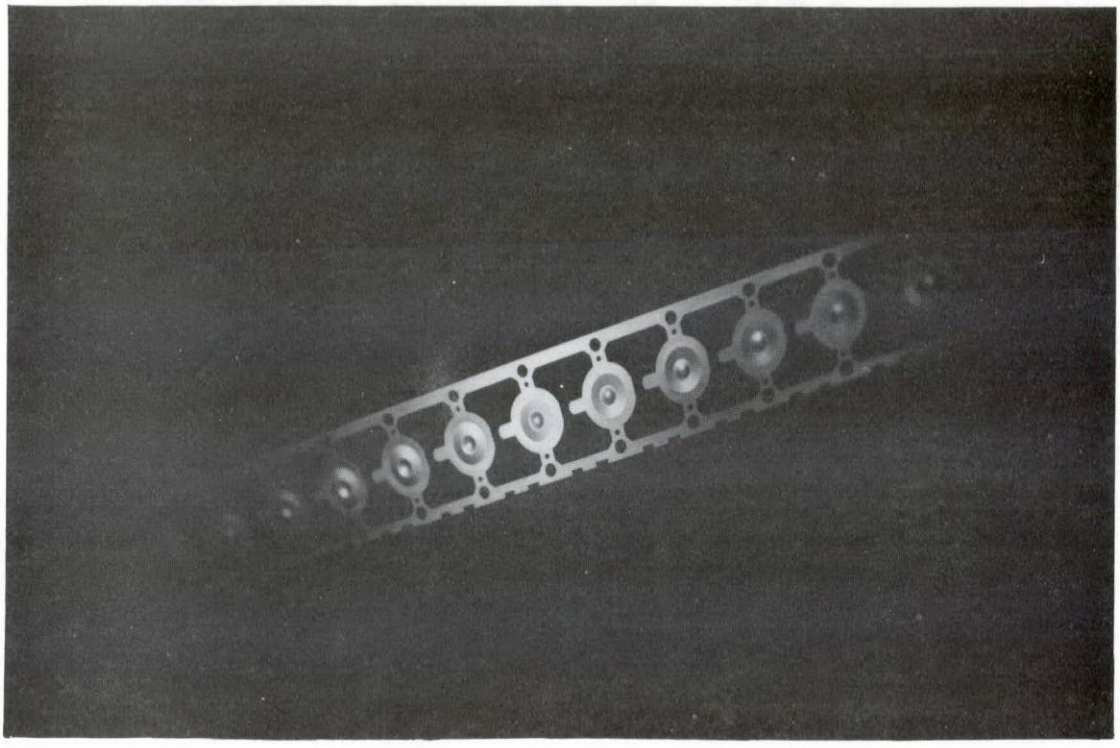


Fig. 9: Part of a push-button contact, all-over silverplated.

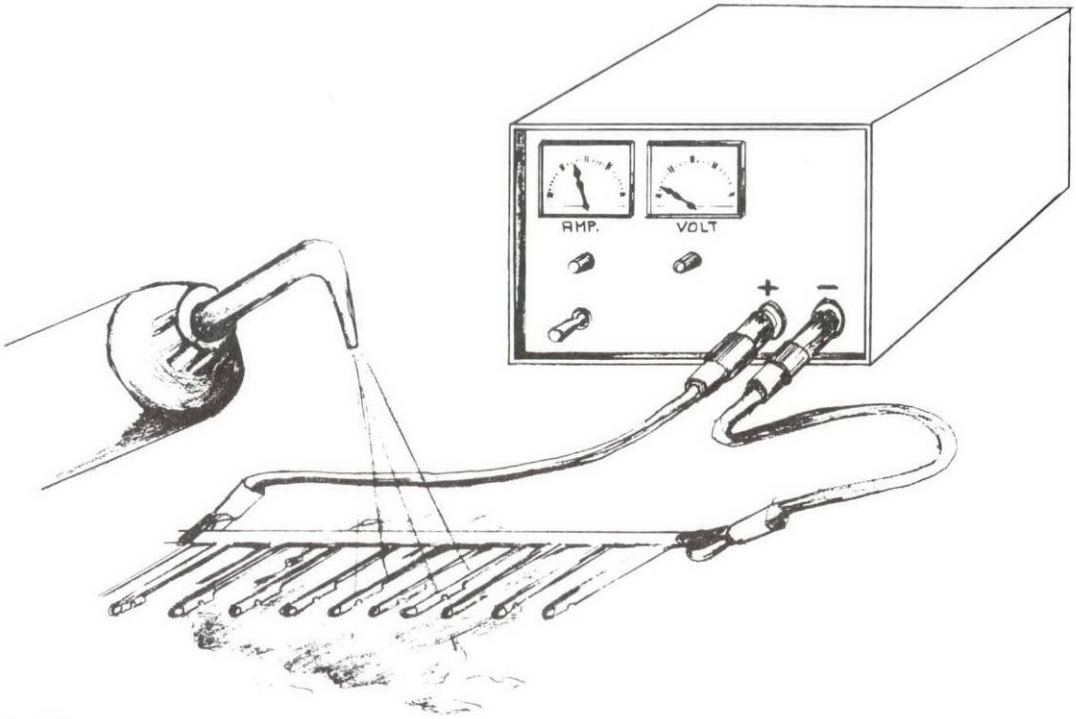


Fig. 10:

To determine CCC of a product, it is clamped between 2 leads of a rectifier. When current is gradually increased, product becomes warm. Spraying some water on it gives impression of approximate temperature.

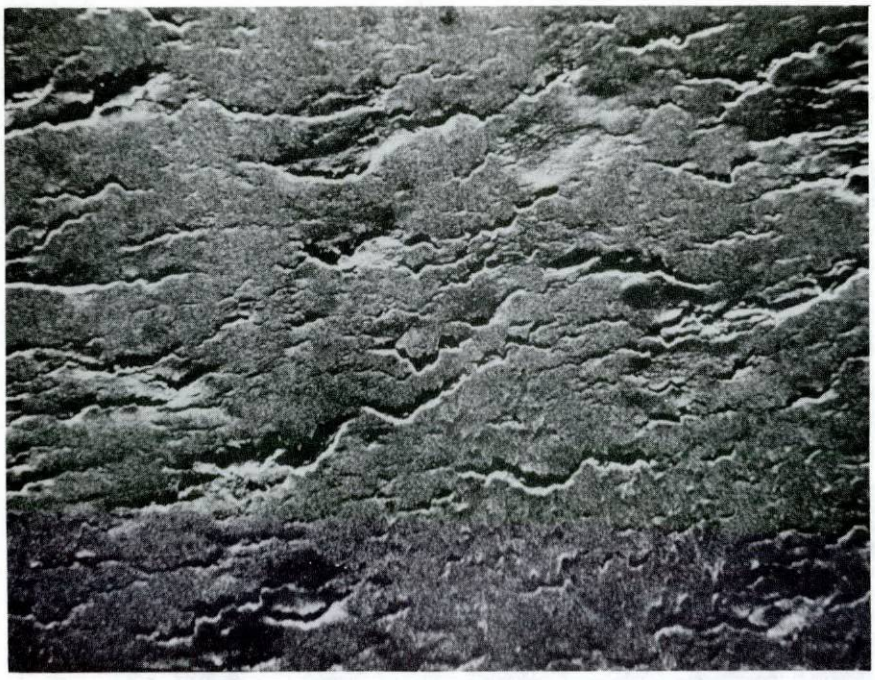


Fig. 11:

Defect in base metal as evident in SEM photograph's. Left picture shows base metal with cracks. Right picture after plating and heat test. Small blisters and original cracks are visible



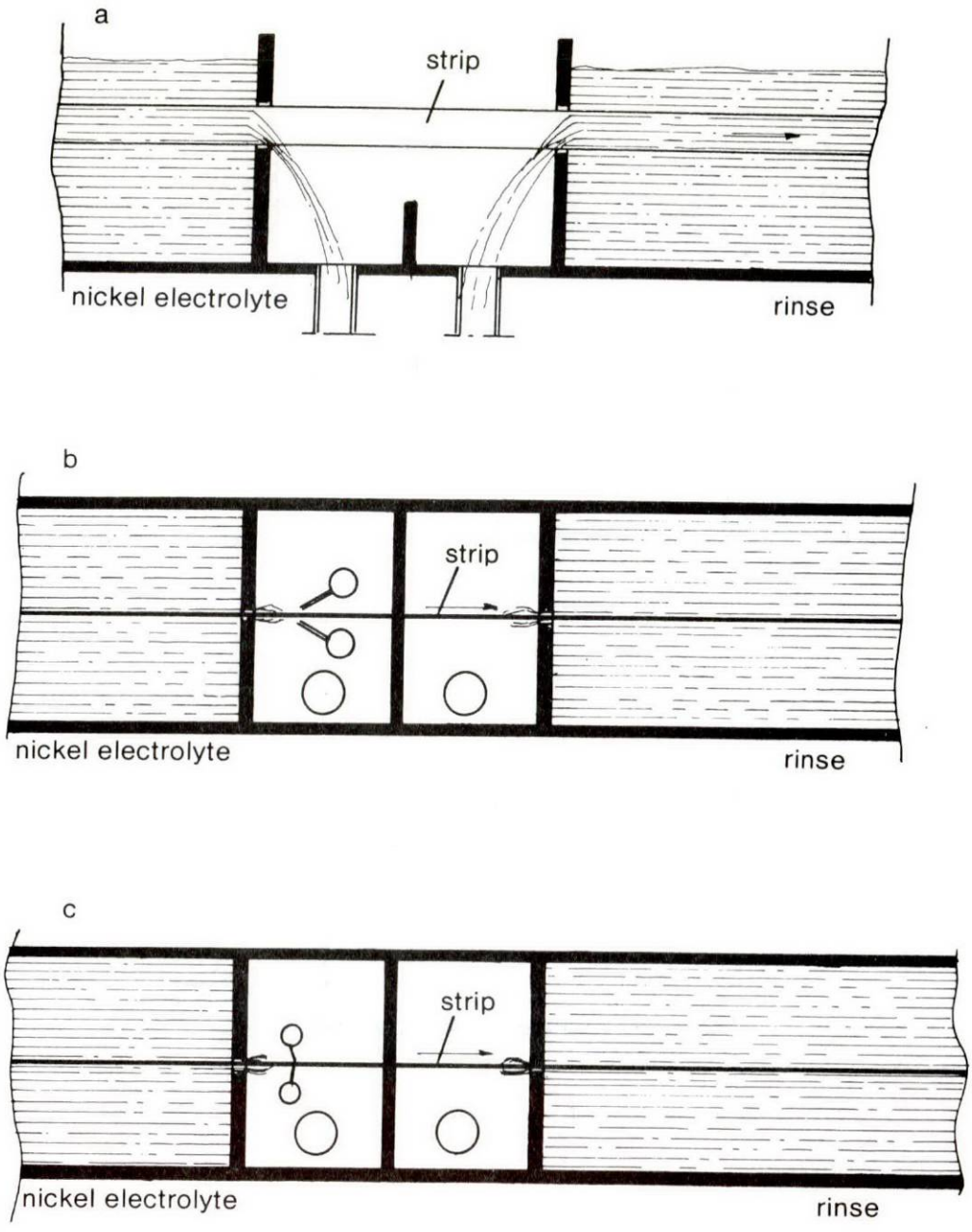


Fig. 12:

Schematic view of section of a reel to reel plater, with left nickel bath and right rinse tank.

a) no provisions (side view)

b) with air wipe (top view)

c) with mechanical wipe (top view)

Air or mechanical wipe reduces drag-over with 60-90%.

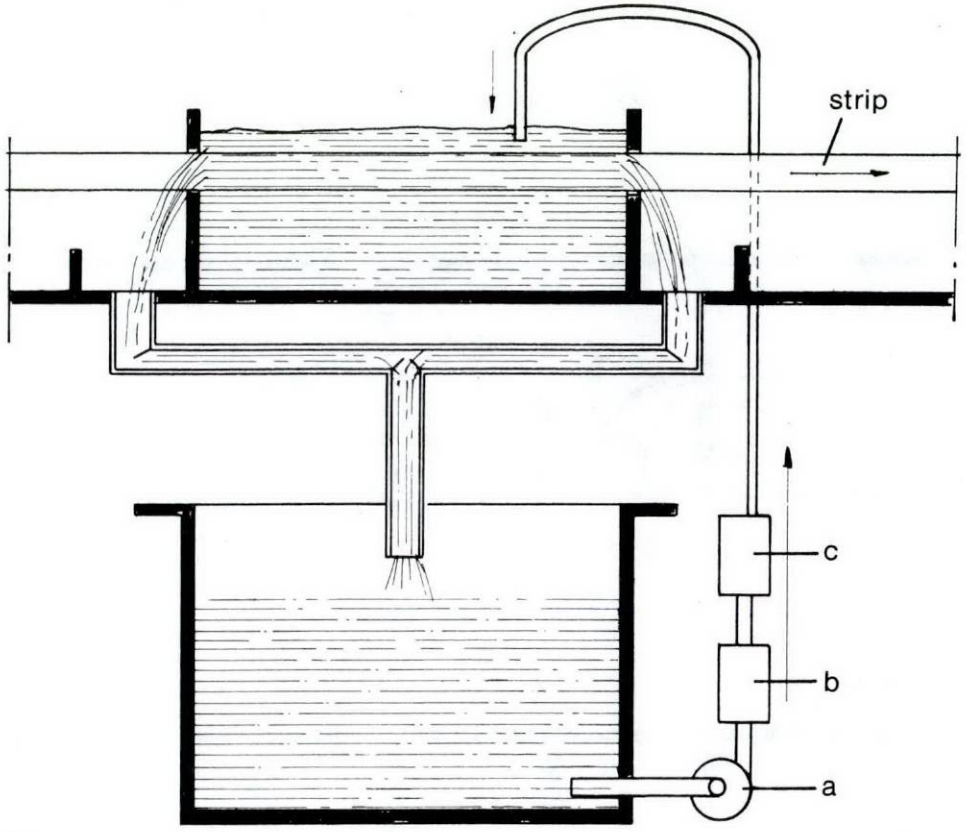


Fig. 13:

CLOSED RINSE SYSTEM;

a = circulating pump

b = ion exchange, mixed bed

c = carbon filter

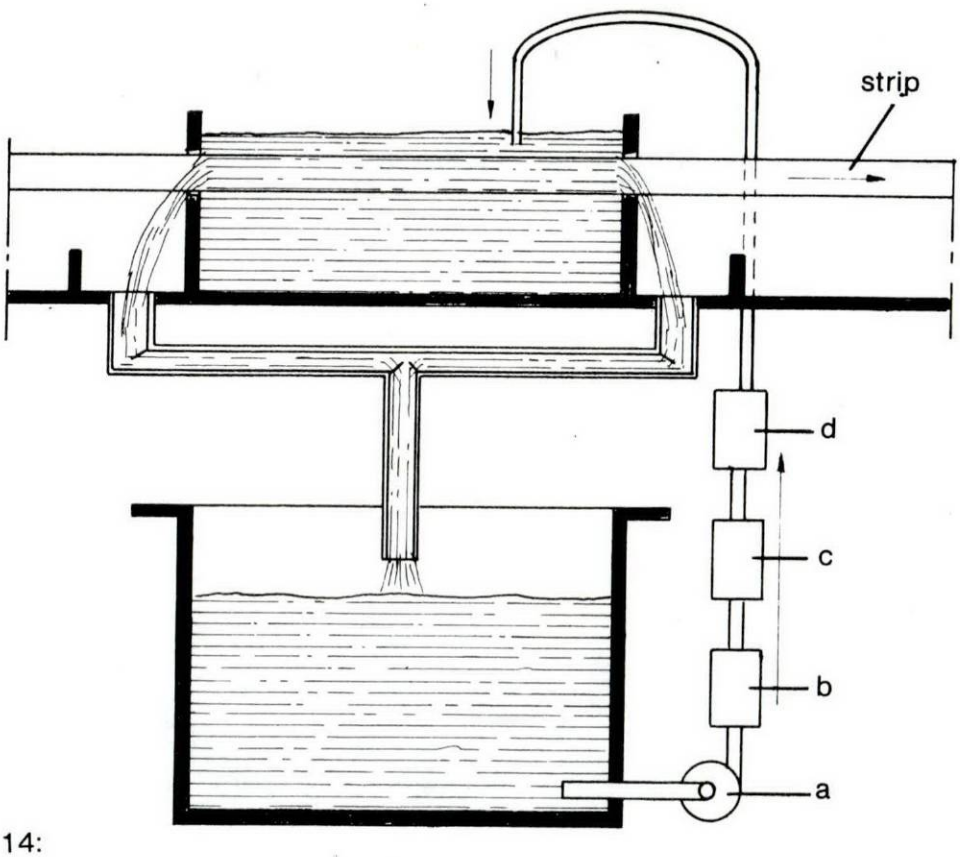


Fig. 14:

Rinse system after gold plating;

a = circulation pump

b = gold ion exchange

c = mixed bed ion exchange

d = carbon filter

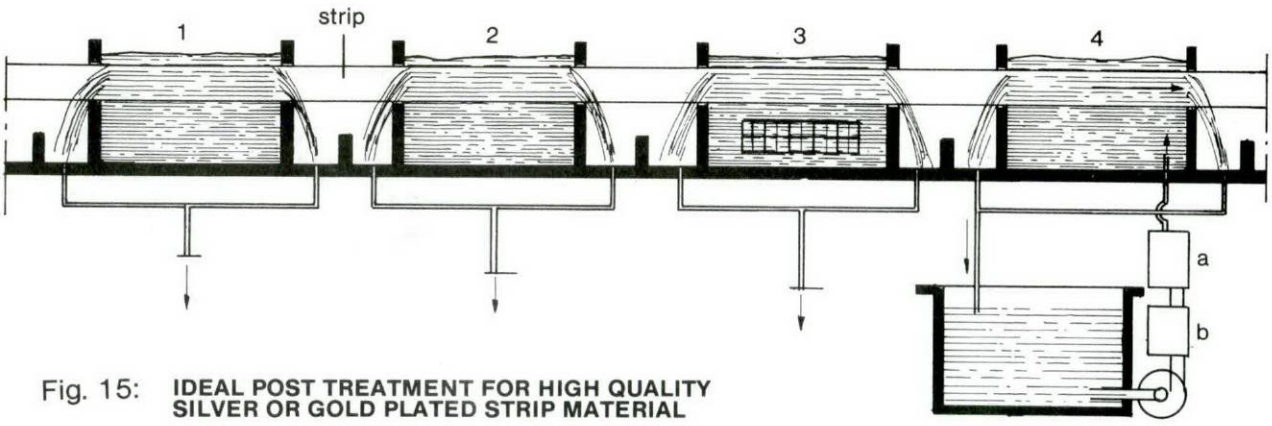


Fig. 15: **IDEAL POST TREATMENT FOR HIGH QUALITY SILVER OR GOLD PLATED STRIP MATERIAL**

1. Fresh water rinse
2. Cold rinse deionised water
3. Warm rinse deionised water with Ultrasonic agitation
4. Cold rinse deionised water recirculated over mixed bed resin column (a) and carbon cartridge (b)

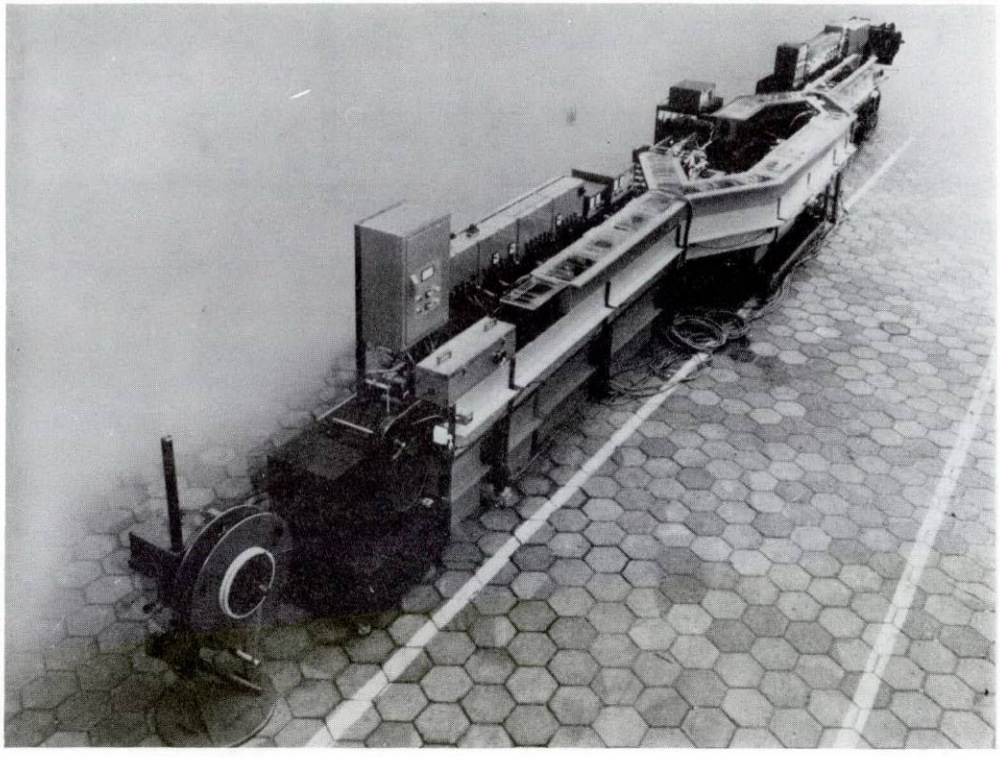


Fig. 16: View of reel to reel plater with alternative possibility of full silver or selective gold plating in two paralel sections.

ELECTRONICS
SESSION F

Some Properties of Palladium Electrodeposits for Engineering Applications

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SOME PROPERTIES OF PALLADIUM ELECTRODEPOSITS FOR ENGINEERING APPLICATIONS

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ABSTRACT

Morphological, crystallographic, electrical and electrochemical data are presented for Palladium electrodeposits from a mildly acid phosphate electrolyte. The deposits are bright and fine-grained, but are subject to microcracking, the extent of which is determined by bath temperature, current density, and deposit thickness. At bath temperatures above 55°C, deposits are substantially microcrack-free. Contact resistances of the deposits vs. a hemispherical gold probe at ordinary contact pressures are substantially identical to those of corresponding gold deposits.

Extensive environmental testing indicates that palladium deposits are somewhat less galvanically active toward copper and nickel than corresponding deposits of gold or rhodium. Electrochemical polarization curves for these systems are shown. Porosity vs. thickness plots are shown to be somewhat higher than, but of the same form as, those of corresponding gold deposits.

I Introduction

Electrodeposited metals are commonly subject to some variation in physical properties such as hardness, ductility, and apparent stress as the conditions of deposition are varied. In palladium electrodeposits, the ease with which codeposited hydrogen can be incorporated into the metallic crystal lattice can cause such variations to become very large. In consequence, a wide variety of plating formulations have been proposed for palladium over the years, several of which have achieved commercial success. A critical review of a number of palladium plating solutions was provided some years ago by Reid (1). The object of this current work is to present detailed data concerning some physical, chemical, and electrical properties of palladium electrodeposits plated from a mildly acid phosphate electrolyte containing palladium in chelated form.

Some operating parameters of the plating bath are shown in Table I. As indicated, the electrolyte is a phosphate system at a pH of approximately 6. An organic brightening system is employed for grain refinement. Control of deposit brightness may be maintained by adjustment of the brightener concentration

and/or the bath temperature. In general, deposit brightness and hardness are increased by operating at lower temperature in this system. Increasing the bath temperature favors increased current efficiency and plating range. Operation at slightly acid pH permits direct deposition of palladium on copper, nickel, and copper-based alloys without the use of a gold or silver strike, although such may be employed if desired.

Table I

Bath Operating Parameters - Technic Pallaspeed

pH:	5.5 - 6.5
Temperature:	25-70°C (70-160°F)
Specific Gravity:	1.09 (12° Baume') minimum
Palladium Content:	2.0-20 grams/liter
Anodes:	Platinized
Anode/Cathode Ratio:	$\gg$1.0
Agitation	Recommended
Current Efficiency:	85-98 percent
Hardness (typical):	250-300 Knoop (25 gm.load)

II Deposit Morphology and Crystallography

Specimens for Hull cell testing were prepared from commercial 66 x 99 mm panels of highly polished brass. These were given a final mechanical polish with jeweller's rouge on a four inch wheel, after which they were cathodically cleaned, activated, and finally struck for 30 seconds at 20 mA/cm^2 in a phosphate-citrate gold striking solution at pH 4.2 containing 2.0 grams gold per liter and operated at 55°C. It had been shown in previous work (2) that specimens prepared in this manner provide a reproducible (111) oriented substrate for deposits to be examined by x-ray diffraction.

Specimens prepared as indicated above were individually palladium-plated in a 267 ml Hull cell for 10 minutes at a cell current of 0.5 ampere. Bath temperatures for the various plating runs were 22°, 38°, and 49°C, controlled in each case to ± 2°C. Agitation was by means of a Plexiglas rod stirrer oscillated at a distance of 1 cm from the substrate surface. Palladium concentration in the plating bath was 7.92 grams/liter.

Following plating, the various specimens were retained at room temperature for several days in a desiccator to allow maximum development of such microcracking as would take place. The specimens were then cut up along the lateral midline into 1 cm^2 sections centered at indicated current densities of 2, 4, 6, 10, and 15 mA/cm^2. These were then examined by x-ray diffraction using copper K_α radiation in a Siemens Crystalloflex IV

instrument, and by scanning electron microscopy using an ETEC "Autoscan" instrument.

The x-ray diffraction pattern for a randomly-oriented palladium powder specimen is shown in Table II. Diffraction data obtained from the electroplated specimens are shown in Table III. In all cases, diffracted signal intensities are expressed as intensity ratios normalized to the diffracted intensity from the (111) crystal plane.

Comparison of Tables II and III reveals a very high degree of (110) preferred orientation for the electrodeposits plated at 22°C. Deposits plated at 38° and 49°C show a much lesser degree of (110) preference, in both cases tending to approach a (111) preferred orientation with increasing current density. Such differences are highly significant because palladium, like gold, is a face-centered cubic material, and in f.c.c. crystals the (111) is the most densely packed crystal plane. Previous work (2) has shown that in gold electrodeposits, preferred orientation of the densely-packed (111) crystal planes parallel to the substrate surface yields high covering power (low deposit porosity at low thickness) and good wear performance in sliding friction, whereas a preferred orientation with less densely packed crystal planes such as (100) or (110) parallel to the substrate surface is accompanied by a very high microthrowing power. Such deposits show strong leveling effects and tend to "build brightness" with increasing deposit thickness, but show generally poorer covering power and poorer wear performance than their (111) oriented counterparts. In the palladium plating system discussed here, it is evident that a range of deposit orientations from strongly (110) to strongly (111) can be achieved by controlling the plating conditions.

Table II

X-ray Diffraction Data: Polycrystalline Palladium

(A.S.T.M. File 5-0681)

"d" spacing	Crystal Plane	Intensity Ratio
2.246 Å	(111)	100%
1.945	(200)	42
1.376	(220)	25
1.173	(311)	24
1.1232	(322)	8
0.9723	(440)	3
0.8924	(331)	13
0.8697	(420)	11

The last column of Table III shows the halfwidth of the diffraction peak from the (111) crystal plane, measured in degrees.

Table III

X-ray Diffraction Data: Electroplated Specimens

Temperature °C	Current Density mA/cm^2	Relative Diffracted Intensity				Halfwidth of (111) peak degrees
		(111)	(200)	(220)	(311)	
22	2	100	-	55	-	0.7
	4	100	-	135	-	0.65
	6	100	3	215	9	0.65
	10	100	7	245	9	0.6
	15	100	10	415	-	0.6
38	2	n/r	-	-	-	-
	4	100	12	30	11	0.5
	6	100	7	43	13	0.6
	10	100	2	7	12	0.65
	15	100	-	-	12	0.65
49	2	n/r	-	-	-	-
	4	100	32	95	30	0.45
	6	100	12	45	15	0.45
	10	100	8	42	16	0.65
	15	100	3	8	11	0.6

This parameter increases with increasing internal stress of the deposit, and also with decreasing average grain size. In the present measurements, the (111) halfwidth shows a generally decreasing trend with increasing deposition temperature. It will be seen subsequently that those deposits of (111) halfwidth less than 0.5° are apparently free of microcracking.

A series of scanning electron micrographs of the palladium electrodeposits plated at 22°, 38° and 49°C are shown in Figures 1, 2, 3 and 4. Some observations concerning microcracking and topography in these deposits are as follows:

1. The density of microcracks per unit area decreases with increasing deposition temperature.
2. At 22° and 38°C, the density of microcracks per unit area decreases with increasing current density. At 49°C, no clear trend is established.
3. At all temperatures investigated, the size and depth of individual microcracks appear to increase with increasing current density. This effect is felt to be an artifact resulting from the increase in thickness of the Hull cell deposit with increasing current density. Assuming that microcracking in these deposits results from the volume increase due to recombination of hydrogen atoms diffusing out of the palladium lattice, an increase in deposit thickness per unit area will result in an increase in the volume of gas evolved per unit area per unit time.
4. The microcracks observed do not propagate in any preferred direction, but apparently randomly along grain boundaries. This suggests that recombination of hydrogen atoms may take place preferentially at grain boundaries.
5. The surface smoothness of the deposits is greatest at low deposition temperature. As deposition temperature is increased, the surfaces become increasingly nodular in texture, which may indicate the development of faceting.

III Contact Resistance Measurements

The bulk resistivity of palladium, approximately 10.8 microohm-cm at room temperature (3) is the highest of any metal in the platinum group. In applications involving electrodeposits, however, the contact resistance (4) is likely to be far more significant than the bulk value.

OFHC copper specimens for contact resistance testing were obtained from Bell Telephone Laboratories, Inc., Columbus, Ohio.

Table IV

Contact Resistance: Palladium Flat vs. Gold Probe

Palladium thickness, Microinches	Underplate	Contact Resistance, Milliohms			
		25 gm.load	50 gm.load	100 gm.load	200 gm.load
22 ± 3	none	1.2 ± .09	0.85 ± .15	0.57 ± .08	0.37 ± .06
19.5 ± 2	nickel	1.3 ± .10	0.90 ± .10	0.63 ± .09	0.40 ± .04
92 ± 9	none	2.0 ± .70	1.20 ± .30	0.70 ± .10	0.44 ± .06
81 ± 12	nickel	1.5 ± .20	1.10 ± .10	0.70 ± .10	0.42 ± .04

These were 5x5 cm in size and had been provided with an abraded finish on one side. Two of these specimens were cathodically cleaned, activated, and plated with palladium to nominal thicknesses of 0.5 and 2.5 micrometers. The palladium bath temperature was 49°C, and the current density employed was 5 mA/cm^2. A further two specimens were similarly plated with palladium after having been plated with 2.5 micrometers of additive-free sulfamate nickel as an underplate. Following plating, the deposit thickness was determined by beta backscatter in a "tick-tack-toe" pattern at nine points on the abraded side of each specimen. The specimens were then returned to Bell Laboratories, where they were probed for contact resistance in an "autoprobe" device (4) using a 1/8 inch hemispherically-ended gold rod as the probing element. Contact pressures of 25, 50, 100 and 200 grams were used, and the specimens were probed using the same nine-point grid as employed for thickness measurement.

The results of this series of experiments are shown in Table IV. For brevity, mean values are shown for each specimen.

In general, the contact resistance results indicate that the effect of the nickel underplate is negligible. Except at the lowest contact pressures the effect of increasing palladium thickness is very small. Measurement of the effects of environmental exposure on the contact resistance of palladium electrodeposits was not attempted in this work. Such studies are known to be in progress in other laboratories.

IV Deposit Porosity and Corrosion Resistance

Porosity calibration curves for palladium deposits on copper were prepared by corrosion potential measurements (5). A 99.9% palladium foil of dimensions 5x5x0.025 cm was prepared by soaking for 10 minutes in a hot (60°C) solution of 0.35 M K_2HPO_4. The foil was rinsed in deionized water, then soaked for 30 minutes in 3.0 M HCl. After a further deionized water rinse, the specimen was suspended by means of a 99.99% gold wire in a solution of air-equilibrated 0.1 M NH_4Cl, and its corrosion potential was read versus that of a saturated calomel reference electrode using a Keithley Model 610C electrometer voltmeter. A short length of No. 44 AWG uninsulated copper wire was prepared by cathodic cleaning, rinsing, and activation in 3.0 M HCl. The wire was mounted at one end into a pin vise affixed to the shaft of a calibrated micrometer head by means of which it could be immersed into the NH_4Cl test solution to a known depth.

When the corrosion potential of the palladium foil had reached a steady value, the mounted copper wire was immersed into the test solution. An electrical connection was made from it to

the palladium foil, so that now the electrometer was reading the corrosion potential of the coupled palladium and copper specimens, the immersed area of each of which was known. The copper wire was then withdrawn in known increments from the solution by adjustment of the micrometer head. The corrosion potential of the coupled specimens and the micrometer settings were noted for each incremental withdrawal. From the micrometer settings and the known diameter of the wire, the area of copper immersed at each step, and also the area fraction of copper, expressed as

$$A_a = \frac{\text{Area of copper}}{\text{Area of palladium + area of copper}}$$

could be calculated. A plot of corrosion potential vs. the logarithm of the copper area fraction is shown in Figure 5.

To assess the validity of the calibration curve in Figure 5 for use with electroplated, rather than wrought palladium, a 99.99% gold coupon of area 40 cm^2 was plated with 7.5 micrometers of palladium from the phosphate bath. Using this plated specimen in place of the palladium foil, the determination of the calibration curve was repeated, and both curves are shown in Figure 6. The agreement between these curves is considered excellent, particularly considering that the surface roughnesses of the foil and electroplated palladium specimens are almost certainly different.

The slopes of the calibration curves in Figures 5 and 6 are approximately 51 millivolts per decade, which is equal to the anodic Tafel slope β_a of copper in 0.1 M NH_4Cl (5). It had been shown by Mansfeld (6) that such a slope is indicative that the cathode (oxygen reduction) reaction in the galvanic couple of interest is controlled by the rate of diffusion of oxygen through the electrolyte.

A calibration curve for gold-copper couples in 0.1 M NH_4Cl had been published previously (5) and is reproduced in Figure 7. The gold-copper calibration curve has a slope of approximately 35 millivolts per decade, which is equal to the ratio

$$\beta_a \beta_c / (\beta_a + \beta_c)$$

of the cathodic and anodic Tafel slopes of gold and copper in 0.1 M NH_4Cl. It had been shown earlier by Stern (7) that such a slope indicates that the cathode reaction is controlled not by diffusion, but by charge transfer. It might also be noted from a comparison of Figures 5 and 7 that at the same area fraction of copper, the corrosion potentials of gold-copper and palladium-copper couples in 0.1 M NH_4Cl will differ from each other by 130 millivolts or more, the palladium-copper couples being the more positive.

In view of the above, one might well wonder why gold-copper and

palladium-copper couples should behave so very differently under the same conditions in the same test electrolyte. In order to investigate this, we determined the cathodic polarization curves of rhodium, palladium, and gold foil samples, each of area 50 cm^2 and of purity $\geq$ 99.9%, in 0.1 M NH_4Cl. The apparatus and methodology for such determinations have been described previously (8) and need not concern us here. For comparison purposes, an anodic polarization curve of a 2.5 cm^2 specimen of 99.9% copper was also obtained. All of the various polarization curves are plotted in the form potential vs. log current in Figure 8.

The type of plot shown in Figure 8 is known as an Evans diagram. The point of intersection of the cathodic (potential driven negative) curve of the cathodic member in a given galvanic couple with the anodic (potential driven positive) curve of the anodic member yields, on the potential axis, the corrosion potential of the actual couple in the test electrolyte; and on the current axis, the galvanic current passing between them at that potential. Precious metal cathodes in neutral salt solutions tend to act as oxygen electrodes, and the long near-vertical segments observed in the cathodic curves of rhodium, palladium, and gold in this system are all clearly indicative of such behavior, as well as of diffusion-limited kinetics at the cathode. It may be noted that the anodic curve of copper crosses the gold curve before the onset of the diffusion-limited region, whereas it crosses both the palladium and rhodium curves well within the diffusion-limited region. This explains the difference in slope of the palladium-copper and gold-copper calibration curves shown in Figures 5 and 7, and also why the calibration curves are displaced from each other on the potential axis.

Having arrived at the porosity calibration curve of Figure 5, plating runs were carried out to determine the porosity versus thickness characteristic of the palladium electrodeposit. The samples used were small copper electrical terminals (AMP, Inc., No. 30697). These were prepared by cathodic cleaning, rinsing, and pickling in 3.0 M HCl, followed by bright-dipping in a solution consisting, by volume, of

4 parts concentrated H_2SO_4

2 parts concentrated HNO_3

3 parts water

with about 1 ml of concentrated HCl added per liter to control the etching rate. After rinsing and drying, the specimens were loaded into a small plating barrel, reactivated, and plated with palladium at a current density of 2 mA/cm^2. Bath temperature was 49°C.

At intervals, the plating operation was interrupted, the barrel

removed from the solution, and a group of 15 specimens removed at random from the top of the barrel load. These were rinsed, marked, and set aside, after which the barrel plating operation would be resumed. We thus obtained a series of groups of specimens having various deposit thicknesses. Each of the various groups was then subdivided into subgroups of 5 specimens. The corrosion potential of each subgroup was determined versus S.C.E. in 0.1 M NH_4Cl solution, and the area fraction of exposed copper calculated from the calibration curve in Figure 5. The deposit thicknesses for the various specimens were determined by beta-backscatter and average values calculated for each subgroup.

A plot of the logarithm of the exposed area fraction of copper versus the logarithm of deposit thickness for these specimens is shown in Figure 9. The upper plot in Figure 9 is for palladium on copper. The lower plot is data previously reported (9) for a pure unbrightened gold deposit plated on copper in a procedure substantially identical to that reported here. Over the thickness range from 5 to about 30 microinches the porosities of the gold and palladium electrodeposits are approximately comparable. Over 30 microinches, however, the porosity of the gold deposit decreases at a much more rapid rate than that of the palladium.

Palladium electrodeposits have been reported (10,11) to be less porous, thickness for thickness, than corresponding gold deposits; or at least to provide a greater degree of protection, particularly when plated over nickel. With regard to porosity, the present results indicate that the reverse is true: gold deposits appear to be much less porous than palladium, particularly at thicknesses over one micrometer or so. With regard to protection, it should be noted that the positive displacement of corrosion potential amounting to 100 millivolts or more exhibited by palladium-plated specimens with respect to their gold-plated counterparts is sufficient, in many environments, to passivate the exposed underlayer; this being particularly true for the case of exposed nickel. It is thus possible under certain conditions for a palladium electrodeposit to provide a degree of corrosion protection equal to or greater than that afforded by a corresponding gold deposit, even if the porosity of the gold deposit is lower. This will not, however, represent the general case, and will have to be verified experimentally for any given combination of plating, substrate, and environment.

V Summary

In this paper we have attempted to present specific data regarding some properties of palladium deposits plated from one specific electrolyte/brightener system. These will certainly vary to some degree from the properties of deposits from other electrolyte systems, but it is hoped that from studies of this type a "variance band" can be established for palladium electro-

deposits in general. In view of the present near-chaotic pricing situation with respect to precious metals, and to gold in particular, substitute materials assume increasing importance daily. We hope that the data herein will prove both timely and useful.

Acknowledgement

The writer is grateful to Professor Henry Leidheiser, Jr., of the Center for Surface and Coatings Research, Lehigh University, Bethlehem, PA., for performing the x-ray and scanning micrographic experiments, and to Dr. Morton Antler of Bell Telephone Laboratories, Inc., Columbus, Ohio, for providing the contact resistance measurements.

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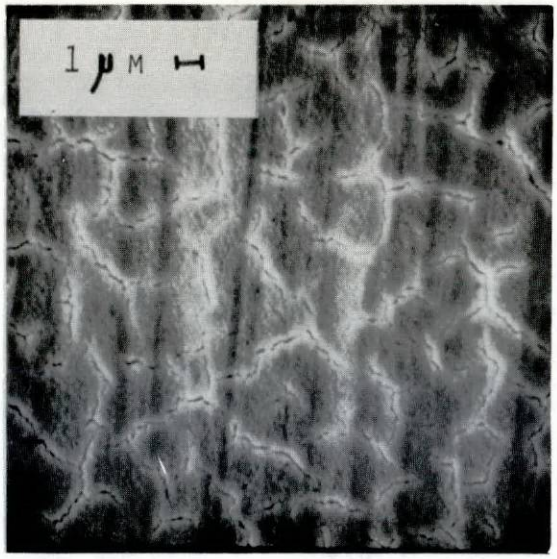

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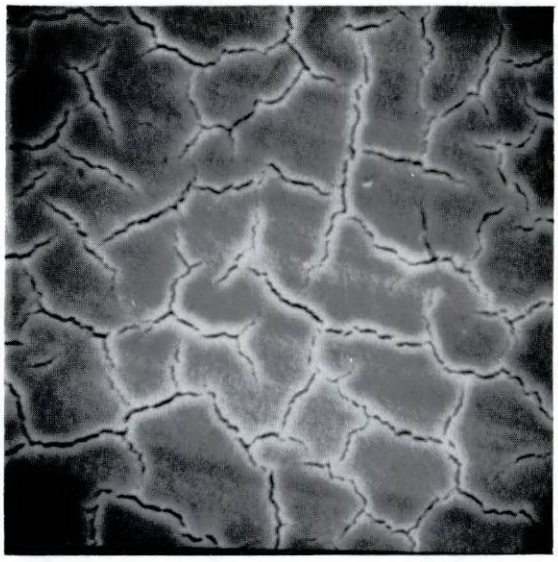

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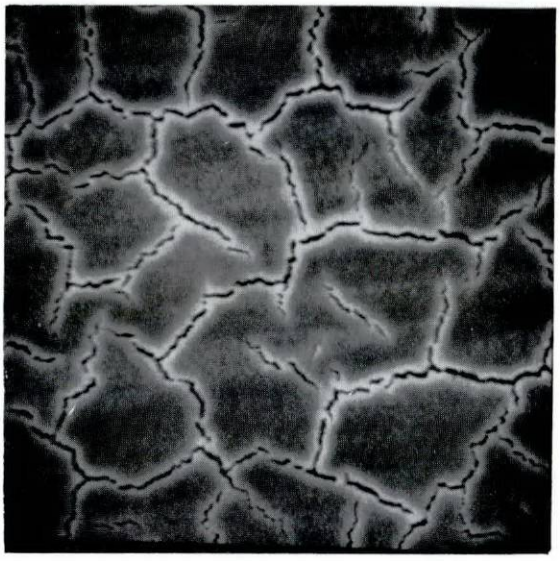

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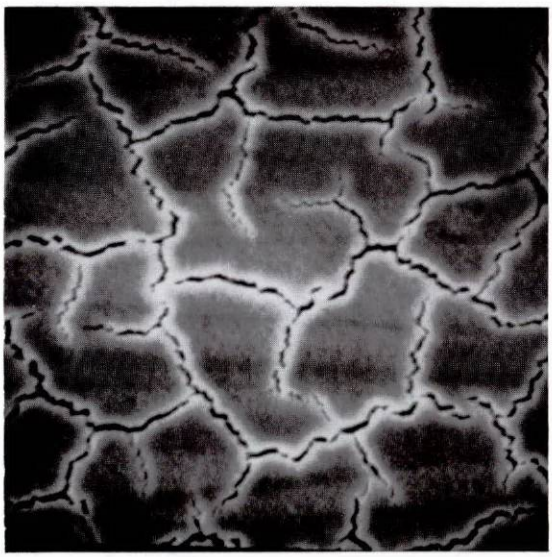

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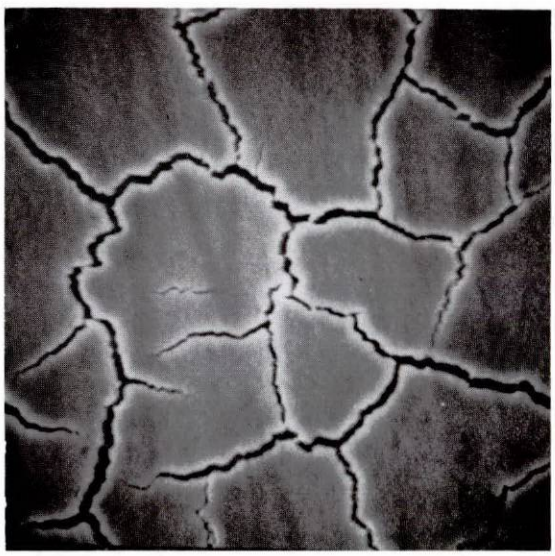

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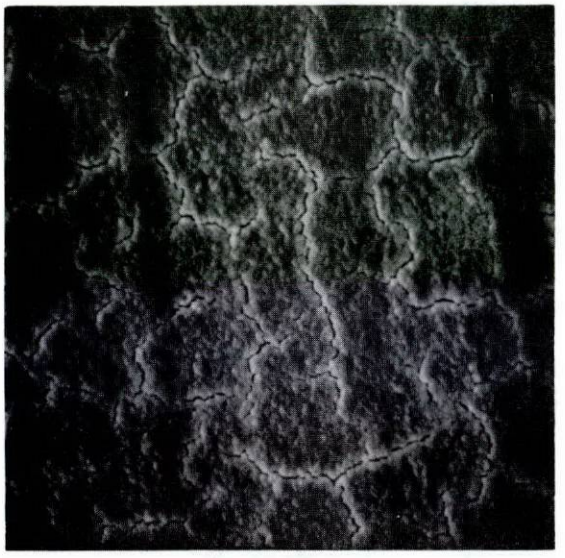

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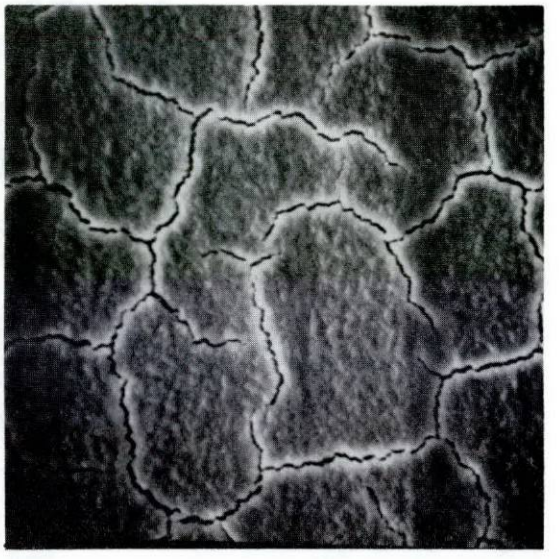

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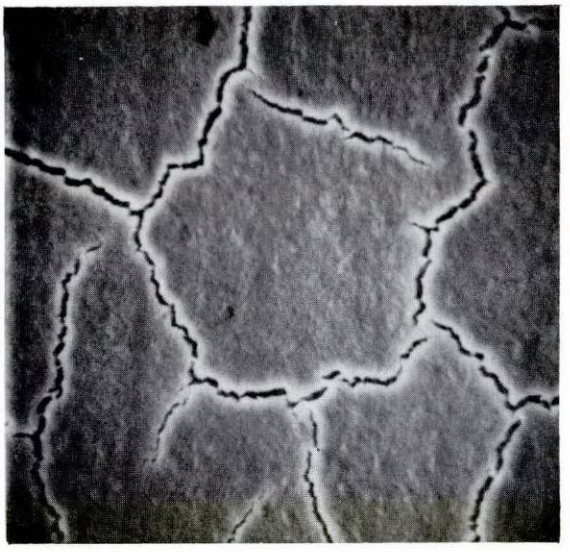

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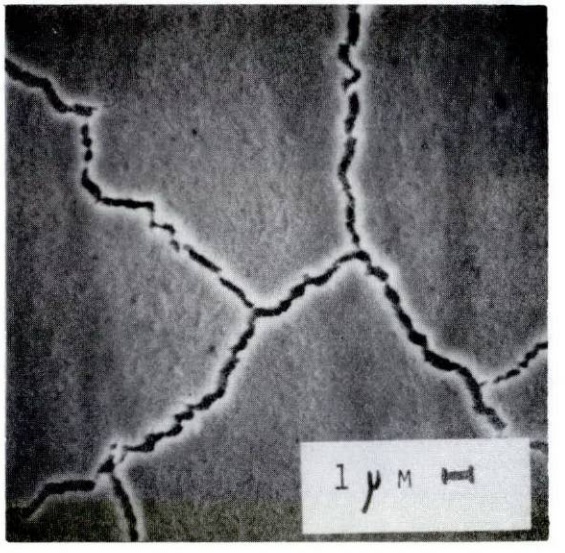

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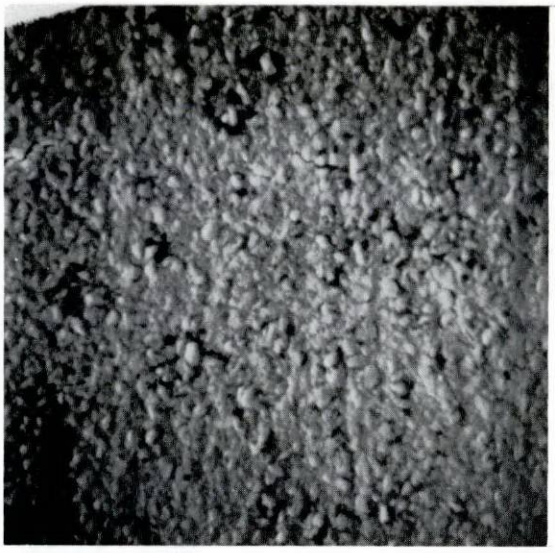

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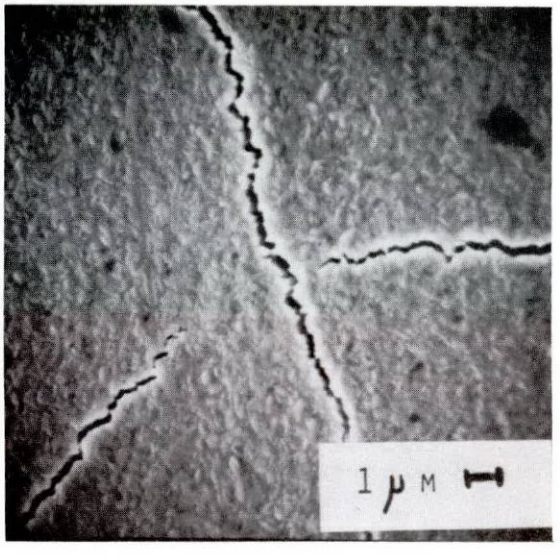

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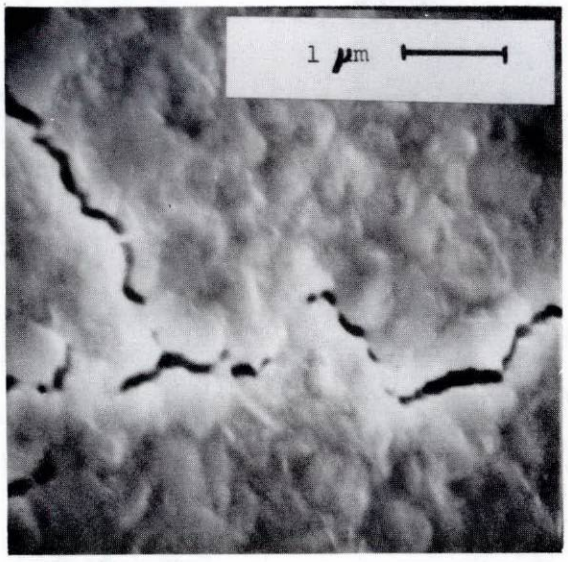
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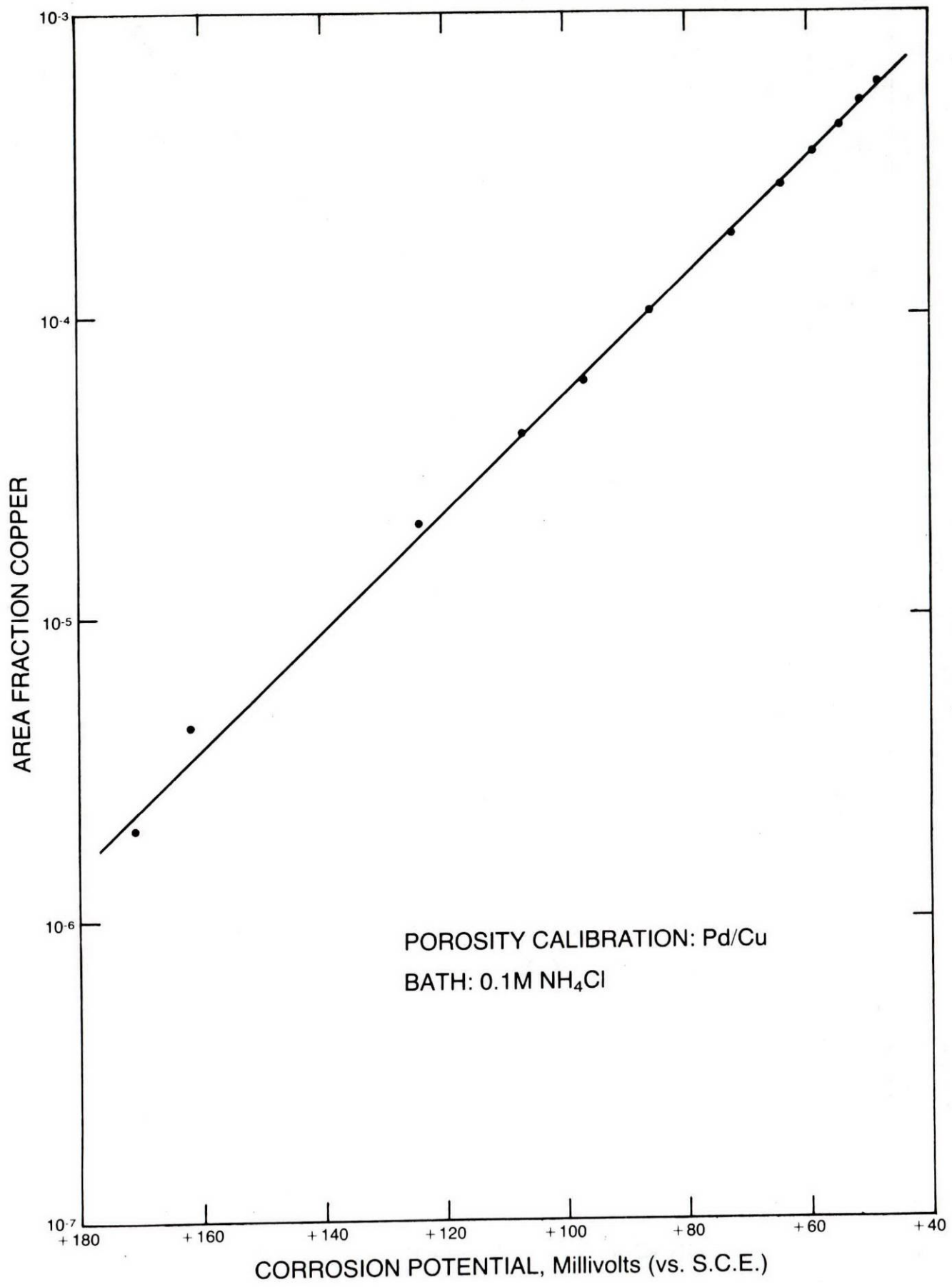
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10-4
10-5
10-6
10-7
AREA FRACTION COPPER
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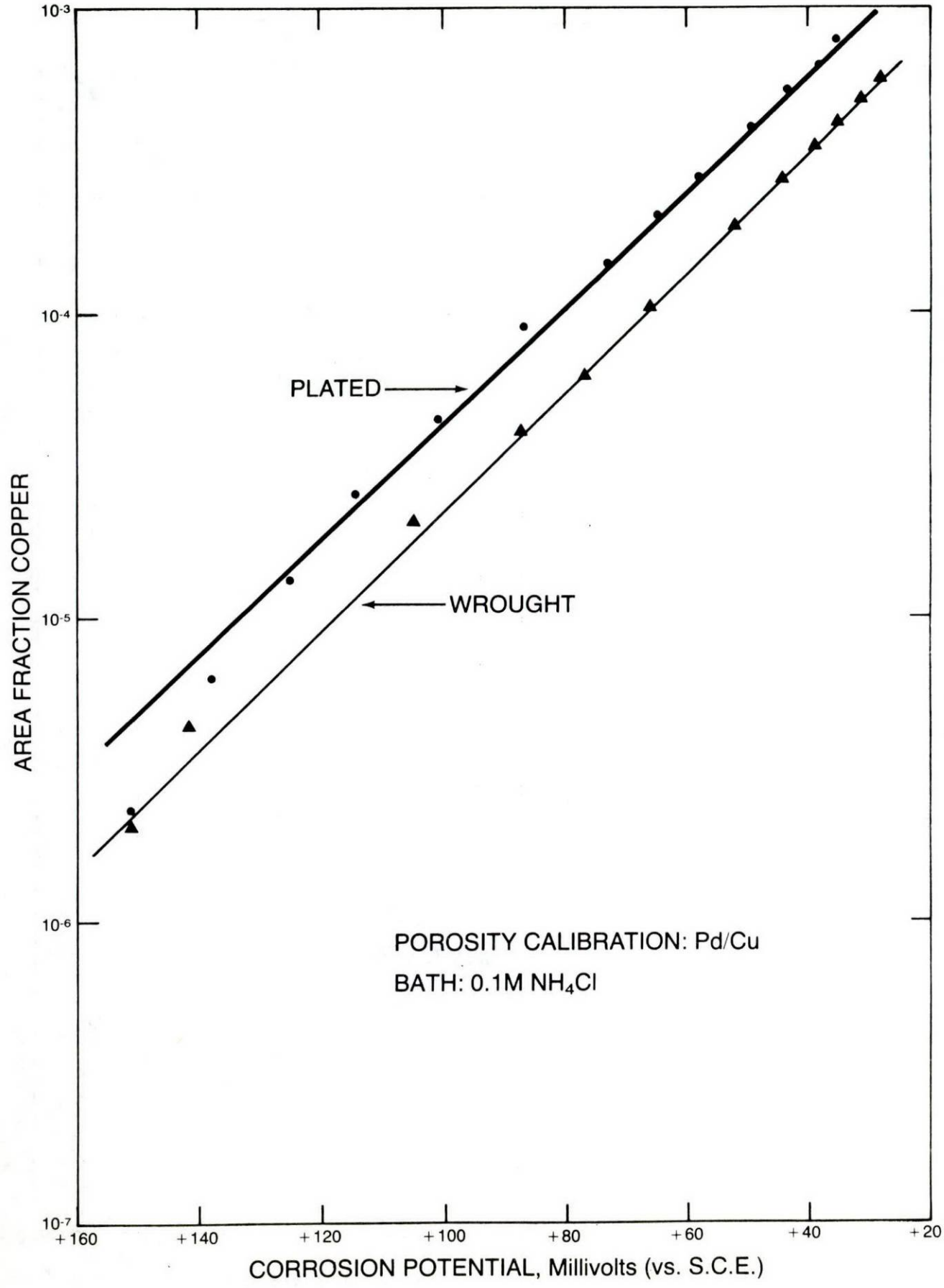
+160
+140
+120
+100
+80
+60
+40
CORROSION POTENTIAL, Millivolts (vs. S.C.E.)
POROSITY CALIBRATION: Pd/Cu
BATH: 0.1M NH4Cl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10-4
10-5
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10-7
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PLATED
WROUGHT
POROSITY CALIBRATION: Pd/Cu
BATH: 0.1M NH4Cl
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+120
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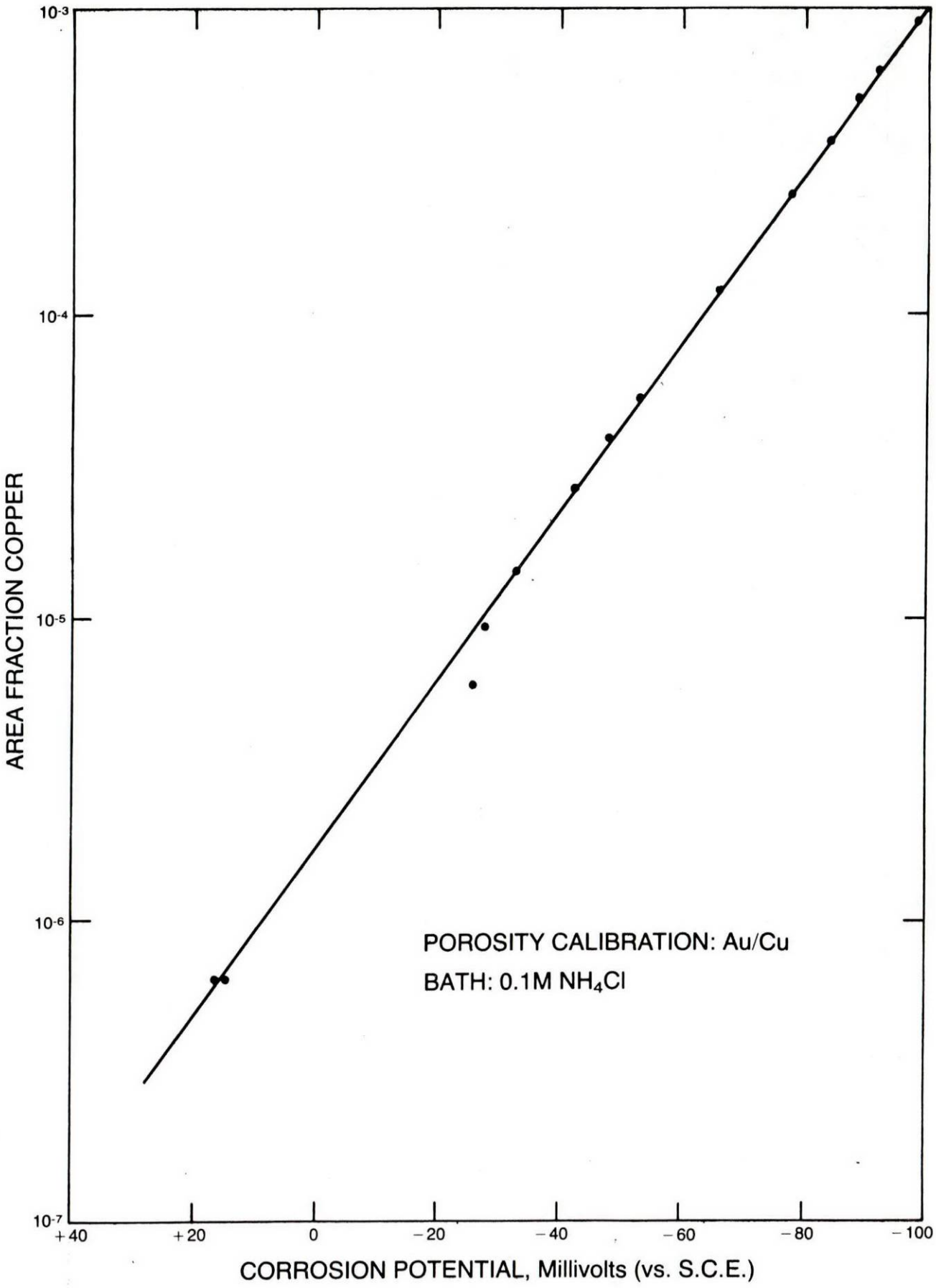
+80
+60
+40
+20
CORROSION POTENTIAL, Millivolts (vs. S.C.E.)


AREA FRACTION COPPER
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
POROSITY CALIBRATION: Au/Cu
BATH: 0.1M NH_4Cl
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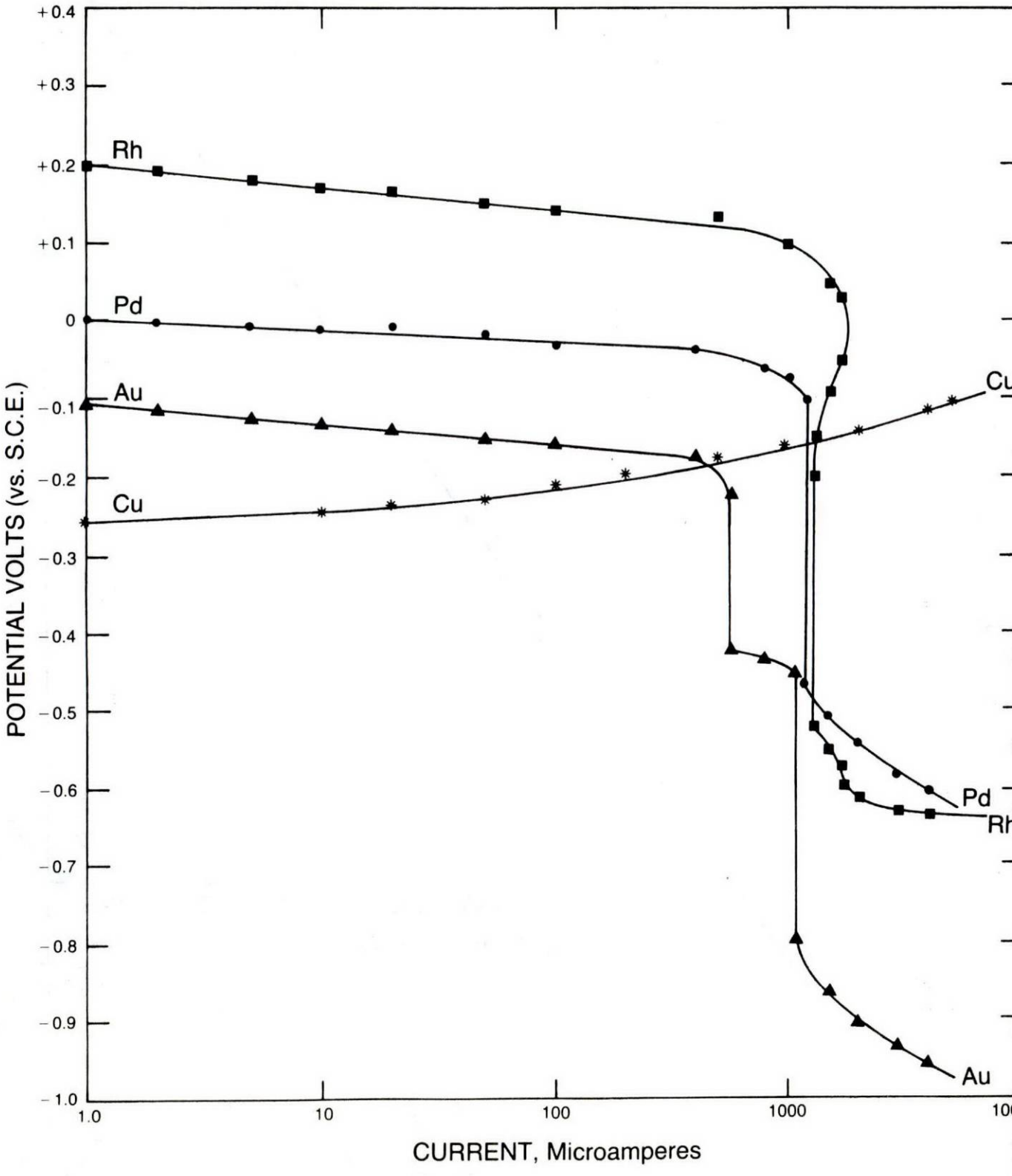
+20
0
−20
−40
−60
−80
−100
CORROSION POTENTIAL, Millivolts (vs. S.C.E.)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+0.1
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−0.7
−0.8
−0.9
−1.0
POTENTIAL VOLTS (vs. S.C.E.)
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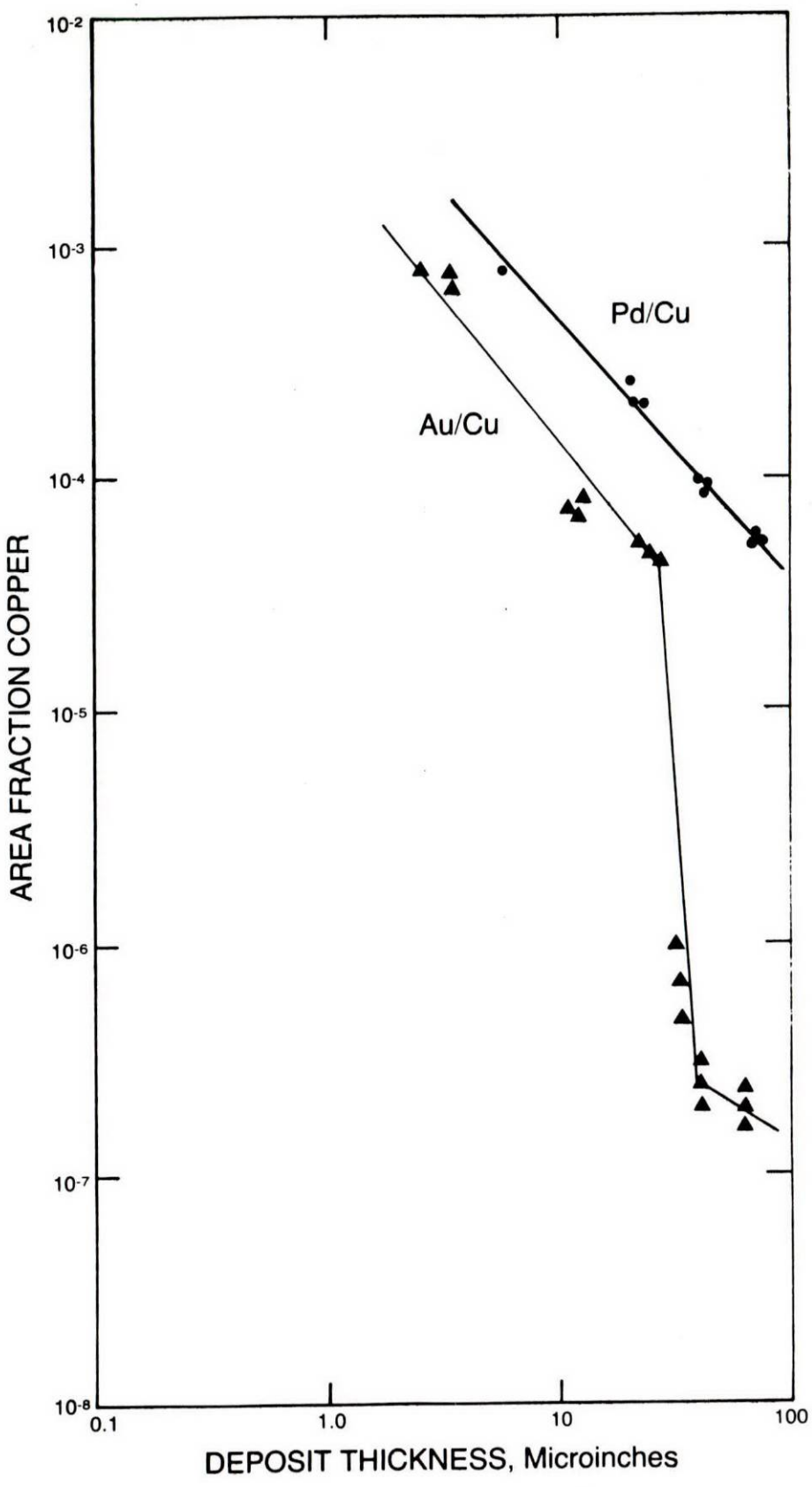
Pd
Au
Cu
Cu
Pd
Rh
Au
1.0
10
100
1000
CURRENT, Microamperes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10-4
10-5
10-6
10-7
10-8
AREA FRACTION COPPER
Pd/Cu
Au/Cu
0.1
1.0
10
100
DEPOSIT THICKNESS, Microinches

F-4

ELECTRONICS
SESSION F

A New Silver Plating Bath Containing No Free Cyanide for Electronic Applications

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A NEW SILVER PLATING BATH FOR ELECTRONIC APPLICATIONS

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Harrisburg, Pennsylvania

ABSTRACT

A new silver plating bath containing no free-cyanide has been developed especially for high-speed plating in the electronics industry. Silver plated from this bath has good contact properties, and was found generally to be less susceptable to tarnishing than silver plated from a conventional alkaline cyanide bath. It was also found that surface treatment can further reduce tarnishing and reduce or eliminate electromigration.

Introduction

The accelerated increase in the price of gold and related noble metals has brought about a renewed interest in silver platings for electronic applications. In addition to its economic advantages, silver exhibits properties that are generally associated with good contact materials. It has high electrical and thermal conductivity, moderate hardness, and good wear characteristics. Silver does not undergo fretting corrosion nor does it form frictional polymers at low loads. It also can withstand high environmental temperatures and a certain amount of corrosion and still function as a satisfactory electrical contact surface.

Present-day requirements of the electronics industry, however, call for platings which, in addition to these favorable properties, are also capable of being applied with automatic strip-line plating equipment over a fairly large range of line speeds and current densities. Furthermore, the potential usefulness of such platings would be enhanced if they could be made less susceptible to tarnishing and electromigration.

The Plating Bath

A system that meets the requirements of high speed strip-line plating has recently been developed. This new silver plating bath can be formulated as either a high speed (200+ ASF) or standard (5-30 ASF) system. It produces acceptable high-purity, high efficiency deposits from baths containing as little as one troy ounce to as much as five troy ounces of silver per gallon. In addition, baths formulated to contain as little as 4-5 troy ounces of silver metal per gallon can produce, under the proper conditions, acceptable electrodeposits at current densities up to 400 ASF.

The bath is an aqueous solution that contains no free cyanide, i.e., no cyanide compounds are used in the bath except for potassium silver cyanide

($KAg(CN)_2$). The only other components are monobasic and dibasic potassium phosphates. The concentrations of these components vary, depending on the requirements of the system.

By minimizing the number of components, and without the requirement of organic additives, analytical and bath maintenance procedures are simplified. Maintenance, on a day to day basis, requires only three relatively simple procedures: specific gravity measurement to control electrolyte concentration, pH measurement, and metal replenishment based upon the use of an ampere-hour meter. For complete quantitative analysis, all components can be determined gravimetrically, although the silver can also be determined by atomic absorption spectroscopy.

An added advantage of this plating system is that it lends itself to less complicated waste treatment procedures than the high cyanide systems. It also allows quantitative precipitation of silver, as AgCN, by merely reducing the pH to about 3 with H_3PO_4. The AgCN can then be re-used to make metal additions to the operating plating bath by dissolving it with the required amount of KCN to re-form the soluble $KAg(CN)_2$ complex.

Tarnishing Comparisons

Certain other advantages are inherent in a no free-cyanide, low metal, neutral pH, silver bath. In the plating process, the low metal concentration of the bath minimizes dragout losses (with the obvious economic advantages of reduced inventory investment and reclamation costs), while the

neutral pH, no free-cyanide properties cause the system to be free-rinsing, thereby reducing the probability of leaving residual cyanides and other bath components on the finished parts.

This reduction of surface contamination may be the main reason for the relatively stain-free appearance of parts plated in the no free-cyanide system. The plated parts also showed less of a tendency toward discoloration in the presence of hydrogen sulfide. In contrast, when these parts were immersed in a KCN solution, thereby simulating surface conditions of a high-cyanide system, they showed discolorations that were similar to those observed on parts plated from a standard, high-cyanide silver bath.

A quantitative comparison of tarnishing of the two types of silver deposits is shown in Table I . The data in this table show the thicknesses of silver sulfide (Ag_2S), as determined by constant-current coulometric reduction of silver-plated coupons that had been exposed to various field environments. Silver chloride was also found in all of the tarnish films. These data show that, in nearly all instances, the amount of silver sulfide tarnish on the coupons plated from the no free-cyanide bath is less tha that of the corresponding coupons plated from the high-cyanide bath.

Table I . Silver Sulfide Thicknesses After Field Exposure

Exposure Site	Days	Ag_2S Thickness, Angstroms: Without Inhibitor, High Cyanide	Without Inhibitor, No Free-Cyanide	With Inhibitor, High Cyanide	With Inhibitor, No Free-Cyanide
A	70	44	27	12	28
	168	60	43	15	50
	363	46	84	79	121
B	208	31	3	3	3
	361	35	21	23	37
C	250	176	287	104	213
	313	1030	596	590	670
D	172	214	109	130	56
	316	284	85	310	---
E	35	1570	1370	579	1120
	167	3580	2250	2550	2490
	308	8920	6140	4230	5220

Site A - Control room of a steel mill pickling line.
Site B - Airport traffic control and computer facility.
Site C - Control cabinet on the process floor of paper mill.
Site D - Outdoor exposure along seacoast of eastern Florida.
Site E - Effluent treatment area of a petrochemical complex.

In a similar manner, coupons plated from the no free-cyanide bath exhibited a lower contact resistance, when probed with a gold-plated ball after field exposure, than did coupons plated from the high-cyanide bath. These contact resistances are listed in Table II. Comparison of these contact resistances with the sulfide film thicknesses listed in Table II shows that a contact resistance of less than 2 milliohms can generally be maintained even when the sulfide film reaches a thickness greater than 1500 A^{o}. In the few instances where high contact resistances were observed on coupons with relatively thin sulfide films, there was also a significant quantity of silver chloride present on the coupon surface. For example, the high-cyanide silver coupon exposed at site D for 316 days had a silver chloride thickness of 2080 A^{o} after the same exposure.

The effect of treating electroplated silver coupons with a commercial tarnish inhibitor is shown in Table I. These data indicate that the benefits of the tarnish inhibitor were greater at the sites having less corrosive environments (A, B, and D). In highly corrosive environments, however, the tarnish inhibitor reduced the rate of sulfide formation but did not lower it sufficiently to allow the treated silver to function satisfactorily as an electrical contact. Also, the data in Table II indicate

that the tarnish inhibitor was somewhat more effective on the high-cyanide silver than on the no free-cyanide silver. However, in mild environments, the thickness of silver sulfide on untreated no free-cyanide silver was similar to that on high-cyanide silver that had been treated with the tarnish inhibitor. This again indicates that the rate of sulfide formation is lower on the no free-cyanide silver than on the high-cyanide silver.

Table II. Contact Resistances of Silver Exposed Without Tarnish Inhibitors

Exposure Site*	Days	100g Contact Force		200g Contact Force	
		High Cyanide	No Free-Cyanide	High Cyanide	No Free-Cyanide
A	70	1.8	0.7	1.1	0.6
	168	1.0	0.8	0.8	0.7
	363	2.2	0.8	1.3	0.7
B	208	1.0	0.8	0.8	0.6
	361	1.7	1.2	1.3	1.0
C	250	0.8	1.1	0.6	0.9
	313	1.1	1.4	0.9	0.9
D	172	1.3	1.2	1.0	0.8
	316	---	---	---	---
E	35	1.4	1.4	0.9	0.9
	167	21.	35.	4.1	19.
	308	---	---	---	---

*Site descriptions are listed in Table I.

Electromigration

In addition to tarnishing, the other major limitation to silver platings in electronics has been the tendency for silver to undergo electromigration in certain environments.

Silver electromigration, as defined in this paper, is an electochemical phenomenon, involving the transport of silver from one conductor to another, through a non-metallic medium, under the influence of an applied electrical field.[1,2] The mechanism is electrolytic, and may occur when the insulator separating the polarized conductors (as on a printed circuit board) has acquired sufficient moisture to allow electrolytic conduction.

In practice, electromigration can produce two separate, but not always distinct, phenomena, both of which can lead to impairment of a circuit's electrical integrity. These are colloidal silver "staining" and dendritic bridging. Colloidal silver deposits appear as brownish stains on insulator areas where migrating silver ions have been chemically or photolytically reduced to metallic silver. Silver dendrites, on the other hand, are the

result of preferential deposition of the metal at localized sites on the negatively-charged conductor, forming individual, spike-like protrusions. Once these nuclei have formed, the higher current density at their tips will greatly increase the probability of further deposition. This will be manifested as an accelerated growth outward from the tips in the form of thin black filaments of silver, extended from the cathode back toward the positive conductor. (Figure 1) In the course of this growth, branching usually occurs at definite crystallographic angles, resulting in a characteristic "dendritic" structure. (Figure 2)

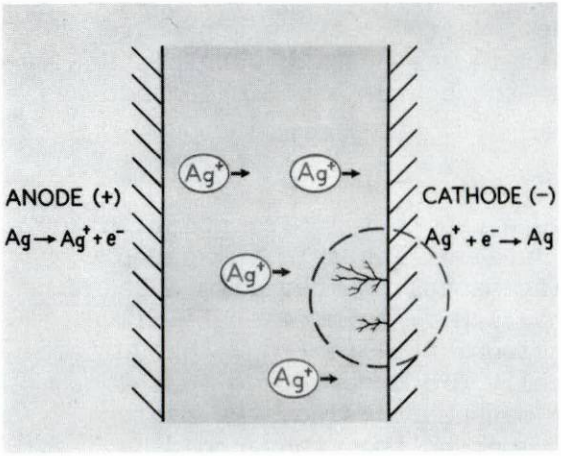

Figure 1. Schematic diagram of early stage of dendrite growth.

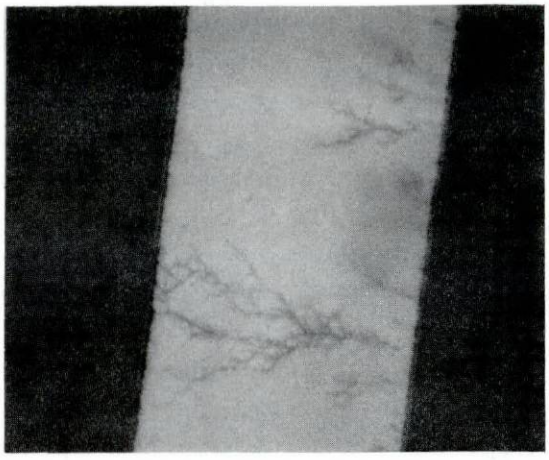

Figure 2. Photomicrograph of a silver dendrite bridging a 0.030 inch spacing.

When a filament finally bridges the gap between conductors, a sudden drop in resistance will occur. Although the magnitude of the resistance drop will be small (because of the small cross-sectional area of a single filament), a rapid increase in additional bridges---as would be expected when dendrites are present---will soon lower the resistance sufficiently to produce circuit failures.

An extensive investigation of electromigration in currently-used materials systems has been conducted in our laboratory . The primary operating parameters promoting electromigration problems were found to be:

- Contamination on the insulator surface
- Moisture (i.e., high relative humidity)
- Elevated temperatures
- Voltage difference between conductors
- Small spacing widths

Although the tendency towards electromigration had also been found to be dependent on the nature of the insulator material (and its surface) and the type of silver plating used, more recent work has shown that these effects

could be prevented or inhibited. In addition, the same techniques were often effective in inhibiting the tarnishing of the silver plating.

Silver electromigration was studied experimentally using silver-plated printed circuit boards. They were prepared using commercial glass-epoxy to copper laminates. The copper was etched to form the circuit pattern, prior to silver plating, using standard photoresist printing and etching techniques. The circuit pattern was connected to a common busbar on the edge of the boards, which was trimmed off after plating. Thus, the etched edges of the copper circuit pattern were also silver plated. The only exposed copper on the boards was across the ends of the fingers where they were attached to the busbar. This edge was inserted into an edge-card connector housing. The leaf-spring contacts in the housing were plated with the same type of silver as was used on the board to which contact was being made.

The edge-card connectors were wired in such a way that a d.c. polarization voltage could be applied between adjacent parallel lands on the circuit boards. The boards were placed in an environmental chamber with a relative humidity of 90 percent and an elevated temperature, to accelerate silver electromigration. During the period of environmental testing, the voltage applied to the circuit boards was periodically disconnected so that the resistance between adjacent lands could be measured. Also, the boards were removed periodically from the test chamber so that they could be examined microscopically for evidence of silver migration. Photomicrographs were taken to provide a permanent record of the nature and extent of migration on a particular board after a certain time of environmental exposure. Most of the boards were then placed back on test so that further growth of small silver dendrites could be observed.

In addition to the effects of different types of glass-epoxy boards and different types of silver plating, the use of surface treatments was also investigated. In general, the boards that were silver plated from a high-cyanide bath on type G-10 glass-epoxy substrates had the lowest rate of silver electromigration, as had previously been reported[3]. The highest rate of silver migration was observed on boards with type FR-4 glass-epoxy substrates plated with silver from a no free-cyanide bath. However, when these boards were dipped into a commercial silver tarnish inhibitor, silver electromigration was prevented. Figure 3 shows comparison photographs of two FR-4 boards plated with the no free-cyanide silver; both of these boards were tested simultaneously for the same length of time. The board that was treated with the tarnish inhibitor shows no dendrite growth while the untreated board has obvious dendrites between the silver-plated lands.

In no case was migration ever found at the silver-plated contacts or in the connector housing.

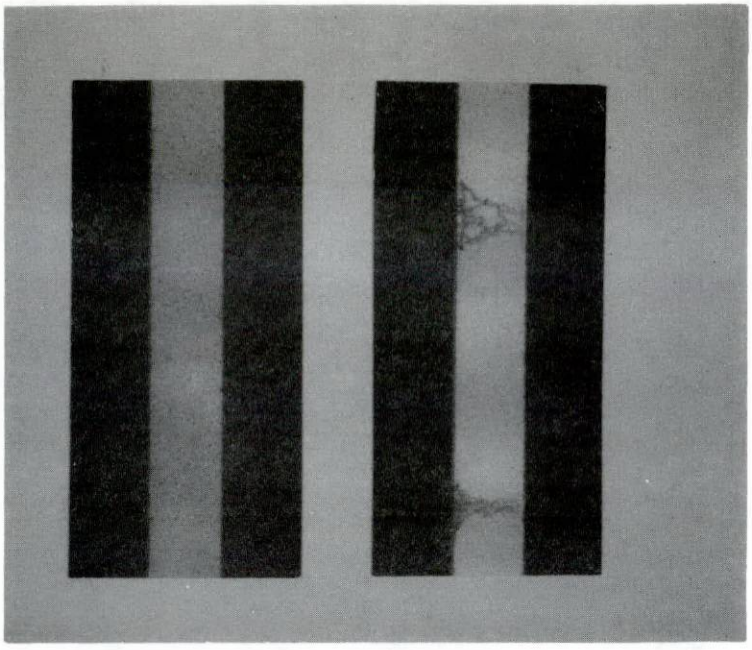

Figure 3. Comparison of printed circuit boards treated (left) and untreated (right) with a commercial tarnish inhibitor to reduce silver electromigration.

Ackowledgements

The authors wish to acknowledge the assistance of Dr. W. Kwalwasser for conducting the initial tarnish exposures. Mr. C. Sieber made the contact resistance measurements and Mr. D. Lehman did the coulometric analyses.

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F-5

ELECTRONICS SESSION F

Use of Strategy of Experimentation in Gold Plating Studies

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USE OF STRATEGY OF EXPERIMENTATION IN GOLD PLATING STUDIES

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Introduction

Presently at Sandia, we use a cyanide-citrate gold solution similar to that described by Ehrhardt[1] for some of our plating work. With the ever increasing cost of gold and the impetus to reduce plating thickness variations to minimize cost we felt we needed to better understand the influence of various plating variables on efficiency, throwing power and appearance. To this end we decided to apply the methodology of statistical experimental design to the gold plating studies.

Although plating experiments lend themselves very nicely to modern methods of experimental design, very little has been published in the plating literature on this topic. We are aware of only four papers: Ginberg et al[2] utilized a Box-Wilson[3] method for selecting the optimal conditions for electroplating nickel-iron alloy, Eisenmann[4] used factorial experiments to determine the effects of eight plating variables on selective properties of hard gold deposits, Goldman and Sykes[5] used a factorial experiment for determining the effect on plating thickness and rate of immersion time in activator and electroless copper solutions and Tomassi et al[6] determined the optimal cadmium sulfate formulation for best throwing power via factorial experimentation.

The strategy we used in this work is based on ideas presented in a recent three-day course given to some Sandia Livermore personnel[7]. The chosen approach-the particular experiments and the analysis-was a design due to Plackett and Burman[8]. The Plackett-Burman design helped to screen the most important variables from the larger number of possible ones with a minimum of testing. In one instance after completing the 6-variable Plackett-Burman analysis we discovered that only 3 variables were important. These were then evaluated via a full factorial experiment (2^3). Thus our factorial experiment involved only 8 trials, a significant reduction from the 64 required by a complete factorial scheme with 6 variables.

The first step was to fix the limits of the six independent variables; gold concentration, ammonium citrate concentration, ammonium sulfate concentration, current density, pH, and temperature. Agitation could also be considered an independent variable. However, for this work it was kept constant by using an electric stirrer since earlier work in our laboratory with a similar gold solution revealed that agitation was not a critical variable influencing efficiency, appearance or throwing power. The lower and upper values for each independent variable for the experiments are given in Table I, columns 1 and 2 respectively. The actual choices are based on personal experience intuition, and work by others. There is nothing particularly significant about any of the selections and the method applies with any reasonable set of limits.

The Plackett-Burman design for 6 independent variables calls for 12 experiments (Table II)[8]. Columns X_1 through X_6 of Table II show the set of parameters to be used in each experiment, while the remaining columns X_7 through X_{11} are for estimating the experimental error during the analysis of the data. Using the limits (+ and -) defined in Table I and the design of Table II, 1-litre solutions were mixed and tested per the requirements of Table III. The experiments were randomized, to exclude any ordering bias, by using a random numbers table.

TABLE I

GOLD PLATING INDEPENDENT VARIABLES

(The first and second columns give the limits chosen for this work; the third column shows the composition recommended by Rehrig[9])

	Lower Limit (-)	Upper Limit (+)	Recommended Conditions
X_1 = Potassium Gold Cyanide (g/l)	6	36	20
X_2 = Ammonium Citrate (g/l)	50	200	75
X_3 = Ammonium Sulfate (g/l)	50	200	75
X_4 = Current Density (A/m^2)	11	65	32
X_5 = pH	3.8	6.8	5.5
X_6 = Temperature (°C)	49	71	60

TWELVE-RUN PLACKETT-BURMAN DESIGN

(See Ref. 7 or 8 for further details.)

		Independent Variables						Error Analysis Variables				
Trial	Mean	X_1 (gold)	X_2 (Ammonium Citrate)	X_3 (Ammonium Sulfate	X_4 (Current Density)	X_5 (pH)	X_6 (Temp.)	X_7	X_8	X_9	X_{10}	X_{11}
1	+	+	+	-	+	+	+	-	-	-	+	-
2	+	+	-	+	+	+	-	-	-	+	-	+
3	+	-	+	+	+	-	-	-	+	-	+	+
4	+	+	+	+	-	-	-	+	-	+	+	-
5	+	+	+	-	-	-	+	-	+	+	-	+
6	+	+	-	-	-	+	-	+	+	-	+	+
7	+	-	-	-	+	-	+	+	-	+	+	+
8	+	-	-	+	-	+	+	-	+	+	+	-
9	+	-	+	-	+	+	-	+	+	+	-	-
10	+	+	-	+	+	-	+	+	+	-	-	-
11	+	-	+	+	-	+	+	+	-	-	-	+
12	+	-	-	-	-	-	-	-	-	-	-	-

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TABLE III

PLACKETT-BURMAN DESIGN FOR THE
STANDARD EFFICIENCY MEASUREMENTS

Trial	Pot. Gold Cyanide (g/l) X_1	Ammonium Citrate (g/l) X_2	Ammonium Sulfate (g/l) X_3	Current Density A/m^2 X_4	pH X_5	Temperature °C X_6
1	36	200	50	65	6.8	71
2	36	50	200	65	6.8	49
3	6	200	200	65	3.8	49
4	36	200	200	11	3.8	49
5	36	200	50	11	3.8	71
6	36	50	50	11	6.8	49
7	6	50	50	65	3.8	71
8	6	50	200	11	6.8	71
9	6	200	50	65	6.8	49
10	36	50	200	65	3.8	71
11	6	200	200	11	6.8	71
12	6	50	50	11	3.8	49

Upon completion of the Plackett-Burman analysis for efficiency, a 2^3 factorial-type experiment was run (Table IV) which incorporated the three most important variables. In order to estimate curvature (i.e., departure from a linear dependence on a variable), points were included at the middle value of all factors. These were the only additional tests required since the other eight tests needed for the 2^3 factorial experiment were covered in the initial Plackett-Burman screening design (Table II).

Experimental Details

Measurement of Efficiency

Efficiency measurements were based on the standard established by a copper coulometer connected in series with each plating solution. The coulometer contained 200 g/l copper sulfate, 100 ml/l sulfuric acid, and 50 ml/l of absolute ethyl alcohol. Two efficiency measurements were made for each experiment listed in Table III. Cathode material was brass sheet with an exposed are of 40 cm^2. Plating time at 10.8 and 65 A/m^2 (1 and 6 asf) was 43 and 7.5 minutes, respectively. The panels used for the efficiency tests were the same ones subsequently used for the appearance tests discussed below.

Measurement of Appearance

Appearance was measured by assigning number ratings from 10 to 100 to the panels used for the efficiency tests. The lowest rating (10) represented the worst appearance (dark foxy brown typical of burnt gold) while a rating of 100 represented the ultimate in appearance (yellow gold). Five people with varying experience in plating rated the panels.

Measurement of Throwing Power

Throwing power, which is the ability of a solution to plate uniformly regardless of cathode configuration, was measured by using a Haring[10] 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 was calculated by use of the equation,

$$\frac{P-M}{P-1}$$

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). Efficiency was also measured during these tests by use of a copper coulometer connected in series with the Haring cell.

TABLE IV

2^3 FACTORIAL DESIGN

Trial	Mean	X_1 (gold)	X_2 (Current Density)	X_1X_2	X_3 (Temp.)	X_1X_3	X_2X_3	$X_1X_2X_3$
1	+	-	-	+	-	+	+	-
2	+	+	-	-	-	-	+	+
3	+	-	+	-	-	+	-	+
4	+	+	+	+	-	-	-	-
5	+	-	-	+	+	-	-	+
6	+	+	-	-	+	+	-	-
7	+	-	+	-	+	-	+	-
8	+	+	+	+	+	+	+	+

Results

Efficiency--Standard Test Results

The measured values from the standard tests of efficiency are displayed in Table V, column 1. While the efficiency of the citrate-gold solution under normal operating conditions as defined in Table 1 is 90 - 100 percent, values ranging from 33 to 114 percent were obtained in this set of experiments. We will return to the meaning and significance of the values exceeding 100 percent later in this section.

The Plackett-Burman analysis of these results is given in Table VI. The numbers shown are the so-called "factor effects." A factor effect is computed by taking the sum of the measured values for which the independent variable assumed its lower limit, and dividing the difference by the number of trials for which the independent variable assumed its upper limit (6 in all cases here). The absolute value of the factor effect is to be compared with the "minimum significant factor effect," which is calculated from the experimental error, the number of degrees of freedom, and the confidence level. Additional details of the Plackett-Burman computation method are included in the appendix.

The minimum significant factor effect at a 90 percent confidence level is 16.3 for the standard efficiency-test measurements. Any variables in Table VI with absolute effect values greater than this minimum are, therefore, of significance. This means that current density, gold concentration and temperature clearly have statistically significant effects on efficiency. Ammonium citrate concentration, ammonium sulfate concentration, and pH do not influence efficiency to any degree of importance.

Figure 1 shows a graphical analysis of the three factors (gold concentration, current density and temperature) which have significant effects. The conclusion drawn from this presentation of the data is that maximum efficiency is obtained regardless of current density when the gold concentration is kept high. At low gold concentration, the only way to obtain good efficiency is to plate at low current density.

Figure 1 also reveals that efficiencies much higher than 100 percent were obtained at low current density when the solution contained high amounts of gold. This suggests that there may have been some experimental difficulties at the low current density and/or some electroless deposition. A literature search revealed that our experimental use of the copper coulometer was less than optimum. For example, it is recommeded by Mantell[11] that the cathode current density in the coulometer be maintained within the range of 20 to 200 A/m^2 (1.9 to 18.6 asf) by adjusting the cathode area. We did not make adjustments to the cathode area, so our current density varied from 10.8 to 65 A/m^2 (1 to 6 asf). Since we exceeded Mantell's recommended range at low current density this may also have contributed to the higher efficiencies. Subsequent experiments with throwing power and efficiency discussed in a later section of this report support this statement since with a constant cathode current density (65 A/m^2) no unusually high current efficiencies were obtained. The important point is that the graphical presentation of the data (Figure 1) clearly showed that this was an area worthy of further investigation.

TABLE V

EFFICIENCY, APPEARANCE, AND THROWING POWER RESULTS[a]

Packett-Burman Trial No.[b]	Efficiency[c] (%)	Appearance	Throwing Power (%)	Efficiency[d] (%)
1	95	86	66	97
2	92	20	62	94
3	33	12	86	26
4	106	82	98	100
5	114	94	93	103
6	89	54	78	85
7	84	22	82	54
8	98	100	89	93
9	50	10	89	30
10	97	60	69	99
11	99	100	98	102
12	94	84	89	89

[a]Each value is the average of two data points.

[b]See Table II for test matrix.

[c]From the standard-technique measurement.

[d]Taken in conjunction with the throwing power measurement.

TABLE VI

FACTOR EFFECTS, ESTIMATE OF EXPERIMENTAL ERROR, AND THE MINIMUM SIGNIFICANT FACTOR EFFECTS FROM A PLACKETT-BURMAN ANALYSIS[a]

	Efficiency[b] (%)	Appearance	Throwing Power (%)	Efficiency[c] (%)
Potassium Gold Cyanide	22.5	11.3	-11.2	30.7
Ammonium Citrate	-9.5	7.3	10.2	-9.3
Ammonium Sulfate	-.2	4.0	.8	9.3
Current Density	-24.8	-50.7	-15.2	-28.7
pH	-.8	2.7	-5.8	5.0
Temperature	20.5	33.3	-.8	20.7
S_{FE} (Size of Experimental Error)	8.1	12.5	3.0	9.8
[MIN] (minimum significant factor effect at 90% confidence level)	16.3	25.0	6.0	19.8

[a]The boxed values are ones exceeding the minimum significant factor effect.

[b]From the standard-technique measurements.

[c]Taken in conjunction with the throwing power measurements.

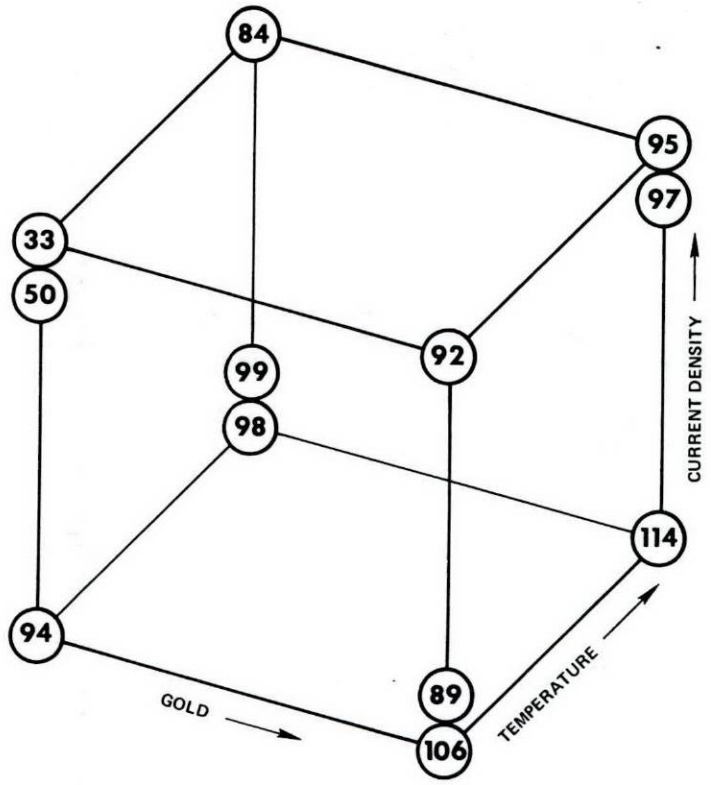

Figure 1. Graphical Analysis of the Variables Which Affect Efficiency

A 2^3 factorial experiment was then performed with the three independent variables of gold concentration, current density, and temperature. The results are shown in Table VII. The minimum significant factor effect at a 90 percent confidence level was calculated to be 3.7 and all three independent variables as well as all interactions have factor effects greater than this. This corroborates the conclusion of the Plackett-Burman analysis that all three variables have statistically significant effects. The interactions that are indicated include: gold and current density (X_1X_2 = 15.0) gold and temperature (X_1X_3 = -7.0), current density and temperature (X_2X_3 = 6.0) and gold, current density and temperature ($X_1X_2X_3$ = -17.0). Based on these data, the following regression equation can be used to describe the situation:

$$Y = 87.5 + 10\ X_1 - 11.5\ X_2 + 10.5\ X_3 + 7.5\ X_1X_2$$
$$- 3.5\ X_1X_3 + 3.0\ X_2X_3 - 8.5\ X_1X_2X_3$$

This formula shows that gold concentration and temperature have positive effects and current density a negative effect. Therefore, higher efficiencies can be achieved by increasing gold concentration and temperature while decreasing current density. There is also curvature, i.e., deviation from linearity in the middle point range, since the minimum significant curvature is 4.65 while that obtained from this analysis is -10.5.

Appearance Test Results

Remarkably good agreement was obtained among the five individuals who rated the panels (Table VIII) even though their plating experience varied widely (from 1 to 30 years of experience). The averages appear in Table V and Table VIII while the Plackett-Burman analysis results are shown in Table VI. The minimum significant factor effect at a 90 percent confidence level is 25.0. This means that current density (-50.7) and temperature (33.3) are the only variables that have statistically significant effects. All other variables-gold concentration, ammonium citrate concentration, ammonium sulfate concentration and pH have values quite less than 25.0 and hence are not significant.

A graphical analysis of the three variables current density, temperature, and gold is shown in Figure 2. This very clearly reveals that if the current density is kept low and the temperature high, optimum appearance is obtained regardless of gold concentration.

Combined Throwing Power and Efficiency Test Results

Throwing power values (Table V) ranged from a low of 62 to a high of 98 with a mean value of 83. For a better understanding of the significance of these numbers, reference is made to a summary of throwing power of plating

TABLE VII

PLATING EFFICIENCY 2^3 FACTORIAL EXPERIMENT

(The boxed values are ones which exceed the minimum significant factor effect. The center-point efficiencies were found from measurements using values of the independent variables in the middle of their normal range (Table I). Curvature was calculated by taking the difference between the mean factor effect and the center-point average. For details on the calculation of [MIN C], see Ref. 7.)

Trial	Mean	X_1 (Gold)	X_2 (Current Density)	X_1X_2	X_3 Temp.	X_1X_3	X_2X_3	$X_1X_2X_3$	$\bar{Y}$
1	+	-	-	+	-	+	+	-	94
2	+	+	-	-	-	-	+	+	89
3	+	-	+	-	-	+	-	+	33
4	+	+	+	+	-	-	-	-	92
5	+	-	-	+	+	-	-	+	99
6	+	+	-	-	+	+	-	-	114
7	+	-	+	-	+	-	+	-	84
8	+	+	+	+	+	+	+	+	95
Sum +	700	390	304	380	392	336	362	316	
Sum -	0	310	396	320	308	364	338	384	
Overall Sum	700	700	700	700	700	700	700	700	
Difference	700	80	-92	60	84	-28	24	-68	
Effect	87.5	[20]	[-23]	[15]	[21]	[-7]	[6]	[-17]	

Center Point Average: (100 + 98 + 96)/3 = 98
Curvature: 87.5 - 98 = -10.5

[MIN] = 3.70 (90% confidence level)
[MIN C] = 4.65

TABLE VIII

APPEARANCE RATINGS
(The rating range was 10 for the worst-looking result to 100 for the best appearance)

Trial No.	Rating[a]					Average
	A	B	C	D	E	
1	90	90	90	80	80	86
2	10	20	20	30	20	20
3	10	10	10	20	10	12
4	90	90	80	70	80	82
5	100	90	90	100	90	94
6	50	60	60	50	50	54
7	20	20	10	40	20	22
8	100	100	100	100	100	100
9	10	10	10	10	10	10
10	50	70	60	60	60	60
11	100	100	100	100	100	100
12	90	80	90	80	70	84

[a] Panels were those used for the efficiency experiments. Ratings were performed by five individuals coded A-E.

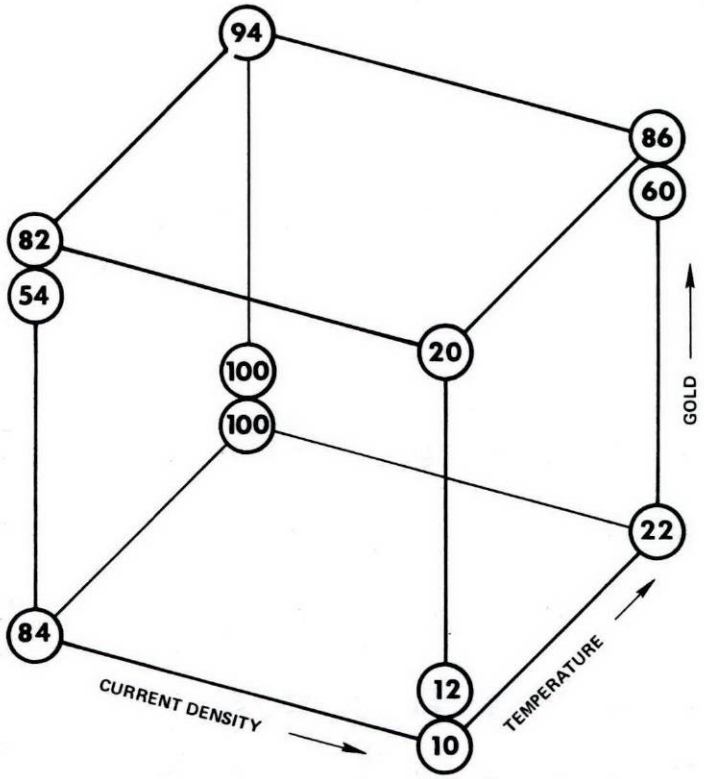

Figure 2. Graphical Analysis of the Variables Which Affect Appearance

solutions published by Schaefer and Pochapsky[12]. The solutions lend themselves to four separate groups: Chromium, which has very poor throwing power (less than 0 percent), is in a group by itself. The next category in terms of increasing throwing power contains most acid baths of single metals or alloys (0 to 25 percent). The third category includes most cyanide solutions (25 to 50 percent), and the fourth category contains stannate tin and its alloys, with throwing power values of 50 percent and greater. It is important to note that the average throwing power values obtained for the citrate solution rank among the best available in providing good throwing power. It clearly belongs in the top category. The point is that only for a relatively small subset of the values of the independent variables will there be a significant decline in throwing power.

The Plackett-Burman results (Table VI) indicate that current density, gold concentration, and ammonium citrate concentration are the variables which have statistically significant effects on throwing power. In addition, since the value -5.8 for the pH effect is quite close to the 6.0 value for the minimum significant factor effect, this suggests that pH also be considered as potentially significant. From a physical standpoint current density should be significant because it influences polarization characteristics, which in turn are very important in determining current distribution. Increasing the ammonium citrate concentration and/or decreasing the pH increases the conductivity of the solution and this technique has been shown by others to be one of the standard methods for improving throwing power of plating solutions.[13] The concurrently obtained efficiency results (Table VI) show that gold, current density and temperature are by far the most critical variables. These data provide very close duplication of the efficiency work discussed earlier and thus support the conclusions drawn from the analysis of the standard approach tests.

Summary

Experimental design strategy has been demonstrated to be a powerful tool for understanding plating. A specially chosen series of experiments was run to assess statistically the influence of a number of plating variables--gold, ammonium citrate, and ammonium sulfate concentrations, current density, pH, and temperature--on efficiency, appearance and throwing power. The conclusions that can be drawn are:

1. Gold concentration, current density and temperature are the key variables which affect efficiency.

2. Current density and temperature are the critical variables which influence appearance.

3. Current density, gold concentration, ammonium citrate concentration, and pH are the variables which affect throwing power.

This work provides an understanding of the influence of gold plating variables on efficiency, appearance, and throwing power that heretofore did not exist. Good gold plating practice typically dictates that for optimum

results, metal ion concentration and temperature should be kept high and current density kept in the low to intermediate range, which has all been verified here. In addition, the influence of ammonium citrate, ammonium sulfate, and pH was defined.

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APPENDIX

COMPUTATION OF THE FACTOR EFFECT FOR A TWELVE-RUN PLACKETT-BURMAN EXPERIMENT ON PLATING EFFICIENCY (Illustrated in Table A-I)

1. Write the average response (measured dependent variable) for each run to the right of the table (column heading $\bar{Y}$, Table A-I).

2. Total the values of the response on the lines with a plus sign for each column. Write the total on the line called Sum +. Do for all columns including the unassigned ones.

3. Do the same for the responses on the lines with minus signs. Write the total on the line called Sum -.

4. For each column subtract Sum - from Sum +. Write the result on the line called Difference.

5. For each column divide the Difference by the number of plus signs in that column (six for this work). This number is the "effect" for that column. For those columns with assigned factors this number is the factor effect. For the extra columns to which no factor is assigned, this number is an estimate of experimental error.

6. Square each of the unassigned factor effects (columns X_7 to X_{11}).

7. Add them together and divide by the number of unassigned factor effects.

8. Take the square root; this gives S_{FE}, which is the size of the experimental error.

9. To calculate the minimum significant factor effect, use $[MIN] = t \cdot S_{FE}$, t being 2.01 for 5 degrees of freedom at the 90 percent confidence level (from a table listing the fractiles of t for varying proability levels and degrees of freedom).

RESULTS FOR TWELVE-RUN PLACKETT-BURMAN PLATING EFFICIENCY EXPERIMENT

(Significant effects are shown in boxes)

Trial	Mean	X_1 (gold)	X_2 Citrate	X_3 Sulfate	X_4 (Current Density)	X_5 (pH)	X_6 (Temp.)	X_7	X_8	X_9	X_{10}	X_{11}	$\bar{Y}$
1	+	+	+	-	+	+	+	-	-	-	+	-	95
2	+	+	-	+	+	+	-	-	-	+	-	+	92
3	+	-	+	+	+	-	-	-	+	-	+	+	33
4	+	+	+	+	-	-	-	+	-	+	+	-	106
5	+	+	+	-	-	-	+	-	+	+	-	+	114
6	+	+	-	-	-	+	-	+	+	-	+	+	89
7	+	-	-	-	+	-	+	+	-	+	+	+	84
8	+	-	-	+	-	+	+	-	+	+	+	-	98
9	+	-	+	-	+	+	-	+	+	+	-	-	50
10	+	+	-	+	+	-	+	+	+	-	-	-	97
11	+	-	+	+	-	+	+	+	-	-	-	+	99
12	+	-	-	-	-	-	-	-	-	-	-	-	94
Sum +	1051	593	497	525	451	523	587	525	481	544	505	511	
Sum -	--	458	554	526	600	528	464	526	570	507	546	540	
Overall Sum	1051	1051	1051	1051	1051	1051	1051	1051	1051	1051	1051	1051	
Difference	1051	135	-57	-1	-149	-5	123	-1	-89	37	-41	-29	
Effect	87.6	22.5	-9.5	-.2	-24.8	-.8	20.5	-.2	-14.8	6.2	-6.8	-4.8	

S_{FE} = 8.1

[MIN] = 2.01χ 8.1 = 16.3 (90% confidence level)

8312A-A19b/ws

G-1

ELECTRONICS
SESSION G

Liquid Photoresist Process for Subtractive and Semi-Additive Printed Circuitry

G. G. Perrin, A. Price, S. Simoliunas
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LIQUID PHOTORESIST PROCESS FOR SUBTRACTIVE AND SEMI-ADDITIVE PRINTED CIRCUITRY

Gordon G. Perrin, Jr., Alan Price, and Saulius Simoliunas

ABSTRACT

Polyvinyl cinnamate negative working photoresist process has been established for fabricating plated through hole printed circuitry. Copper conductors and plated through holes are protected from etchants by crosslinked photoresist without plating a dissimilar metal resist. Copper circuitry of 1 mil thickness and 2 mil line/space width can be routinely produced.

In the early seventies there was an attempt to produce a 1 mil thick (or above) copper circuitry with 5 mil wide lines and spaces, and to produce these circuits by rapid (1 mil per hour) electroless plating. The key for this process was the nickel catalysis. Continguity of a copper metal foil produced by aldehyde reduction of an alkaline copper ion complex is related to the presence of nickel ions in the electroless plating solution.[1,2,3,4]

However, there were too many problem areas in this fabrication scheme.

1. The electroless copper deposit produced from dilute aqueous solution of copper EDTA complex, nickel chloride, sodium hydroxide, and formaldehyde only approaches, but never becomes identical to plain copper sulfate electrolyte copper foil in mechanical properties. To produce 1 mil (or greater) deposits without porosity is very difficult.

2. To produce adequate bonding between the substrate and the electroless copper deposit is difficult without unduly roughening the substrate. This roughening later adversely affects the resolution of the photo sensitive film prior to electroless deposition of the metal.

3. If a photoselective metal deposition technique is not used, and also if no catalyst impregnated boards are used, then one is forced to use screened resists or photoresists. In that case, an alternative method would be to use subtractive technology, which is the main technology today and where screened resists and/or photoresists are used.

The popular dry film photoresists are limited in their resolution because of their thickness and their protective mylar coatings. The maximum resolution achieved with this type of photoresist is only 5 mil lines and spaces. We know from semiconductor technology that liquid photoresists can achieve a resolution limit of 80Å.

Because of the difficulty of exposure within the plated through holes, negative liquid photoresists, until recently, were not utilized in fine line printed circuit production. Now the technical difficulties have been overcome, and a workable process has been announced.[5]

The older positive liquid photoresist[6] process to produce print-and-etch circuitry was too sensitive to light and quite subject to etchant attack. It is not used today.[7]

The new negative working liquid photoresist process yields printed circuitry without solder electroplating. In other words, photoresist is substituted for solder electroplate. It is a contracted form of the standard subtractive technology, and this contraction makes the new method more elegant, cheaper, and reliable. The resolution is very high - 2 mil wide line and 2 mil space 1 mil thick copper circuitry can be routinely produced. 1 mil wide line and 1 mil space 0.5 mil thick copper circuitry has also been successfully produced. In fact, it is the only subtractive method to yield fine line printed circuitry comparable only to fully additive processes without the attendant problems of obtaining consistently metallic, thick (1 mil or above) copper plate, via electr less copper deposition as opposed to electrolytic copper deposition Also it eliminates solder electroplating with its attendant problem of peptone inclusions, variations in composition, poor throwing power in long narrow holes, adhesion to copper, melting under solde mask and the subsequent rupturing of the solder mask in the wave soldering operation, conductor undercutting due to dissimilar metal during etching, operation, etc. Solder electroplating is replaced by electroless tin and where needed to meet mil spc. 275c, by hot air solder leveling with or without solder mask.

The photoresist used is the proven old standby of photoresist technology - polyvinyl cinnamate.[8,9,10,11,12] Now it has been modified by new catalysts and processing steps to provide an etch resist for conductor patterns and plated through holes in printed circuit production. The new process substitutes for and surpasses the more costly dry film photoresist tenting and etching technique. It also compensates for holes which have been drilled off-center, and very narrow annular rings, since the photoresist is fully crosslinked within the hole-even if 90% of the hole opening is obscured by the negative.

Here is the procedure in detail with pertinent comments.

1. Drilling of the copper clad laminate by manual or NC methods. 1/4 to 1/2 oz. copper cladding is preferred. If NC methods are not available, then after shearing laminate to size, vapor degrease in chlorinated solvents, flow coat with photoresist, dry in an oven with air circulation at 250 F for 1 hour. After removing the board, cool it to room temperature, plate it on the printing machine with the negative on top with emulsion side on the board for 2 to 10 minutes, develop in the degreaser, dye in gentian violet in toluene, rinse off the rest of unexposed resist with water spray, then rinse in isopropyl alcohol, spray with water, 5% HCl acid rinse, air dry.

This provides a good contrast, reliable pattern which can be used in a hand drilling operation. The resist pattern is only 0.1 mil thick. It is quite pliable and does not chip as dry film photoresist (which is quite brittle and a magnitude thicker) can. A good driller can thus provide prototype cards by manually drilling 3 or 4 card stacks.

2. Electroless copper deposition cycle. The photoresist pattern has to be stripped in common solvents, such as 50% by volume methylene chloride, 50% by volume water, ammomium hydroxide, and a surfactant. Rinse in water spray. Dry in an oven at 212 F to drive out water. Degrease in chlorinated solvent. Etch in ammonium persulfate etch, the ammonium persulfate being in aqueous solution at 10% by weight. Rinse, 10% by volume H_2SO_4 dip, rinse, stannous chloride, rinse palladium chloride, rinse cycle can be used. This cycle is preferred, because there are no complexing agents deposited on the board from stabilized palladium-stannous chloride catalysts, which care commercially available. If stannous chloride, rinse, palladium chloride, rinse cycle is used, care must be taken to keep these solutions in dark.

As for electroless copper itself, the preferred formulation was described above. Its salient point is the added nickel ions. In regard to commercial electroless copper solutions no preference is indicated. They are all loaded with stabilizers and produce porous films, but the solutions last longer. From engineering viewpoint, bath stability at the expense of mechanical properties of the deposit does not make sense. The porosity has a savings grace. That is, it provides for subsequent keying of electroplate to the original foil. The recommendation is to sand off the electroless copper deposit altogether, since structurally electroless copper is different from the original electroplated copper foil and thus provides the "weak link" in the subsequent sandwich. Thus, the logic of having contiguous electroless copper films inside the holes, where they are only needed and none on the surface. Just this realization that adhesion is best between the same crystallographic structures and doing everything to mate similar materials avoids a plethora of problems. Since light sanding is used to remove electroless copper from the surfaces, the control of electroless copper

thickness becomes unnecessary. Large savings can be realized by making and maintaining one's own solutions.

3. Copper panel electroplating, light sanding of the printed circuit surfaces, then water rinse, 10% by volume H_2SO_4 dip, water rinse and go into air agitated cathode-moved plain copper sulfate electroplating tank. Copper electroplating should be done from plain copper sulfate electrolyte to simulate and surpass the commercial foil in higher tensile strength and bending ductility.[13]

It has been twenty years since a new plating philosophy, which may be called "the antibrightener and antileveler approach", was demonstrated in electroplating baths without additives. These baths yielded superior mechanical properties of the deposits.[14] Today superior mechanical properties have been found in additive-free gold.[15]

Hence, the recommendation is for additive-free gold and nickel sulfate with bromide ions for tab plating. The copper sulfate electrolyte should be about 10 oz/gallon copper sulfate, 20 oz/gallon of sulfuric acid, 50 ppm chloride ion, 20-30 asf to produce 1 mil circuitry with cathode and air agitation. The reason for plain copper sulfate electrolyte is also that it yields an unpassivated copper, which provides superior adhesion for photoresist and which is evenly etchable.

4. Photoresist application. Light sanding of copper electroplated panels. Photoresist can be sprayed on, or one may dip boards in it, let dry at 250 F for 1 hour in air circulated oven. One may apply after the first 15 minutes drying a second coat for insurance in multilayer application. The printing and developing are the same as outlined above. Log relative sensitivity is around 1.7 at 300-320 nanometers and 1.5 at 400-420 nanometers.

Adhesivity is excellent. The adhesivity of a photoresist to the copper is an important factor when performing precise etching. The photoresist adheres so well that no penetration of the etchant can be observed between resist pattern and copper surface if it is baked at 250 F for 1 hour. Here, the great superiority of wet-film photoresist is demonstrated against dry-film photoresists.

The thermal stability of this type of photoresist is very good.

The photoresist has a viscosity of about 12 centistokes, solids about 7% by weight, specific gravity about 1.01. Thew trick is in the molecular weight of polyvinyl alcohol and the amount of esterification with cinnamic acid. It has to be dried at 250 F for a long time. Thus, the holes are solidified, although they may even be blocked by photoresist. Air drying (oxygen inhibition of polymerization-crosslinking) is a must.

This method opens a myriad of possibilities for new photoresist development with greater resonance structures than cinnamic acid; uv, e beam, laser printing methods, etc. However, the main method will remain intact. For a 100% reliability the printed board may be given ultrasonic shock before etching, but the long drying at 250 F is already a good test of whether or not the photoresist and the new electroplate have good adhesion.

5. Etching is done in common etchants. All are suitable. The recommendation is for cupric chloride with excess hydrochloric acid. It is a cleaner and smoother etchant than ferric chloride. Also the etchant yields a pure compound. The anodic etching process,[16] which reuses solution and retrieves copper, eliminates all undercutting and yields 0.5 mil wide line and 0.5 mil space 0.5 mil thick printed circuitry.

6. Stripping of the photoresist in common solvents (such as methylene chloride type), nickel and gold electroplating, electroless tin or hot air solder leveling with or without solder mask.

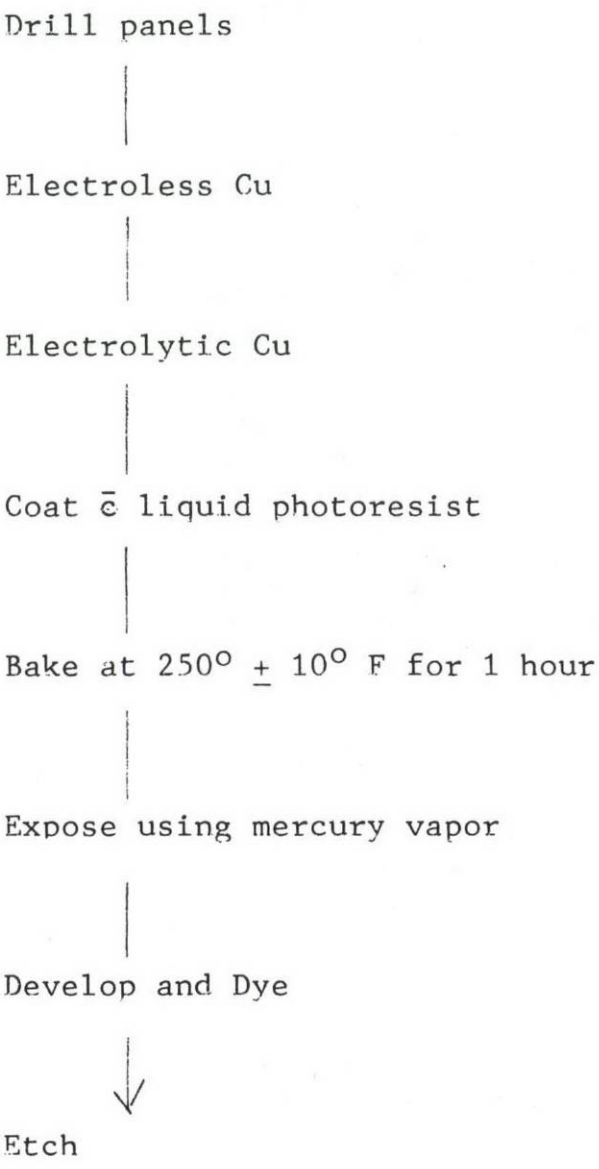
Hot air solder leveling provides pure eutectic solder, which cannot be produced by electroplating. The boards, which were fabricated with hot air solder leveling were superior in solderability and resolution to those made with the standard solder electroplating process. The recommendation is for the industry to embrace hot air solder leveling far and wide; the industry may eventually not even have a choice.

Thus a printed circuit has been produced in a short time and with relative ease.

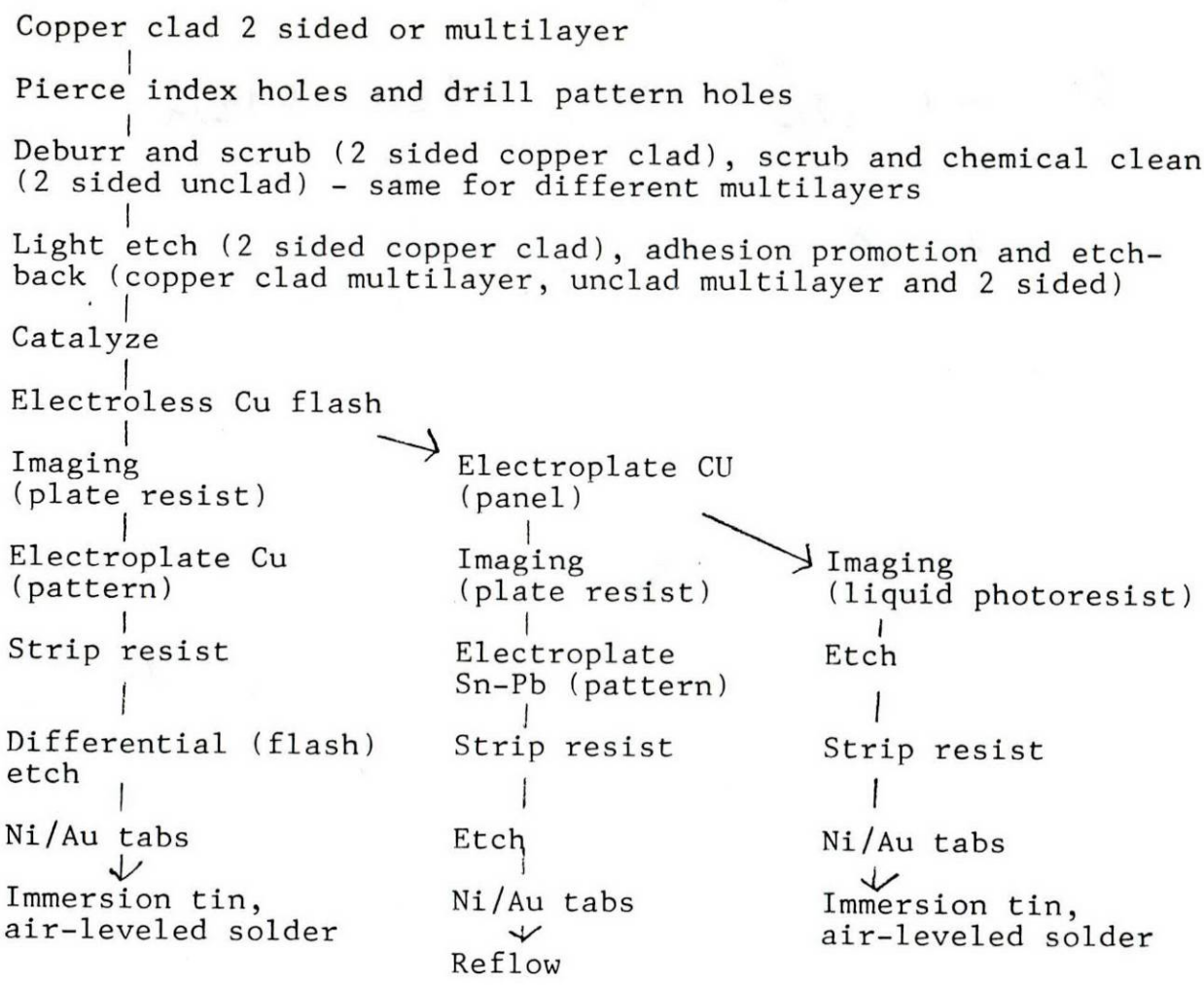
An important variation of this process is using pattern plating, then stripping of photoresist and depositing new photoresist for protecting conductors and plated holes. This requires very good registration and superior cleaning cyle for pattern plating. However, 5 mil thick conductors of 10 mil width reducing from 12 mil width were obtained using the standard liquid photoresist process. Tin-lead, being a metal mask, sets up a half cell in etching operation and large undercutting is a common result.

In effect, liquid photoresist has returned to printed circuitry. Its use now seems so obvious that one may wonder why it was not invented and used before. It seems that plating in electronics is slowly, but surely coming of age.

Liquid Photoresist Process

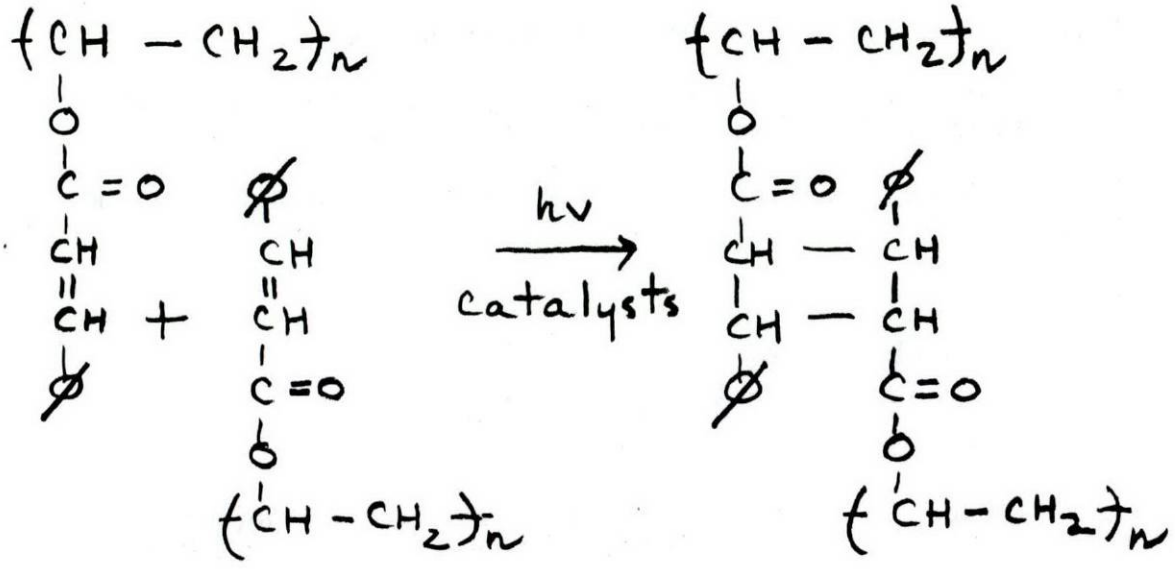


PTH SUBTRACTIVE AND SEMI-ADDITIVE PRINTED CIRCUITRY
(2 sided and multilayer)



DWG. NO.

CROSSLINKING OF POLYVINYL CINNAMATE



(main product)

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G-2

ELECTRONICS SESSION G

The Use of U. V. Inks in a Solvent Free PWB Shop

K. B. Reber
Western Electric Co.
Columbus, OH

THE USE OF U.V. INKS IN A SOLVENT FREE PWB SHOP

K. B. Reber
Western Electric Company
Columbus, Ohio

In 1961, we started making printed wiring boards used in the first Electronic Switching System. By today's standards those single sided, single family, high volume print and etch boards were very simple.

In the past several years, our product line has changed considerably. We still make a few Electronic Switching type boards, but the majority of our production is mixed. We make boards ranging in size from a 1/2 square inch to several square feet; we ship yearly quantities ranging from 1 board to 6 million boards per code and hundreds of different shapes and sizes. The boards may be any combination of solder plated, resin coated, soldermasked, gold plated, single sided, some double sided, designation printed, terminal inserted, made from thin foil, 1 ounce, 2 ounce or 5 ounce copper on polyester glass, epoxy glass, epoxy paper, or phenolic paper, and since were in the phone business, our boards are used in home phones, pay phones, Mickey Mouse phones, power equipments, hung on poles, mounted in central offices and thrown around in beeping softballs. And of course each phone system has a name EADAS, SLC8, PTD2-A, PSS, RTA, JEDDA, TSPS, ETA, COMKEY, SCC, KBR, AMARS, ANI-B, BDT, CCIS, LAMDA C, WADS, DCDP and several hundreds more. We like some of our own names better -- the baby foot board, the duck board, the Italian boot, Mother Hubbards shoe and the Boom-Boom board.

Some unknowing person may point out that although most printed wiring designs are varied, we are blessed with some fairly common manufacturing techniques -- drilling, etching, plating and screen printing.

Printing is a PWB process, common to most manufacturing facilities, but the techniques of printing are as numerous as the PWB shops themselves. This is a result of the variety of inks, screen wire, emulsions, etchants, and a dozen other variables that come into play depending on the type of product made, the equipment used and the economic and environmental considerations that are of prime concern to us all. Today, I am going to briefly tell you how we screen print with emphasis on our present and planned use of Ultra Violet light curable inks.

Successful circuit screen printing depends greatly on preparation of the copper surface. Several years ago we installed an inline three station cleaning machine to replace the existing solvent cleaning of the raw material. The first station is a spray unit that cleans organic residues and dirt with an alkaline cleaner. The panels are conveyed directly into a Scrubber where copper oxides are removed by an abrasive scrub. The last station is a dilute acid spray with a

water rinse followed by a drying section. This last spray removes traces of the alkaline cleaner and provides a slightly acidic surface which is more compatible with alkaline strippable inks.

Our screen making room has facilities for screen stretching, coating, exposing and screen storage. We also have an ultrasonic tank to strip the screen emulsion to reclaim screens for reuse. We use only glass masters for exposing screens in order to guarantee a minimum dimensional change in the stepped phototool during storage.

Our screening area, is 36 by 41 feet in size and is enclosed with a filtered air system controlled to 75 $\pm$ 3 degrees F with a relative humidity of 45% minimum, 55% maximum, and contains eight automatic printers. The printed panels are cured in either a UV unit or an infrared oven depending on the ink being used. Adequate space is also provided for storage and screen clean up.

Since 1972, we have been using alkali soluble resists and at the present time we use the same resist for both etching and plating. We had the usual problems most people experience when changing inks. No two inks have the same consistency, consequently, screens and printer set-up techniques had to be changed to get the best results from the new ink. The viscosity of this ink can be adjusted by adding several different additives in the ester or glycol ether family. Which one you use is dependent on your desired drying rate. Prior to the conversion to our present ink system, we had been using a solvent strippable ink. The conversion resulted in a substantial savings in reduction of solvent usage.

A copper board that will be coated with a protective resin is printed with the alkaline ink, dryed in the I.R. oven, etched with cupric chloride and conveyed into a spray stripping machine at 7 feet per minute where the ink is removed with a 2% solution of sodium hydroxide and water. The sodium hydroxide solution is run at temperatures ranging from 90 degrees to 120 degrees. The 80 gallon capacity machine is recharged after 4 hours of use. The machines are exhausted through fume scrubbers, the same scrubbers that are used for the etchers.

A solder plated board is printed with the same ink and solder plated using a low metal plating bath. The ink is then stripped from the board by the same process previously described. It is etched using an alkaline etchant.

The benefits of the alkaline ink system are obvious. It saves money. The trichlorethelene cost is several dollars a gallon and sodium hydroxide in bulk is only several pennies for the same amount. The second big benefit is the easy compliance to the Ohio and Federal EPA Emissions Standards and OSHA threshold limitations.

For these reasons our work with UV inks has been channeled along the

same line -- UV curable resist that will strip with alkaline solutions. Printed circuit UV screening inks fall into three categories:

1. Solder mask inks
   A. Over copper
   B. Over solderplate

2. Designation or legend inks
   A. Over bare laminate
   B. Over circuitry

3. Etch and plating resist ink

Our first exposure to UV curable screening inks came about when our board customers suddenly added soldermask requirements to their product. Rather than increase our capacity to print and cure epoxy soldermask, we looked closely at the UV materials that were available and several polymers being developed by our laboratories. The board design was changed from solder plate to bare copper with the use of a modified commercial UV soldermask with a protective resin over the bare copper lands. The only equipment needed was a curing unit, costing approximately $8,000. This unit has two, 200 watt per inch bulbs with parabolic reflectors and a wire mesh belt with speeds up to 30 feet per minute. We print the UV polymer using a 180 mesh stainless steel screen wire coated with 2 coats of liquid emulsion. To control the relatively low viscosity UV material, the print cycle was changed to a flood first mode to reduce the flow of ink through the screen. A flood first mode leaves the screen bare of ink while the operator is loading and unloading the machine. The boards are cured at 10 feet per minute and tested for cure by running them through a wave solder machine and inspecting for adhesion failures.

Because of adhesion difficulties, a different UV polymer was developed for use over solder plate, thus completing our conversion from epoxy soldermask to UV soldermask.

UV curable designation or legend printing inks, or silk screening inks as some people call them, by the nature of what they are intended to do, have some problems. They must be legible, must adhere to both paths and substrate and must not adversely affect insulation resistance. To be legible, they must be fairly opaque and that may affect adhesion. The more opaque the material the lower the transmission of light to the layer of material next to the substrate that must be cured to create the bond of the ink to the board.

Also, the dyes or pigments may affect the insulation resistance of the board. The product made at our location that requires designation printing is conveniently single sided so no paths are bridged by ink, therefore, with proper artmaster design, insulation resistance is not critical. Several commercial inks have been tested and the ink that

has been most successful to date for adhesion is a black ink with a carbon pigment. Tests are continuing to find a material that will meet all of our insulation resistance requirements so that we can print on both sides of double boards.

The third and most important use of UV inks in a PWB Shop is for etch and plating resists. What we were originally looking for was:

1. One ink for both and plating
2. Alkaline strippable
3. Able to use existing equipment
4. Prints without major process changes

We did not find an ink that met all the requirements, in particular Item 3. We have concluded that a new stripping machine is necessary.

We have extensively tested four inks. Panels were printed, cured, etched or plated and stripped and here's where the problem arose. The stripping was not adequate in our existing machines at 130°F with the solutions modified with various amounts of butylcellosolve with no success.

Our other requirements were totally met. The printing was excellent with line definition comparable to photo resist. Only screen wire was changed to obtain the best results from each ink.

The parts were cured at conveyor speeds ranging from 5 to 20 feet per minute. The cure was sufficient to allow the parts to drop onto a stacking device without scratching the cured resist. The durability of the ink is also reflected in its resistance to breakdown in the plating bath. Tests have shown resistance to plating breakdown or pinholing to be several hundred times better than conventional heat dried inks.[1]

Using UV ink as an etch resist can result in problems if the exposure is not properly controlled. A "cure window" must be emperically established and maintained for the particular resist used. Under cured resist will be removed by the etchant and over cured resist is impossible to strip.

Although most of the ink manufacturers specified that their inks would strip at 130°F, we found that in practice the time required in the machines was unreasonable and would limit capacity. After running several trials we decided to order a high temperature (160°F) double chamber stripper. This unit is designed with a moving belt filter to pull the stripped strings of resist out of the solution flow so that the stripper solution stays active longer. The machine is equipped

[1]Test completed by Mr. Doug Reed of Tektronix, Inc., Beaverton, Oregon, published in the October, 1977, issue of Insulation/Circuits.

with three rinse chambers, two water rinses with a dilute acid rinse to neutralize the sodium hydroxide stripping solution.

Our tests indicate that this machine, with several other modifications, will strip an alkaline strippable UV ink and also have the ability to strip aqueous photo resist.

In summary, the benefits of UV resins used in circuit board manufacture:

1. Speeds up processing - fast cure rate, no wait time for processing second side of double sided board.

2. Cuts down dropout - cured ink is durable, reduces defects due to handling and plating.

3. No drying of ink in the screens. Ink covered screens can remain set up in the printers between shifts and overnight until the particular printing run is completed. This results in fewer screen setups and less ink waste. Also, printing voids due to clogged screens are virtually eliminated.

4. Saves electricity - we expect a savings of $18,000 a year in electricity alone by turning off our infrared ovens.

5. Floor space savings - our infrared system takes up 680 square feet of space compared to 30 for the UV.

6. Solvent free - essentially no exhaust to worry about except ozone and a small amount of the polymer that is vaporized.

7. Alkaline strippable - costly solvents not required.

G-3

ELECTRONICS
SESSION G

Acid Copper Sulfate Deposit Characteristics For Printed Wiring Board Applications

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ACID COPPER SULFATE DEPOSIT CHARACTERISTICS FOR PRINTED WIRING BOARD APPLICATIONS

By
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SEL-REX DIVISION OF OMI, NUTLEY, NJ

ABSTRACT

Acid copper solutions exhibiting high throwing power were developed primarily for printed wiring board applications. These systems produce 1:1 hole-to-surface deposit thickness ratios. Presently, the industry requires copper plating to provide (1) uniform thickness distribution, (2) deposit leveling, and (3) thermal shock resistance. This paper summarizes recent developments in acid copper sulfate deposit characteristics for printed wiring board applications.

INTRODUCTION

Brief History of Copper Electroplating For the Printed Wiring Board Industry.

From the 1940's to the 1960's copper pyrophosphate electroplating systems were used almost exclusively by the printed wiring board industry. The pyrophosphate system was widely accepted because it produced a 1:1 throwing power ratio.[1] This ratio represents equal thickness of copper on the surface and in the center of the hole on printed wiring boards. Throwing power requirements originated from the following needs:

1. Economic

If throwing power is inadequate, the minimum thickness requirement for the hole center would require an increase in the copper surface thickness, thereby, increasing cost. Cost increases would result not only from increased copper surface thickness, but also from increased usage of copper etchants.

2. Design

Uniformity of copper thickness in holes is important for acceptable component insertion. Poor throwing power can result in non-uniform copper thicknesses in holes which will result in poor component contact.

Uniformity of copper thicknesses across the board is also important since varied copper thicknesses will cause a preferential copper etch and result in undercutting circuit lines.

Despite their widespread early use, pyrophosphate copper systems exhibit the following undesirable features: (1) narrow pH range (8 to 8.6), (2) bath temperatures of 120-130°F, (3) need for waste treatment, (4) stringent analytical maintenance, and (5) pyrophosphate hydrolysis to orthophosphate, thereby requiring bailout. (Should the orthophosphate concentration reach 100g/l, the bath must either be diluted or discarded.)

Acid copper systems exhibiting a throwing power ratio of 1:1 have become widely accepted by printed wiring board manufacturers due to their benefits which include eliminating bail out, operation at room temperature, ease of control and waste treatment.

In this paper, we will discuss the following attributes of state-of-the-art acid copper systems: throwing power, distribution, leveling, thermal shock, resistance to contamination and deposit stress and hardness. These performance features are responsible for the widespread field acceptance and use of acid copper.

THROWING POWER

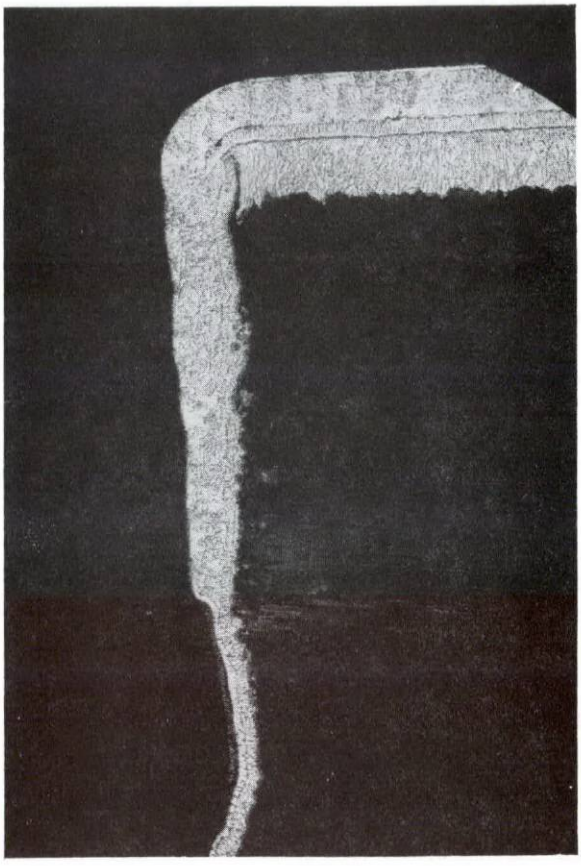
Throwing power is a key requirement due to economic and design needs. Traditional acid copper systems (used in decorative applications) did not meet throwing power requirements,[2] therefore, the electrolyte constituents were varied in order to improve throwing power. The following table contains constituents and amounts for "traditional" acid copper and "high throw" acid copper electrolytes.

	TRADITIONAL	HIGH THROW
Copper (Cu^{++}) (as sulfate)	56 g/l	19 g/l
Sulfuric Acid (H_2SO_4)	56 g/l	190 g/l
Chloride (Cl^-)	60 mg/l	60 mg/l

FIGURE 1

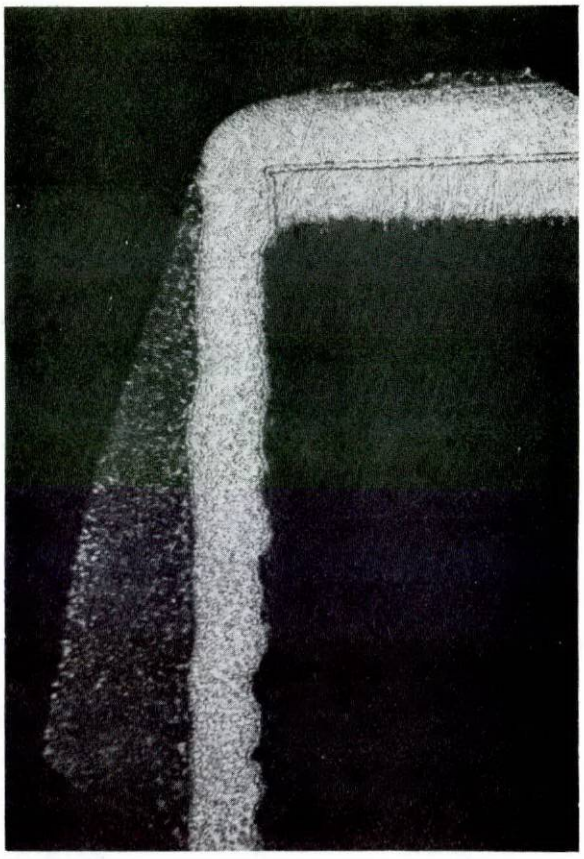
The key to good throwing power in acid sulfate systems is the ratio of acid to copper. A 10 (acid) to 1 (copper) ratio yields a 1:1 (hole to surface) copper thickness. The recommended range for copper concentration in "high throw" acid copper electrolyte is 15 to 23 g/l. Throwing power will decrease as the acid to copper ratio decreases. A minimum acceptable ratio is 8:1. At a less than 8:1 acid to copper ratio, throwing power will begin to degrade and the effect will be proportional to board thickness. Fig. 1 illustrates the throwing power ability of traditional and high throw acid copper systems.[2]

Routine analytical testing is used to monitor copper and sulfuric acid concentrations. From these quality control results, proper maintenance of a 10:1 (acid to copper) ratio will insure that throwing power requirements are fulfilled.



Less than 1:1 hole to surface deposit thickness.

HIGH THROW



1:1 Hole to surface deposit thickness.

THICKNESS DISTRIBUTION

The distribution of the copper deposit is to a large extent controlled by three main physical parameters of the plating system.

Anode-to-Cathode Ratio - In pattern plating, cathode area can vary from one side to the other. Anode-to-cathode ratio should be similar for each side to insure equal copper thicknesses. In production situations, this can be accomplished by alternating the image patterns of multiple boards on each rack. Distribution should be acceptable if a 1:1 to 3:1 anode-to-cathode ratio is maintained. A ratio of over 4:1 will increase the concentration of copper in the bath which will decrease the acid-to-copper ratio and adversely affect throwing power.

ANODE POSITIONING

Anode-to-cathode positioning should be eight inches nominally and not less than four inches. Anodes should be approximately three inches shorter than the cathodes. If the anodes exceed the three inch limit, copper will be preferentially plated at the lower edge of the cathode; thereby creating poor distributuon.

Racking

Poor rack design (for example, one contact point per board) will lead to varied current density on the cathode, thereby creating extreme thickness differences throughout the cathode. Good rack design (illustrated by spine-type racking containing multiple contact-points) will produce similar thicknesses throughout the cathode. Excellent racking (illustrated by envelope-type racking containing continuous contact points) will produce uniform thicknesses throughout the cathode. Distribution can be optimized by controlling the three main physical parameters. For example, a relatively difficult situation such as the plating of a 46x62 cm (18x24 inches) multilayer board having a thickness of 3.2 mm (0.125 inch) will produce the desired thickness across the board and within the holes within ± 15%.[9] Typical situations such as the plating

of a conventional double-sided board can produce the desired thickness within ± 10%.

STRUCTURE, LEVELING AND THERMAL SHOCK

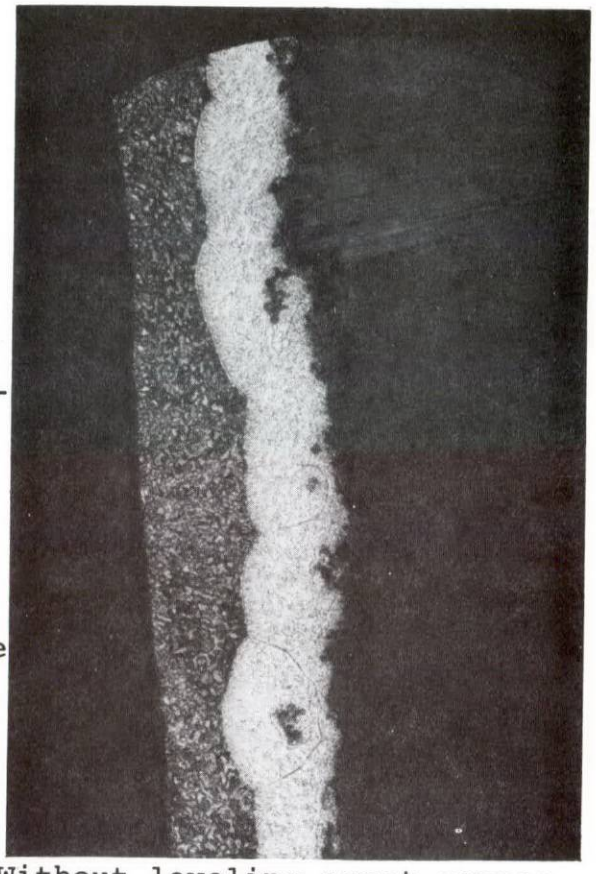
Additives are used in "high throw" acid copper systems to impart certain desirable characteristics such as equiaxed structure, leveling and resistance to thermal shock. A widely used system is a process consisting of 3 additives, they are: 1) carrying agent, 2) leveling agent, and 3) ductility promoting agent.

Deposit structure is important since an equiaxed type of grain structure has been found to be beneficial in thermal shock testing. Leveling is necessary to produce uniform wall surface throughout the hole and eliminate "fold-overs" in multi-layer boards.[7] Poor leveling can also lead to thermal shock failures. Thermal shock resistance is important to maintain copper continuity after reflow of printed wiring boards. A "cracked" copper deposit can lead to a discontinuous electrical circuit (open circuit).

All three additives contribute to the desired equiaxed copper structure.[3] The primary additive functions as a "carrying agent". The main function of the carrying agent is to guide the other two components to create an equiaxed structure. With insufficient levels of carrying agent, striations occur and other components can not function; therefore, the key to a well functioning acid copper is the carrying agent. Original acid copper systems used thiourea and related compounds as the carrying agents. Their stability in the high acid media was poor; therefore, a major concern in synthesizing a new carrying agent was to insure it's stability in the "high throw" acid copper electrolyte.

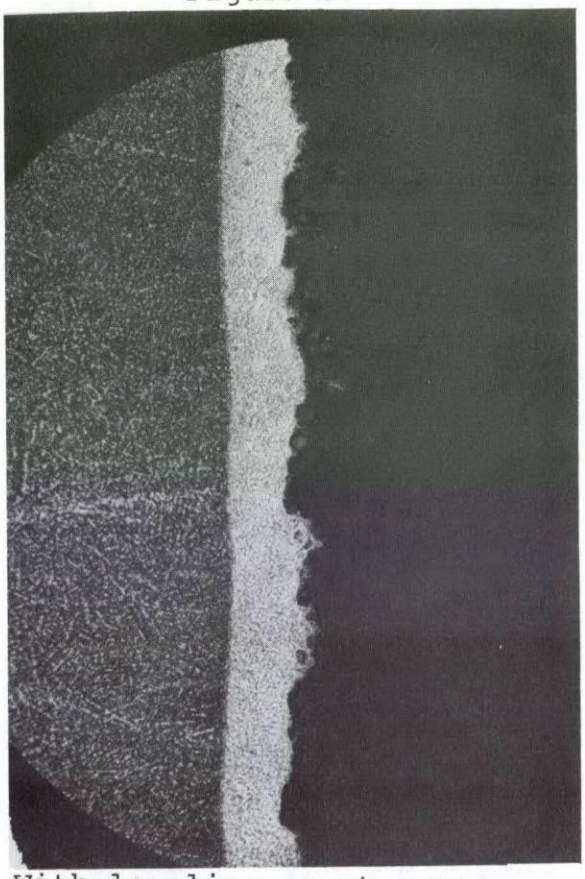
The leveling agent smooths over most barrel imperfections. This additive will increase copper coverage in deep drill tears. Figures 2 and 3 illustrate the role of the leveling agent.

Figure 2



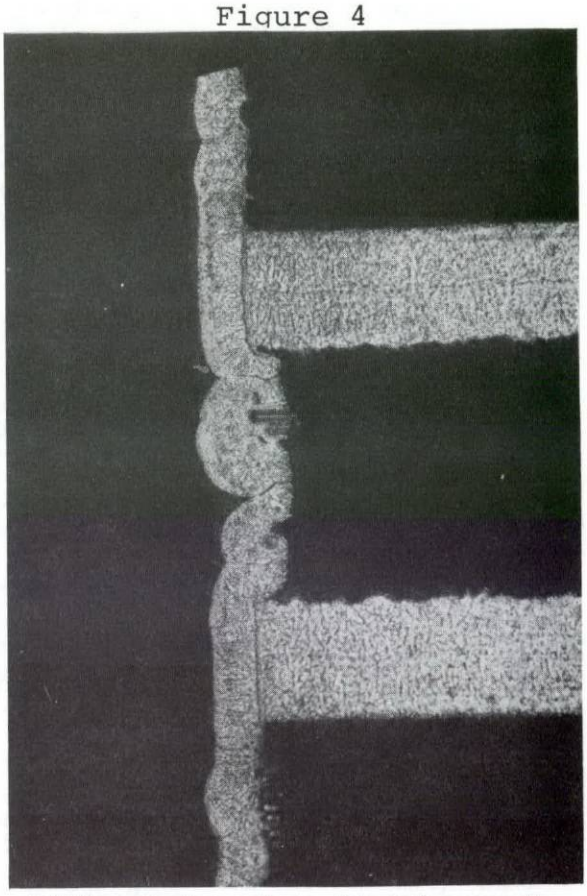
Without leveling agent copper deposit reproduces drilling imperfections

Figure 3



With leveling agent copper deposit smooths over drilling imperfections

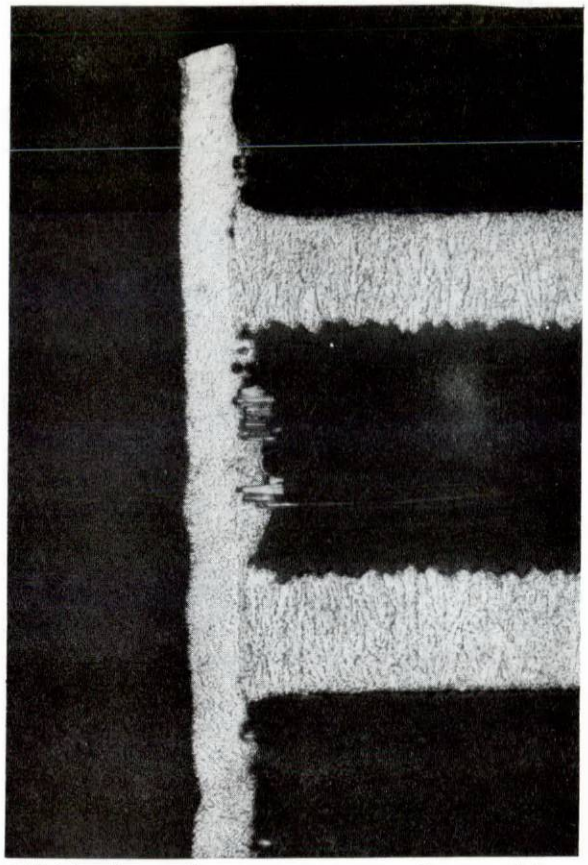
Figure 4



Without leveler "fold over" creates failures by non-uniform (bridged) copper deposits.

Figures 4 and 5 illustrate the roll of the leveling agent in eliminating "fold over" problems[4] in multilayer boards.

Fiqure 5



With leveler, copper deposit is uniform.

Dyes such as the Azo Class[8] have been used as leveling agents. Dyes present several problems such as, 1) possible harmful breakdown products, and 2) cross contamination into other tanks by leach-out from the racks. New leveling agents are polymers which do not stain or produce harmful breakdown products.

The third component functions as a ductility promoting additive to enhance thermal performance. This additive will produce uniform corners and create a deposit with equiaxed grain structure which consistently passes thermal shock testing.

Leveling, thermal shock and equiaxed structure are maintained by proper replenishment. In general, all three additives are combined into an optimized blend to facilitate replenishment. In unusal cases, special additive blends can be formulated-for example:

1. In multilayer boards a special blend favoring the thermal shock additive is used to insure acceptable thermal shock performance for boards with a 3.5 to 1 aspect ratio (depth to diameter).[3]
2. If drilling is a problem, the leveling agent can be favored to increase copper covering in deep drill tears.
3. To accommodate bath temperatures exceeding 80°F, special additive blends have been formulated to compensate for increased conductivity.

Acid copper systems are formulated with carrier, leveling and ductility promoting additives in order to fulfill printed wiring board requirements for copper deposits. All three contribute to the desired equiaxed structure and resulting properties.

RESISTANCE TO CONTAMINATION

An additive-free acid sulfate copper system has the capability of producing some of the desired deposit characteristics such as an equiaxed grain structure. The major drawback to an additive-free system, however, is that any contaminant introduced may produce an adverse effect such as striations. Since contamination in plating baths is not unusual, high throw acid copper systems were designed to be resistant to contamination. This resistance is related to

the following concept: Introducing preferential organics (such as additives) will outweigh the adverse effects of contamination and thereby impart the desired deposit characteristics.

Trace metallic contamination can alter the copper structure at hole/surface interface (corner). For example, iron contamination at 100 ppm is tolerable when the leveler and ductility promoting agent are present in the recommended range. If the leveler and ductility promoting agent are below the minimum required amounts, iron contamination produces columnar deposit structure at hole corners which can result in thermal shock failures.

In general, certain organic contamination (resist breakdown) can result on laminar copper deposits. Organic contamination is not as readily measurable as trace metallic, yet one can evaluate resistance to organic contamination by the infrequent need for carbon treatment. "High throw" acid copper systems have experienced a field life of over one year without any need for carbon treatment.

Deposit tensile strength and elongation measurements have been used as a means to predict the need for carbon treatment. Carbon treatment is generally necessary if elongation measurements fall below 8%. However, values above 8% do not necessarily assure good thermal shock performance.

A functioning acid copper system should produce the following values for a copper foil of 1 mil thickness: 275 to 310 Mpa tensile stress and (40,00 PSI to 45,000 PSI) 10 to 20% elongation.

To summarize, "high throw" acid copper systems were designed to combat amounts of contamination which could normally occur in a printed board manufacturing facility.

THERMAL SHOCK, STRESS AND HARDNESS

Since thermal shock has become a primary concern to printed wiring board manufacturers, the industry is looking for a means to predict acceptable thermal shock results. Among the methods investigated were stress and hardness measurements.

A study to determine whether stress or hardness values can predict thermal shock performance was conducted. Four systems were evaluated:

1. Electrolyte = no additives
2. Leveling System = carrying agent and leveling agent
3. Thermal shock system = carrying agent and ductility agent
4. Thermal shock and leveling combined system = carrying agent, leveling agent, and ductility agent.

The following table presents the results of this study.

Note: All measurements were taken at 1.5 mil copper thickness. In accordance with standard practice, positive tensile stress is represented by (+) and negative by (-).

SYSTEM	ELECTROLYTE	LEVELING SYSTEM		THERMAL SHOCK SYSTEM		THERMAL SHOCK LEVEL COMBINED	
ACTERISTICS	(NO ADDITIVES)	NEW *D	USED	NEW	USED	NEW	USED
NESS *A (25)	95	100	140	92	100	115	107
RNAL SS *B	+7.9 MPa	+19.7	+6.9	+ 35.2	-8.3	-16.6	-36.2
	+1140 PSI	+2850 PSI	+1000 PSI	+5100 PSI	-1200 PSI	-2400 PSI	-5247 PSI
AL SHOCK*C	POOR	POOR	POOR	GOOD	GOOD	GOOD	GOOD
ING *E	POOR	GOOD	GOOD	POOR	POOR	GOOD	GOOD

*A - Hardness measurements done using Knoop indenter with a 25g load.

*B - Internal Stress measurements done by I.S. meter.[5]

*C - 5cm x 5cm circuit board coupons were plated in a 3 liter test cell at 3 ASD for 1½ hours, then subjected to thermal shock testing.

*D - Testing done on "new" systems was performed at 0 ampere hours per 3 liters. "Used" systems were tested after 200 ampere hours per 3 liters.

*E - "Poor" leveling is characterized by the deposit's conformity to the irregularities of the circuit board surface. "Good" leveling is characterized by a smooth deposit, void of any influence of board irregularities.

To summarize these results: Hardness values were similar in all four systems; thermal shock performance could not be estimated by hardness testing. Systems which were formulated to withstand thermal shock testing exhibited stress values from 35.9 MPa compressive to 34.5 MPa tensile, yet systems failing thermal shock testing produced stress within these limits; therefore, thermal shock performance could not be estimated by measuring internal stress.

From the table, one can conclude that at present, the best way to determine whether copper

deposits have acceptable thermal shock results is to test them for thermal shock.

Modified stress or hardness testing may eventually lead to a way to estimate thermal shock results, but failures from epoxy smears or voids[6] may not be detected from these measurements; therefore, a thermal shock test followed by microsection appears to be the most reliable method for evaluating a copper deposit.

Future Requirements of the Printed Wiring Board Industry

A 15% growth rate in the industry indicates that printed wiring board manufacturers will require improved productivity. Obviously, manufacturers will prefer to increase production capacity while utilizing existing equipment. This goal can be accomplished through high speed plating, i.e., higher current densities which decrease plating time. Present high throw acid copper systems have been modified to operate at 6-9 ASD. These high speed formulations can double or triple present production capabilities for typical double sided rigid boards with only minor changes in electrolyte and physical parameters. Carrying agent, leveling agent and ductility promoting agent can be combined into an optimized blend for high speed applications. This system will continue to fulfill the current requirements for leveled deposits, quality thermal shock performance and uniform thickness distribution.

CONCLUSION

State-of-the-art acid copper systems have been developed to meet the demands and requirements of today's printed circuit board industry. Such characteristics as throwing power, thickness distribution, structure, leveling, thermal shock and resistance to contamination, have been optimized as they relate to electrolyte formulations, additives and physical parameters of the plating system. Correlation studies of internal stress and hardness with thermal shock performance indicate the need for functional tests on plated through holes as the preferred method for determining high reliability.

Our present knowledge of the capabilities of the high throw acid copper process leads to the optimistic projection that these versatile systems will meet future requirements of the printed wiring board industry.

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G-4

ELECTRONICS SESSION G

An Analysis of Procedures For Preserving Solderability

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AN ANALYSIS OF PROCEDURES FOR PRESERVING SOLDERABILITY

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SOLDERABILITY DEFINED

Solderability indicates the ease with which molten solder will wet the surface of the metals being joined. Wetting is a surface phenomenon which depends, among other factors, on surface cleanliness. When molten solder leaves a continuous permanent film on the metal surface, it is said to wet the surface. Wetting is facilitated by fluxing and solderability depends on the condition of the base metal. A more detailed discussion on wetting, fluxes, and solderability testing may be found in the literature. (References 1-2-3)

FLUXES

Most metals and alloys can be soldered provided a strong enough flux is employed. However, in most electronic applications, there are restrictions on the activity of the flux in order to protect the board and components and reduce contamination. The purpose of fluxing is to remove tarnish and oxide films from metals to be soldered and prevent further reoxidation before wetting takes place. Most fluxes are designed to remove only tarnish and oxide films, and not organic films such as oil or grease. If component leads are coated with organic films during fabrication, these must be removed by solvent cleaning before soldering.

When component leads incorporate metals or alloys that passivate, such as nickel iron alloys, fluxes that are active enough to produce a consistent and efficient soldering operation should be selected. In some cases, fully activated rosin fluxes may not be sufficiently active and acid fluxes must be employed. When this occurs the metal or alloy is usually coated with another metal so that soldering can be performed without highly corrosive acid fluxes.

Organic water soluble fluxes are the strongest type normally used in electronic soldering. The use of these types of fluxes have increased since recent improvements in their removal with water have been achieved. They can solder component leads that activated rosin fluxes cannot, but it is essential that their residues be thoroughly removed after soldering.

PRESERVING SOLDERABILITY

Since an organic water soluble flux that is cleanable is the strongest flux normally used in electronic soldering, the normal procedure is to coat a difficult-to-solder material with one that can be soldered with the flux used in the process.

Solderability indicates the ease with which molten solder will wet the surface. Environmental factors can affect solderability. The degree of oxidation of a particular metal is a major factor in its ability to be soldered. Conditions such as elevated temperature during fabrication can deteriorate the solderability of a component lead. Storage conditions in high humidity or a corrosive atmosphere are another major cause of solderability problems. (Reference 4)

The purpose of organic, electroplated, and hot solder coatings, is to prevent oxidation or tarnishing of the metal to be soldered. If this is acomplished then the soldering operation can be completed with efficiency with the relatively mild fluxes that are required for electronic soldering.

ROSIN COATING

Rosin or resin type protector coats can preserve solderability of the copper during in plant processing. However, such coatings were never intended for long term storage. If tarnishing of the copper occurs during storage, soldering can be a problem because the coating, although a mild flux, dilutes the activator content of the soldering flux. If soldering problems arise when this type of coating is present on a printed circuit board, it is usually suggested that the coating be removed and the copper surface precleaned prior to the soldering process. In wave soldering it is also important that adequate preheating be employed so that the activator in the soldering flux can be dispensed into the protective coating prior to soldering.

PRESERVING SOLDERABILITY WITH GOLD

Electrodeposited gold possesses superior corrosion and chemical resistance. Because of its high cost, however, relatively thin coatings are used. Coatings under 50 μ in. (1.3 μm) tend to be porous, thereby lowering the protective value of gold. Corrosion of the basis metal or barrier plate through the pores causes soldering problems because the gold dissolves completely during soldering, and it is difficult to wet the corroded basis metal underneath. Solderability also decreases with the amount of alloying elements that are codeposited with gold to increase hardness. Since most gold processes are proprietary, a solderability test is essential to determine if the codeposited addition agents are detrimental to solderability. Gold may cause brittleness in the solder connection because of the formation of the gold-tin intermetallic compounds, when the gold content of the solder fillet is over 5 per cent. Although the quantity of gold is small relative to the solder fillet, the compound forms at the interface between the plating and the gold. There is a complete loss of strength. This is not to say that gold, properly employed and controlled, has no place as a solderable coating. (References 5-6-7-8)

The escalating cost of gold in recent years has limited the use of this coating as a method of preserving solderability. However, there are

still some who feel that the cost of gold plating is compensated by other processing advantages. The widespread use of alkaline etching solutions enables a nickel coating with thin gold deposit 5-10 micro-inches to serve both as the etch resist coating and eliminates the need for a separate plating operation for the contact fingers. Nickel is essential for a barrier coating because gold in low thicknesses over copper would be too porous to act as an etch resist.

The main reason for use of nickel gold is to reduce cost by simplifying processing steps and improve reliability of the completed Printed Circuit Board.

IMMERSION TIN

Immersion tin is a coating applied over copper by a chemical process. The problem with this process is that it is not a true electroless process and there are limitations on the thickness of the coating. Normally a thickness of 30-50 microinches is the practical thickness that can be applied. The solution that deposits this coating acts as a cleaner and renders the copper solderable. However, a tin coating of under 50 microinches is normally not sufficient to provide corrosion protection for long term storage. Also, the tin alloys with the copper and can create an unsolderable condition during long term storage.

There is often a misunderstanding of the electroless process. It can be employed provided its limitations are thoroughly understood. If it could be applied with a thickness of 200-300 microinches, it would be an excellent process, but to date the technology to do this in a production process has not been developed.

SOLDER AND TIN PLATING

Tin and solder electrodeposits are employed to preserve solderability and to provide a solderable coating over metals that are difficult to solder. On printed circuit boards they also have the function of serving as etch resist metals.

BASE METAL PREPARATION

Cleaning the base metal prior to plating is extremely important when plating to preserve solderability.

During the soldering operation these coatings become completely molten and the quality of the bond formed (between the molten layer and the basis metal) depends entirely on the wetting mechanism. The cohesive forces that originally caused the plated layer to adhere to the basis metal surface are no longer present. The basis metal before plating must be a solderable surfce, or else dewetting is likely to result during subsequent soldering operations.

In any operation involving solder or tin plate, a simple solderability test of the basis metal immediately prior to plating is essential to determine the adequacy of the cleaning cycle. It is more economical to check a few parts than to have an entire day's production rejected for lack of solderability. Remember, repairing means stripping the plate and replating.

A proper cleaning cycle must be compatible with the basis metal and all other materials on the part, and it also must remove all organic and inorganic material from the basis metal. In addition, with a clean surface, a pore-free plate is assured. Therefore, cleaning is performed for two reasons -- to assure an active surface that will solder well at a later time and to protect against porosity that will cause corrosion during etching or during subsequent storage. Without cleaning, there is no purpose in plating.

Care should be taken in selecting a compatible cleaning cycle, one that will remove all foreign material from the surface, i.e., the cleaning materials must neither soften nor lift the plating resist nor dissolve the plastic laminate. Once such a cycle is established, it must be maintained. The concentrations of all solvents, cleaners, and acids should be maintained, and periodic dumping schedules must be established in order that the solutions do not become contaminated to the point of inefficiency. Solvents, cleaners, and acids are not expensive so it is economical and sensible to use fresh materials as required to eliminate the production of inferior work.

One method of determining the adequacy of a cleaning cycle is to take a part just before plating, dry it, apply water white rosin flux, and dip it into a solder pot. If its solders without dewetting, it is clean. If this simple test were performed more often, there would be a tremendous decrease in soldering problems occurring during the late stages of manufacturing.

Although the majority of soldering problems with both tin and solder electrodeposits are caused by inadequate cleaning prior to plating, control of the plating solution and use of both high purity chemicals and anodes, are essential for good results.

In both solder and tin coatings, organic addition agents must be controlled within narrow limits and periodic removal of organic breakdown products is required. If occluded organics are not minimize, outgassing during soldering will occur. (see Photomicrographs 1-2-3)

In most bright tin plating processes, it is essential to keep the operating temperature of the solution low to minimize the amount of occluded organics. In many cases refrigeration is used to keep both temperatures under (60°F 16°C).

In solder plating control of alloy composition is important. Current

density, type of addition agent, amount addition agent, and solution formulation, must be carefully controlled.

The alloy composition should be close to the eutectic alloy 63/37 to minimize reflow problems. A more detailed discussion may be found in literature.

Bright tin deposits have the advantage of providing a better contact surface than solder plate. They are also less susceptible to staining by handling. On printed circuit boards this coating over nickel is sometimes employed to eliminate gold on the contact fingers.

FUSED COATINGS

Tin-lead electrodeposits that are reflowed are usually between 300 to 500 microinches in thickness. This thickness provides adequate protection with a minimum of reflow problems. When printed circuit boards are reflowed, the tin-lead deposit forms a meniscus on the conductor pad. Because of this, the edges of the pad have a much thinner coating than the original plating, while the center is thicker. The average thickness is the same but it is distributed differently. As the plating thickness increases over 500 microinches, the surface forces are not always sufficient to hold the solder in this meniscus - especially on wide pads, the solder shifts upon solidification and the deposit appears uneven. On inspection, this may be mistaken for a dewetting condition, but it actually is a shifting of the molten solder before solidification.

When reflowing tin-lead with a thickness over 500 microinches, the boards must be in a horizontal position and withdrawn in a smooth manner. Otherwise, shifting of the molten solder is inevitable. Because of this problem, there is a practical limit on the coating thickness.

Improvements in infrared reflow equipment have increased the use of thick fused coatings in recent years. Reflowed tin-lead electrodeposits offer several advantages. One they provide is a 100% quality control check immediately after etching. By examining the boards after reflow, problems in hole drilling, cleaning procedures, plating, and etching can be detected and corrosive action taken immediately. This procedure has had a dramatic effect in improving PC board reliability.

Another benefit is that solder slivers are eliminated. During etching there is undercutting where the tin-lead coating overhangs the conductor pad. Under certain vibration conditions, this overhang can fall off and cause a short circuit. Fusing eliminates this condition and adds to circuit board reliability. (See Photomicrographs 4-5-6)

PROBLEMS IN REFLOWING PLATED COATINGS

Co-deposited impurities, especially copper in tin-lead, can cause dewetting in a reflowed deposit. Variations in alloy composition raise

the melting point and cause reflow problems. This is particularly true when organic contamination causes poor solution throwing power and resultant high lead deposit in the plated-thru holes. Heavy oxidation or tarnish films that result from chemical attack by etching solutions must be removed prior to reflowing. (Reference 9)

HOT SOLDER COATINGS

Hot solder coatings are becoming very popular since air leveling techniques for clearing the plated-thru holes of solder have been successful in keeping sufficient solder on the board to preserve solderability for extended periods of time. Before this method, the holes were cleared with hot oil or wax. The pressure required to do this caused most of the solder to be removed. The relatively thin coating that remained provided only limited shelf life.

The air leveling process requires a high purity solder and a flux that is designated for this process. The flux that has provided the best results to date is an organic water soluble flux with a non-volatile vehicle to reduce generation of smoke. It also should have residues that are easily removed by water and are biodegradable.

Roller tinning is a process that can apply a solder coating on one-sided and non-plated-thru hole printed circuit boards. The boards are fluxed and then passed through rollers coated with molten solder. Good solderability of the boards is essential because it is possible to apply the solder coating over an unsolderable surface.

SHELF LIFE

Work conducted at the Tin Research Institute in England using accelerated aging tests, indicated that both tin and solder electrodeposits provided the best shelf life. Roller tinning was fair but solderability rapidly deteriorated with immersion tin gold plating and rosin coating.

Fused coatings and hot dipped coatings that are air leveled were not listed. It expected that these coatings would provide better protection than tin or solder plating.(Reference 10)

SUMMARY

The most important ingredient for preserving solderability is base metal preparation, and the next is sufficient thickness. At least 250 microinches of either tin or solder is essential to preserve solderability for extended periods of time. Avoiding high humidity and sulfur containing environment, will also aid in providing better shelf life.

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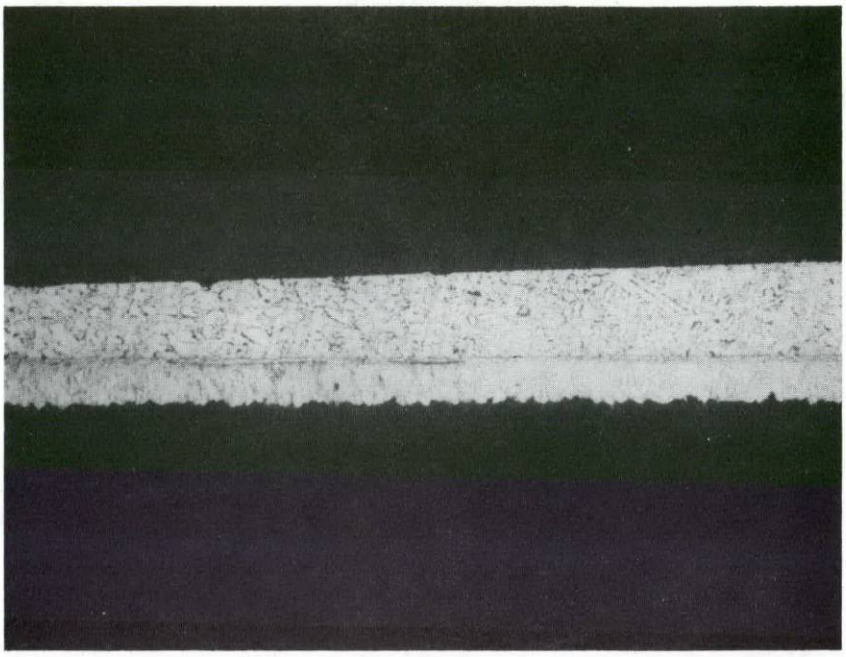

Figure 1, normal reflowed tin-lead deposit (80X magnification)

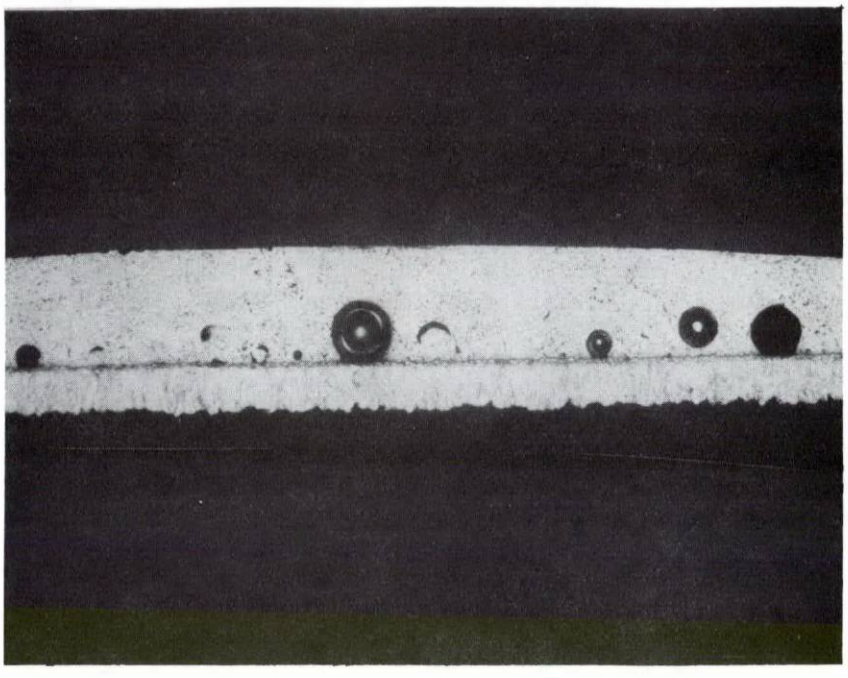

Figure 2, reflowed tin-lead with excess occluded organics (80X magnification)

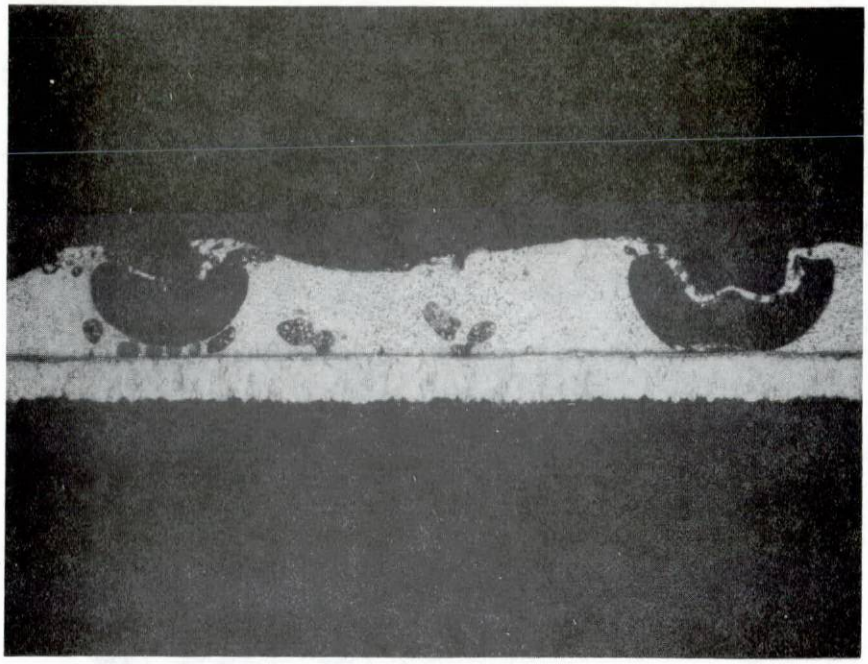

Figure 3, reflowed tin-lead with excess occluded organics causing outgassing (80X magnification)

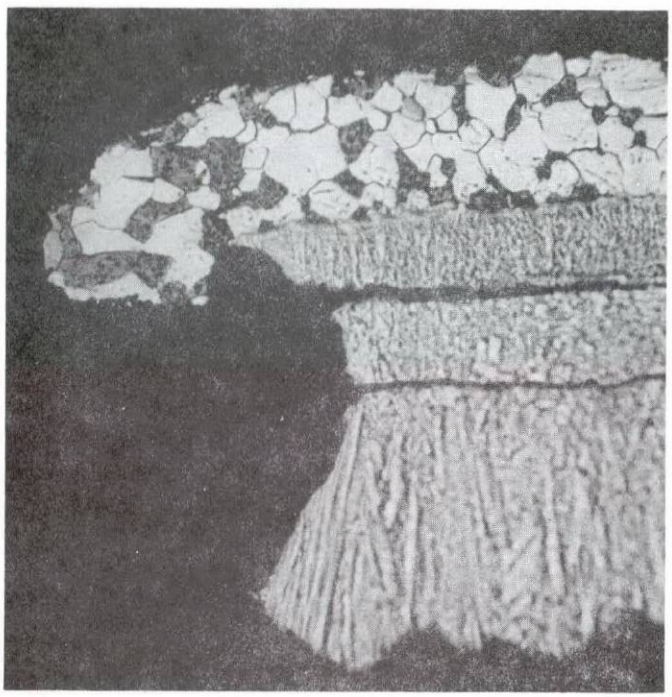

Figure 4, conductor pad after etching where tin-lead is the etch resist material. Note that undercutting causes solder sliver (667X magnification).

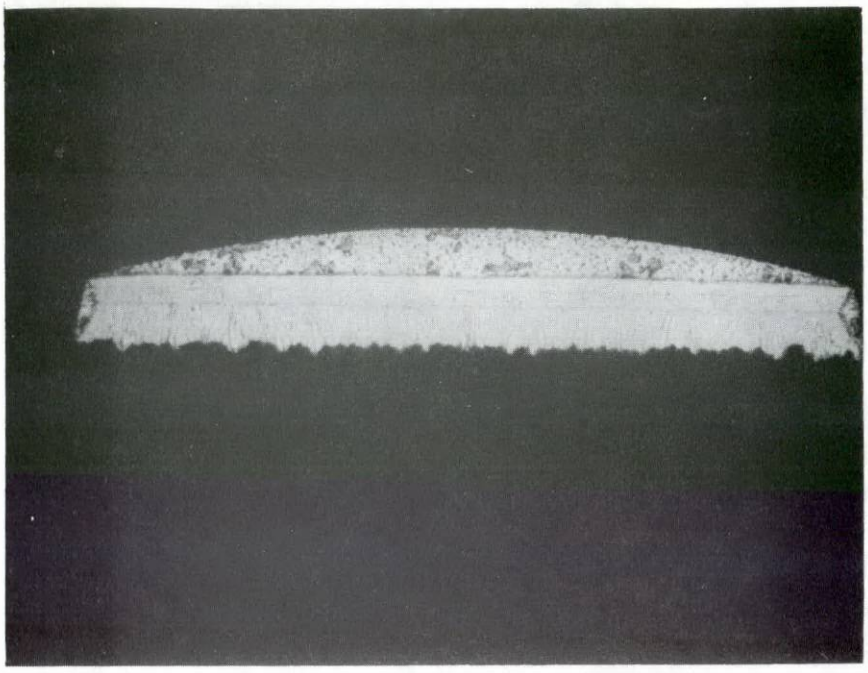

Figure 5, tin-lead deposit after reflow to remove solder sliver (200X magnification)

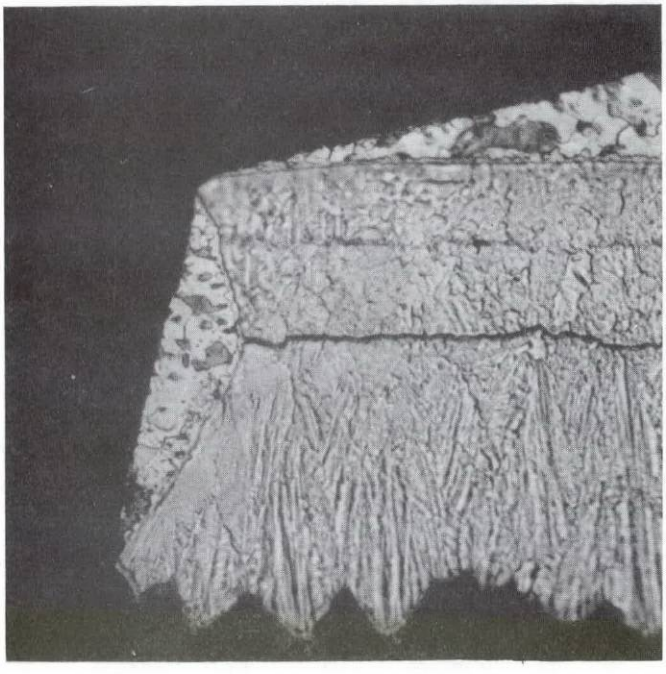

Figure 6, side of conductor pad after reflow. Fusing flux cleaned side of pad, causing solder coating (750 modification)

H-1

GENERAL INTEREST SESSION H

The Efficiency and Throwing Power Of Different Chloride Zinc Plating Baths

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"The Efficiency and Throwing Power of Different Chloride Zinc Plating Baths"

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Pavco Inc.
Cleveland, Ohio

Abstract

This study was undertaken to obtain quantitative values for the two most talked about properties of chloride zinc plating baths - high cathode efficiency and poor throwing power. The efficiency and throwing power measurements were made at three different current densities using a Haring cell. Three different alkaline zinc baths were also run in this study for the purpose of comparison.

Introduction

Chloride zinc plating baths are constantly gaining greater and greater acceptance in the U.S.A. There are many reasons for this but the two major ones are reduced waste treatment and improved economics. There is, however, one major drawback to chloride zinc systems, namely their poor throwing power, which is keeping them from even greater success and acceptance. In fact it is estimated that the chloride zinc market could be increased by up to 30 to 35% by the elimination or significant reduction of this one problem alone. It was for this reason that a study was undertaken to measure the throwing power and efficiency of different chloride zinc plating baths as compared to different alkaline zinc plating baths.

Since there tends to be some confusion as to what the term throwing power means, the meaning of this term is best explained at this time. Throwing power is, for all practical purposes, the ratio of metal deposited in the high current density versus the amount deposited in the low current density. It is not, as some people believe, the ability of a bath to "throw" into or cover deeply recessed areas. This later bath property is actually referred to as its covering power, which unlike throwing power, is very good for most chloride zinc baths.

Experimental

There is no laboratory method of measuring throwing power that exactly duplicates production results. There is however a commonly used laboratory method for measuring throwing power which has been shown to be good for comparison studies. This method was developed by Haring and Blum[1] and uses what is commonly referred to as a Haring cell. The Haring cell consists of a rectangular cell with cathodes at either end with an anode located at some point in between. The positioning of the anode is such that it is usually between 3 and 15 times further from one cathode than the other.

1) H.E. Haring and W. Blum, Trans. Electrochem. Soc., 44, 313 (1923)

The Haring cell used in this study was 6.7 cm. (2.6 in.) wide, 42.2 cm. (16.6 in.) long and 8.3 cm. (3.3in.) high. The anode to cathode distances were 7.0 cm. (2.8 in.) and 33.9 cm. (13.3 in.). A zinc slab 0.6 cm. (0.3 in.) thick, 6.7 cm. (2.6 in.) wide and 8.3 cm. (3.3 in.) high with 64-0.3 cm. (0.1 in.) holes for solution and current distribution was used as the anode. The cathodes were galvanized steel panels 6.4 cm. (2.5 in.) wide and 8.3 cm. (3.3 in.) high. For all tests, a solution volume of 1850 mls. was used which gave a solution depth of 6.7 cm. (2.6 in.).

Each of the plating baths was prepared in a 3 liter quantity using commercial grade chemicals. The composition of these baths is given in Tables 1 and 2. Three different chloride zinc baths were prepared representing the three major chloride electrolyte systems currently being used (see Table 1). The only factors which were varied between these baths were: 1) the type and level of electrolyte in order to maintain an approximately constant chloride content, 2) the use of boric acid in the potassium chloride bath, 3) the level of starter and brightner in the ammonium chloride bath were raised in order to get a commercially acceptable bath.

Three different alkaline zinc plating baths were prepared for use as comparisons for the chloride zinc baths (see Table 2). One of these was a typcial non cyanide formulation while another was a standard mid cyanide bath and the third was a low metal - high cyanide ratio bath. This later bath is used primarily in barrel plating where high throwing power is required.

Before the actual experimental runs were started, a series of throwing power and efficiency measurements were made to determine the reproducibility of the test method and technique used. The results of these runs are listed in Table 3 which shows the reproducibility of the test results to be quite acceptable.

Each bath was tested for throwing power and efficiency at three different current densities. The amperage for each run was set using a standard 0 to 5 amp. ammeter. An acid copper bath was also placed in series with the Haring cell for use as a coulometer. All of the efficiency and throwing power calculations in this study were made using the coulometer measurements as standards.

The acid copper bath used in the coulometer had a composition of:

Cupric Sulfate ($CuSO_4 \cdot 5H_2O$) gms./L (oz/gal) 209.7 (28.0)

Sulfuric Acid (SpG. 1.84) gms./L (oz/gal) 52.4 (7.0)

The coulometer itself was a standard duplicell with dimensions of 8.7 cm. (3.4 in.) wide, 10.2 cm. (4.0 in.) long and 6.8 cm. (2.7 in.) high. This cell was fitted with copper anodes, on each side (lenghtwise), and the

Table 1

CHLORIDE ZINC BATH COMPOSITIONS

COMPONENT	POTASSIUM CHLORIDE	MINI AMMONIA	AMMONIUM CHLORIDE
Zinc gms./L. (oz./gal.)	19.5 (2.6)	19.5 (2.6)	20.2 (2.7)
AMM. CHL. gms./L. (oz./gal.)		30.0 (4.0)	131.8 (17.6)
POT. CHL. gms./L. (oz./gal.)	185.0 (24.7)	151.3 (20.2)	
BORIC ACID gms./L. (oz./gal.)	33.7 (4.5)		
pH	5.1	5.1	5.2
STARTER %	3.0	3.0	3.5
BRIGHTENER %	0.1	0.1	0.2
TEMP. °F	73 ± 2	73 ± 2	73 ± 2
CHLORIDE gms./L. (oz./gal.)	109.1 (14.6)	113.0 (15.1)	109.3 (14.6)

Table 2

ALKALINE ZINC BATH COMPOSITIONS

COMPONENT	NON CYANIDE	MID CYANIDE	HI THROW CYANIDE
ZINC gms./L. (oz./gal.)	**11.2 (1.5)**	**19.5 (2.6)**	**11.2 (1.5)**
SOD. CYANIDE gms./L. (oz./gal.)		**47.9 (6.4)**	**33.7 (4.5)**
CAUSTIC gms./L. (oz./gal.)	**104.9 (14.0)**	**77.1 (10.3)**	**77.1 (10.3)**
STARTER %	**3.0**		
BRIGHTENER %	**0.2**	**0.25**	**0.25**
PURIFIER %		**0.15**	**0.15**
TEMP. °F	**73 ± 2**	**73 ± 2**	**73 ± 2**
CN / Zn RATIO		**2.46**	**3.0**

Table 3
REPRODUCIBILITY

	$\overline{X}$	σ_{n-1}
Throwing Power	**19.8**	**0.15**
% Average Efficiency	**96.2**	**0.36**
% Actual Efficiency	**94.6**	**0.69**

$$\sigma_{n-1} = \sqrt{\frac{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}{n-1}}$$

cathode was a copper plated steel panel 10 cm. (3.9 in.) by 6.5 cm. (2.6 in.) suspended parallel and halfway between the two anodes. A solution volume of 400 mls. was used, giving a depth of 5.5 cm. (2.2 in.).

Both near and far cathodes were used in the Haring cell for the determination of the throwing power and the average efficiency. For the determination of actual efficiencies, however, only the far cathode was used. The equations used to calculate the throwing power and efficiencies are show in Table 4. There are any number of equations that can be used to calculate throwing power, for this study however we used the equation proposed by S. Field[2] since this seems to be the most accepted and the one with which most people are familiar. With this equation, the condition of zero throwing power is defined as a plate distribution ratio equal to the ratio of the cathode to anode distances. A throwing power of 100% is defined as a plate distribution ratio equal to one.

Results

The results of the throwing power and efficiency measurements for the three chloride zinc baths are shown in figures 1, 2, and 3. The fourth plot on each of the graphs is an average of the three baths. Figure 1 is a plot of throwing power versus current density. This shows the potassium chloride and the mini ammonia baths to have the best throwing power in the barrel plating range of 0.5 to 1.2 A/dm^2 (4.6 to 11 A/ft^2). In the rack plating range of 1.5 to 4.5 A/dm^2 (14-42 A/ft^2) the potassium chloride and the ammonium chloride baths have the best throwing power. In general, all three baths decrease in throwing power with increasing current density. Although displaced slightly from each other, the average and actual efficiencies, as shown in figures 2 and 3, show the same trends for each bath. The average efficiency is the most significant of the two since it should be more representative of actual production conditions. The efficiency plot of the potassium chloride bath is different from the others in that it starts with the lowest average efficiency and steadily decreases with increasing current density. The average efficiency of the ammonia bath on the other hand decreases slightly, then increases slightly, with increasing current density -- while that of the mini ammonia bath remains fairly constant over the current density range tested.

Figures 4, 5, and 6 show the throwing power, average efficiency, and actual efficiency for the three alkaline zinc baths. Included with each figure is also a plot of the average values of the chloride zinc baths for comparison. Figure 4 shows the throwing powers of the various baths versus current density. In the very low current density range, the high throw cyanide bath has far superior throwing power, while the other two alkaline baths and the average chloride zinc baths are about the same. As the current density increases however, the throwing power of the alkaline baths also increases while that of the chloride zinc baths

2) S. Field, J. Electrodepositors' Tech. Soc. 7, 83 (1932)

Table 4
CALCULATIONS

$$\textbf{Throwing Power} = \frac{4.84 - D}{4.84 + D - 2} \times 100 \quad \textbf{(Field's Equation)}$$

$$4.84 = \frac{\text{Distance of Anode from Far Cathode}}{\text{Distance of Anode From Near Cathode}}$$

$$D = \frac{\text{Grams of Zinc Deposited on Near Cathode}}{\text{Grams of Zinc Deposited on Far Cathode}}$$

$$\textbf{Efficiency and Average Efficiency} = \frac{\textbf{Total Grams of Zinc Deposited}}{\textbf{Grams of Copper Deposited}} \times \frac{100}{1.2196} \times 1.1854$$

1.1854 = Grams of Cu^{++} Deposited in 1.0 Amp. Hr.

1.2196 = Grams of Zn^{++} Deposited in 1.0 Amp. Hr.

Figure 1

CHLORIDE ZINC THROWING POWER

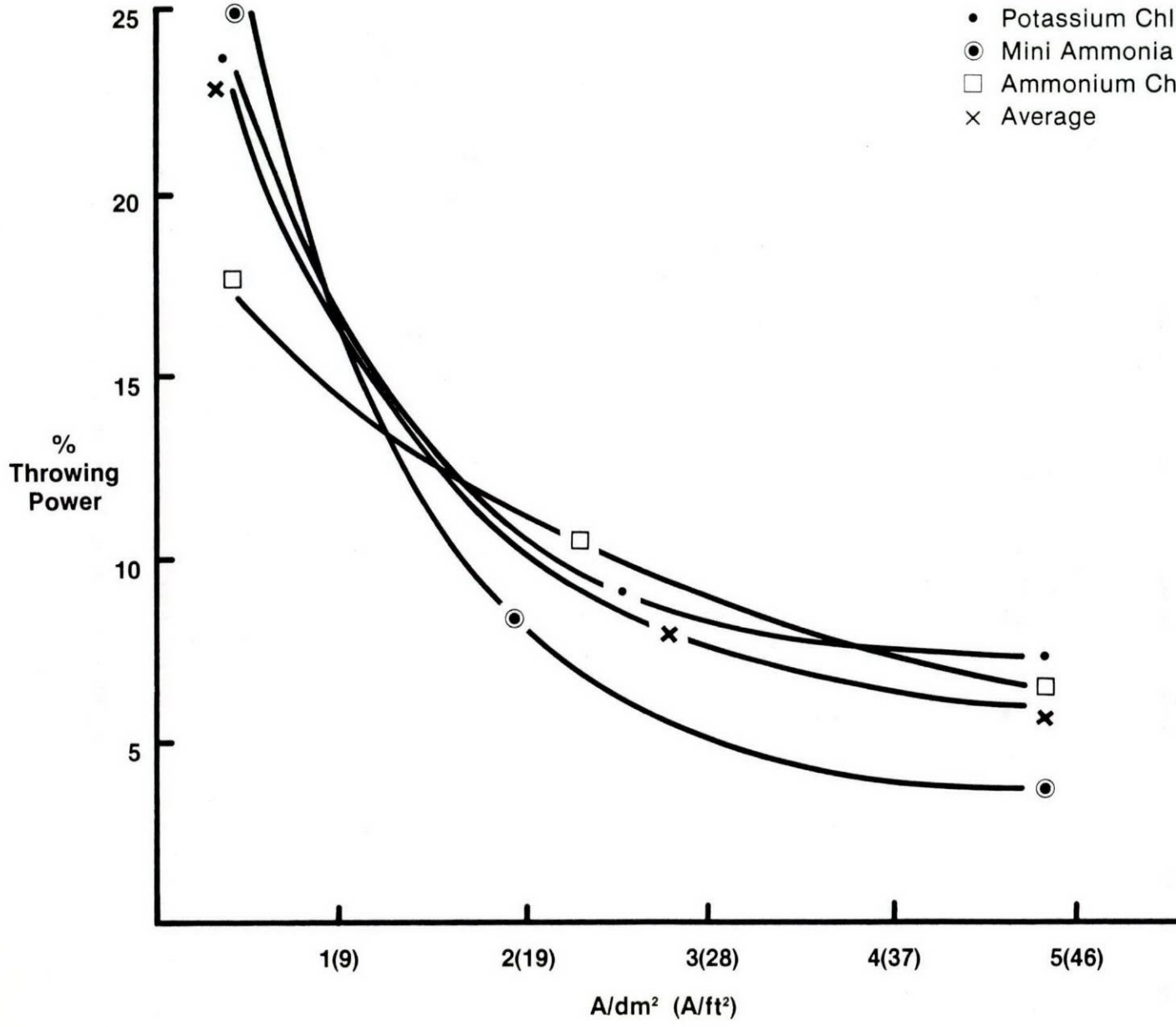


Figure 2

% AVERAGE EFFICIENCY OF CHLORIDE ZINCS

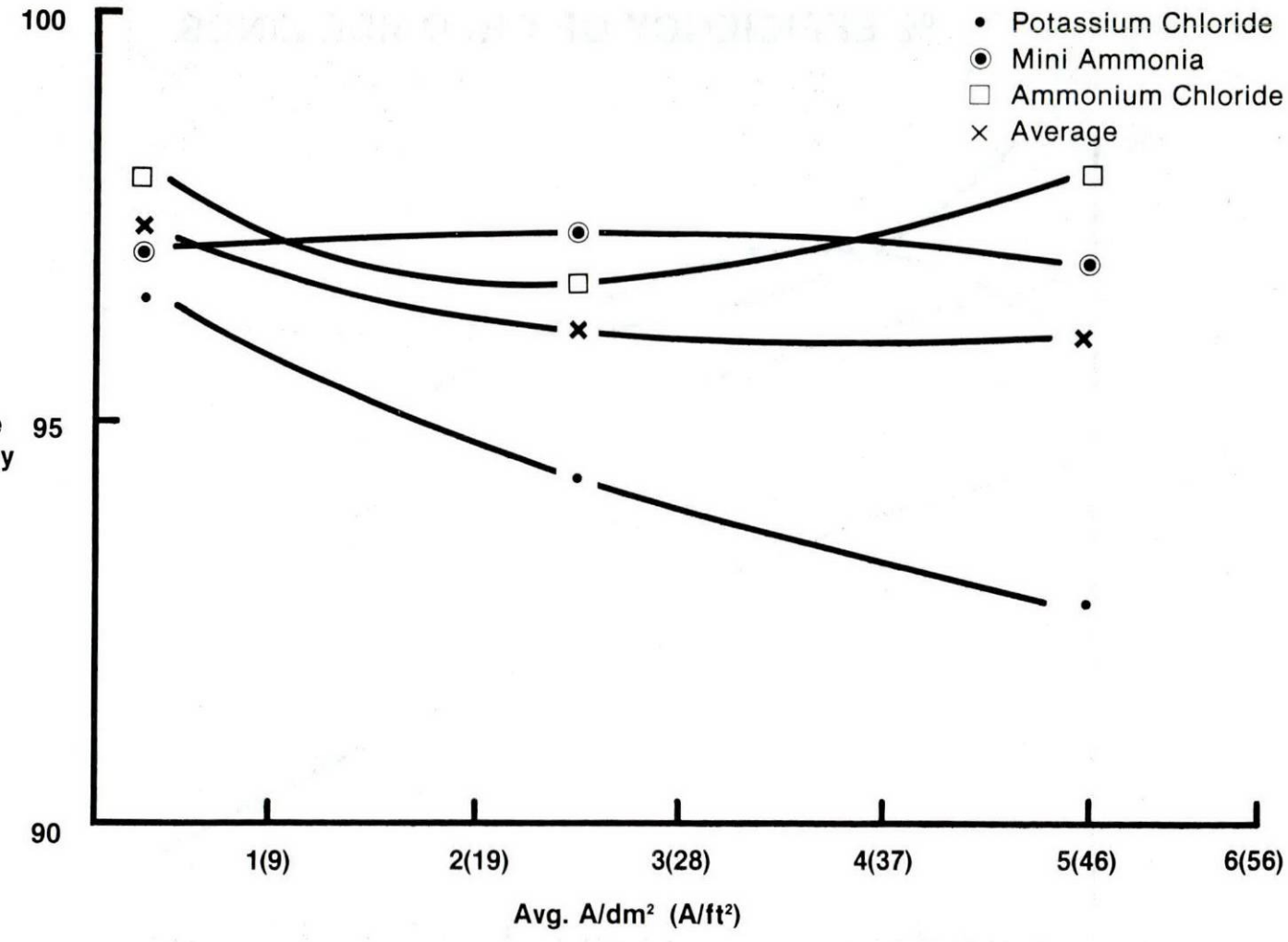


Figure 3

% EFFICIENCY OF CHLORIDE ZINCS

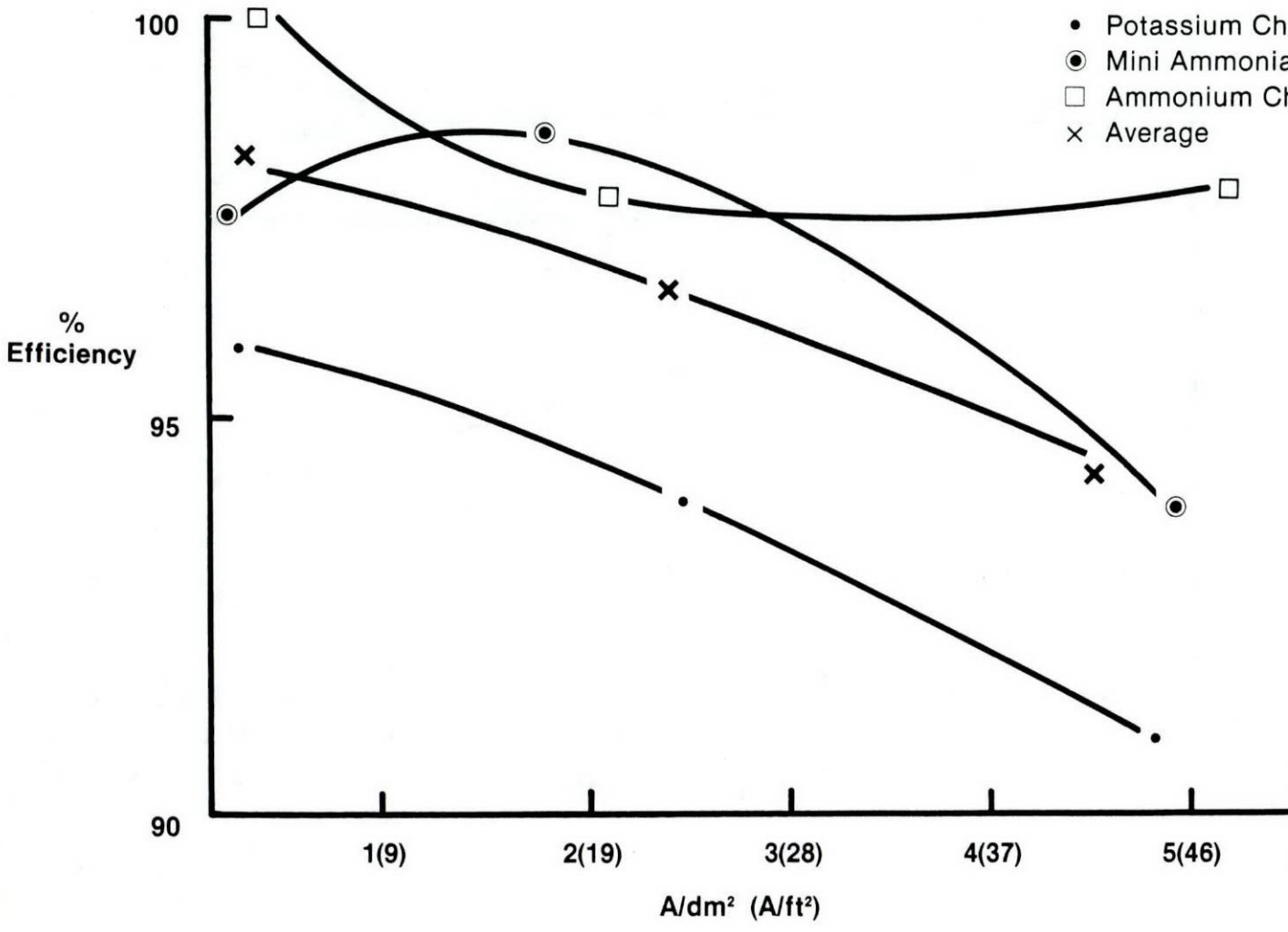


Figure 4

% THROWING POWER OF ALKALINE ZINCS

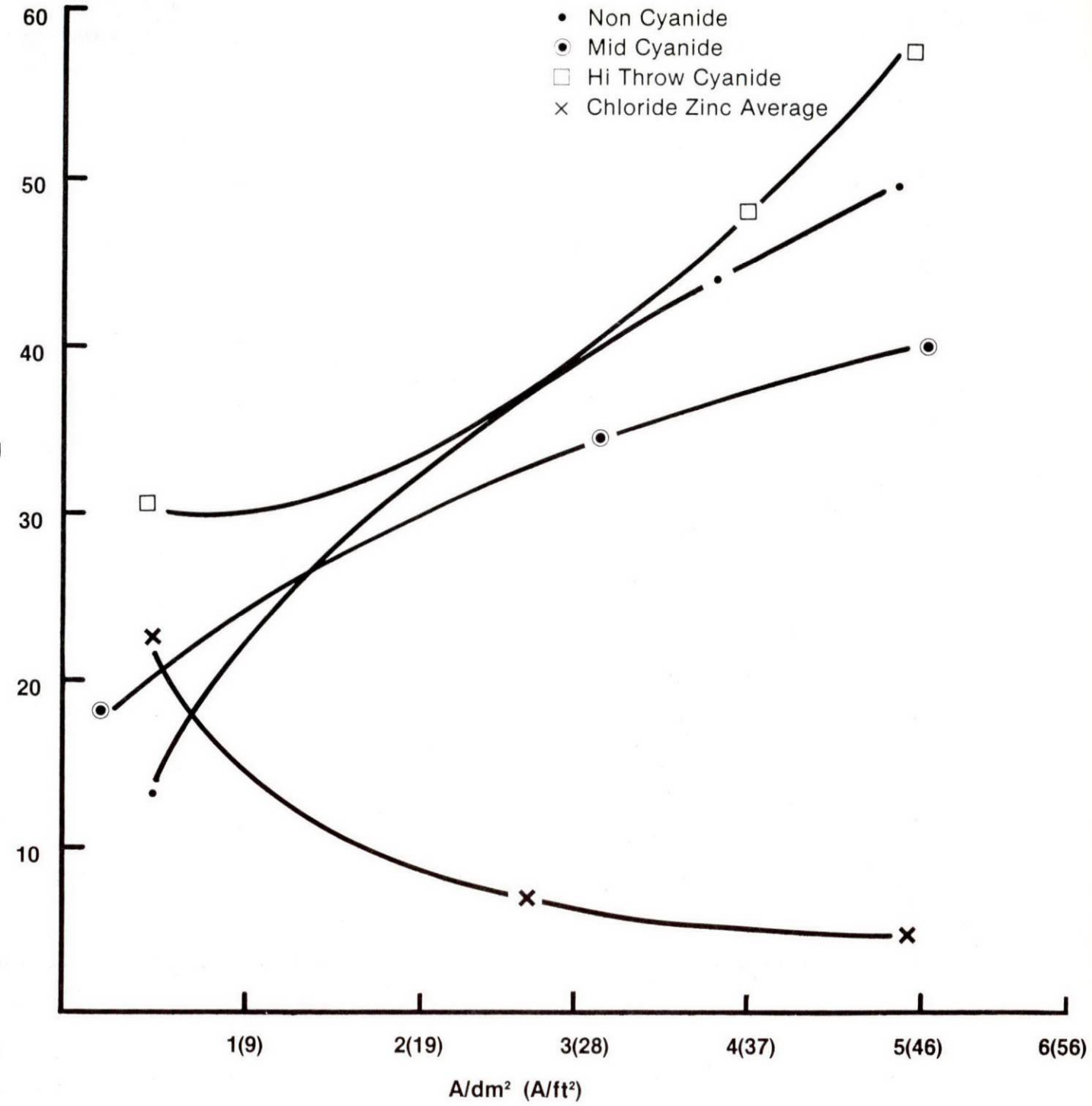


Figure 5

% AVERAGE EFFICIENCY OF ALKALINE ZINCS

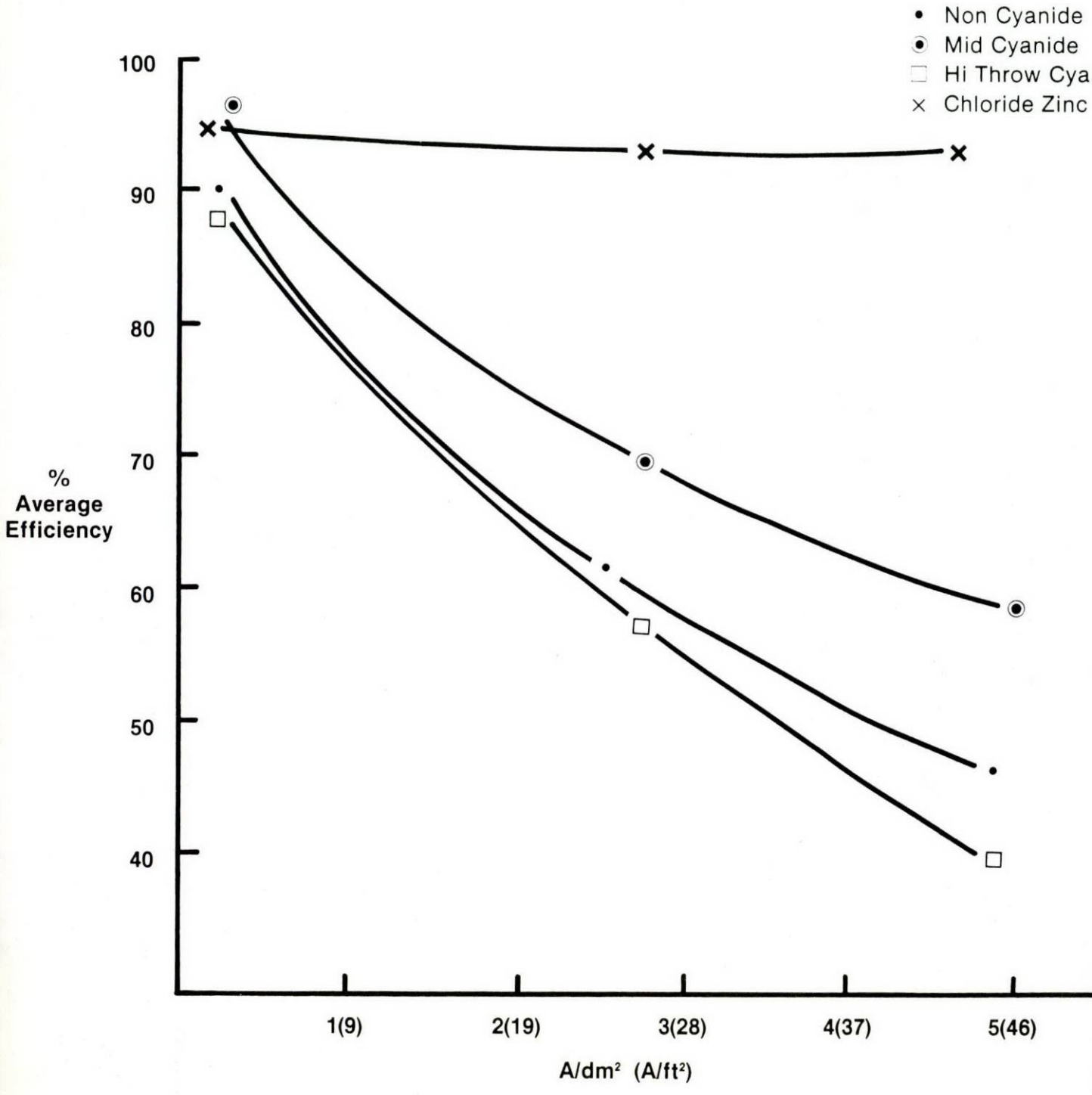
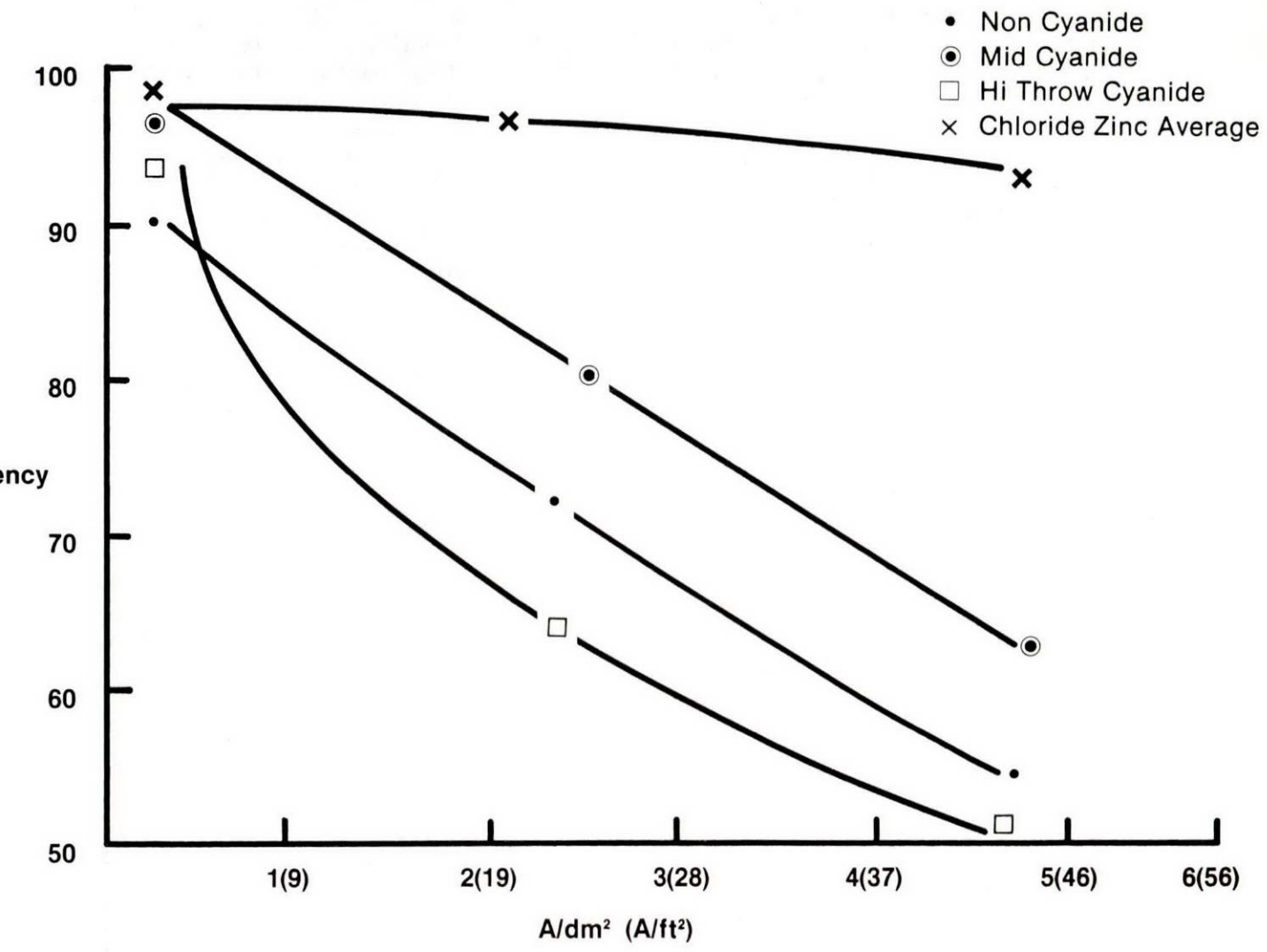


Figure 6

% EFFICIENCY OF ALKALINE ZINCS



decreases. As the current density increases, the non cyanide and the high throw cyanide converge, then diverge again in favor of the high throw cyanide bath. In the higher current density ranges, the mid-cyanide bath has the poorest throwing power of any of the alkaline baths but is still far better than the chloride zinc systems. Once again, the average efficiency and the actual efficiency results plotted in tables 5 and 6 show the same trends for all the alkaline baths. The average efficiency results (figure 5) are again of the most interest since they should be closer to actual production results. The average efficiency plots show that at low current densities, the chloride zinc and the mid-cyanide efficiencies are fairly close while the other alkaline baths are somewhat lower. As the current density increases, the chloride zinc efficiency remains fairly constant while the alkaline zinc efficiencies decrease drastically. All three alkaline baths lose efficiency at about the same rate with the mid-cyanide having the best efficiency and the two other baths being about equal to each other.

Conclusions

The following conclusions can be drawn from the data presented in this paper:

1) The throwing power of chloride zincs decreases with increasing current density while the opposite is true for the alkaline zincs.

2) All of the chloride zinc systems performed about the same except for the lower efficiency of the all potassium chloride system and the flatter throwing power curve of the all ammonium chloride system.

3) The efficiency of the chloride zinc systems is not significantly affected by current density but the efficiency of the alkaline systems drops considerably with increasing current density.

4) While some inprovement in the throwing power of the chloride zinc systems may be achieved by adjustment of the bath chemistry, it will not be as good as the alkaline zinc systems because of the differences in the shapes of the efficiency versus current density curves.

H-2

GENERAL INTEREST SESSION H

Electroplating of Bright Cadmium From a Non-Cyanide Bath

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ELECTROPLATING OF BRIGHT CADMIUM FROM A NON-CYANIDE BATH

Mirza L. Baig
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ABSTRACT

Bright cadmium is being plated commercially from a bath containing ammonium sulfate and a small quantity of chloride ions. The pH of the bath is maintained at 6.5 to 8.5. Over-all cathode efficiency of the bath with respect to the concentration of metal ions, sulfate ions, etc., is reported. The removal of cadmium metal from effluent by precipitation and filteration is discussed. Other features of the bath are also mentioned.

Introduction

Electroplating of cadmium from non-cyanide electrolytes has been known for quite some time, 1,2,4. Recent stress on cleaning of our environment through municipal, state and Federal regulatory agencies, more rigorous research efforts were directed towards the development of a practical bright cadmium plating process. As a result several processes have emerged, over the years, as alternatives to the well known cyanide based cadmium plating bath. In Table I are listed the approximate compositions of four of the more popular baths. Of these the bath No. IV only will be discussed in this paper.

This bath has been in commercial use since 1971 in automatic and manual barrel installations and in a manual rack plating line. Work plated in these baths ranges from stampings and fasteners to heat treated forgings and powder iron parts.

This study is primarily intended for the practical electroplaters most of whom do not have access to sophisticated research equipment. For this and other reasons the study of the plating current efficiency and the removal of cadmium metal from the effluent rinse water are the only aspects that are reported here.

Experimental Procedure

The electrolyte was prepared in distilled water, using USP grade ammonium chloride and ammonium sulfate and commercial grade cadmium oxide. The various additives were commercial grade chemicals either used as such or reacted in production quantities before use. The chemical nature of these additives

TABLE I

Compositions of Some Non-Cyanide Cadmium Plating Baths

Ingredients	Bath No.I Sulfate	Bath No.II Fluoborate	Bath No.III Neutral Chloride	Bath No.IV Neutral pH Sulfate
Cadmium	3.0 oz/gal 22.5 g/l	12.6 oz/gal 94.5 g/l	2.0 oz/gal 15 g/l	2.0 oz/gal 15 g/l
Amm. Fluoborate	--	9 oz/gal 60 g/l	--	--
Amm. Chloride	--	--	19-24 oz/gal 140-180 g/l	2-3 oz/gal 15-22.5 g/l
Amm. Sulfate	--	--	--	12-16 oz/gal 90-120 g/l
Make up Additive or Buffer	?	?	13% by vol.	10-15% by vol.
Boric Acid	--	3.6 oz/gal 27 g/l	--	--
pH	3.5 to 4.5 with Sulfuric Acid	3-3.5 with Fluo-Boric Acid	6.3 - 7.0	6 to 8.5

is of proprietary significance which prohibits their public disclosure.

Cathode current efficiency experiments were carried out in a 267 ml Hull Cell. D.C. power source was a laboratory size rectifier with an out-put of zero to 10 volts and zero to 25 amperes. An ampere meter with a zero to five ampere scale and calibrated to read 0.05 amperes was employed to measure plating current. The steel Hull Cell panels were cleaned, wiped dry with a clean towel and were weighed before and after plating on an analytical balance to determine the weight of electroplated cadmium.

The pH measurements were made with a Beckman "xero matic" pH meter.

The concentration of cadmium metal in the electrolyte before and after treatment was determined by an independent laboratory utilizing an atomic absorption apparatus.

To duplicate various effluent concentrations, one volume of the electrolyte of test No. 1 Table I was diluted respectively, with 1, 2, 4, 9, 29, 49 and 99 volumes of distilled water. Varying quantities of sodium hydroxide was added to known volumes of diluted samples to precipitate cadmium ions as cadmium hydroxide. Cadmium ions were also precipitated as cadmium sulfide by adding excess of sodium polysulfide solution. One of the above treated and filtered solutions and two untreated solutions to which only a very small amount of sodium hydroxide had been added (pH 9-10) were treated with polysulfide solution. Flocculent was added to enhance the settling of precipitated cadmium sulfide in two instances. The filtered solutions were analyzed to determine the unremoved cadmium.

Results

Plating efficiencies were measured for electrolytes containing varying amounts of cadmium metal, ammonium sulfate and buffering agent. Plating currents and plating times were as follows: 0.5 ampere and 1.0 ampere for 10 minutes each and 1.5 ampere for five minutes. Concentration of chloride ions as ammonium chloride was kept constant at 22.5 g per liter (3 ounces per gallon). These results are given in Table II and are plotted in Figs. 1, 2, 3 and 4.

Per Cent Cathode Efficiency = $\frac{w \times F}{2.097}$, where w is the weight of cadmium in grams deposited under experimental conditions; 2.097 is the weight of cadmium in grams deposited for one ampere-hour of plating current, if all the current had been used for depositing it; and F is the factor to convert ampere-minutes to one ampere-hour, $F = 60/i \times t$, where i is the plating current in ampere and t is the plating time in minutes.

In Table III are reported the concentrations of cadmium metal before and after treatment of the diluted electrolyte samples.

Discussion

"The cathode current efficiency is the ratio of the weight of metal actually deposited to that which would have resulted if all the current had been used for depositing it." In actual production plating the cathode efficiency which is influenced

TABLE II

Cathode current efficiency at various current densities with respect to concentration of cadmium metal, ammonium sulfate and buffering agent, concentration of ammonium chloride being constant at 22.5 g per liter and brightener at 1% by volume: pH 8.3.

Test No.	Cadmium g./l	Amm.Sulfate g./l	Buffer % by Vol.	Plating Current Amp	Plating Time Mins.	Per cent Cathode Efficiency
1.	7.5	90	10	0.5	10	72.0
2.	"	"	"	1.0	10	65.3
3.	"	"	"	1.5	5	66.5
4.	"	112.5	"	0.5	10	71.8
5.	"	"	"	1.0	10	71.1
6.	"	"	"	1.5	5	65.6
7.	"	90	15	0.5	10	68.2
8.	"	"	"	1.0	10	57.0
9.	"	"	"	1.5	5	48.3
10.	"	112.5	"	0.5	10	70.3
11.	"	"	"	1.0	10	62.0
12.	"	"	"	1.5	5	62.0
13.*	"	"	"	0.5	10	59.8
14.*	"	"	"	1.5	5	56.4
15.	11.25	90	10	0.5	10	76.5
16.	"	"	"	1.0	10	71.7
17.	"	"	"	1.5	5	67.3
18.	"	112.5	"	0.5	10	72.6
19.	"	"	"	1.0	10	75.6
20.	"	"	"	1.5	5	71.2

TABLE II- continued

Test No.	Cadmium g./l	Amm.Sulfate g./l	Buffer % by Vol.	Plating Current Amp	Plating Time Mins.	Per cent Cathode Efficiency
21.	11.25	90	15	0.5	10	70.0
22.	"	"	"	1.0	10	67.5
23.	"	"	"	1.5	5	66.75
24.	"	112.5	"	0.5	10	74.5
25.	"	"	"	1.0	10	71.8
26.	"	"	"	1.5	5	66.0
27.	15	"	10	0.5	10	84.0
28.	"	"	"	1.0	10	78.8
29.	"	"	"	1.5	5	80.2
30.	"	"	15	0.5	10	88.9
31.	"	"	"	1.0	10	78.6
32.	"	"	"	1.5	5	76.3
33.*	"	"	"	0.5	10	79.4
34.*	"	"	"	1.0	10	76.8
35.*	"	"	"	1.5	5	77.5
36.**	-	-	-	0.5	10	80.8
37.**	-	-	-	1.0	10	75.0
38.**	-	-	-	1.5	5	75.8
39.***	-	-	-	0.5	10	83.5
40.***	-	-	-	1.0	10	64.4
41.***	-	-	-	1.5	5	57.1

* Excess brightener

** Barrel plating bath (cadmium metal = 19.85 g/l, ammonium chloride = 19.5 g/l, ammonium sulfate = 80 g/l, iron as Fe = 0.217 g/l).

*** Cyanide rack plating bath (cadmium metal = 13.5 g/l, total sodium cyanide = 97.5 g/l, sodium hydroxide = 19.85 g/l).

TABLE - III

CONCENTRATION OF CADMIUM IN DILUTED

ELECTROLYTE BEFORE AND AFTER TREATMENT

Sample No.	Dilution	Before Treatment Calculated		Cadmium After Treatment Analyzed	Sodium Hydroxide Addition
		Buffer PPM	Cadmium PPM	PPM	g/L
1	1/1	25,000	3,750	100	200
2	1/1	25,000	3,750	50	250
3	1/2	16,667	2,500	452	200
4	1/2	16,667	2,500	60	256
5	1/4	10,000	1,500	1000	160
6	1/4	10,000	1,500	580	167
7	1/4	10,000	1,500	130	200
8	1/4	10,000	1,500	100	250
9	1/4	10,000	1,500	50	300
10	1/4	10,000	1,500	51	160*
11	1/4	10,000	1,500	less than 1	10**
12	1/9	5,000	750	61	300
13	1/29	1,667	250	35	220
14	1/29	1,667	250	24	250
15	1/49	1,000	150	30	200
16	1/99	500	75	2	0.5**

* Filtrate of sample No. 7 was further treated with excess of sodium polysulfide solution. Precipitated cadmium sulfide filtered.

** Cadmium sulfide precipitated with sodium polysulfide solution. Flocculent added to enhance settling and filtered.

by the distribution of the plating current on the entire surface of the work piece (cathode) is of real importance[3,5]. Because of the geometry of a cathode and its spacial relation to the surrounding cathodes, co-existance of current densities of differing magnitudes on its surface is imperative. These co-existing current densities would influence the distribution of the depositing metal. The use of robbers or thieves in electroplating is a consequence of this phenomenon. Under the light of this knowledge it is assumed that the cathode efficiency determined by means of the Hull Cell would predict the actual plating process more closely. Hence the adoption of this method for the determination of cathode efficiency of the bath No. IV. The plating efficiency thus obtained may be termed "the over-all cathode efficiency."

It is apparent from Fig. 1 that an electrolyte having metal concentration of about 7.5 g/l (one ounce per gallon), ammonium sulfate concentration of 112.5 g/l (15 ounces per gallon) and buffer concentration of 10% by volume exhibits higher over-all cathode efficiency. An increase in buffer concentration to 15% by volume reduces this value in all cases. But simultaneously lowering the ammonium sulfate concentration to 90 g/l lowers the cathode efficiency at all current densities; and more so for higher current densities. This is very essential for better uniformity of deposit on a part with complex geometry. The excess amount of brightening agent also reduces current efficiency at lower current densities but increases this value for higher current densities.

Analysis of Fig. 2 indicates an unpredictable pattern. Fig.3 shows that the performance of the electrolyte becomes more predictable when the concentration of cadmium metal reaches 15 g/l (2 ounces per gallon). Changes in concentration of ammonium sulfate, buffering agent and of brightening agent have similar influence on the over-all cathode efficiency as when concentration of cadmium metal in the electrolyte is about 7.5 g/l (one ounce per gallon).

A comparison of Figs. 1, 2 and 3 shows that if the concentration of ammonium sulfate is held at 112.5 g/l (15 ounces per gallon) and that of buffering agent at 15% by volume, the over-all cathode efficiency of the electrolyte with respect to metal concentration acquires a mathematical characteristic. This behavior is shown graphically in Fig.4. It can be seen that the plating efficiency of Bath No. IV increases with an increase in metal concentration and decreases with an increase in cathode current density.

Preliminary tests indicated that precipitation of cadmium hydroxide started slowly and only when the sodium hydroxide concentration reached 150 g per liter of the diluted solution

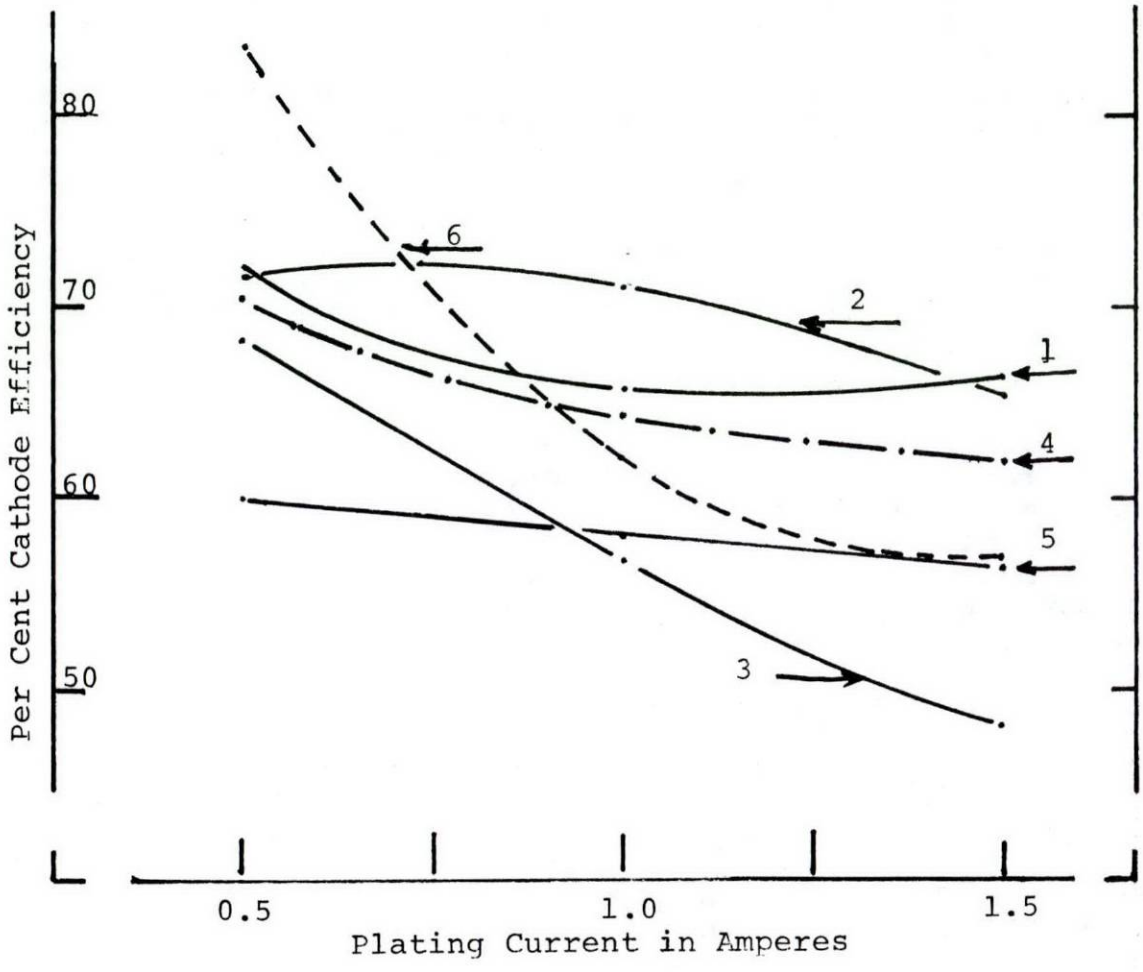

Fig. 1 Cadmium metal = 7.5 g/l,

	Ammonium Sulfate	Buffer
Curve 1	90.0 g/l	10% by vol.
Curve 2	112.5 "	10% "
Curve 3	90.0 "	15% "
Curve 4	112.5 "	15% "
Curve 5	112.5 "	15% " + Excess brightener
Curve 6	Cyanide Based Plating Bath	

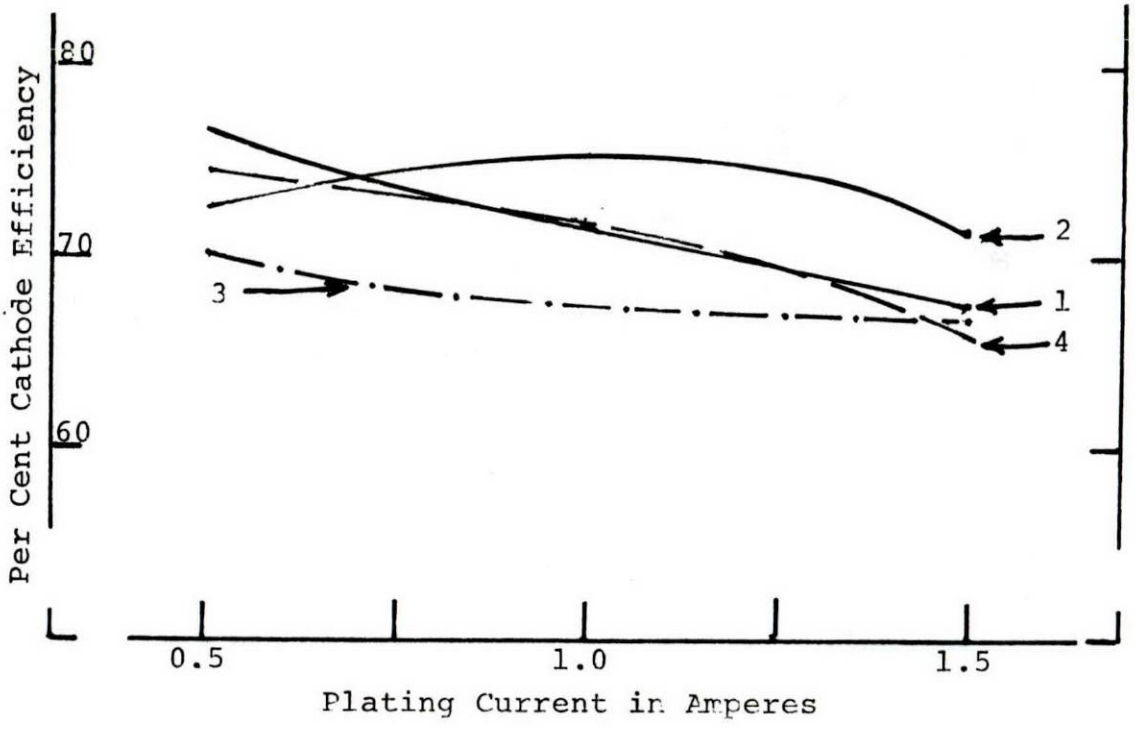

Fig. 2 Cadmium metal = 11.25 g/l

	Ammonium Sulfate	Buffer
Curve 1	90.0 g/l	10% by vol.
Curve 2	112.5 "	10% "
Curve 3	90.0 "	15% "
Curve 4	112.5 "	15% "

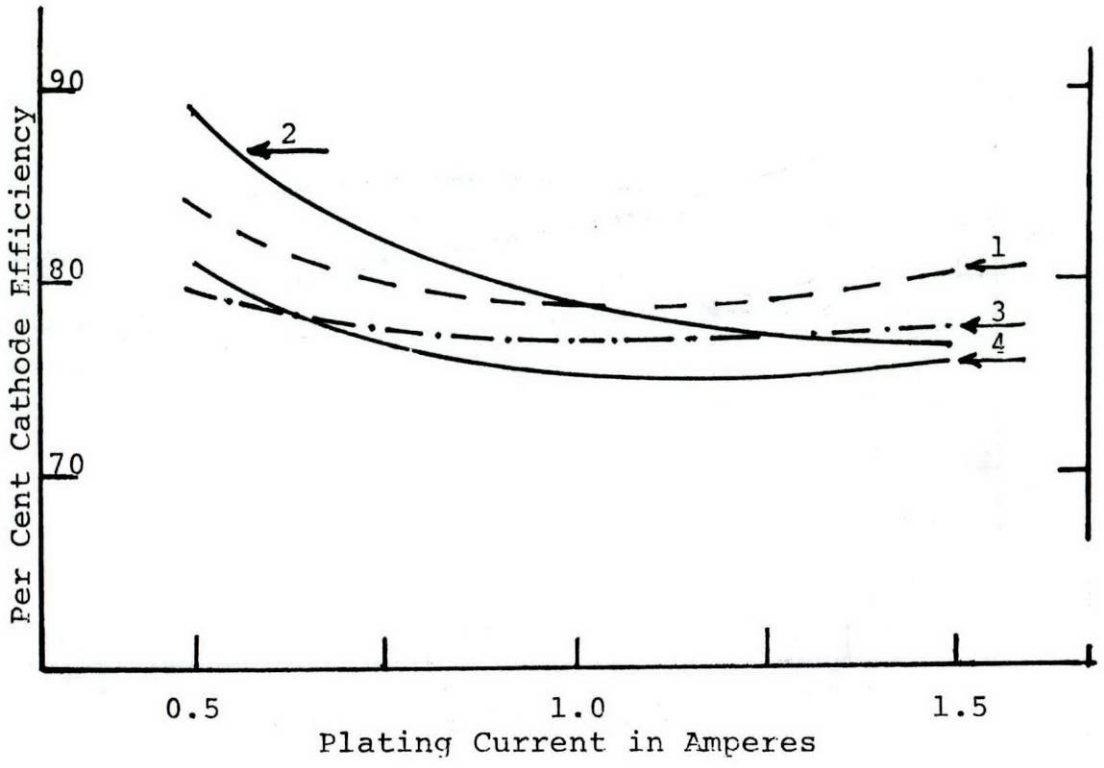

Fig. 3 Cadmium metal = 15 g/l

	Ammonium Sulfate	Buffer	
Curve 1	112.5 g/l	10% by vol.	
Curve 2	112.5 g/l	15% "	
Curve 3	112.5 "	15% "	+ Excess Brightener
Curve 4	80.0 "	?	+ Brightener ?

Cadmium metal= 19.85g/l

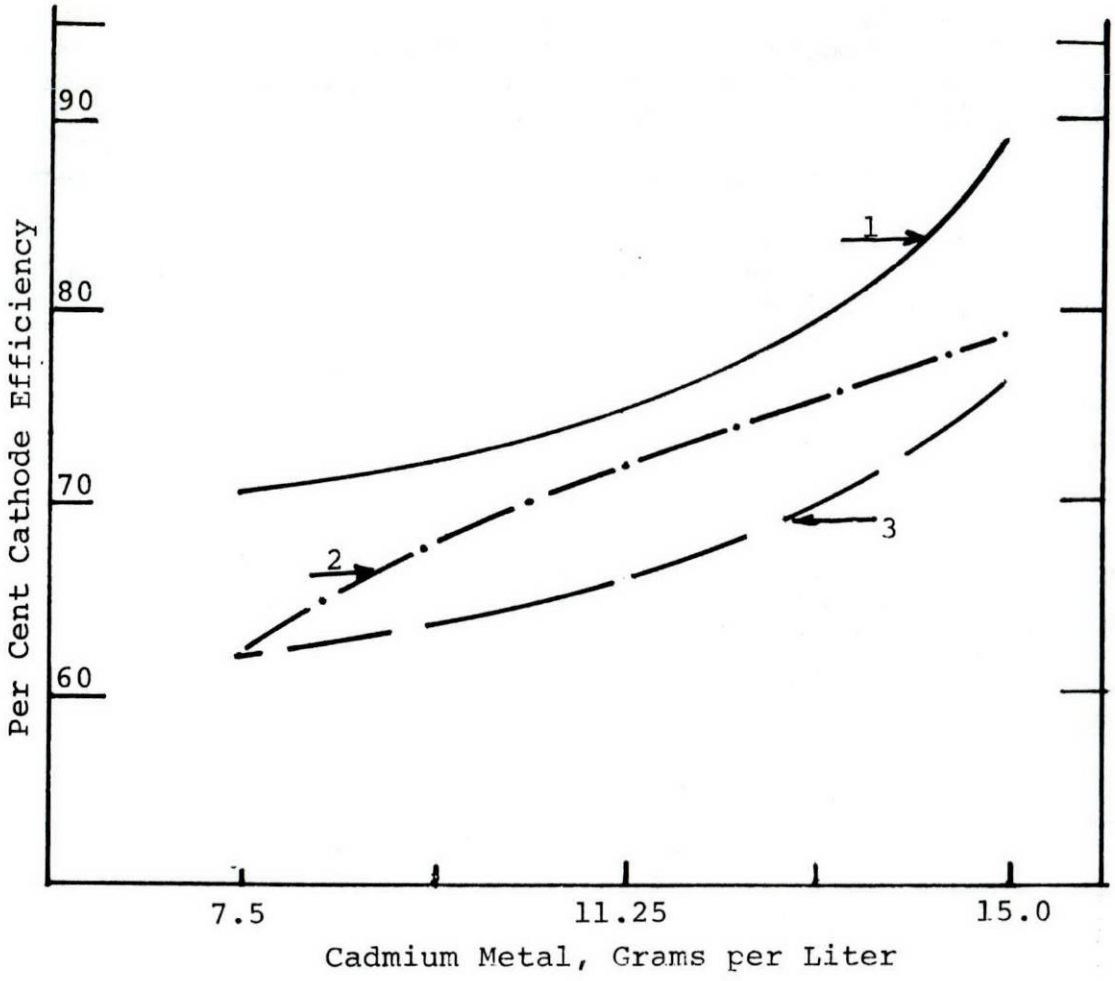

Fig. 4. Ammonium Sulfate = 112.5 g/l, Buffer = 15% by vol.

Curve 1 0.5 ampere, plating current
Curve 2 1.0 " " "
Curve 3 1.5 " " "

irrespective of the dilution factor. Precipitation was faster the higher the amount of sodium hydroxide added. When 250 g to 300 g of sodium hydroxide was added per liter of the diluted sample precipitation of cadmium hydroxide was instant and the separation of the precipitate from the mother liquor was rapid.

Data of Table III suggest that 200 g of sodium hydroxide per liter of diluted electrolyte is satisfactory for maximum removal of cadmium ions at all dilutions. However, at lower dilutions, 1/1 thru 1/9, higher the concentration of sodium hydroxide larger the removal of cadmium.

Sodium polysulfide treatment appears to be very effective on samples 11 and 16. In case of sample 10 the removal of cadmium is not encouraging. Perhaps, higher concentration of sodium hydroxide interferes in the precipitation of cadmium sulfide.

Present data are not sufficient to give conclusive results. However, there is enough information that may lead to a certain course of further study.

For the recovery of cadmium, drag-outs may be collected in a drip tank and treated in the manner of samples 1, 2, 4, 8 or 9, Table III. The precipitate may be filtered, washed and used to replenish the plating bath. The pH of the filtrate may then be reduced to between 9 and 10 (samples 11 and 16) and treated with excess solution of sodium polysulfide, or sodium sulfide to precipitate most of cadmium to meet effluent requirements.

If recovery of cadmium is not desired then diluted effluent may be treated with sodium sulfide or polysulfide solution and precipitated cadmium sulfide may be filtered.

Conclusion

An examination of data of Table II and III and of Figs. 1, 2, 3 and 4 leads to the following conclusions.

1. Electrolyte represented by curve 3 Fig. 1 would perform similar to the cyanide based electrolyte, curve 6 Fig. 1.
   Both electrolytes would tend to produce more uniform deposit in rack plating of parts of complex shape. However, it will take about 20% longer time to deposit x mm thick deposit from Bath No. IV as compared to the cyanide type electrolyte mentioned here.

2. For barrel type plating operation the metal concentration of the bath should be greater than 11.25 g/l, preferably 15 g/l for maximum production.

3. An increase in ammonium sulfate concentration increases the over-all cathode efficiency; so does an increase in metal concentration.

4. An increase in buffering agent concentration reduces cathode efficiency.

5. Excessive amount of brightener additions tend to reduce the cathode efficiency.

6. More data is needed to establish an efficient and economical procedure for effluent treatment. Nevertheless, the data collected so far and described here do suggest the possiblity of such a process.

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1. Metal Finishing Guidebook and Directory, Metal and Plastic Publication, Inc. 1979 issue, Page 186.

2. Modern Electroplating, editor, F.A. Lowenheim, Pub. Wiley-Interscience, 3 rd ed. 1973, pp 74, 80-81.

3. ibid., Page 7, Current Efficiency, Page 28, Current Distribution, Page 30, Metal Distribution.

4. Electrolplating Engineering Handbook, Editor, A.K. Graham, Pub. Reinhold Publishing Corp., 2nd. ed. 1962, Page 239, Table 4.

5. ibid., Chapter 16, PP. 480-490.

ACKNOWLEDGEMENT

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I-1

ELECTROLESS PLATING SESSION I

Evaluation of Nickel Boron as a Primary Finish on Component Leads

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EVALUATION OF NICKEL BORON AS A PRIMARY FINISH ON COMPONENT LEADS

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ABSTRACT

Electronics Laboratory has been involved in an evaluation of electroless nickel boron plating. Phase I involved the development of processes for the electroless deposition of nickel boron on Kovar. Phase II concerned itself with the plating of nickel boron on electronic component leads: flatpacks, TO-5 headers, and DIP's. The nickel boron coating on the component packages underwent testing to evaluate its use as a primary lead finish.

Introduction

During the past few years, electroless nickel plating has become increasingly popular for electronic parts. This is because no electric current is required and, therefore, more substrate materials can be plated, including plastics, ceramics, metals, and non-conductors. There are two principal types of binary electroless nickel solutions on the market: electroless nickel-phosphorous and electroless nickel boron. To date, the majority of information and knowledge accumulated about the use of electroless nickel has to do with nickel-phosphorous alloys. Since there has been a lack of manufacturing data regarding electroless nickel boron and its applications, the Physical Metallurgy Section of Electronics Laboratory had been committed to an intensive evaluation of nickel boron plating during the past year.[1]

The work effort being presented in this paper had been a two-fold study. Phase I concentrated on the cleaning and surface activation of Kovar base metal, and an in-depth study of the nickel boron plating parameters. Two nickel boron baths were evaluated. Bath I[2] produced deposits containing a maximum of 1% boron and Bath II[3] deposits contained 2-3% boron. The result of Phase I was the establishment of manufacturing process technology for electroless nickel boron plating on Kovar.

The second phase of the program tested the manufacturing process instruction developed in Phase I by plating electroless nickel boron on microelectronic packages, essentially flatpacks, TO-5 headers and dual-in-line packages. The nickel boron coating on the component packages underwent testing in order to evaluate its use as a primary lead finish. The tests included visual inspection, metallographic examination, adhesion, corrosion resistance, ductility, and solderability.

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[1] This work was supported by the Air Force Materials Laboratory, Dayton, Ohio, contract number F33615-78-C-5084.
[2] Shipley Company's NIPOSIT 468.
[3] Allied Kelite Company's NIKLAD 740.

Experimental Phase I

Nickel boron alloy can be obtained from an electroless plating solution through the chemical reduction of nickel ions from solutions containing boron. The boron in this study was dimethylamineborane (DMAB). This reaction takes place on an activated substrate, and requires no electric current as in electroplating, thus the ability is provided to plate on a variety of substrates. The substrate of interest throughout the program was Kovar, an iron (53%), nickel (29 ± 1%), cobalt 17 ± 1%) alloy which is widely used in the electronic industry for component leads.

1. Cleaning and Activation. Due to a tenacious oxide layer often found on Kovar components before plating, the cleaning and activation of the base metal was thoroughly investigated. All Kovar test samples were initially cleaned in a hot alkaline cleaner.[4] The parts were soaked at varying temperatures (60°-90°C) for varying times (3-15 minutes). Hot (80°-85°C) concentrated hydrochloric acid and dilute (25%-50%) hydrochloric acid solutions, operated from room temperature to 60°C, were evaluated for the activation of Kovar. Cathodic activation in a potassium nickel cyanide solution,[5] the use of a bright dip (1 part H_3PO_4, 1 part HNO_3, 1 part water), and a 25% sulfuric acid solution (70°C) were also evaluated following the hydrochloric acid soak. The cleaning and activation process selected for use is given in Table I.

TABLE I

Cleaning and Activation for Kovar

Solution	Conditions
1. Alkaline Soak Cleaner	80°C-85°C, 5-10 minutes, mild air agitation
Cold water rinse	2 minutes
2. 50% Hydrochloric Acid	55°-60°C, 5 minutes mild air agitation
Cold water rinse	2 minutes
3. 25% Sulfuric Acid	68°-72°C, 5 minutes, mild air agitation
Cold water rinse	1 minute

2. NiB Plating Bath Parameter Study. The electroless nickel boron solution parameters that were studied for Bath I and Bath II included pH, temperature, agitation, loading rate, and bath component composition. The percent boron in the nickel boron deposit was monitored by atomic absorption

[4] Enplate PC-453, Enthone, Inc.
[5] Sel-Rex Company process.

methods for each lot plated. A correlation was then drawn between bath parameters and deposit composition.

Two methods of agitation were evaluated, work rod agitation (moving the parts being plated through the NiB solutions) and a recirculating pump. They were evaluated individually and in combination. The work rod agitation moved the parts through the solution at varying rates between 6 and 15 feet/minute (1.6 ft/min intervals). Pumping rates of 25, 35, and 50 gallons/hour were used (25 gallons/hour is equal to 10 bath turnovers/hour). Results of these studies indicate that agitation is necessary to plate a pit-free deposit. As the amount of agitation is increased, the plating rate reaches a maximum (7 ft/min and 35 gal/hr) and then decreases with further increase in agitation.

Although sufficient agitation to maximize plating rate and minimize deposit pitting can be obtained by pumping the solution through a sparger, this method of agitation causes premature, spontaneous decomposition of the plating bath. Plating on tank walls is accelerated and plating on the interior of the pump system takes place. Mixing air into the solution through the pumping action is believed to be the cause of this increased solution activity. The manufacturers' technical data on the two plating baths (I and II) warn against the use of air agitation for this reason. Therefore, throughout the remainder of the program, work rod agitation at the rate of 11 ft/min (3.35 m/min) was used.

The operating temperature and pH of Bath I were varied over the entire range recommended by the manufacturer. At constant pH, the plating rate and boron content in the deposit increased with elevated temperature. At constant temperature, the pH does not significantly affect the deposition rate but the boron content in the deposit decreases as the pH is increased.

The operating temperature and pH of Bath II were varied over the entire range recommended by the manufacturer. At constant pH, the plating rate and boron content in the deposit increased with elevated temperature. At constant temperature, the plating rate increased and the boron content in the deposit decreased as the pH of the nickel boron solution rose. Loading of Bath I was varied from 0.1 to 0.8 ft^2/gal, (manufacturer's recommended range 0.25 to 0.50 ft^2/gal), while the loading of Bath II was varied from 0.1 to 1.0 ft^2/gal (manufacturer's recommended range 0.25 to 1.0 ft^2/gal with 0.6 ft^2/gal the optimum). No significant effect on deposition rate was evident. Only with Bath II, the boron content in the deposit decreased as the loading rate was increased.

The last parameter to be investigated was the nickel boron solution's composition. Bath I is controlled by quantitative analysis (titration) to determine the bath activity; that is, the amount of metal (nickel) and reducer (boron) present in solution relative to the manufacturer's recommended amounts for the bath (100% activity). In this study, the bath activity was varied from 60% to 120% with both components in balance and also an imbalance of $\pm$ 10% of each component.

Bath II was also controlled by determination of bath activity by quantitative chemical analyses. In this study, the metal component activity was varied from 80 to 120% and the reducer component was varied from 4 to 7% (5% optimum) at each metal component activity level studied. Table II gives the results of the nickel boron bath activity study and Table III lists the optimum plating process for Bath I and Bath II.

TABLE II

Nickel Boron Bath Activity

Bath I

1. Deposition rate increases with increased bath activity.
2. Boron content in the deposit decreases with increased bath activity.
3. Imbalance of bath components increases boron content in the deposit.
4. An excess of reducer component increases the amount of cracks in the deposit.

Bath II

1. No trends were evident in the data from the study of bath activity and reducer.

TABLE III

Plating Process for Nickel Boron

Parameter	Bath I	Bath II
pH	7.0 - 7.2	5.9 - 6.1
Temperature	66° ± 1°C (150° ± 2°F)	71° ± 1°C (160° ± 2°F)
Activity	95 ± 1%	95 ± 1% (RM 4.8 - 5.0%)
Agitation	Work Rod 3.35 ± .15 m/min (11 ± .5 ft/min)	Work Rod 3.35 ± .15 m/min (11 ± .15 ft/min)
Loading Rate	61.4 to 122.7 cm^2/l (0.25 to 0.50 ft^2/gal)	61.4 to 122.7 cm^2/l (0.25 to 0.50 ft^2/gal)

3. Deposit Testing. In addition to the optimization of the plating process in Phase I, some preliminary testing of the nickel boron deposit was done. The tests included metallographic examination, adhesion testings, ductility and solderability. Deposit cracking as shown by metallographic cross-section (microcracking) was visible in the nickel boron deposit from both baths. Some transverse cracks were seen in the deposit on all samples cross-sectioned from both baths and varied from an occasional crack (Fig. 1a) to heavily cracked (Fig. 1b). Longitudinal cracks were most evident in deposits with heavy transverse cracking (Fig. 1b). The deposit thickness in Figure 1a is 250 µin, evenly distributed, and has a good interface with the substrate, Kovar. Figure 1b is 250 µinches thick.



Figure 1a 400X

Nickel boron as plated on Kovar.

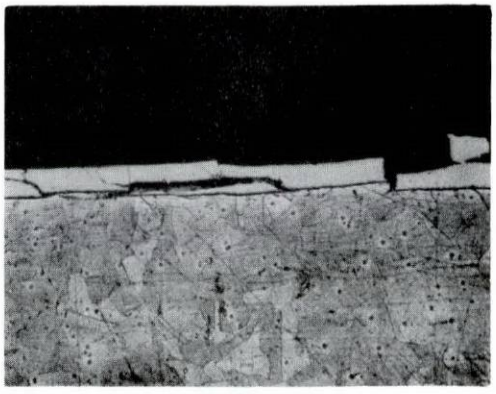


Figure 1b 400X

Nickel boron as plated on Kovar.

Adhesion testing of the nickel boron deposit was accomplished by bending the panel through an angle of 180° over a diameter equal to the thickness of the specimen. The area was then examined at 14X magnification and showed no flaking or peeling of nickel boron from the Kovar.

Ductility tests were conducted by bending the deposit 45°-90° and viewing at 14X magnification for cracks in the deposit bend area. Two (2) types of crack formation were always noted. Figure 2a is an example of transverse cracking in the bend area and Figure 2b is an example of network cracking.

Initial solderability test results, using 63 tin solder and flux types R, RMA and RA were not encouraging, as evidenced by the pictures in Figures 3a and 3b.

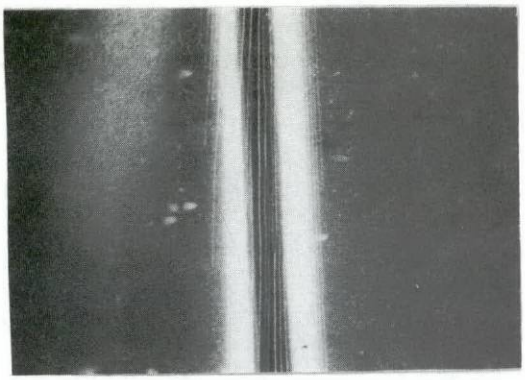


Figure 2a. Transverse Crack

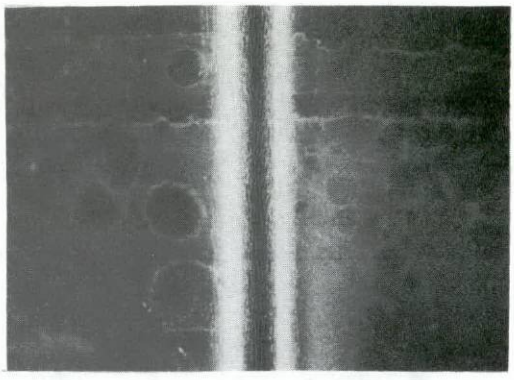


Figure 2b. Network Crack

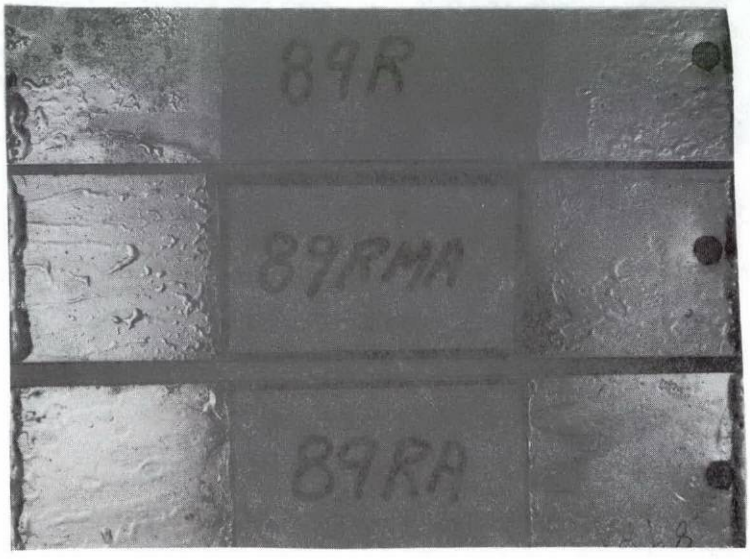


Figure 3a. Bath I Solderability



Figure 3b. Bath II Solderability

The right side of the sample was tested before aging and the left side after 1 hr steam-aging. Only 30% of the as-plated samples passed solderability criterion using an RA flux. Less than 10% of the samples passed after steam-aging with an RA flux. No samples passed with R or RMA flux.

The final result of Phase I was the establishment of an optimum nickel boron plating process that can be reproduced and applied to manufacturing technology.

Experimental Phase II

1. Verification of Nickel Boron Manufacturing Technology. Phase II concerned itself with applying the nickel boron manufacturing technology developed in Phase I to the plating of nickel boron coatings on electronic component leads, essentially flatpacks, TO-5 headers, and dual-in-line packages (DIP's). To simulate production conditions, a pilot nickel-boron plating line was designed, as shown in Figure 4.

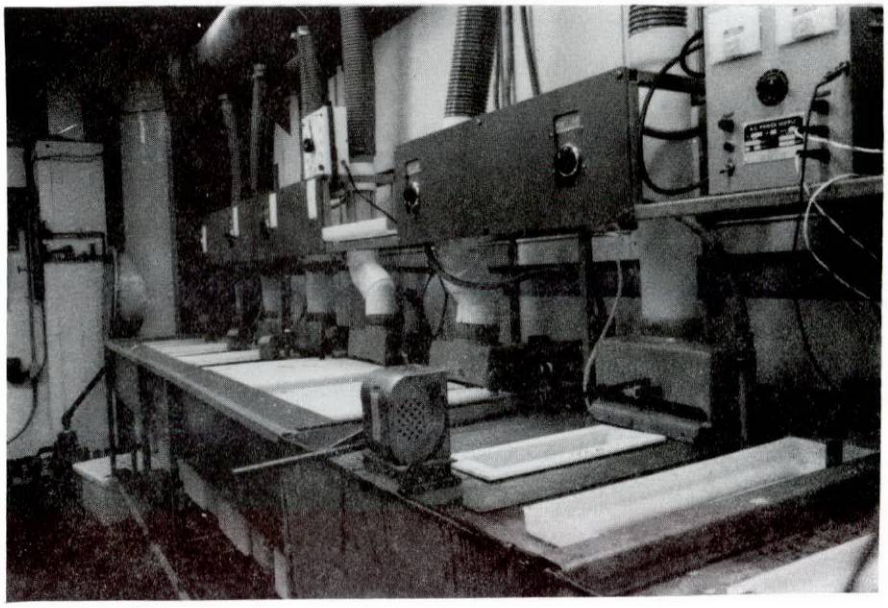


Figure 4. Electroless Nickel Boron Plating Line

The pilot plating line consists of five 15 gallon polypropylene tanks, two stainless steel hot-water jacket tanks, and seven running water rinse tanks. Immersion heaters and controls are installed where needed, as is the capability for air agitation. The two water-jacket tanks have automatic cathode rod agitators. The nickel boron solutions are heated in the hot water jacket tanks so that localized overheating of the plating bath is prevented. To eliminate potential environmental hazards and to insure personnel safety, a scrubber and ventilation system were also installed. The plating line accommodates a production rack of component parts, 85 pieces per rack. A total of 255 pieces of each type of compo-

nent were plated in Bath I and Bath II.

2. Testing of Nickel Boron as a Lead Finish. Besides establishing the fact that the nickel boron plating process developed in Phase I is amenable to manufacturing technology, Phase II evaluated the nickel boron deposit as a primary component lead finish. The test series for nickel boron deposited on component leads is given in Table IV. The nickel boron deposit characteristics obtained from the results of the test series confirmed the preliminary data obtained in Phase I.

TABLE IV

Lead Finish Test Series

Test	Type of Sample	No. of Samples Tested/Lot	No. of Samples Per Lot
Visual (14X)	Component Package	All	155-255
Adhesion (180° Bend)	Leads	20	155-255
Thickness (Metallograph)	Leads	5	155-255
Glass-to-Metal Seal (Metallograph)	Glass/Metal Seals	5	155-255
Lead Integrity (45°-90° Bend)	Leads	20	155-255
Salt Spray (24 hours, 5% NaCl)	Component Package	40	155-255
Steam Age (1 hr, Steam)	Component Package	20	155-255
Burn-in Plus Steam Age (100 hr, 150°C)	Component Package	20	155-255
Solderability As-Plated (60/40 solder)	Leads	20	155-255
Solderability Steam-Aged	Leads	20	155-255
Solderability Heat-Aged	Leads	20	155-255

Scanning Electron Microscope pictures were taken[6] of the bend area of a flatpack lead after lead integrity (ductility) testing. At 160X magnification in Figure 5a, numerous cracks were seen and this is shown further at 2800X, Figure 5b, indicating a brittle deposit with no ductility.

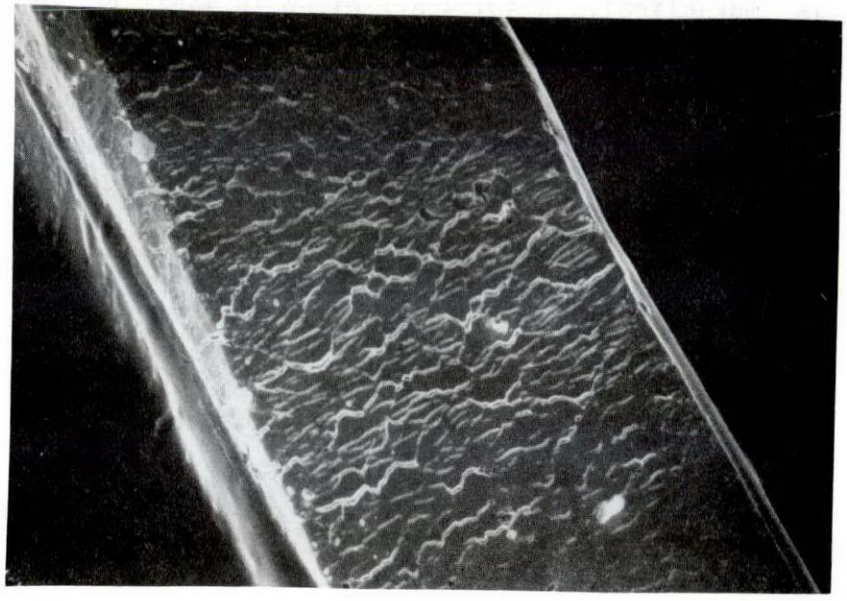


Figure 5a. SEM photo 160X

Nickel Boron Deposit on Flatpack Lead at 90° Bend

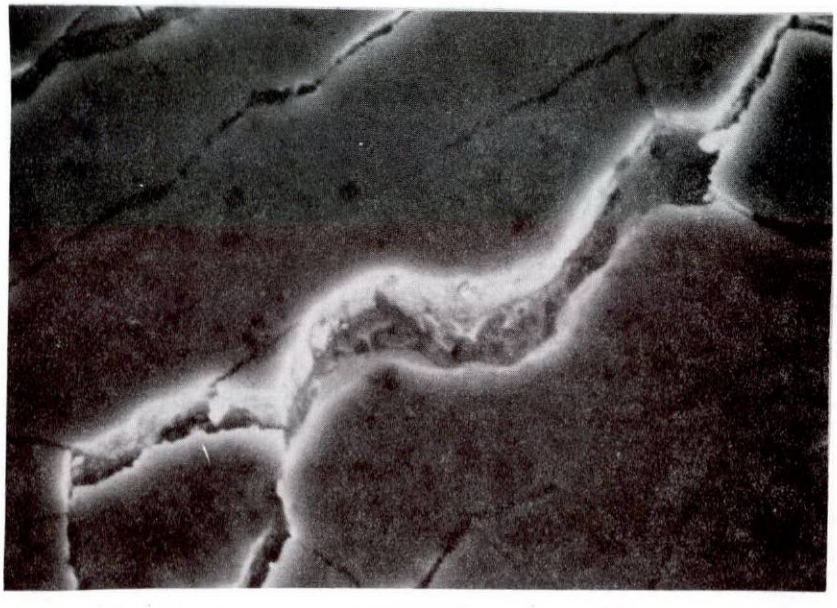


Figure 5b. SEM photo 2800X

Nickel Boron Deposit on Flatpack Lead at 90° Bend

[6] SEM work by D. Calabrese, Physicist, Rome Air Development Center, New York.

In an attempt to improve ductility of the nickel boron deposit, samples from lots with varying percent boron were heat-treated at 600°C and 800°C and then tested for ductility (bending stress 45°-90°). At 800°C all of the samples were ductile; no cracks were viewed in the bend area at 20X magnification. However, for electronic lead applications, heat-treating at 800°C is impractical. Results are given in Table V.

TABLE V

Ductility Study

Lot No.	Deposit Thickness (μin)	% Boron in Deposit	Formability* After Heat Treat 600°C	800°C
95	350	0.34	T**	Good
113	170	0.38	Good	Good
101	160	0.39	Good	Good
93	260	0.56	T	Good
92	460	0.76	T	Good
121	170	0.89	Good	Good
127	90	0.91	Good	Good
102	160	2.3	T	Good
98	160	2.5	T	Good
106	230	2.6	T	Good

* Specimens bent through an angle of 90°C over a 1/8" diameter mandrel and examined at 20X magnification for deposit cracking in the bend area.

** Transverse type cracks observed in bend area of specimen.

Corrosion tests included a pre-bending stress of the leads through an arc of 45°-90° and then exposure to a 5% salt fog atmosphere for 24 hours. The results were not good. Samples showed rust and varying amounts of blue-green salts. Figures 6a and 6b are representative of all test samples.

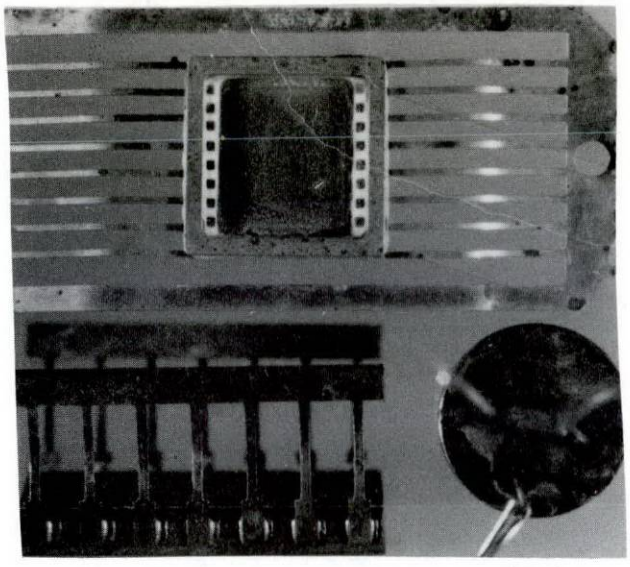


Figure 6a. 24 hr Salt Spray (5%) NiB from Bath I

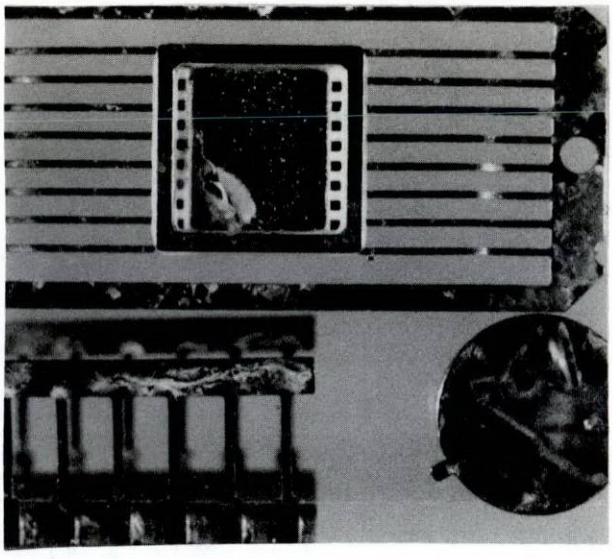


Figure 6b. 24 hr Salt Spray (5%) NiB from Bath II

For solderability tests, a 60/40 tin-lead solder was used at 260°C. A mechanical device was constructed that controlled the rate of immersion (1 in/sec), emersion (1 in/sec) and dwell time (5 sec). An RA flux[7], which meets MIL-F-14256, was used for the nickel boron plated components. Twenty samples were tested for solderability from each lot. Three conditions were used to test nickel boron deposits: after plating, following one hour exposure to steam aging, and after a 100 hour bake at 150°C with 1 hour steam aging. Due to an excess of dewetting, non-wetting, and the presence of pinholes, the nickel boron components failed solderability tests for each condition. The following pictures (Figures 7a, b, c, d) are illustrations of such.

In an attempt to quantify some of the solderability data, a few flatpack components were soldered using a meniscograph, which gives an easy-to-read graph that recorded the entire wetting process, a typical diagram for good solderability is given in Figure 8a. Test results for flatpack samples plated from Bath I and Bath II are shown in Figures 8b, c, respectively.

[7] Kester 1511 Mil RA.

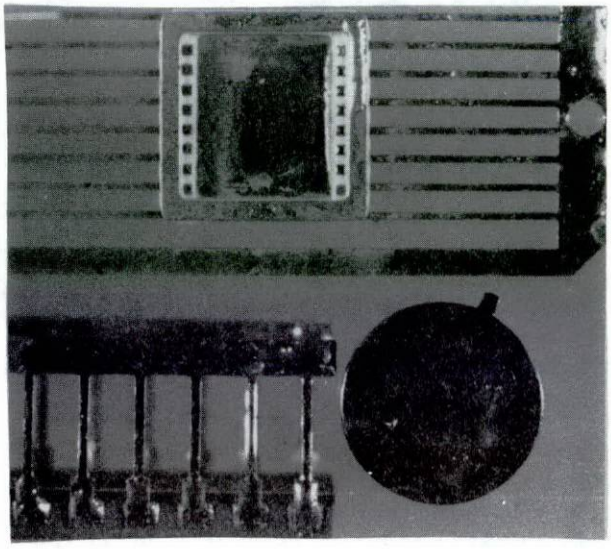


Figure 7a. As plated from Bath I

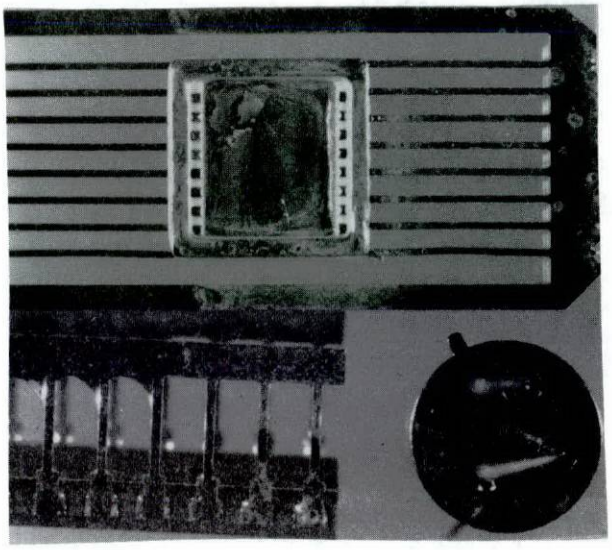


Figure 7b. As plated from Bath II

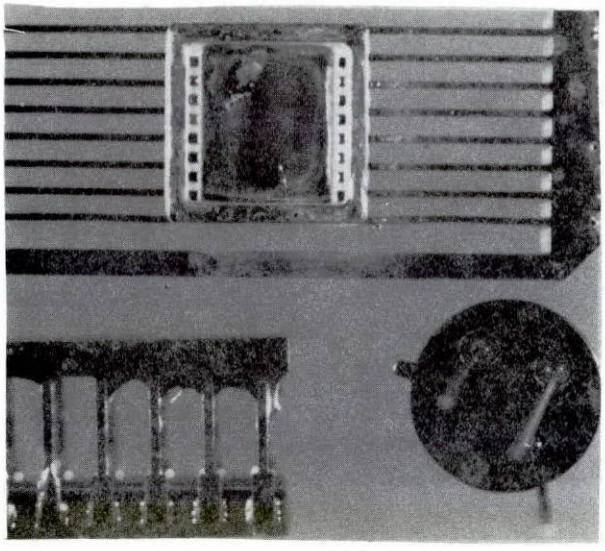


Figure 7c. Steam-aged from Bath I

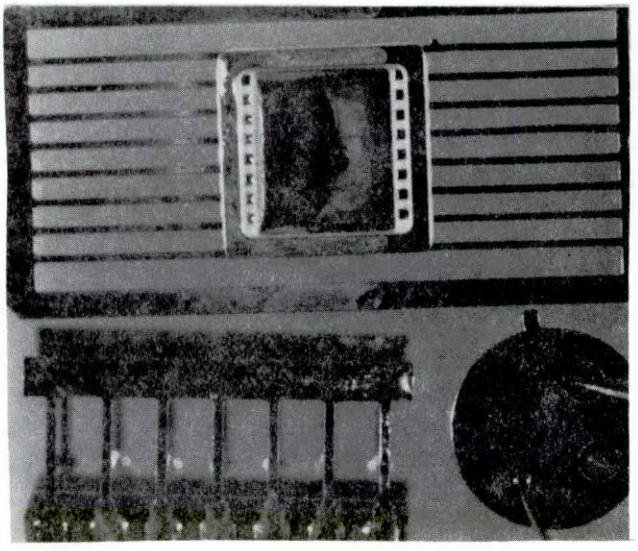
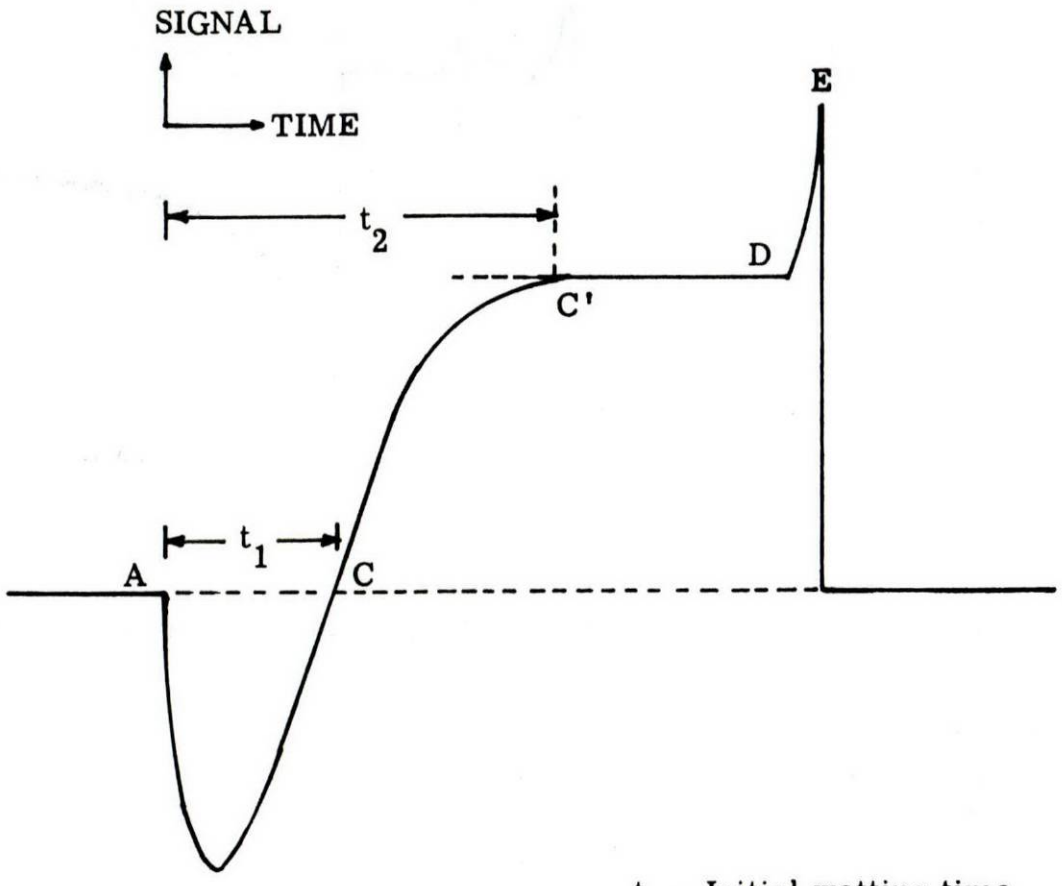


Figure 7d. Steam-aged from Bath II



t_1 - Initial wetting time

t_2 - Maximum wetting time

A - Specimen entering the solder
AB - Buoyancy force of solder
BC - Initial wetting
CC'D - Final wetting
C - Initial wetting achieved (crossover with initial condition)
C' - Final (maximum) wetting achieved (point of tangency with horizontal)
DE - Withdrawal

Note: Drawing not to scale - for illustration only.

Figure 8a. Representative Meniscograph for Good Solderability.

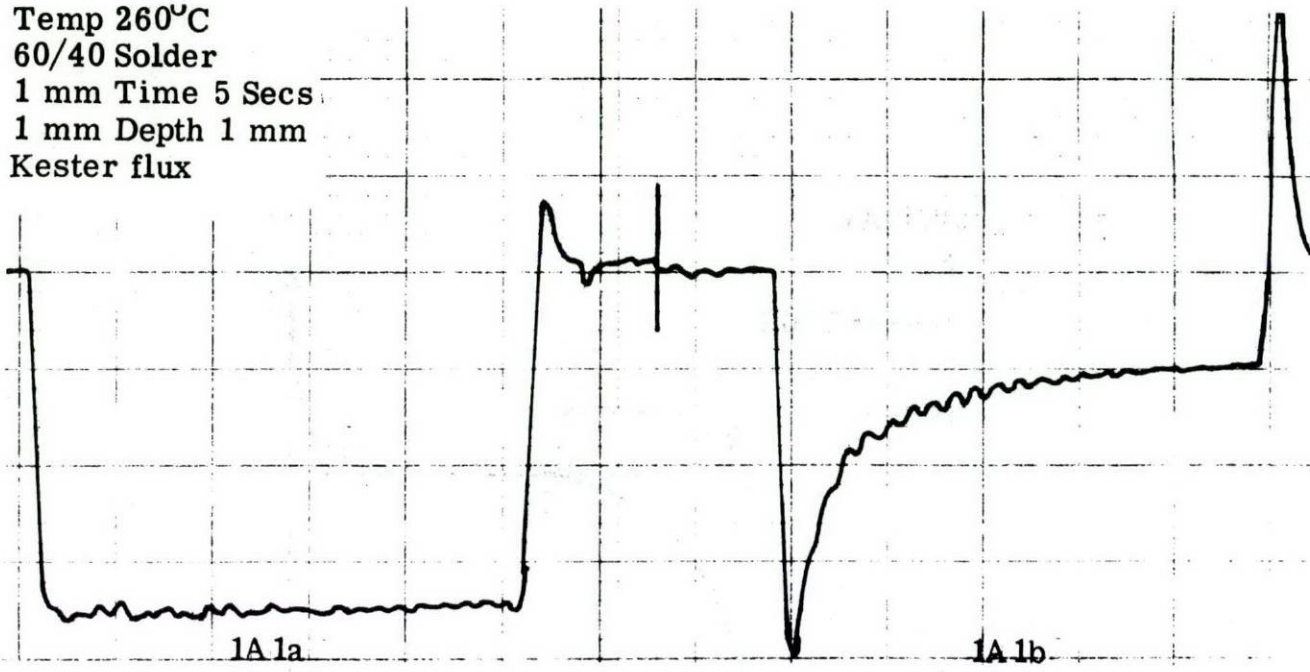


Figure 8b. Meniscograph for Solderability of Bath I's Plated Flatpack

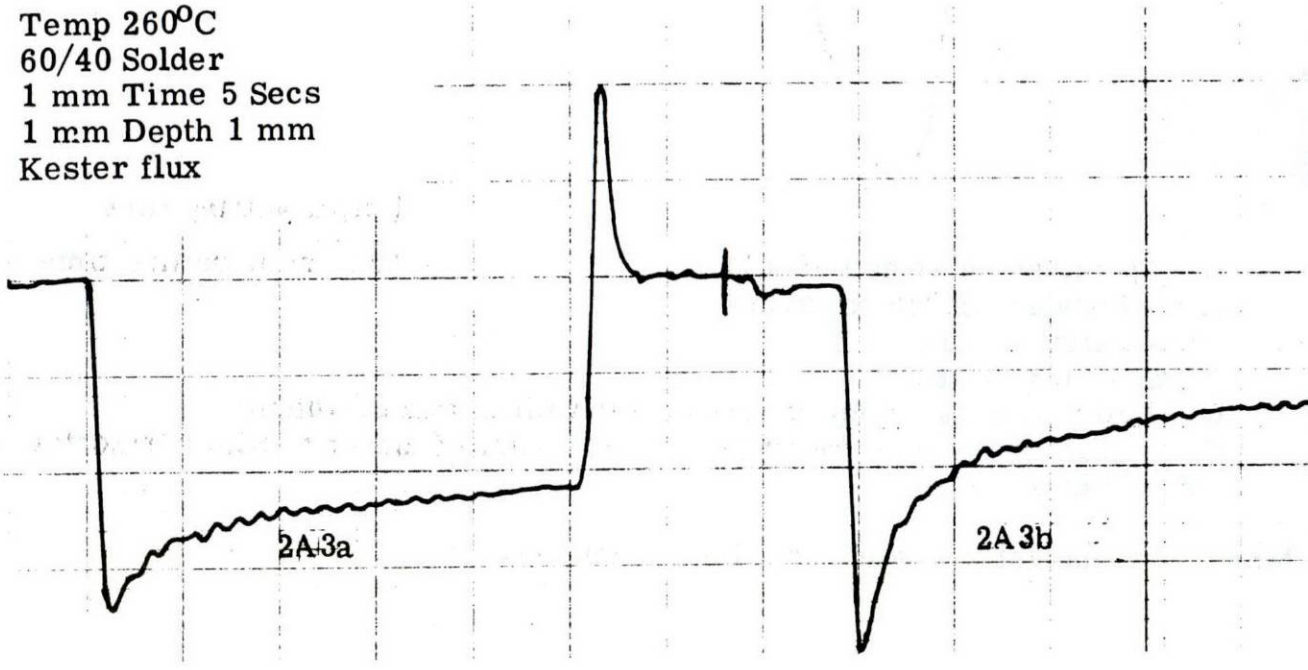


Figure 8c. Meniscograph for Solderability of Bath II's Plated Flatpack.

Conclusions

From the test results obtained in Phases I and II, the nickel boron deposit traits can be characterized as shown in Table VI. Although the metallurgical properties of nickel boron deposits do not enhance its potential use as a primary lead finish, the electroless coating may be of value in an alternate electronic application, as a thin undercoat or where a hard wear-resistant surface is needed. The plating process itself is amenable to manufacturing technology and the deposit plates evenly with good adhesion.

TABLE VI

Nickel Boron Traits

Characteristic	Bath I	Bath II
Adhesion	Excellent	Excellent
Deposition Rate	150-300 µin/hr	300 µin/hr
Deposition Uniformity	Very Good	Very Good
Bath Stability	Good	Good
Deposition Appearance	Semibright - Matte	Bright - Semibright
Hardness	High	High
Ductility	Poor: brittle	Poor: brittle
Solderability	Poor	Poor
Corrosion Resistance	Poor	Poor

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I-2

ELECTROLESS PLATING SESSION I

Electroless Nickel Deposition in an Ultrasonic Field

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ELECTROLESS NICKEL DEPOSITION IN AN ULTRASONIC FIELD

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ABSTRACT

The application of ultrasonic irradiation to an electroless nickel plating system is discussed in this paper. The effects of ultrasound on the plating rate, internal stress, as-plated hardness and deposit composition are reported. Comparisons are made on Ni-P deposits plated with and without ultrasound. Mixed potentials as functions of stabilizer concentration are determined. Procedures are described for the development of empirical rate laws for the plating bath with ultrasound and in the absence of the ultrasonic field. The ultrasonic experiments were run at two resonant frequencies, 25 kHz and 40 kHz.

INTRODUCTION

In 1955, S. R. Rich[1] published the results of studies on metal deposition in ultrasonic fields.* Rich investigated the effects of ultrasonic irradiation on both electrolytic and electroless deposition. Rich reported that the plating rate of an (unspecified) alkaline hypophosphite electroless nickel plating bath was increased five-fold in an ultrasonic field of 20 kHz.

Recently, Mallory[2] described the effects ultrasound has on the physical properties of electroless Ni-P alloys deposited in ultrasonic fields. Concomitant with rate enhancement, the as-plated hardness of the deposits was reported to be increased about 100 VHN with ultrasound. The X-ray diffraction patterns of ultrasonically produced Ni-P deposits were distinguished by the presence of the (200) reflection plane. The (200) reflection is normally absent in the X-ray diffraction patterns of deposits formed without ultrasound. Additionally, the phosphorus content of these deposits was observed to be lower than deposits produced without ultrasound.

Although the studies cited have definitely shown that ultrasound has an effect on electroless nickel plating, more data are required to determine which, if any, of the effects are uniquely the result of the ultrasonic field. This paper represents a beginning toward this goal.

EXPERIMENTAL

The plating bath used throughout this investigation is similar to the formulation referred to as Bath No. 5 in reference 2. Its composition is as follows:

$NiSO_4 \cdot 6H_2O$	–	0.1 mole/L (variable)
Lactic Acid	–	0.3 mole/L (constant)
Citric Acid	–	0.07 mole/L (constant)
$NaH_2PO_2 \cdot H_2O$	–	0.28 mole/L (variable)
Thiourea	–	0-1.5 ppm
pH (adjusted with KOH)	–	4.8 (variable)
Temperature, °C	–	87 (variable)

* The ultrasonic frequency range is defined to extend from about 16 kHz to several thousand kHz.

With the exception of the complexing agents, the concentrations of the bath components were varied to ascertain the effects of ultrasound on an empirical rate law derived for the plating system without ultrasound. Except when determining the activation energy, all experiments were carried out at 87°C.

The solution volume-to-surface area ratio was kept purposefully large to minimize the effects of changes in bath composition during the course of the plating tests. The concentrations of the reactants in the plating bath did not change more than 1 percent during plating.

Plating rates were determined by measuring the weight gain per unit time per cm^2, i.e., mg/cm^2-min.

The composition of the test deposits was determined by a difference technique. The nickel metal content of plated foils was analyzed using dimethylglyoxime, the balance assumed to be phosphorus.

Microhardness of the deposits was determined with a Wilson Tukon Indenter under both 50- and 100-gram loads on the cross-section of deposits at least 75 μm thick.

The mixed potentials were determined using working steel electrodes versus a silver-silver chloride electrode.

The method of Feldstein and Weiner[3] was used to determine the variations in mixed potential when the plating bath is titrated with various stabilizers with and without ultrasound. The potential measurements were made using a PAR Model 173 Potentiostat/Galvanostat.

X-ray diffraction studies were performed with a Norelco X-ray diffractometer equipped with a single crystal monochromator.

The relative magnitudes of the internal stress were determined with a Brenner-Senderoff Spiral Contractometer.

The ultrasonic equipment used in this investigation were two Branson E-Module ultrasonic systems consisting of LTH and ATH transducerized, heated, stainless steel tanks of approximately 10-liter capacity, operating at 25 kHz and 40 kHz, respectively, with maximum power output of 450 watts, respectively.

All results reported are the average of several tests.

RESULTS AND DISCUSSION

The values for phosphorus content, as-plated microhardness, and the internal stress of the experimental deposits are given in Table I.

The internal stress of electroless Ni-P deposits has been observed by several investigators[4,5] to be inversely related to the phosphorus content of the deposits. It is further claimed that there is no significant difference in the as-plated hardness of Ni-P alloys containing 2 to 11 percent phosphorus. However, unpublished data indicate that the as-plated hardness is directly related to the internal stress of the deposits. It follows then, that the as-plated hardness is inversely related to the phosphorus content of deposits when there are differences in the internal stress between alloys of different phosphorus content. The data presented in Table I are examples of these relationships. The effect of ultrasound on the composition of the deposits will be discussed in more detail later.

Table I. Phosphorus Content, As-Plated Hardness and Internal Stress of Deposits

	Ultrasonic Field		
	None	*25 kHz*	*40 kHz*
% Phosphorus	9.5	8.5	7.2
As-Plated Hardness			
VHN_{50}	500	600	590
VHN_{100}	525	625	600
Internal Stress, Tensile (psi x 10^3)	4.1	10.8	17.6

The X-ray diffraction patterns of the deposits formed with and without ultrasound show a low-ordered structure with crystallite diameters measuring about 17Å. The deposits formed in the ultrasonic fields of 25 kHz and 40 kHz show the strong (111) reflection as does the normal deposit. However, the (200) reflection plane observed in a previous study[2] is not present in the X-ray diffraction pattern of the 25 kHz and 40 kHz deposits of these experiments. There are at least two possible explanations for the absence of the (200) plane in the ultrasonically produced deposits of this investigation:

1. Changes in microstructure occur when plating takes place in an ultrasonic field with resonant frequency greater than 40 kHz. (The previous studies were performed at the resonant frequency of 49 kHz.)

2. The appearance of the (200) plane was an experimental artifact resulting from the physical conditions of the previous experiments.

Brenner and de Minjer[6] observed that the addition of thiourea at very low concentrations would increase the plating rate through a maximum, and further additions of thiourea would completely inhibit the plating reaction. Mallory[2] observed that when ultrasound is applied to the plating system, the concentration of thiourea necessary to cause these changes is considerably less than otherwise required. Figure 1 shows the manner in which the plating rate varies with thiourea concentration with and without ultrasound. The maxima in the plating rate versus thiourea concentration curves are at lower concentration values of thiourea for ultrasonic irradiation than without ultrasound.

The maximum in the rate curves occur at 0.05, 0.7 and 1.0 ppm thiourea for 40 kHz, 25 kHz and no ultrasound, respectively.

Feldstein and Lancsek[7] have shown that the phosphorus content of Ni-P deposits decreases with increasing thiourea concentration. It is assumed that ultrasonic irradiation accelerates the diffusion of the stabilizer, in this case thiourea, to the reaction surface. We can define an apparent or effective stabilizer concentration C_E by the relation:

$$C_E = C_B\ f(R_A) \qquad (1)$$

such that when $R_A = 0$, $f(R_A) = 1$ and where C_B is the actual or bulk concentration of stabilizer in the solution and $f(R_A)$ is some monotonic increasing function of the diffusion rate. For a constant C_B, the diffusion rate increases as $f(R_A)$ increases. The limiting value of C_E is that point at which the plating reaction stops. This relation holds for most stabilizers used in electroless nickel

plating. For example, Figure 2 and Figure 3 show the variation in the mixed potential when the plating bath is titrated with KIO_3 and $Bi(NO_3)_3$, respectively. When ultrasound is applied, the endpoint of the titration corresponds to smaller bulk concentration values than obtained without ultrasound.

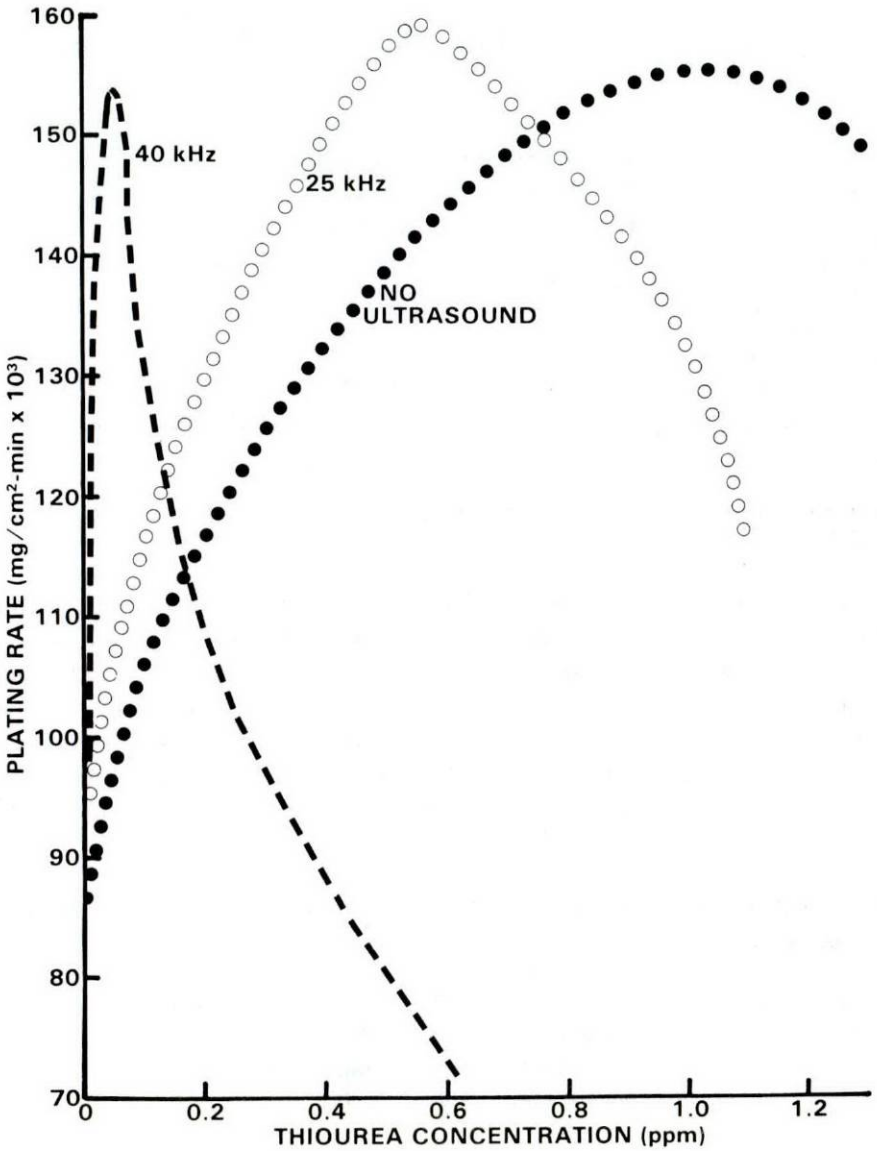

Figure 1. Plating Rate Versus Thiourea Concentration Without Ultrasound and at 25 kHz and 40 kHz

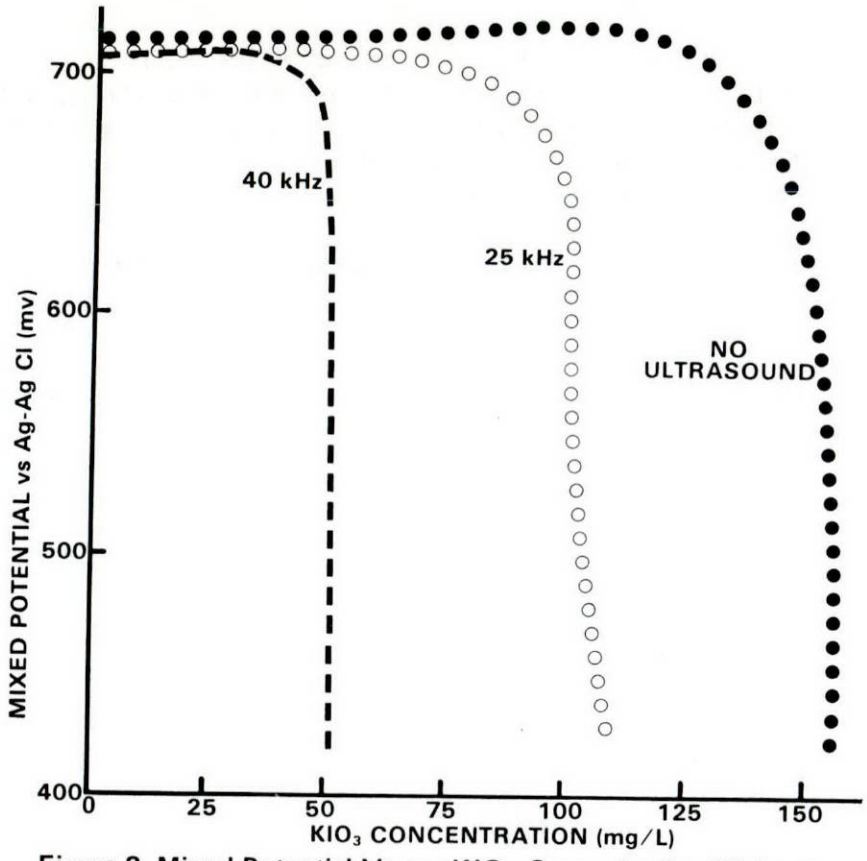

Figure 2. Mixed Potential Versus KIO_3 Concentration Without Ultrasound and at 25 kHz and 40 kHz

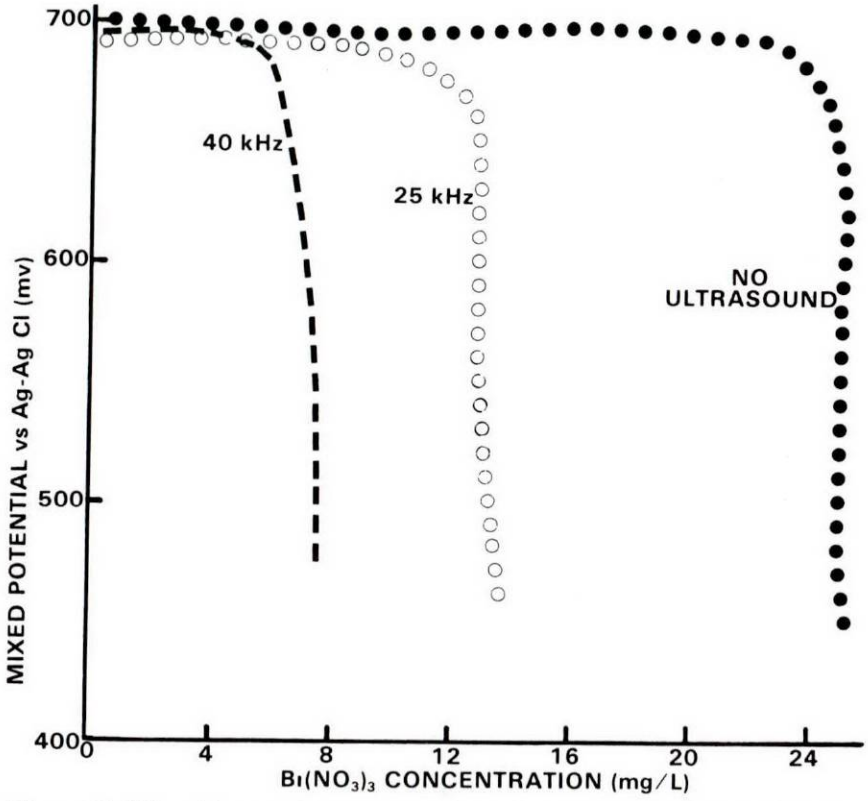

Figure 3. Mixed Potential Versus $Bi(NO_3)_3$ Concentration Without Ultrasound and at 25 kHz and 40 kHz

Gutzeit[8] states that by increasing the velocity of agitation in the plating bath, the rate of deposition is increased up to a maximum (roughly equal to twice the original rate), and with increasing velocity the rate starts decreasing steadily. Since the hydrogen ion concentration constantly increases as the plating reaction proceeds, the rate increasing phase is interpreted to be due to the rapid transfer of H^+ away from the catalytic surface.

Gutzeit further postulated that the second or rate decreasing phase is due to the rapid translation of the nickel ions past the catalytic surface. The test data in Figures 1, 2 and 3 indicate that the rate decrease observed by Gutzeit can be attributed to the presence of stabilizing agents intentionally added or inadvertently added as contaminants with the bath chemicals used. Therefore, as agitation is increased, the removal of H^+ from the surface causes an increase in rate of deposition. However, from the data obtained in these experiments it is postulated that after passing through the first phase (maximum rate) the plating reaction becomes dominated by the effective concentration of a stabilizing substance according to equation (1).

If sufficient data are taken on an electroless nickel plating system when the concentrations of the reactants are varied in some prescribed manner, a useful, albeit empirical, rate law can be derived. The general form of the empirical rate equation is:

$$\text{Rate} = r = k_1 [Ni^{++}]^a [H_2PO_2^-]^b [H^+]^c [C_3H_6O_3]^d [C_6H_6O_7]^e \exp\left(-\frac{E^\ddagger}{RT}\right) \qquad (2)$$

where a, b, c, d, and e are the reaction orders and $E^\ddagger$ the activation energy. In the case of the present experiments we can set

$$k_2 = k_1 [C_3H_6O_3]^d [C_6H_6O_7]^e$$

so that

$$r = k_2 [Ni^{++}]^a [H_2PO_2^-]^b [H^+]^c \exp\left(-\frac{E^\ddagger}{RT}\right) \qquad (3)$$

Taking the logarithm of equation (3), yields

$$\log r = \log k_2 + a \log (Ni^{++}) + b \log [H_2PO_2^-] + c \log [H^+] - \frac{E^\ddagger}{2.3RT} \qquad (4)$$

Equation (4) can be used as a basis for the determination of the reaction orders and the activation energy. That is,

$$\left(\frac{\partial \log r}{\partial \log [Ni^{++}]}\right) = a \; ; \; H_2PO_2^- \text{ and } H^+ \text{ constant}$$

$$\left(\frac{\partial \log r}{\partial \log [H_2PO_2^-]}\right) = b \; ; \; Ni^{++} \text{ and } H^+ \text{ constant}$$

$$\left(\frac{\partial \log r}{\partial \log [H^+]}\right) = c \; ; \; Ni^{++} \text{ and } H_2PO_2^- \text{ constant}$$

Since log $[H^+] = -pH$, we can write

$$-\left(\frac{\partial \log r}{\partial pH}\right) = c$$

$$\left(\frac{\partial \log r}{\partial 1/T}\right) = -\frac{E^{\ddagger}}{2.3R} \; ; \; Ni^{++}, H_2PO_2^-, \text{ and } H^+ \text{ constant}$$

When the log rate of deposition is plotted as a function of the log concentration of the varied reactant, e.g., log r versus log $[Ni^{++}]$, a straight line is obtained. The slopes of the straight lines so obtained are the values of the respective reaction orders. Similarly, the plot of log rate versus 1/T yields a straight line whose slope is equal to $-\frac{E^{\ddagger}}{2.3R}$, from which the activation energy can be easily calculated.

The reaction orders and activation energies computed from experimental data using the methods described above are given in Table II.

Table II. Empirical Parameters

	Ultrasonic Field		
	None	*25 kHz*	*40 kHz*
Reaction Orders			
a	1.4	1.38	1.4
b	1.0	1.05	1.0
c	0.25	0.50	0.47
Activation Energy, k cal/mole	13.6	13.6	15.1

The reaction order, b = 1, with respect to the hypophosphite ion corresponds to previously reported first-order dependence for hypophosphite ions[9]. The order of the reaction with respect to hydrogen ion concentration, c = 0.25, for the system with no ultrasound is also in agreement with the previously reported values. When ultrasound is applied to the plating system, the value of the reaction order with respect to H^+ doubles, i.e., c = 0.5.

The rate laws derived from the experimental plating bath used by Gutzeit[9], Lee[10], and later by Donahue and Yu[11], show zero-order dependence on the nickel ion in the concentration range studied. The plating bath these investigators used was a sodium acetate-acetic acid buffered system containing no chelating agents. The bath used in this present study contains complexing agents that chelate the nickel ions. Levy[12] points out that the plating rate is a function of the free nickel ion activity (concentration) at the catalytic surface. The complexing agent controls the nickel ion concentration or availability for reduction at the catalytic surface. Therefore, the reaction order with respect to the nickel ion is probably related to the complexing agents present in the bath. This would account for the zero-order dependence of acetate-acetic acid bath and the reaction order of 1.4 for the chelating system of this study.

The activation energies obtained in this study lie in the range of values reported elsewhere.

The empirical rate law can be written as

$$\text{rate} = k_2 [Ni^{++}]^{1.4} [H_2PO_2^-] [H^+]^{0.25} \exp\left(-\frac{13.6}{RT}\right)$$

for the system without ultrasound, and

$$\text{rate} = k_2 [Ni^{++}]^{1.4} [H_2PO_2^-] [H^+]^{0.50} \exp\left(-\frac{13.6}{RT}\right)$$

when ultrasound is applied to the system.

CONCLUSION

From the data obtained to this point, it can be concluded that the effects of ultrasound on electroless nickel plating is unique only in the method of solution "agitation."

From the data on the effect of stabilizers in the ultrasonic field, it appears that only the low end of the ultrasonic frequency range is practical when applied to electroless nickel plating. Ultrasonic frequencies greater then 50 kHz should be investigated to determine if there are any unique effects other than agitation.

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I-3

ELECTROLESS PLATING SESSION I

Plating on Plastics

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PLATING ON PLASTICS

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ABSTRACT

This paper describes a new and revolutionary proprietary method for plating on plastic materials. This method does not involve the conventional preparation involving chromic acid etching and sensitization followed by catalytic plating of engineering metals. In this method the plastic substrate is treated in a matter of seconds in a mixture of organic liquids, treated in another step with a metal slurry and dried after washing off the excess. A nickel coating can then be applied to this metallic substrate in an immersion nickel bath after which bright nickel and chrome plates are applied in the usual manner. The obvious advantages of this method are discussed, stressing the fact that this process is not restricted to just ABS plastics, being applicable to a wide variety of other plastics. (Parts finished by such a process will also be passed around for inspection).

Introduction:

Although efforts on successful plating of engineering metals on plastics started nearly three decades ago, the really practical solutions had to wait until the science of plastics had improved to the point where materials like ABS could be mass produced and alongside, the science of metal finishing, especially autocatalytic (electro-less) plating was developed to a stage where it could be applied to metal surfaces. As a result of intense research and development, we have today two commercially applicable processes, both of which are being used in industry with great success. However the fact remains that each of these suffers from certain important disadvantages. In the one, which is primarily suitable only for ABS plastics (disadvantage), a very strong solution of chromic acid is used to etch the plastic, followed by a long series of steps involving expensive chemical solutions toward producing a very thin electroless nickel film over which copper, nickel and chromium are subsequently plated. Chromic acid is a pollution hazard and treatment facilities are found to cost heavily. Special chemicals involved in sensitization, involving palladium, are quite expensive.[1]

In the second process, which incidentally is somewhat similar to the one to be described, the chromic acid etch is eliminated, but the process is apparently suitable only for polypropylene.[2]

The process to be described was developed by the author independently and

will be seen to overcome all the disadvantages mentioned above; in addition some special advantages will also be noted.

THE NEW PROCESS

Plastic articles to be plated are placed in metal trays or racked suitably. Any other method of holding the parts is also satisfactory, provided they do not touch one another. The plastic articles can be of the usual platable ABS grades, polycarbonates, thick-section polyethylene and a wide variety of other materials such as Noryl. Special grades of platable polypropylene can also be used.

Cleaning: No cleaning is necessary if the molding procedure is carried out carefully. A dip in a mild soap solution (even kitchen detergent) followed by a thorough rinsing is satisfactory.

Treating: The parts are now ready for treatment which is the nucleus of this whole process. They are lowered into a container consisting of the following:

90% by volume of trichloroethylene
10% by volume of ethyl alcohol
200-250 g/liter of fine copper powder (50-150 micon size).

This mixture is stirred either mechanically or by a magnetic stirrer so that the copper powder is uniformly distributed in the solvent medium and deposits itself on the softened plastic surfaces. The stirring is carried out in pulses (starting & stopping) and finally shut off so that all the copper powder settles to the bottom and on the parts. The rack or holding device is lifted up gradually and held above the tank allowing the excess slurry to drain into the tank, at the same time drying the parts. The whole process described above can be accomplished in 1 minute. After drying for 30 seconds, the parts are brought into another tank containing the same solvent mixture as described above, but without any copper in it. The parts are dipped and raised quickly so that any excess copper not adhering to the parts comes off and renders the copper coating even. The parts are dried for about 1 minute in a current of warm air (if convenient). This process is found to produce a uniform, adherent copper coating.

The next step depends on the nature of the final cosmetic surface needed on the part. If a decorative cosmetic appearance is needed, the parts are dipped in a 10% Nitric acid solution for 15 seconds and rinsed. (Even a dilute version of a Nitric-sulfuric bright dip for copper can be used here). The articles are now subjected to an immersion nickel solution at room temperature. (70^{0}-90^{0}F) - containing:

50-60 g/ℓ	Nickel Sulfate[3]
50-60 g/ℓ	Ammonium Sulfate
100-120 g/ℓ	Sodium Thiosulfate

(Aqueous solution) for about 15 minutes.

This results in a nickel film of enough thickness and conductvity to be plated in a conventional electroplating bath, with bright nickel and chromium.

All of the above steps can be lumped as 'pretreatment', parts being racked for plating after 'pretreatment'.

Discussion: Obviously, no theoretical discussions are needed, since the pre-plating of copper is achieved by a physical process of softening the surface of a plastic to which a powder of copper is applied, made part of the surface and dried to obtain a thin coating of copper. The subsequent dip process is easily understood, but it must be pointed out that the chemically produced nickel not only produces a surface similar to a 'nickel strike', but helps bridge some of the minute areas which are not completely filled with copper. The problem of adhesion is nonexistent as the initial copper film is firmly anchored to the plastic. In fact, the copper film that is produced can be buffed on a soft wheel to produce a bright, smooth surface.
Possible Modifications: The above process can be modified. Instead of dipping the parts in the agitated slurry, the parts can first be dipped in the solvent mixture, transferred to another chamber and copper powder can be sprayed on the surfaces as in a sandblasting machine. This modification may be found to be better in cases where complicated contours exist on the part, since here all parts of the article are equally covered. Another modification is to add 1% by volume of methylene chloride to the above solvent mixture to make softening better, particularly on platable polypropylene.
Advantages Of The Method: Process steps are reduced to the absolute minimum. No pollution problems arise since all the copper not used in covering articles goes back into the tanks and none is discharged. No oxidizing acids are used. Chemical costs are obviously minimal.

The rate of evaporation of trichloroethylene is slow and solvent loss is minimal since the operation is carried out at room temperature. No chemical analysis is required, as copper powder can be added when needed. No special equipment is needed. Time of pretreatment is very short, compared to the present methods.
Disadvantages: This method is ideal when only one surface or exposed surface is to be plated (as in most decorative applications). Interior or hollow areas cannot be plated by this method. Solvent mixture in treatment tanks has to be kept covered during operation after racks or trays are lowered into them.
Conclusions: The above - described method seems to have more advantages than disadvantages and it is the conclusion of this author that it can be easily incorporated in an industrial plating shop.

Acknowledgments: The author wishes to thank Sunbeam Corporation for allowing him to present this paper. Thanks are due to Mrs. Cindy Anthony for typing the manuscript.

Note:

The specifications presented here have been submitted to the US Patent Office for issuance of a patent.

A few articles plated by this method can be circulated among the members of the audience for their examination.

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   (b) "Molder Plater Upgrades Facilities", Prod. Finishing, Feb. 1977, pp. 34-42
2. "Technology For Plating On Plastics", Prod. Finishing, Jan. 1976, p.84
3. This formula is a modified version of the formula on page 483, Metal Finishing Guidebook & Directory, Vol. 77, No. 13, 1979

(Proprietary or patent information must be obtained before attempting to use formula referred to in any commercial operation).

General Note

Since this paper describes an independently developed, new process and not a subject already in the public domain, the number of references is necessarily limited.

APPENDIX

TEST RESULTS

At the time of writing, only one set of 12 each of *ABS, *Noryl, *Lexan, Polyethylene, and Polypropylene substrates plated with copper and nickel by the above method have been tested in thermal cycling (ASTM B553-71). No table of results is thus given, but it can be stated that upto 1 mil (0.001") of nickel on copper (0.0003"), the testswere withstood

upto	1 cycle	(very severe)
upto	2 cycles	(severe)
upto	4 cycles	(moderate)
upto	6 cycles	(mild)

by each set of 12 of the above. (More data on pull tests, thermal and corrosion resistance should be available by the time this paper is presented).

*These are the generally well-known commercial plastics.
ABS: Acrylonitrile butadiene styrene
Noryl: Polyarylene ether
Lexan: Polycarbonate resin
(Noryl and Lexan are trade names of General El. Co.)

J-1

GENERAL INTEREST SESSION J

Status of Metrication in the United States

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United States Metric Board
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"Status of Metrication in the United States"
"Plans and Actions of the United States Metric Board"

Henry Kroeze
Member United States Metric Board
Representing the Engineering Profession

The United States Metric Board was established by an Act of Congress, that was signed into law on December 23, 1975. Extensive research by the National Bureau of Standards and many hearings by House and Senate Committees, which revealed that "Going Metric" was in the best interest of our country preceded the passage of this Public Law 94-168, commonly referred to as the "Metric Conversion Act of 1975".

It took until April 1978 before the board was finally confirmed by the United States Senate. Its seventeen citizen members represent various sectors of our society such as business, labor, science, engineering, small business, the construction industry, education, weights and measures groups, retailing, the National Governors Conference and Consumers, as prescribed by law.

The act declares that the policy of the United States shall be to coordinate and plan the increasing use of the Metric system in the United States. The Board has no mandatory powers: it is strictly a coordinating agency. However, the law gives an outline of what the board is expected to do. In order to carry out this task the board established a policy, that is strictly based on the law, that was passed by congress.

In order to carry out its task the following board Committees were formed:

1. Budget and Personnel
2. Policy
3. Public Information and Education
4. Research Coordinating
5. Private Sector Liaison
6. Standards Liaison
7. Government Agencies Liaison
8. Annual Report

The Budget and Personnel Committee first selected candidates for the position of the Boards' Executive Director, from which the complete board made its selection. This committee than, with the assistance of the executive director, selected our staff. In this process we had to go through the required government procedures. All postions had to be posted and follow "civil service" requirements. Of our staff only the executive director and his confidential secretary do not come under civil service rules.

The Budget and Personnel Committee also establishes a budget for the various board activities outlined in the law. It has to follow the general rules of O.M.B. (the Office of Management and Budget) and has to justify its recommendations before House and Senate budget committees.

The policy committee was one of the first committees that was established. Its task was to clearly interpret the law, and may be come up with recommendations for reenforcing or adjusting the Metric Conversion Act of 1975. I served on this committee, and wrote the original draft. Writing it was a pleasure and an honor, but since I did it when I spent a week in a hospital with a leg infection it was not too much fun.

The Public Information and Education Committee is charged with informing the public about metrication, where it is all about, its progress, its pro's and con's, its "guts". The law requires us to give every citizen the opportunity to become familiar with the metric system of measure, so that everyone can for him or herself make a decision whether he or she want to go metric or not. This is a tremendous task, which explains that a major part of our very small budget is spent on this effort.

The Research Coordinating Committee, of which I am a member, is looking into the effects that metrication will have in specific areas. For instance: What will be the effect on skilled workers who will have to replace some of their tools? What are the effects on foreign trade and productivity? What were the effects when the wine and liquor industry changed to metric and how to prevent the mistakes that that industry made, when for instance milk packaging goes metric? What are the effects on consumers? Should we have dual pricing, at least temporarily?

Our private sector committee encourages private interest groups to take the initiative. Many of such groups have already established timetables. The automobile manufacturers are way ahead of most groups. The Metric Coordinating Committee of the American Society for Engineering Education, which is the secretariat for the engineering education group, has established a timetable for converting engineering education to metric. The American Congress on Surveying and Mapping has established a timetable for its areas of interest. Many of the sector committees of the American National Council are the secretariats for their particular groups. The United States Metric Board encourages the activities of these groups, who submit their conversion plans to our board. Our Private Sector Liaison Committee will look at these plans and check it for possible harmful effects on other sectors including the general public before submitting it to the full board for a recommendation, which may be positive or negative.

Our Standards Liaison Committee, of which I am also a member, deals with metric engineering standards and the over 250 standards writing organizations in this country. Unfortunately these various organizations don't always agree with each other. Our job, and it is quite a job, is to keep the peace between them. Of course we support ANSI, the American National Standards Institute, which officially represents the United States at international standards conferences. We believe, that our engineering standards in most cases are superior and should be adopted internationally, in metric language. Our committee has become involved with NATO standards and with controversies caused by other countries trying to get the Republic of China to adopt their particular engineering standards for certain imported products.

Our committee that deals with government agencies is charged with coordinating the metric activities within the various government agencies and have them take part in the metric activities of the private sector groups in their areas of interest. Before this committee was established, every government agency went more or less on its own as far as metrication was concerned. The committee has done a tremendous job in establishing a uniform metrication policy for government agencies. It does take in consideration the interests of the private sector.

The law requires us to provide an "Annual Report" to the President and to our Congress. The Committee charged with this task collects data on what we as a board have accomplished, and also may give some recommendations for additional legislative action. This years report should be completed this spring, so that copies should be available in May or June.

During the last few months more and more major companies, such as General Motors, IBM, Texas Instruments, Combustion Engineering, Dupont, Inland Steel, etc. are releasing data on how they accomplished productivity improvement and/or cost reductions by going metric. Seven-up increased its sales and profits by taking advantage of metrication at the right time. Several companies including those classified as "small business", have reported increased export opportunities as a result of going metric. More data on these efforts should be available shortly. As a member of the U.S. Metric Board I will bring you up to date on the latest developments in this area at your National Convention.

J-2

GENERAL INTEREST SESSION J

Changeover to Metric for the Plating Industry

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CHANGEOVER TO METRIC FOR THE PLATING INDUSTRY

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Sooner or later the Plating Industry will "Go Metric." The decision to do so may be as a result of:

... Doing business in a world wide market place and the need for a common technical measurement language.

or

... Doing business with a domestic industry which has converted to metric usage.

or

... Doing business with a country which has the use of the metric system as a legal requirement in that country.

or

... A decision in the form of a law passed by the U.S. Government that the country convert on a mandatory, planned basis.

or

... Various combinations of the above reasons.

However, regardless of whether or not the Government passes a bill to that effect, any business - large or small - will convert when the times, business and legal conditions, so dictate. This is already the situation which was faced by the many multinational companies which have already announced their changeover plans.

The Plating Industry, like other "service" type industries, has already been faced with the need to work from metric documents provided by their "customers." ("Service" type industries in this context means any industry which provides a service to a prime customer in the form of plating, machining, raw material supply, assembly, drafting, design, testing, inspection, etc.) Some of these documents have been dual dimensioned (metric and inch or vice versa) or else metric only. Likewise, the standards used by the industry are becoming more and more preferred metric to satisfy the needs of the "customer" who, as previously stated, had to go metric for business or legal reasons.

When faced with metric only documents, the plating industry or, for that matter, any small company, has two options:

- Refuse to take the business opportunity because the job is metric.

OR

- Take the business opportunity and find the best and/or least costly way to handle the metric situation.

Any company which takes the first option in the face of increasing use of metric throughout the U.S. and the world by large and small companies is merely hiding its head in the sand and throwing good business opportunities to its competitors who have already faced up to metrication and have taken the second option. A company taking the first option will probably not stay in business very long.

Of course, taking the second option means that an investigation into the metric problem is needed, and some action plans will have to be set in place. Early planning will have to take place so that a plan of all tasks, objectives and timetables are covered to insure an orderly transition from the customary system to the metric system. This will permit a selection of the activities which must take place, their sequence and prioritization.

The foregoing assumes that there will be sufficient time to take such definitive action prior to getting involved with metrication. In practice, this will probably not be the case because most small businesses are prone to ignore the fact that metrication is taking place until they are faced with metric documents from which they must quote and/or manufacture. In fact, many small businesses are hoping that going metric is a fad that will go away.

Regardless of whether there is time for early planning or if suddenly faced with metrication, there is no need to panic. Many other companies have already found themselves in the same situation and have come through with few, if any, scars. Why is this so? It can only be attributed to good old American business ingenuity which almost daily is faced with changing work situations in the form of new and/or different demands by various customers, new government regulations, new standards and other new challenges. Metrication is no different; it is merely the adoption of a new measurement system and metric standards. After all, didn't we all go through the adoption of the decimal inch in the late fifties and early sixties (remember all the arguments pro and con for that change?).

Now let us take a look at this thing called "Metric" and see what it's all about. First, and foremost, the metric system adopted and being used world wide is not the metric system with which most people who have been educated in metric or have used metric in their work until recently are familiar. Because one of the main reasons for going metric has been to have a common technical measurement language, the metric system now in use is the internationally agreed upon International System of Units (SI) which is reflected in the International Standards Organization (ISO) standards 1000 and 31-0 through 31-XIII. These standards concern themselves with Style, the SI Units and Derivatives, and the correct technical units for the various disciplines.

Style is concerned with the proper use of symbols, abbreviations, format, and so forth, of the units of SI in normal usage so that everyone will be communicating about SI in a consistent manner.

The SI Units of Measurement deals with the seven base units for length (metre), mass (kilogram), time (seconds), electric current (ampere), temperature (kelvin), luminous intensity (candela) and amount of substance (mole) and their abbreviations. Of the seven, only the measurement for length, mass, and temperature are new to most people. The other units are in common usage. There are, however, some very important differences in the technical units which are used in SI, for instance: power is expressed in watts; energy is expressed in joules; force is in newtons; pressure is in pascals. These are just a few of the differences which must be learned.

The field of standards is an area very often ignored or forgotten when discussing metrication. Most people feel that the measurement system is all that is involved in going metric. This is a very serious oversight since nearly all standards reflect the use of some measurement system or systems. In the United States, our standards are customarily "inch" dimensioned or else dual dimensioned with the "inch" system preferred. Most U.S. standards activity has been slow or non-existent when it comes to metricating the needed standards.

The plating standards appear to be an exception since they appear to have already been converted to metric, which is a big plus for the industry because a good base of metric standards is an absolute necessity for the metric changeover.

Plans for the change to metric may be very simple or very complete depending upon the thought and time applied to the planning process. The most simple plan would appear to be the decision to simply convert the metric documents to "inch" dimensions and work accordingly. This kind of plan is usually arrived at when an order is received for parts to be quoted,

machined, plated or otherwise processed and the documents are in metric dimensions only; furthermore, the work is needed and the customer needed the parts last week. It is a reasonable plan because the only cost involvement appears on the surface to be the time involved in making the measurement conversions. There is no manufacturing or inspection equipment involved. The cost is also found to be very low since the time involved for converting 45 dimensions and tolerances is about 15 minutes or less. On most orders, this is negligible considering the overall cost of the order.

This plan has some very serious risks involved. The most important being the potential for errors in conversion and the rounding of the conversions, in which case costly scrap or at best costly rework is the final result. Another problem is that the converted dimensions are not backed up with inch "unless otherwise noted" standards for Geometric Form Dimensioning and Tolerancing or other standards because the customer has supplied metric only backup documents. This means additional conversions and potential errors. Discussions with the customer in regard to questions and problems on the order also become a problem because the customer is thinking and talking metric and you are thinking and talking inch. More confusion and errors result unless extreme care is taken during discussions.

It appears, therefore, that a better plan needs to be put in place in order that all parties are using the same measurement language and standards. The plan will cover 4 phases:

Phase I	Develop a Changeover Policy and Plan
Phase II	Obtain or Develop a Base of Metric Standards and Informaion
Phase III	Implement in All Areas
Phase IV	Phase Out the Inch System

Taking these phases separately and in detail:

Phase I - Develop a Changeover Policy and Plan

The first step, of course, is to develop the company policy. This will include decisions on: Accepting or not accepting metric business opportunities (as stated before)? What will be the extent of the changeover? Will it be simply to convert all documents back to inch? Or, will all manufacturing and inspection equipment be converted to metric capability? Will the entire company or just affected departments or portions thereof be changed over?

The plan with target dates should be put in place to implement the policy, and an organization should be assigned to oversee implementation. This organization may be only a single individual who does this as part of his regular duties. It may consist of several individuals if the company is large enough. This person or group will need to become familiar with the SI Metric Measurement System and everything that is affected by it -- especially as it applies to the company or to specific functions of the company to which metrication applies.

This will be a good time to also review the regular day-to-day operations to see where they can be improved while changing over to the SI system. This could probably be done without going metric, but there just doesn't seem to be sufficient time on a day-to-day basis to take as good a look at these operations as will be possible while changing over to metric. Such improvements can offset the costs of going metric and result in a more efficient operation.

Phase II - Obtain or Develop a Base of Metric Standards & Information

The base of standards should include very specifically all applicable customer standards, applicable industry standards (U.S. and ISO) and the company's own standards. Any customer who has gone metric will have available any standards applicable to their work. These should not only be obtained but also should be thoroughly understood by all employees who will work on the customer jobs. The same applies to all other necessary standards.

Suppliers' catalogs are also a necessary source of metric information. More and more suppliers are now providing such material.

Phase III - Implement in All Areas

Implementation will consist of both education of employees and also conversion of equipment. Education will vary from familiarity of the very basic metric units being used (for example, the millimeter in engineering and manufacturing operations) to full knowledge of the SI system and applicable standards.

Equipment conversion plans will vary considerably because there are two aspects which must be considered. First, some equipment will not need conversion because it is not measurement sensitive (example: broaching machines and some drill presses). Other equipment is mainly dependent upon the tool or process used to create the metric dimension (for example, drills, reamers, broaches, gang mills, etc.). Some equipment will need to be

converted to provide at least dual metric and inch capability using one of several readily available commercial units. Digital readout conversion units, although more costly, can, on most model shop or tool room equipment, improve operator efficiency to the point where this is not a cost of going metric but a real return on the investment.

The extent of equipment conversion will vary from basic metric capability on the least number of pieces of equipment to full metric capability on all measurement sensitive equipment. The former provides the ability to handle the few orders at the beginning of metrication, whereas the latter provides the ability to load the full shop with metric only orders. This is the desired end position of any company since the country is going more and more metric.

Phase IV - Phase Out the Inch System

This may not happen in the very near future unless the U.S. passes some legislation making the changeover to metric mandatory; and even then, there will be considerable old product which will continue to remain both "inch" dimensioned and active orderwise.

In summary, when it has been decided that there is a definite need for a company to go metric or if costwise the times, business and legal conditions dictate that conversion is necessary, the foregoing problems will be taken in stride as many business problems usually are. However, a sound policy and very thorough planning and coordination, along with a thorough study of the SI units and metric standards as they apply to a particular business or industry, will go a long way to ensure that the change to metric will be successful.

J-3

GENERAL INTEREST SESSION J

An Atomic Absorption Analysis Technique for Gold Comparable to Fire Assay

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AT ATOMIC ABSORPTION ANALYSIS TECHNIQUE FOR GOLD COMPARABLE TO FIRE ASSAY

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The fire assay method has been used for hundreds of years, and is firmly established as the final word in settlement of refining processing.

Atomic absorption spectroscopy (AAS) was born only 25 years ago, and has made only modest progress as an alternative assay method.

Consider this recent comment: "No reputable assayer believes that instrumental methods provide accurate enough determination of fineness" (1).

Consider also, however, that most refiners have instrumental methods in their laboratories for analyzing solutions, and a few will even offer to settle on a mutually-agreed-upon AAS assay. Some refiners are saving time by analyzing cupelled beads by AAS (2).

One expert recently went so far as to say, "Is the fire assay headed for an obscure extinction? I think the answer to this question may be yes, if more training and educational material is not provided to individuals pursuing an understanding of this subject" (3).

Slide 1 shows the steps involved in a fire assay analysis.

SLIDE 1. FIRE ASSAY PROCEDURE

1. Weigh sample
2. Fuse sample with fluxes, lead, and (possibly) silver
   a. Flux dissolves base metals
   b. Lead alloys with precious metals (P.M.)
3. Dispose of flux
4. Fire lead bead in bone ash crucible
   a. Lead oxidizes and is absorbed by crucible
   b. P.M. bead left (possibly weigh)
5. P.M. bead treated chemically to separate individual metals
6. Weigh pure metals

Fire assay has good points, of course, primarily:

1. Any type of sample can be accomodated (ores, bullion,

sweeps, etc.)
2. Few interferences, since each metal of interest is extracted and weighed separately.

Deficiencies of the fire assay method are:

1. "Proof" samples are needed to correct for assay losses which can occur through volatilization, absorption into the cupel, or incomplete fluxing of precious metals by the molten lead during the assay process.
2. Low-grade (< 0.1% gold) samples require preliminary concentration, since direct fusion is impossible with large samples required for a reliable assay (3).
3. Operator skill can affect results.
4. A comparison of costs of routine independent laboratory assays vs. "umpire" assays by the same laboratories attests to the fact that complete recovery of precious metals is more than a routine proposition.

The use of AAS has good and bad points, also, i.e.:

Advantages of AAS for precious metal assay are:

1. Effective for low grade (0.1%) as well as high grade (99+%) samples.
2. Short analysis time, typically 30 minutes from start to finish.
3. Most constituents of interest in the sample can be analyzed by simply changing lamps on the A.A. instrument.
4. Accuracy and precision are not dependent on highly trained operators.
5. Interferences are minimal and can be compensated (2,4).

Deficiencies of AAS for precious metal assay are:

1. Dissolution of high-silver (10%)/gold samples in aqua regia (3:1 HCl/HNO_3) can entrap gold in the insoluble silver chloride skeleton that forms. This can be compensated for by: 1) Increasing the hydrochloric acid level to 6N (2), or: 2) Separating the silver chloride by filtration or decantation, following which the silver chloride is dissolved in CP ammonium hydroxide to release the gold. The silver can then be analyzed by dilution of the ammonium hydroxide solution.
2. If the AA burner is not periodically purged with a dilute cyanide solution, gold deposits can form on the spoiler, and leach out and give high readings on subsequent analyses.

3. Can be used routinely only for bullion, although it can be adapted for ores, etc., by preliminary fusion operations.
4. Can analyze only those metals that can be chemically dissolved. Chemically-resistant metals like rhodium must be fused initially to convert them to water or acid-soluble salts.

When describing methods of analysis, we don't address the problem of obtaining representative samples. Suffice it to say, that inhomogeneous samples are occasionally encountered, and gross lack of precision in replicate samples might be traced to this problem.

After making many unsuccessful attempts to obtain results via AAS analysis that would be comparable to fire assay results, NBS certified glassware was purchased. This was really a last resort, because work had been done previously (5) that indicated that volumetric errors were quite small.

Surprisingly, subsequent results became comparable to fire assay results.

To check on a more absolute basis, equal-sized samples of a single granulated sample were sent to five independent laboratories. These analyses are shown in Slide 2.

SLIDE 2. FIRE ASSAY OF SAME SAMPLE BY INDEPENDENT LABORATORIES

LAB.	GOLD ANALYSIS(p.p.t.)	DELAY TIME	COST
1	35.91	17 days	$35.00
2	35.90	20 "	$50.00
3	35.83	10 "	$30.00
4	35.98	14 "	$18.50
5	36.18	14 "	$25.00

AVERAGE 35.96 BY AAS 33.91

This data may not appear to be too encouraging, but keep in mind that the primary reason that refiners have not accepted AAS results in the past is that they were consistently high when everyday glassware was used. The above sample was analyzed by AAS on many different occasions, with the results consistently the same.

A brief review of the analytical method used follows.

If some previous data is available on the expected approximate gold content, use sufficient sample to yield a maximum of 10 milligrams of gold. As an example, a sample of 1/20 12 Kt gold filled scrap could be expected to yield 25 parts-per-thousand of gold, or 2.5% by weight. A 400 milligram sample would yield 10 milligrams of gold.

Therefore, in this example, weigh out at least three separate 400 mg. samples. Place each sample in a 50-ml. erlenmeyer flask, and add 10 ml. of 3:1 aqua regia. Place on a hot plate set on "low" in a fume hood. Keep samples on the hot plate until all gassing stops. Cool and examine the flask over a white background for the presence of unreacted pieces. Additional heating will usually solubilize them. White silver chloride can be solubilized by the addition of an additional 10 ml. of concentrated HCl.

The samples are washed with deionized water into NBS certified 1000 ml. volumetric flasks, followed by at least three rinses of the erlenmeyer into the volumetric flask. Dilute to the mark, thoroughly mix, and the samples are ready for analysis.

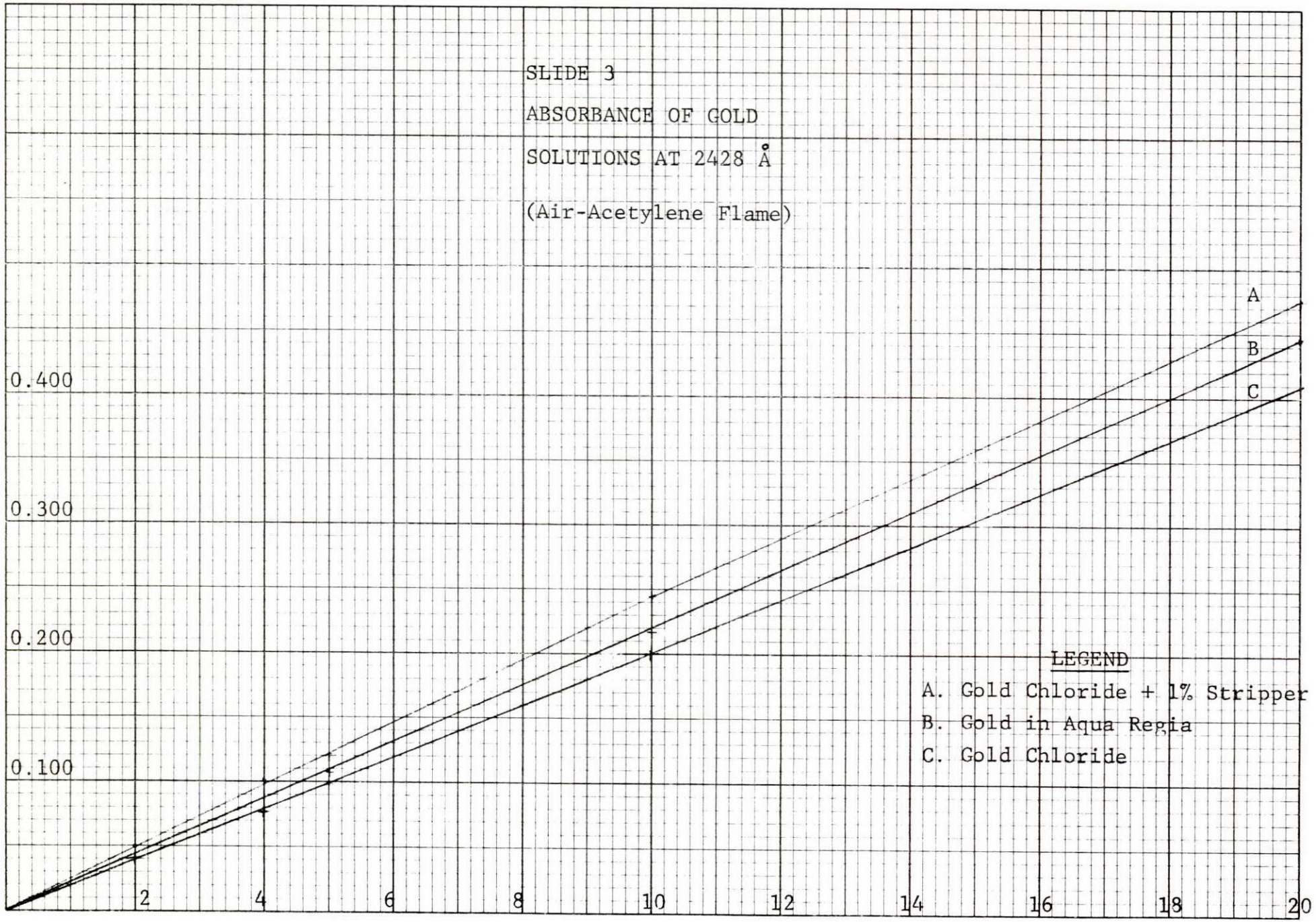
Prepare a standard by pipetting 1 ml. (certified pipet) of 1000 ppm stock gold standard into a 100 ml. certified volumetric flask. Add a little deionized water. Then pipet 1 ml. (don't need certified for this item) of freshly-prepared aqua regia into the flask, dilute to the mark, and mix thoroughly. The standard is 10 ppm with 1% aqua regia, called simply a "10 + 1" standard.

Use a nitrous oxide/acetylene flame (to eliminate interferences), and a wavelength of 242.8 nm. Optimize lamp adjustments, flame, and nebulizer uptake rate for maximum absorbance (using appropriate prescribed instrument procedures), calibrate, and run samples.

If a larger sample is required, as when the gold content is very low, use a larger amount of aqua regia, but match the "+" of the standard to the sample solution.

Gold samples can also be dissolved in proprietary gold strippers, but dissolution proceeds very slowly. Use a nitrous oxide flame, and spike the standard with an equivalent concentration of stripper.

While additives, such as aqua regia and gold stripper themselves may not produce a signal, they can affect gold absorbance (Slide 3) when an air-acetylene flame is used. Matched standards partially offset the effect, while the use


SLIDE 3
ABSORBANCE OF GOLD
SOLUTIONS AT 2428 Å
(Air-Acetylene Flame)
A
B
C
0.400
0.300
0.200
0.100
ABSORBANCE
LEGEND
A. Gold Chloride + 1% Stripper
B. Gold in Aqua Regia
C. Gold Chloride
2
4
6
8
10
12
14
16
18
20

of a nitrous oxide/acetylene flame generally eliminates the effect entirely.

Some laboratory techniques which were found to be helpful are as follows:

1. Make a new standard for each sample run.
2. Don't allow standards or samples to stand, to avoid possible absorption of metals onto walls of flasks.
3. Make final adjustments to volumetric flask fill lines with a medicine dropper. This avoids the problem of inexact filling due to liquid clinging to the walls and running down uncontrollably.
4. Use a nitrous oxide/acetylene flame and a 10 + 1 standard.
5. A 10-second integration time gives best precision, while 0.1 - 1.0 absorbance units on samples insures constant precision (6).

Slide 4 shows the results of using an AAS assay method to cross-check fire assay data with refiners. Slide 5 lists what few splitting limits could be found in print for the purpose of objectively deciding whether assay results are sufficiently close to split the difference. Assays which differ beyond splitting limits are sent to a mutually-acceptable umpire. Generally, if the umpire's assay results fall within the range of the two parties, the umpire assay is accepted for settlement. If the umpire assay is outside the range, the assay nearest the umpire is accepted. Umpire results are always obtained via fire assay. Plasma emission analyses are included in Slide 4 as a third-method cross-check.

CONCLUSIONS

Data has been presented which shows that AAS analysis of refining samples can produce results comparable to fire assay, provided proper preparation procedures are followed. It must be emphasized that averages of assay results are not acceptable as accurate comparisons. Assays must be converted to gold content in the refining lot represented by the assay sample. One high assay on a large lot can balance out low assays on many small lots.

The bottom line analysis of all the listed assays showed the net difference in overall assayed gold content in approximately 900 troy ounces of settlements to be about 1 troy ounce over a 6-month period.

SLIDE 4. ASSAY COMPARISONS (PARTS PER THOUSAND)

SAMPLE #	REFINER FIRE ASSAY	A.A.S. ASSAY	PLASMA* EMISSION	UMPIRE	SETTLE
1	10.40	9.60	10.9	10.64	10.40
2	15.00	16.15	15.7	16.34	16.15
3	22.85	20.80	--	22.2	22.2
4	6.45	6.20	6.16	--	6.325**
5	2.75	3.25	--	2.95	2.95
6	3.85	3.73	3.82	--	3.85
7	13.8	13.5	--	--	13.8
8	9.40	10.5	--	9.39	9.40
9	12.60	12.20	--	12.63	12.60
10	10.45	10.43	11.2	--	10.44**
11	11.15	10.93	--	--	11.04**
12	15.29	15.09	15.9	--	15.19**
13	14.25	14.57	--	--	14.41**
14	4.71	4.49	--	--	4.71
15	4.15	4.18	4.22	--	4.165**
16	1.26	1.47	--	1.24	1.26
17	8.35	8.37	8.64	--	8.36**
18	4.62	4.43	--	--	4.53**
OVERALL AVG.	9.52	9.44			
AVG. OF LOTS UMPIRED	10.61	10.57		10.77	

* Courtesy of H. Griffin, Texas Instruments, Inc.
** Settled on mid-point of refiner and AAS assays

SLIDE 5, SPLITTING LIMITS

REFINER

1. Absolute difference of 0.015 ppt for assays up to 50 ppt
2. 2% relative difference between assays
3. % of mean of both parties depending on total gold content:

to 5 oz.	10%
5-25 oz.	5%
25-50 oz.	3%
50-100 oz.	1%
100-300 oz.	0.5%

4. 0.1 - 0.15 ppt (3)

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J-4

GENERAL INTEREST SESSION J

Insoluble Sulfide Precipitation of Heavy Metals—A Case History

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INSOLUBLE SULFIDE PRECIPITATION OF HEAVY METALS - A CASE HISTORY

BY: T. Lawn/M. Scott and K. Rogers

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even on our health often require new and increasingly more efficient pollution control methods be used. As a result of the new pretreatment standards, many industries will be faced with installing pollution control systems for removal of heavy metals. More recently the low limits required for POTW or direct discharge to surface waters has forced industries to look for more effective processes than conventional hydroxide treatment for heavy metals.

This paper will review a new novel process, which employes insoluble ferrous sulfide for precipitation of heavy and chelated metals. In 1974 a project was undertaken by the E.P.A. under a grant from the National Association of Metal Finishers (NAMF) to demonstrate the effectiveness of insoluble sulfide precipitation over hydroxide precipitation. Since then, over ten(10) systems which utilize the insoluble sulfide process have been installed and this paper will describe one of them.

The conventional method of removing these metals is what is termed as the lime and settle or hydroxide precipitation method. Precipitation of heavy metals by the addition of lime or caustic soda is the most common used practice. With a well-designed and operated system excellent results can frequently be obtained, but the chemistry of treatment has three(3) basic deficiencies. First, the metal hydroxides are amphoteric, or revert into solution at higher pHs. On operating pH ideally suited for efficient removal of one metal is unfavorable for good removal of another. See graph 1. Second, the metals do not respond well to hydroxide precipitation when chelating agents are present in the waste stream. Third, hexavalent chrome must be reduced to the trivalent state by lowering the pH, then raising the pH to precipitate the trivalent chrome as the hydroxide.

When the solubilities of metal sulfides are compared to those of metal hydroxides, one can see the solubilities of metal sulfides are much lower than metal hydroxides, (Figure 1.) therefore can be removed to lower levels. Metal sulfides are not amphoteric, and can be removed at 1 pH level.

CONVENTIONAL SULFIDE PRECIPITATION

An obvious question might be, "If sulfide precipitation is so good why doesn't everyone use it?". The reason might be found

in some practical problems, even though conventional sulfide precipitation is easily accomplished by the addition of a solution of sodium sulfide to the waste stream. Consider that rapid precipitation of very insoluble materials tends to produce colloids that are difficult to separate from water. Even worse, there is no exact method of matching the sulfide feed with the sulfide demand. Addition of a little too much sulfide can produce toxic hydrogen sulfide, from soluble heavy metal complexes, or result in a sulfide ion concentration which makes the treated effluent unsuitable for discharge. What is needed is a method of treatment whereby the sulfide ion concentration can be easily and inexpensively controlled so that the rate of feed matches the sulfide demand of the waste water. Formation of a colloidal precipitate must also be prevented.

INSOLUBLE SULFIDE PRECIPITATION

When using the insoluble sulfide precipitation process, the sulfide ion available to react with the metal is equal to the demand. The sulfide concentration is neither excessive nor deficient. It is rigidly maintained at a concentration of about 0.02 parts per billion. There is not the faintest odor of hydrogen sulfide.

Whereas a conventional system uses a soluble sulfide salt, this process uses an insoluble salt. Just any insoluble sulfide salt will not work. The sulfide salt that does work must have a solubility greater than the heavy metal sulfide that is precipitated. Ferrous sulfide meets this requirement. It works best when freshly prepared, and the manner in which it is prepared eliminates the problem of colloid formation in the process. The only heavy metal whose sulfide is more soluble than Fe S is manganese. In an alkaline solution, the ferrous ions generated in the dissociation of the Fe S will precipitate as hydroxides. Low levels of ferrous ions in the effluent require the pH to be raised to the range of 8.5 to 9.5.

When hexavalent chrome is present in a waste stream, another property of this sulfide process is valuable. At normal operating pH ranges, the hexavalent chromium is reduced to trivalent chromium by the ferrous sulfide. The conventional equipment associated with reduction of chromium such as acid and alkali feeders, ORP sensing and control devices, etc. are not needed.

However, the cost of wastewater treatment with the insoluble sulfide process is higher than the soluble approach from an operating cost standpoint. The additional cost results from increased reagent costs and generation of larger sludge volumes for disposal.

CASE HISTORY

BACKGROUND

Amron is a medium sized Wisconsin company employing approximately 500 at its Waukesha plant and about 150 at its Antigo, Wisconsin plant. The product line is entirely ordinace hardware items in the 20-40 mm ammunition range. Product variety includes cartridge cases, projectiles, grenade piece parts, and occasionally a subassembly. The Waukesha plant is primarily steel working operations including blanking, drawing, extruding, and to a lesser degree, machining. The Antigo plant processes non-ferrous metals, currently brass and aluminum. Production quantities are frequently in the millions per month with each item receiving up to four annealing and drawing operations prior to machining. The material flow is extensively automated. The finishing equipment which generates water borne pollutants is located in the process line where required. There is no isolated or segregated finishing area. The operations generating the pollutants are (depending on the plant) alkaline and acid cleaning, pickling and/or descaling, conversion coatings (primarily zinc phosphate and chromates), reactive soap coatings, cyanide zinc plating, aluminum anodizing, and painting.

WASTE TREATMENT CONSIDERATIONS

Like most companies, Amron was slow in getting started in effluent treatment considerations for a number of reasons - economic, lack of established effluent limitations, the variety of treatment choices with their attendant strength and weakness considerations, and, probably most importantly, a lack of clear cut decision as how to get started. From 1972 until 1975 most of the activity was just talk. A valuable service was accomplished during this time however. Management was educated to the impending regulations and budget planning began to reflect the future costs. Production and Engineering were slowly taught to incorporate pollution effect thinking in their product and processing planning. By late 1975 an approach to the problem had been developed and was in the process of being implemented. The first consideration was the choice of treatment type to be used, for example evaporative recovery, reverse osmosis, thermal destruct, chemical precipitation to name a few. Another consideration was at what point the effluent should be treated - at the end of the pipe, at point source, or at some intermediate point. A final decision had to be made as to where the treated effluent would be discharged, either to the POTW, or to surface waters.

It was our decision to select chemical precipitation as the method best suited for our particular type of manufacturing process. Briefly, comparing this with recovery systems, the decision was based on (1) economic factors that would require

extensive changes in process equipment to incorporate recovery, (2) the lack of costly process materials (we only zinc plate) to justify recovery and (3) the lack of confidence on our part as to the ability of a recovery system to function reliably day after day.

Thermal destruction was discarded as a viable method of treatment because of the high operating costs involved and the lack of proven technology to cope with all our pollutants.

A number of factors were considered in deciding where in the effluent line to perform the waste treatment. As previously mentioned, we have no separate finishing area so treatment could presumably be done either at point source or end-of-pipe. Since we are discharging 2 million gallons a day from our Waukesha plant it was recognized that very large treatment systems would be required to handle the hydraulic load even if the pollutant load was not excessively large. The final decision was a compromise that combined certain like pieces of process equipment that were physically located near each other and to provide waste treatment for them - in effect creating a number of mini-waste treatment centers. Our Antigo plant, with 200,000 gpd, was more conducive to end-of-pipe treatment, so one waste treatment center was planned.

The option existed at each plant to discharge either to the POTW or to surface waters. The choice was made based on economics. Since both the cities of Waukesha and Antigo have received a Federal grant to upgrade their municipal sewage treatment plants the industrial cost recovery and user charge programs required as a condition of the grant would result in significant costs to the company. I recognized that the additional costs resulting from upgrading any selected waste treatment system to allow direct discharge of treated effluent over and above pretreatment requirements would be cost effective. This decision was acceptable to DNR who encouraged methods that would relieve the hydraulic load to the city.

The decisions having been made as to selection of a treatment type, of the point at which treatment was to take place, and the discharge receiving water, the next step was to initiate a program to reduce water usage. This resulted in the use of flow restrictor valves on all running rinses, in many cases reducing usage from 20 gpm to 3 gpm without adversely affecting process quality. In total, the water usage on flowing water rinses was reduced at least 50%.

A sampling program was then initiated and rinse waters and expended dumps were analyzed in order to determine the actual pollutant levels that would require treatment. During this same period of time we were also working with DNR's Industrial Wastewater Section discussing required discharge limits, methods

of treatment, etc. The concept of metal hydroxide precipitation followed by polishing the residual using insoluble sulfide precipitation as previously described was selected as the best method to guarantee the lowest pollutant level for direct discharge.

PROGRAMMED HOIST

Now let's take a look at the source of the waste at our plant and the system that treats that waste. The process equipment is an automated horizontal barrel dip production line used for zinc phosphatizing steel grenade parts. The line produces approximately 800 ft^2 of surface area per hour. It is run 16 hours per day. The flow of rinse water from the line to the waste treatment system is 15 gpm. Contaminants in the rinse water are phosphorous, chromium, nickel, zinc, and iron.

WASTE TREATMENT SYSTEM

(Figure 2.) Dumps and rinse waters flow into below-floor-level sumps. All dumps are collected and slowly metered into the treatment system. This procedure eliminates shock contaminant loads which could not be properly handled by the treatment system. Compartment No. 1 takes the phosphoric acid dump and permits bleeding of this dump very slowly into the rinse water, compartment No. 3. The other dumps are held in compartment No. 2 and subsequently bled into compartment No. 3, the rinse water collection sump.

Neutralization of the waste with lime is accomplished in two steps with pH controllers automatically adjusting the feed of lime. In compartment No. 3 the first step of neutralization occurs. A pH sensing device activates a chemical feed pump for introducing lime. Calcium chloride is also added in this compartment to react with phosphate, precipitating insoluble calcium hydroxyapatite. Effluent flows by gravity to compartment No. 4 where additional lime is added. Compartment No. 4 is small to permit good mixing of the lime. Lime is proportioned on the basis of deviation from set point on the pH control device. Flow from compartment No. 4 is by gravity to compartment No. 5 where further detention and mixing occurs. Compartment No. 5 also acts as a holding tank for filter backwash. This tank will go into recycle at a low level or low pH condition. Effluent from this tank is pumped to precipitator No. 1. To insure good coagulation and settling characteristics, the neutralization system is designed to control the pH within one half unit of set point. A pH probe is located in compartment No. 5 and is used for proportional feedback control of the addition of lime to compartment No. 4. If the pH set point in the second step of the neutralization process is 8.5, we expect the pH of the neutralized waste to be within the limits of 8.0 and 9.0 at all times. The wastewater must be adjusted to a minimum pH of approximately 8.5 in order to assure adequate operation of the

precipitator system. While a pH above 8.5 does not adversely affect the precipitation of metal sulfides it does increase the solubility of chromium hydroxide in the wastewater. Recently we have found that a control pH of 9.0 provides better effluent quality, particularly of iron. The WPDES permit requires an effluent range of 6.0 - 9.5. If the pH range in compartment No. 5 would rise above 9.5 a second stage controller activates a pH alarm and stops the flow of wastewater from compartment No. 5 until the pH is within the acceptable range. Recycle lines with proper valving automatically open so that the system goes to a recycle mode. This condition will shut off the metering pumps for the addition of ferrous sulfide and the two polymers to the wastewaters in the treatment system, but the metering pump for the addition of calcium chloride continues to operate. When the pH of the wastewater returns to within the pH range on the controller in compartment No. 5 the valve settings are reversed so the system returns to operational mode.

The amount of sludge produced by the phosphate, iron, and suspended matter in the waste, and the very poor settling characteristics of the sludge necessitated the use of two precipitator type settling devices. The first precipitator removes the bulk of the suspended matter. It requires an anionic polymer for good coagulation. The second precipitator acts as a polishing system, to which the freshly prepared iron sulfide is added for removal of residual heavy metals. Good flocculation in this step requires a cationic polymer. A dense sludge blanket is maintained in this precipitator at all times. This blanket contains heavy metal sulfides and excess iron sulfide. The concentration of solids in this blanket is about 7,000 mg/l, so there is a large reservoir of active iron sulfide available in the blanket. It acts like a "flywheel", ready to supply all the sulfide ion necessary to accommodate changes in influent metal concentrations. Both precipitators* are designed on the upflow sludge blanket principle. Each unit includes an inlet flume, a mixing compartment, an upflow sludge filter compartment, a sludge concentration zone and an effluent flume. The chemically dosed water is introduced into the inlet flume and is uniformly distributed to the mixing compartment over the entire length of the units. The agitators in the mixing compartment insure intimate contact between water and chemicals and to keep the sludge blanket in suspension. The mixing compartment is separated from the sludge filter compartment by a water tight sloping baffle which serves not only to keep the mechanical agitators from disturbing the sludge blanket, but also provides a gradually increasing area of upward velocity to enhance settling. The resulting sludge blanket provides for entrapment and holding of fine particles.

Chevron shaped settling tubes* are used in precipitator No. 2 and are placed above the sludge blanket to provide more efficient continuous water clarification.

Effluent from the polishing precipitator flows by gravity to a suction tank from which it is pumped to a dual media (anthracite-sand) filter* for additional removal of total suspended solids before discharge. The filter is equipped with an air scour to insure good cleaning. The filter serves two functions: (1) it prevents effluent contamination due to improper coagulation procedures which would cause floc carryover from the precipitators and (2) it removes any fine suspended matter present in the precipitator effluent. The backwash from the pressure filter is returned to compartment No. 5 for treatment with the process wastewaters. Since the system has only one filter and filtration is needed to assure that the effluent limits for TSS, phosphorous, and the various heavy metals will be met at all times the system is designed to shut off the wastewater flow from compartment No. 5 to the remainder of the treatment system during periods when the filter is being backwashed and to store the backwash waters in compartment No. 5 until the backwash is completed.

SLUDGE CHARACTERISTICS

The wet sludge which accumulates at the bottom of both precipitators No. 1 and No. 2 is transported on a periodic basis to a sludge sump. Using compressed air, automatic timers open and close valves on the compressed air lines in order to automatically control the frequency and duration of time that the sludge is transported to the sludge sumps. A sludge pump pumps the wet sludge to a filter press* for dewatering.

The filter press is a plate and frame pressure filter with a cycle time of approximately four hours. A pressure indicator and a high pressure alarm indicate when the filter press is filled with sludge and requires cleaning. A filter cake receiver is located directly beneath the filter press to collect the dewatered sludge. The sludge is periodically hauled by truck to an approved disposal site. The filtrate from the filter press flows by gravity to the inlet of precipitator No. 2 for treatment with other wastewaters.

A totalizing flow meter and a composite sampler are installed on the line from the pressure filter to monitor the effluent as required by the WPDES permit. A certified waste treatment operator, as required by NR114 Wisconsin Administrative Code, is present during all operating hours of the waste treatment center. While the treatment system is designed to operate automatically for the most part, portions of the treatment system are manually operated. The operator is also required for routine inspection and in case of malfunction of the system.

(Figure 3.) This table presents the raw waste and effluent discharge pollutant levels and also shows the effluent quality required by the discharge permit. (Figure 4.) This table pre-

sents a consecutive 6 month period of effluent as measured in pounds per day taken from the WPDES reports. (Figure 5.) This table defines the chemical consumption and sludge generation rates for the system. Treatment of the phosphates in the wastewater accounts for a large percentage of the treatment cost and the phosphate solids constitute the bulk of the sludge generated. The chemical costs for removal of the heavy metals contained in the wastewater was estimated at $2.36/1,000 gallons. Without the presence of phosphates, the solids generation rate would equal 6.4 lbs. per 1,000 gallons of wastewater.

CYANIDE DESTRUCT

The success of this described system resulted in our letting contracts for the purchase and installation of six more treatment centers in Waukesha totaling some 90 gallons per minute. Essentially the systems are similar to that just described with one interesting difference. Two of the waste treatment centers will be on full cyanide zinc rack plating machines. The cyanide treatment consists of three steps. In the first step the pH will be raised to 10.5 - 11.0 and sodium hypochlorite will be added. The feed of hypochlorite is to be controlled by an ORP sensing device and the feed of caustic by a pH sensing device. Excess zinc ion will be provided either from tank dumps or zinc chloride additions as required. Hypochlorite will be added to the second step and controlled by the hypochlorite feed to the first step. The pH in step 2 will be reduced to 7.5 - 8.5. Effluent will then flow by gravity to step three for detention time, about 2 hours.

In this step chlorination effectively converts most of the ferrocyanide complexes to the less favorably treated ferricyanides. Consequently in the next step sodium sulfite will be added to reduce the ferricyanide complexes to ferrocyanides to be precipitated as zinc ferrocyanides. This treatment will furhter reduce the total cyanide discharge by treating those cyanides that are not amenable to alkaline chlorination. The effluent will then be pumped to a filter press to remove the precipitated ferrocyanides. The filtrate then rejoins the non-cyanide rinses for removal of metals by the insoluble sulfide process. This procedure will guarantee an effluent of less than .5 mg/l of total cyanide and less than .05 mg/l of amenable cyanide.

* Supplied by The Permutit Company, Inc.

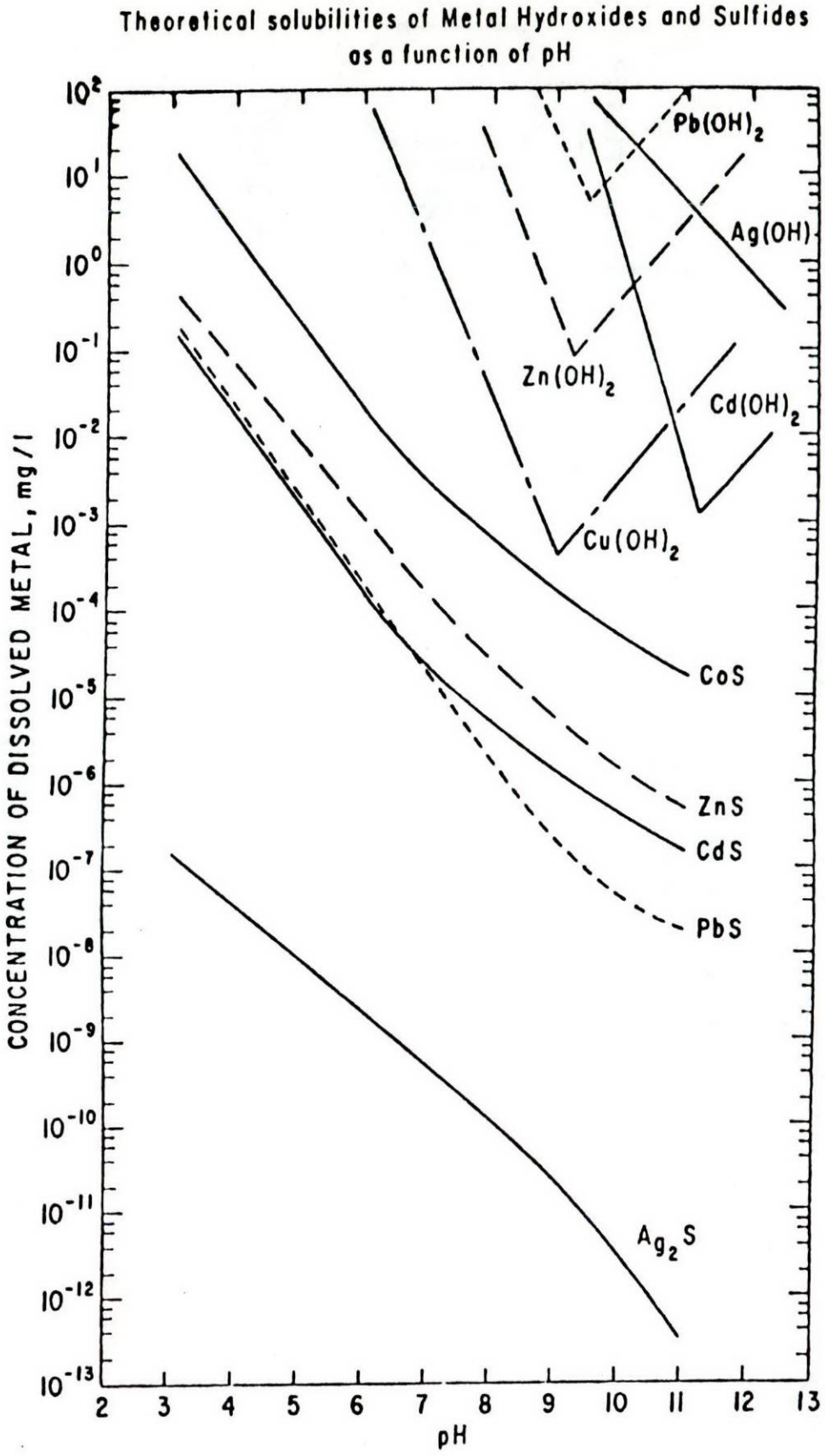
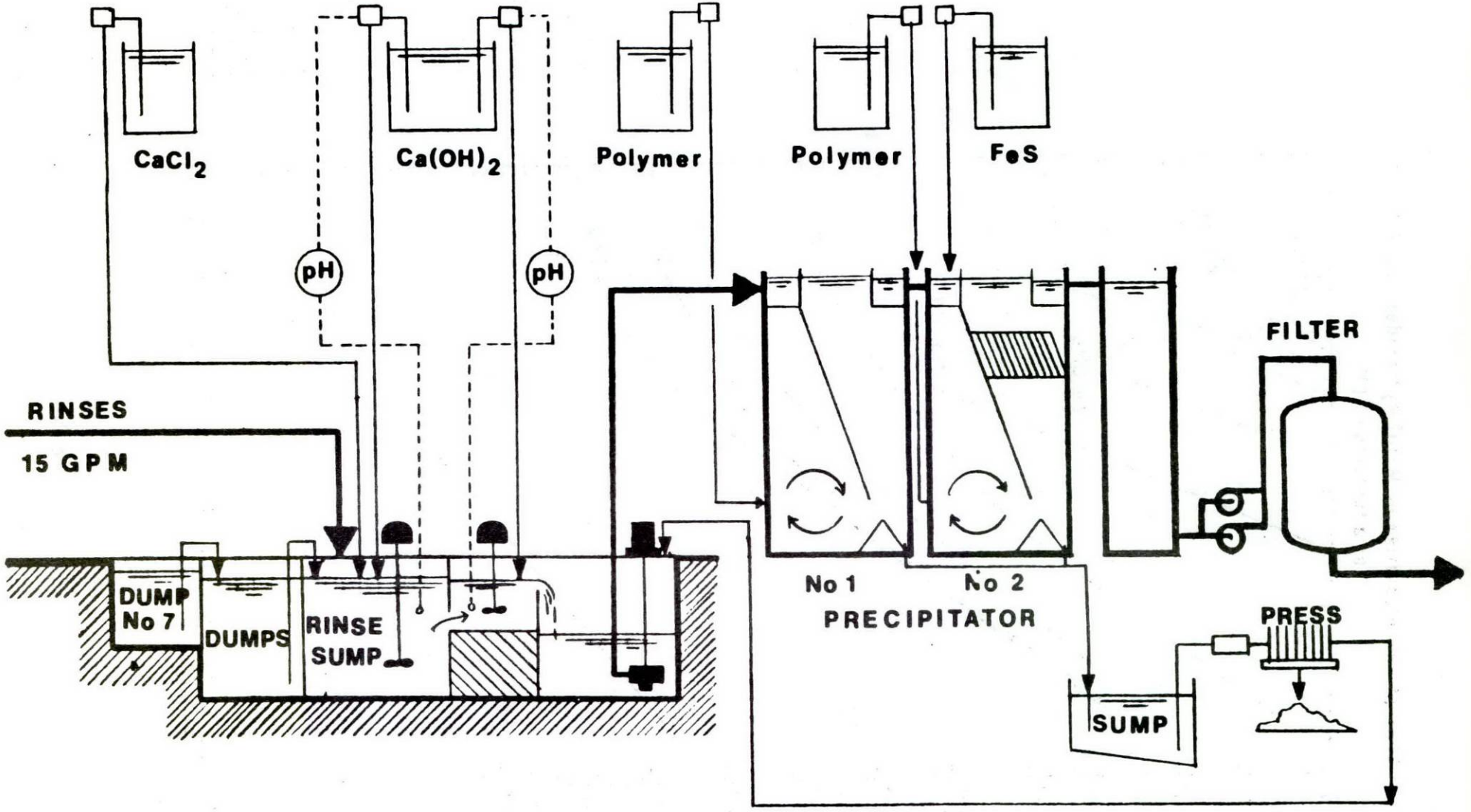

Theoretical solubilities of Metal Hydroxides and Sulfides as a function of pH
CONCENTRATION OF DISSOLVED METAL, mg/l
pH
Pb(OH)2
Ag(OH)
Zn(OH)2
Cd(OH)2
Cu(OH)2
CoS
ZnS
CdS
PbS
Ag2S

Figure No. 1



SULFEX™ TREATMENT SYSTEM

Figure No. 2

Wastewater Analysis[1]

	Influent	Effluent	Permit Requirements[2]
pH	2.9	8.5	6.0 - 9.5
p	289	0.3	1.2
TSS	320	6	23
Cr (Tot.)	8	0.10	0.6
Cr^{6+}	0.07	0.02	0.06
Ni	0.77	0.1	0.6
Zn	24	0.12	0.6
Fe	127	0.60	1.2

1 All values in mg/l except pH

2 Monthly average of daily composite samples

Figure No. 3

WASTEWATER ANALYSIS

Pounds Per Day

	PERMIT REQUIRE:	APRIL 1979	MAY 1979	JUNE 1979	JULY 1979	AUGUST 1979	SEPTEMBER 1979
pH	6.0-9.5	7.45-7.74	7.70-8.21	7.44-8.20	7.71-8.75	7.27-8.00	7.79-8.04
P							
Avg.	.199	.026	.016	.027	.032	.055	.020
Max.	.398	.042	.065	.038	.041	.109	.024
TSS							
Avg.	3.9	.573	.480	.793	.123	.958	.493
Max.	7.81	.634	.713	1.21	.960	1.56	.641
Cr (T)							
Avg.	.099	.015	.016	.018	.019	.015	.014
Max.	.199	.018	.017	.021	.021	.017	.017
Cr (+6)							
Avg.	.0099	.003	.003	.004	.002	.006	.003
Max.	.0199	.004	.004	.005	.003	.017	.003
Ni							
Avg.	.099	.017	.017	.024	.021	.017	.015
Max.	.199	.018	.021	.033	.027	.019	.018
Zn							
Avg.	.099	.015	.016	.018	.037	.017	.014
Max.	.199	.018	.017	.021	.067	.022	.017
Fe							
Avg.	.199	.071	.089	.160	.046	.014	.053
Max.	.398	.090	.100	.392	.054	.322	.074

Figure No. 4

Wastewater Characteristics

Avg. Flowrate	16 gpm	Feed Conc	(avg.)
Feed pH	2.5-- 3.0	P	289 ppm
Effluent pH	7.5-- 8.5	Cr (Total)	8 ppm
		Cr^{6+}	0.07 ppm
		Zn	24 ppm
		Fe	127 ppm

Treatment Chemicals	lb/1000 gal.	$/1000 gal.
$CaCl_2$ (for phosphate removal)	17.0	1.70
$Ca(OH)_2$	5.0	.375
Ferrous Sulfide	.35	.2065
Cationic Polymer (2nd st)	.028	.06
Anionic Polymer (1st st)	.01	.02
Chemical Cost/1,000 gal.		$2.36

Sludge Generation Factors

Dry Solids Generated (lb/1000 gal.)	
1st stage	16
2nd stage	0.4
Dry Solids Generated (lb/1,000 gal. wastewater)	17
30% Solids Generated (lb/1,000 gal. wastewater)	57

NOTE: Without presence of phosphates, treatment cost equals $.81/1,000 gal, solids generation equals 6.4 lb/1,000 gal.

Figure No. 5

WASTE TREATMENT COSTS

Programmed Hoist Waste Treatment Center				$151,460.00
				20 GPM Capacit
Antigo Waste Treatment Center				$484,154.00
				200 GPM Capaci
W.T.C. #1	$178,731.51	$47,522.00		$226,253.51
W.T.C. #2	$321,105.00	$87,500.00	(3/28/79)	$408,605.00
W.T.C. #3	$ 89,144.00	$18,625.00	(3/28/79)	$107,769.00
W.T.C. #4	$168,035.00	$47,222.00		$215,257.00
W.T.C. #5	$600,571.00	$85,111.00		$685,682.00
W.T.C. #6	$ 79,731.00	$16,222.00		$ 95,953.00

Figure No. 6

ENVIRONMENTAL
SESSION K

Determination of the Leaching Properties of Metal Finishing Waste Treatment Sludges

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Reston, VA

DETERMINATION OF THE LEACHING PROPERTIES OF METAL FINISHING WASTE TREATMENT SLUDGES

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ABSTRACT

A program to develop data which would lead to the design of safe, cost-effective methods for disposal of metal finishing wastewater treatment sludges was carried out under the joint sponsorship of the American Electroplating Society and the Environmental Protection Agency. This program consisted of three phases:

- Phase I physically and chemically characterized the sludges from 12 metal finishing plants, selected to represent about 90 percent of the total sludges generated. The sludges were characterized by response to a range of parameters in various static extraction procedures.
- Phase II used laboratory dynamic testing to more closely approximate the conditions in a segregated landfill.
- Phase III involved field tests on two landfills containing electroplating sludges.

The concentration and amount of interstitial fluid and the pH were found to strongly influence the composition of the liquid extract in static tests.

Data from Phase II showed dramatically reduced leaching rates compared to those of Phase I, and Phase III results supported those of Phase II. Limited testing indicates that the age of the sludge has a dramatic impact on its leachability, with leaching rate falling rapidly, and older sludges leaching far less metals.

ACKNOWLEDGMENTS

The EPA project personnel were Alfred B. Craig, Jr. (Project Officer) and George S. Thompson (Branch Chief). Kenneth Coulter served as Technical Project Director and Douglas Thomas served as AES Task Force Chairman. Task Force Members were: Dick Crain, Irv Ireland, George O'Conner and Fred Steward. J. Howard Schumacher served as the AES coordinator.

INTRODUCTION

The American Electroplaters' Society (AES) and the U.S. Environmental Protection Agency (EPA) Industrial Environmental Research Laboratory (IERL) are cooperating in a three-phase study of sludges from electroplating wastewater treatment systems. The ultimate goal of the study is to enable the prediction of the dissolution rate of toxic metals in electroplating sludges in a segregated landfill environment. It is hoped this will lead to environmentally safe landfill designs while avoiding the economic problems associated with overdesign.

Phase I was designed to promote physical and chemical characterization of representative sludges of this type, to test their response to the Extraction Procedure (EP) proposed by the EPA as the primary test of the toxic nature of wastes under RCRA, and to determine the sensitivity of the variables in the EP. Phase II utilized dynamic laboratory testing to simulate actual segregated landfill conditions and to characterize the anticipated performance of electroplating sludges in that environment. Phase III testing provided some validation of the results of Phase II by testing sludges taken from actual landfills.

The AES Task Force recommended a set of 12 waste treatment sludges that adequately represent the electroplating industry, along with the plant sites where the sludges could be obtained. Table I lists the plant code and the major processes at the plant that contributed to the sludge.

Table II illustrates all of the experiments conducted during the testing. Several of the experiments conducted were intended to be screening tests to determine if further investigation would be warranted.

Table I. Description of Experiments

Experiment	Title	Description
I	Effect of pH	Three different sludges were run at pH = 4, 5, 6, 7, 8, 9, 10, and 11.
II	Effect of pH	Nine additional sludges were run at pH = 5, 7, 8, 9, and 10.
III	Effect of Volume of Extraction Water	One sludge was run according to the EP, except that 5 and 10 ml of extraction water per gram of solid were used instead of 16 ml.
IV	Reproducibility	Two sludges were run in duplicate to evaluate the reproducibility of results obtained.
V	Effect of Temperature	One sludge was run at a temperature of 40°C (104°F) which represents the upper extreme allowed by the EP.
VI	ASTM Procedure	A few extractions were run utilizing the ASTM extraction procedures for comparison to the EP.
VII	Effect of Age of Sludge	One sludge was allowed to age for 3 and 6 month periods, then analyzed as in Experiment II.
VIII	Total Metal Content	The total metal content was determined for each sludge.
IX	Anion Content	Anions were tested for because of their potential impact on the solubility of metal ions.
X	X-Ray Diffraction	X-ray diffraction was run on each of the sludge samples to identify the crystalline structures present in the sludge.

Table I
(Continued)

Experiment	Title	Description
XI	Filtrate Analysis and Washing	The initial filtrate from the EP was analyzed to determine the presence of toxic metals and their impact on the results of the EP test. Washing experiments were run to determine the impact of interstitial water quality on EP results.
XII	Filtration versus Centrifugation	Filtration versus centrifugation as separation techniques was evaluated in this test.
XIII	Organic Content	TC and TOC for the sludges were measured to indicate the potential for biological action.

Table II. Plant Descriptions

Plant Code	Primary Plating Process
1A	Segregated Zn
2A	Segregated Cd
3A	Zinc Plating and Chromating
4A	Cu-Ni-Cr on Zn
5A	Al Anodizing
6A	Ni-Cr on Steel
7A	Multi-process Job Shop
8A	Electroless Cu on Plastic, Acid Cu, Ni, Cr
9A	Multi-process with Barrel or Vibratory Finishing
10A	Printed Circuits
11A	Ni-Cr on Steel
12A	Cd-Ni-Cu on Brass and Steel

EXPERIMENTAL PROCEDURE

Sample Collection

The sludge samples were collected in polyethylene carboys. Upon reaching the laboratory, the samples were stored in a refrigerator at 4°C and were withdrawn only to obtain samples for the experimental study. A representative sample for each test was secured by emptying the solid sludges into a large tray, breaking up the solids into smaller pieces (approximately 3/8 inch), and withdrawing portions from several sections of the sample. Slurries were thoroughly mixed prior to sampling. The unused material was returned to the carboy and stored in the refrigerator. The sludges that were collected are described in Table III.

During the sampling visit, an effort was made to collect readily available information concerning plant operations and wastewater handling techniques as they pertained to the sludges. No effort was made to perform an in-depth plant survey or to collect ideal samples. Where possible, the sludge samples were collected as they came out of the dewatering process, although some samples were collected from dewatering beds and may have been several months old. The intent was to collect samples in the form that they would be shipped to a disposal site.

EPA Extraction Procedure

Because the EPA-proposed Extraction Procedure (EP) is used as the basic extraction procedure for the tests in Phase I of this study, a general description of the EP follows to assist in better understanding and interpreting the data.

A 100-gram sample (minimum) of the sludge is separated into its component phases by either filtration or centrifugation. The filtrate is set aside and stored at 1° to 5°C (34° to 41°F). The solid portion is prepared for extraction by reducing the particle size so that it will pass through a standard 9.5 mm (3/8 inch) sieve. After being weighed, the solids are placed in an extraction container where 16 grams of water are added for every gram of solids. This mixture is stirred sufficiently to assure that all sample surfaces are continuously brought into contact with well mixed extraction fluid and to prevent any stratification. The pH is adjusted to 5.0 $\pm$ 0.2, using 0.5N acetic acid. The total amount of acetic acid is limited to 4 ml per gram of solid, beyond which no more may be added. The extraction is maintained between 20° to 40°C (68° to 104°F) for 24 hours.

Table III. Sludge Descriptions

Plant	Initial pH	Percent Dry Solids	Apparent Density (g/ml)	Particle Density (g/ml)	Description
1A	9.3	11			White liquid slurry, rubbery particles
2A	9.8	6	1.08	0.76	Deep brown slurry
3A	8.7	3	1.04	1.56	Yellow-brown slurry
4A	8.5	7	1.04	1.06	Gray-green slurry
5A	7.4	17	1.01	0.81	Gray-gritty paste, with visible water
6A	10.2	34	1.12	0.66	Black paste with visible water
7A	7.4	15	1.24	0.90	Green-brown paste moist, but no visible water
8A	9.0	29	1.25	1.07	Blue-green, clay-like material
9A	9.1	36	1.26	1.06	Gray-green hard lumps, dry appearance and quite compact
10A	9.0	24	1.18	2.44	Dark muddy brown slurry
11A	9.4	19			Homogeneous forest green slurry
12A	9.1	23			Dark blue-grey chunky paste

The mixture is separated as before into solid and liquid components. The liquid is diluted to a total volume equal to 20 times the weight of the initial solid material. To this is added the original filtrate from the raw sludge. This combined liquid is the extraction procedure extract upon which analyses are made for toxic metal ions. The extract is analyzed for silver, arsenic, barium, cadmium, chromium, lead, mercury, and selenium.

Part of Phase I was to determine the sensitivity of the sludges to the variables of the EP. It should be noted that the EPA has defined the EP, and results obtained when EP variables (e.g., pH) are changed are not the results of the EP. Variations from the EP in the testing done during this study are clearly identified.

Dynamic Testing

Dynamic testing done under Phase II of this study was designed to reasonably simulate the environment of a segregated landfill and to test the leaching tendencies of the electroplating sludges in such an environment. The equipment designed for this testing is shown in Figure 1. Simplicity was desired to minimize the test variables; therefore, landfill materials (e.g., clay) are not present because of the complicated attenuation properties of different lining materials. The sludges were subjected to a constant head of deionized water (head = 3 inches of water) to simulate percolation of rainwater through the landfill at a constant rate. Leaching rates, while relatively constant for each sludge, varied from 60 to 2200 ml/day (equivalent to 0.4 to 14 inches of rainfall). The samples were not allowed to run dry as this would result in cracks in the sludge bed which would encourage "short-circuiting" of leaching water when it was reapplied. The leachate was measured periodically for pH and conductance to monitor the extent of leaching present. Leachate was also analyzed for metal concentrations on days 1, 2, 3, 5, 7, and every seventh day thereafter. The leachates were analyzed for all metals known to be in the sludge in significant quantities, based on Phase I testing.

Field Testing

One of the plants that was sampled in the survey (Plant 11A) had two captive landfills where their wastewater treatment sludges were disposed. One of the landfills has not been added to in over six years. Both landfills were sampled at various depths and locations. Additionally, a leachate sample from a drainage pipe on the landfill currently being used and a background soil sample were collected. The solid samples were all subjected

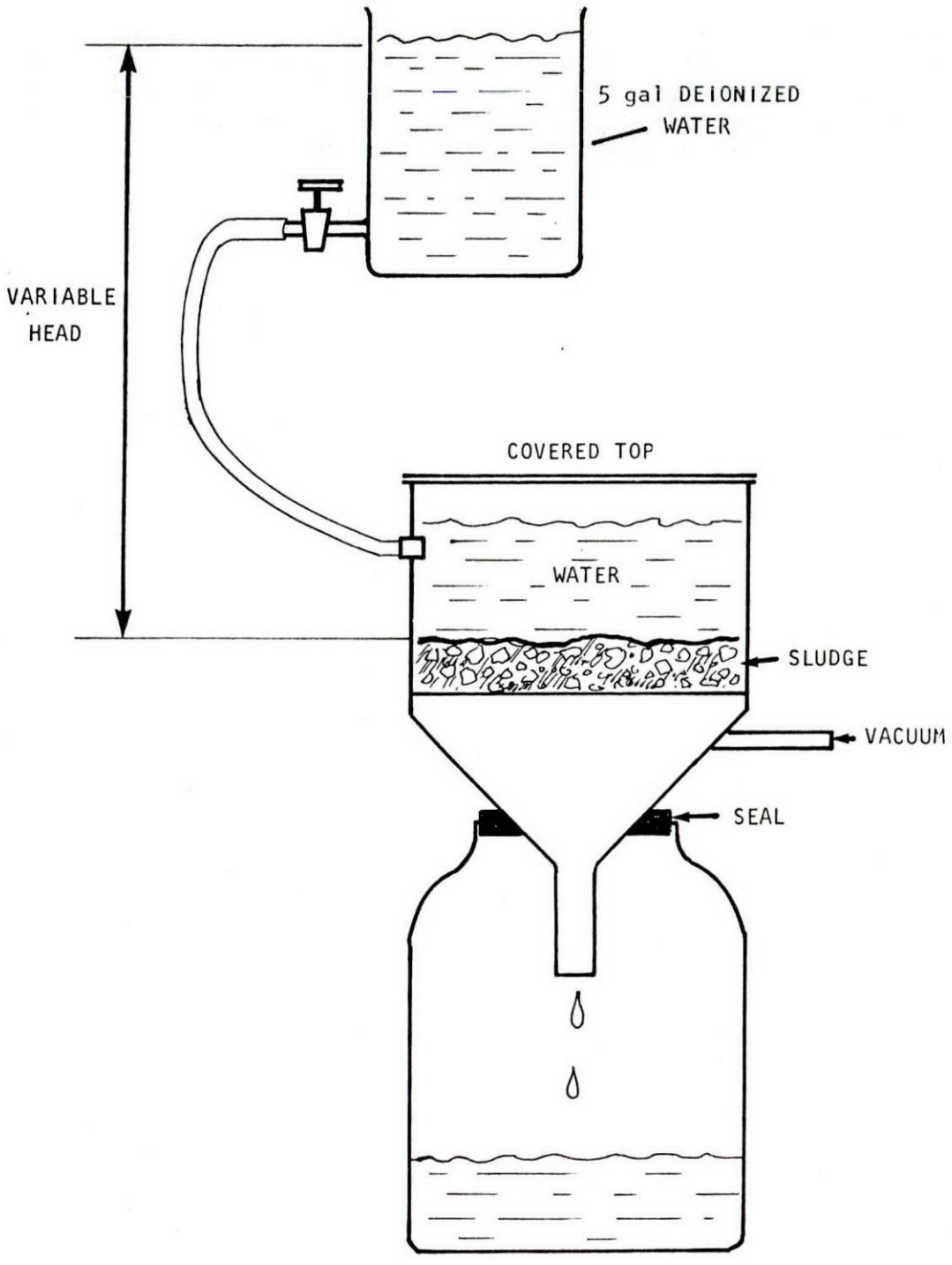


Figure 1. Dynamic Testing Apparatus

to the EP, and the leachate sample was analyzed for the eight toxic metals.

The older landfill had become a pond with about 48 inches of water over the sludge. The pond water was pumped out so that sludge samples could easily be taken. The pond was lined with a heavy growth of cattails and was populated with enough tadpoles to clog the pump being used to drain the pond.

DISCUSSION OF RESULTS

Effect of pH

The results of experiments I and II are shown in Tables IV and V, respectively, and the dramatic effect of pH on metal levels in the extraction extract can be seen. This effect is more clearly seen in Figures 2 through 13.

As a general rule, the metal concentrations followed what would be expected based on general chemistry; i.e., most metals were highly soluble at low pH's and decreased in solubility as pH increased, while some metals reached a minimum and began increasing in concentration again. This is important because, as Table III showed, most sludges had initial pH's of 8.5 or higher.

Several of the sludges have one or two metal concentration levels in the EP extract liquid (pH = 5) higher than the hazardous limits proposed by EPA. Far fewer sludges would have this problem at pH = 8.5 or more.

Age of Sludge

A sample of Plant 7A sludge had been set aside in an open beaker to age for several months. Extractions at pH 5 and pH 7 were run on a portion of the sample after three months, and the results were rather dramatic. Leaching rates dropped by 50 to 90 percent for Cd, Pb, and Cr. The most evident change due to aging was in the dryness of the sample. One explanation for the drop in leachability of the toxic metals may be that some form of curing took place during the drying process which structurally tied up the metals, making them unavailable for dissolution. While these results are very interesting, further testing on other sludges is necessary before firm conclusions can be made.

Table IV. Sludge Characterization - pH Study

Experiment I
(mg/l)

Proposed Hazard Limit[1]		0.1	0.5	0.5
Metal		Cd	Pb	Cr
Plant 6A (34% solids)	pH 4	<0.01	0.027	184
	pH 5	<0.01	0.001	25.4
	pH 6	<0.01	0.002	3.64
	pH 7	<0.01	0.003	1.21
	pH 8	<0.01	<0.001	0.05
	pH 9	<0.01	<0.001	0.06
	pH 10	<0.01	<0.001	0.08
	pH 11	<0.01	<0.001	0.16
Plant 7A (15% solids)	pH 4	0.60	0.006	25.3
	pH 5	2.16	0.003	0.24
	pH 6	0.35	0.002	0.16
	pH 7	0.04	0.005	0.50
	pH 8	1.21	0.25	18.2
	pH 9	1.54	0.28	24.0
	pH 10	2.00	0.40	29.5
	pH 11	1.22	0.28	19.2
Plant 9A (36% solids)	pH 4	0.04	0.020	5.38
	pH 5	0.03	0.010	0.32
	pH 6	<0.01	0.002	0.05
	pH 7	<0.01	0.001	0.05
	pH 8	<0.01	0.002	0.04
	pH 9	<0.01	<0.001	0.05
	pH 10	<0.01	0.001	0.06
	pH 11	<0.01	<0.001	0.09

Note: As, Ag, Ba, Hg, and Se are at or near the detection limits for Plants 6A, 7A and 9A.

[1] As proposed in FR 43, No. 243, pg. 58956.

TABLE V. Effect of pH

Experiment II

Proposed Hazard Limit		0.5	0.1	0.5	0.5	0.02	0.5
Metal		Cr	Cd	Pb	As	Hg	Ag
1A (11% Solids)	pH 5	1.22	0.23	0.041	0.073		<0.01
	pH 7	<0.05	0.01	<0.001	0.076		
	pH 8	<0.05	<0.01	<0.001	0.035		
	pH 9	<0.05	<0.01	<0.001	0.114		
	pH 10	<0.05	<0.01	.007	0.082		
2A (6% Solids)	pH 5	1.89	126	<0.001	0.005		<0.01
	pH 7	1.68	1.42				
	pH 8	1.85	0.48				
	pH 9	1.41	0.20				
	pH 10	1.74	0.25				
3A (3% Solids)	pH 5	85.0	6.00	0.009			
	pH 7	10.4	0.13	0.045			
	pH 8	17.2	0.04	0.146			
	pH 9	20.6	0.02	0.020			
	pH 10	34.2	0.04	0.042			
4A (7% Solids)	pH 5	21.8		0.038			.02
	pH 7	10.8		0.005			.02
	pH 8	15.7		0.012			.02
	pH 9	25.4		0.011			.02
	pH 10	42.2		0.008			.02
5A (17% Solids)	pH 5	<0.01		<0.001			<0.01
	pH 7	0.18		<0.001			
	pH 8	3.67		0.031			
	pH 9	4.28		0.067			
	pH 10	1.58		0.005			
8A (29% Solids)	pH 5	400		0.032		0.0450	.02
	pH 7	1.69		<0.001		0.0395	.01
	pH 8	0.86		<0.001		0.0166	.01
	pH 9	1.34		<0.001		0.0075	.01
	pH 10	0.30		<0.001		0.0047	<.01
10A (24% Solids)	pH 5	0.12		0.88			
	pH 7	<0.05		0.075			
	pH 8	<0.05		0.055			
	pH 9	<0.05		0.082			
	pH 10	<0.05		0.058			

-Continued-

TABLE V. Effect of pH
(Continued)

Experiment II

Proposed Hazard Limit		0.5	0.1	0.5	0.5	0.02	0.5
Metal		Cr	Cd	Pb	As	Hg	Ag
11A (19% Solids)	pH 5	4.22	<0.01	0.004	0.035		
	pH 7	0.18		0.002	0.006		
	pH 8	0.19		0.002	0.039		
	pH 9	0.46		0.002	0.048		
	pH 10	0.35		0.002	0.052		
12A (23% Solids)	pH 5	4.85	268	0.031	<0.001		0.03
	pH 7	0.38	1.65	0.004			0.02
	pH 8	0.38	0.46	0.004			0.02
	pH 9	0.26	0.27	0.002			0.01
	pH 10	0.56	0.34	0.002			0.02

Blanks, Ba, and Se were at or below detection limits.

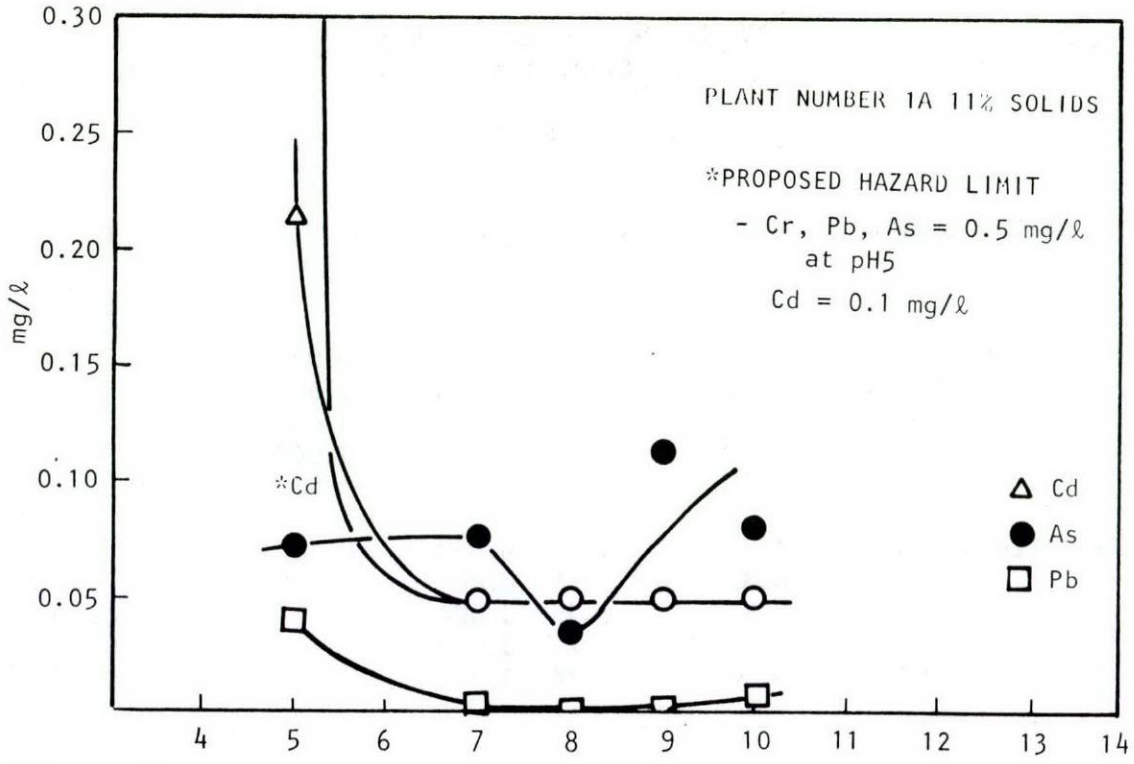
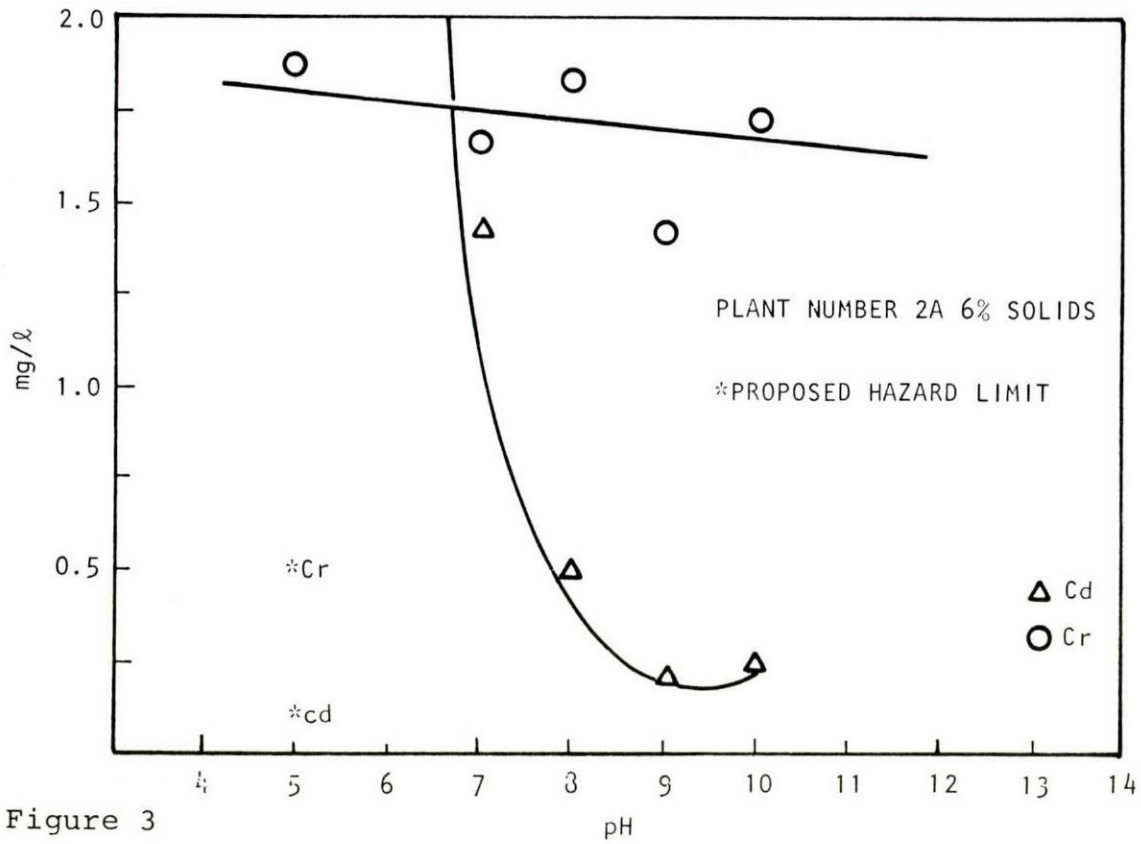


Figure 2



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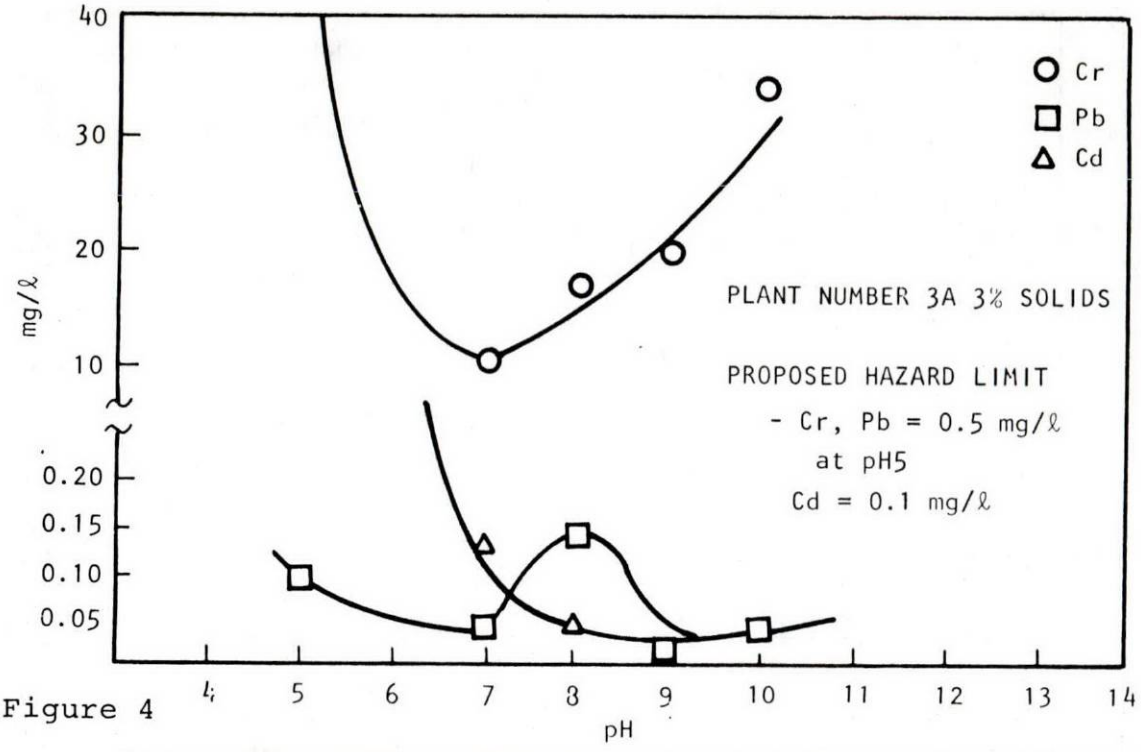
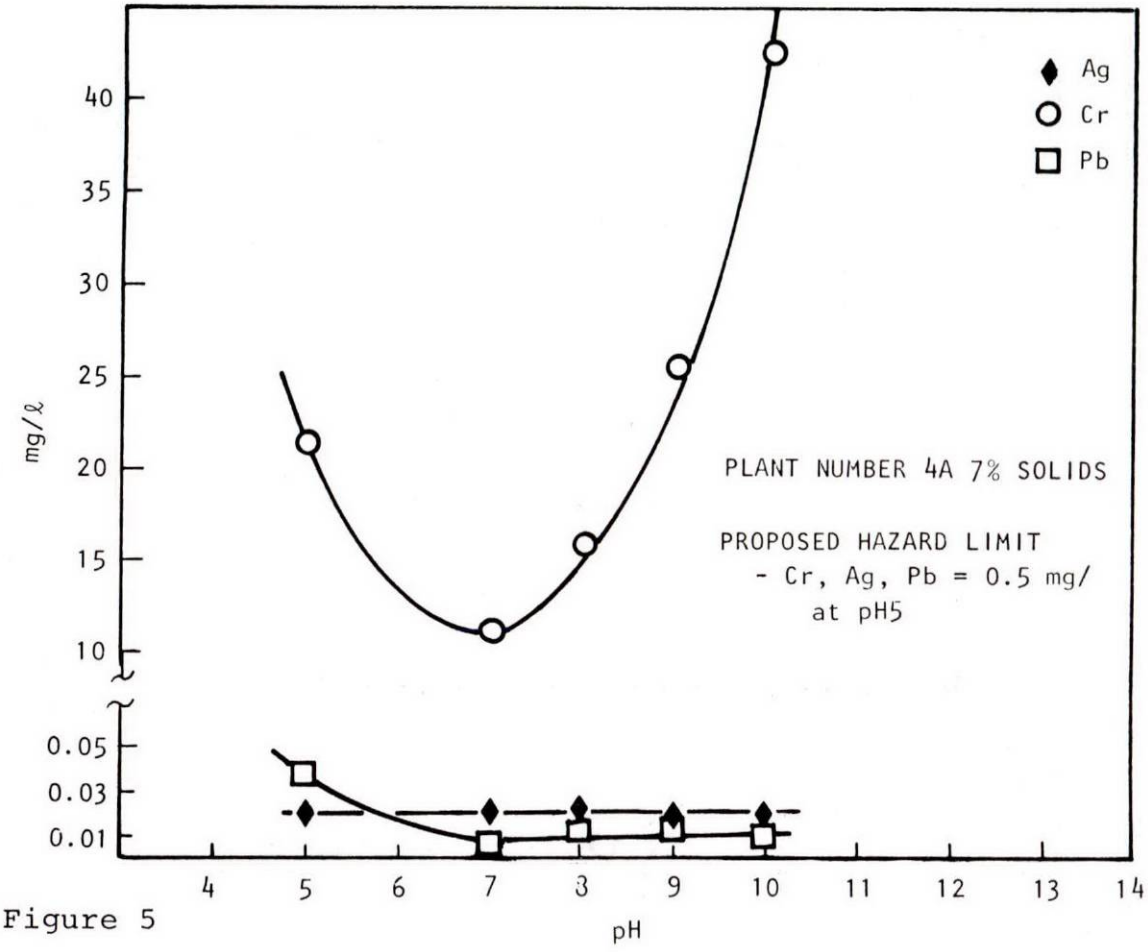


Figure 4



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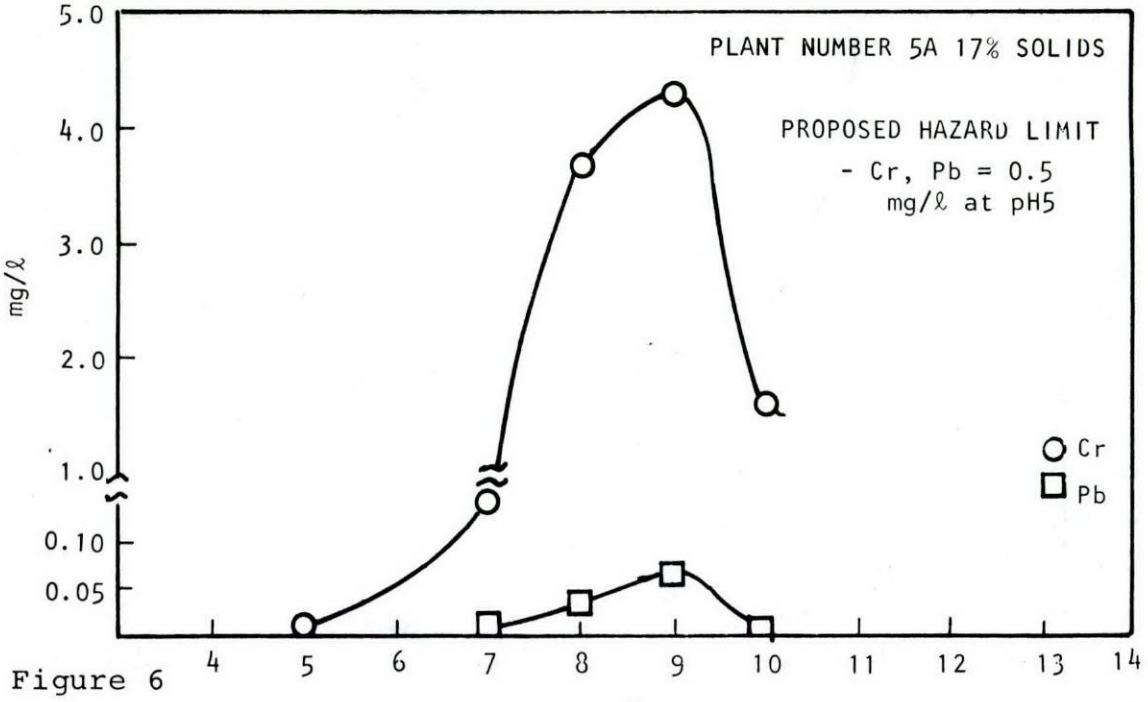

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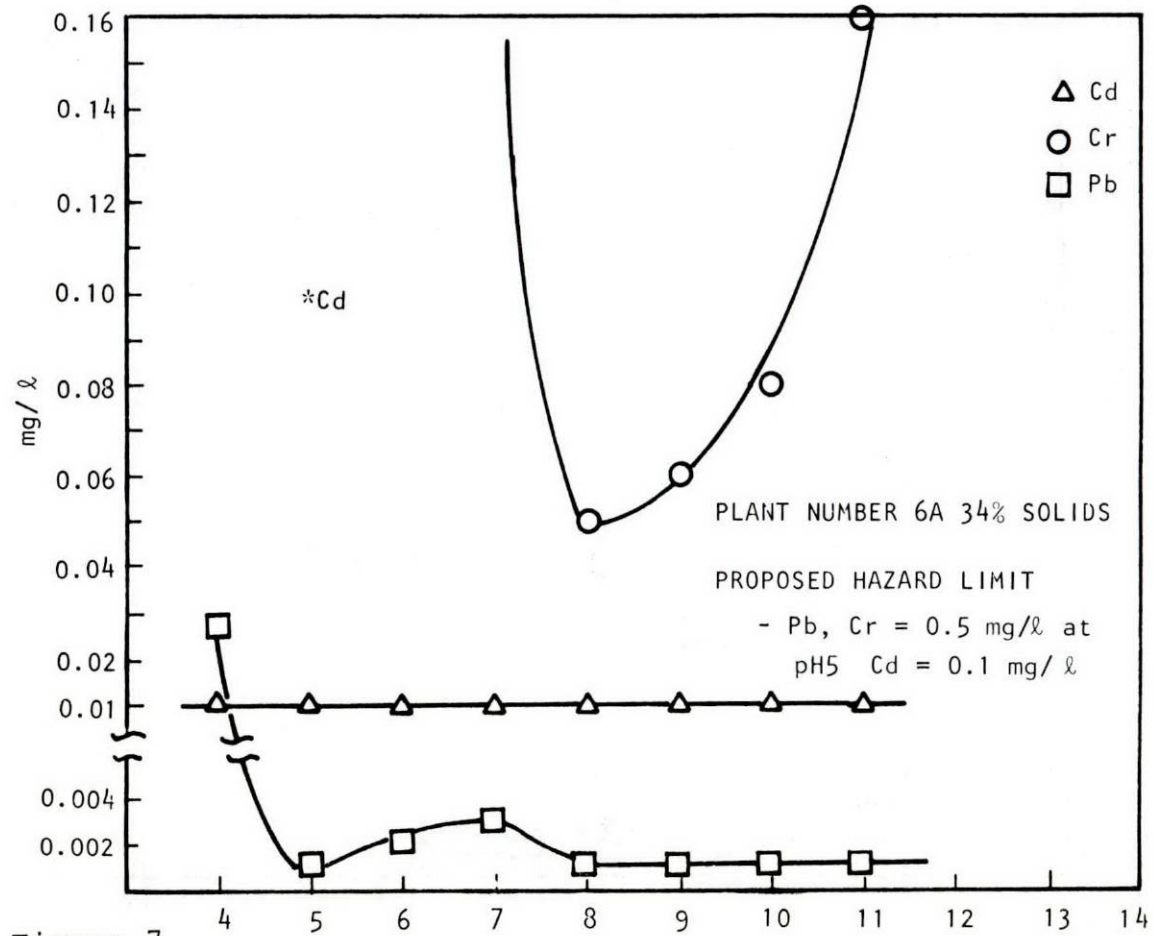

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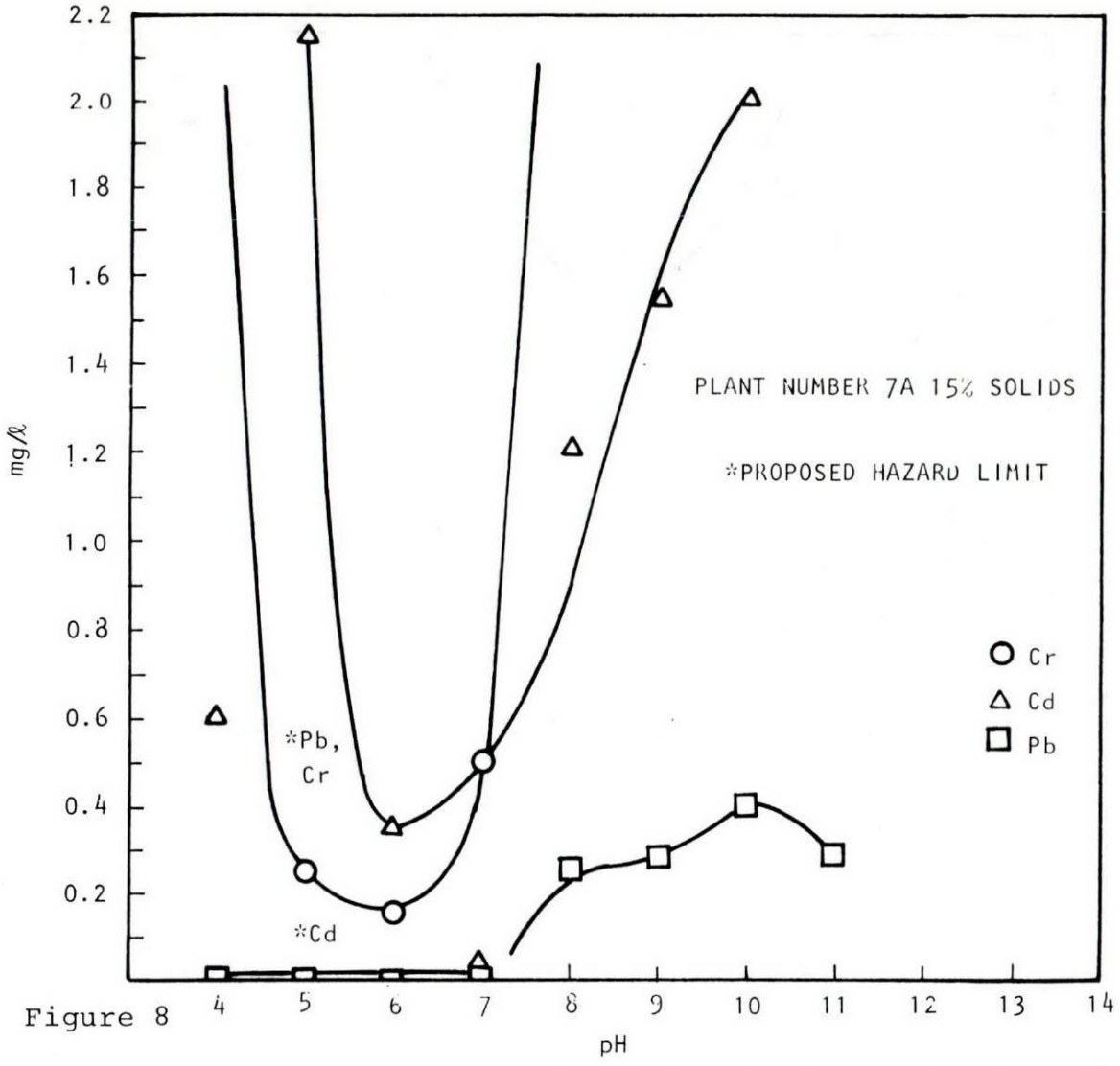

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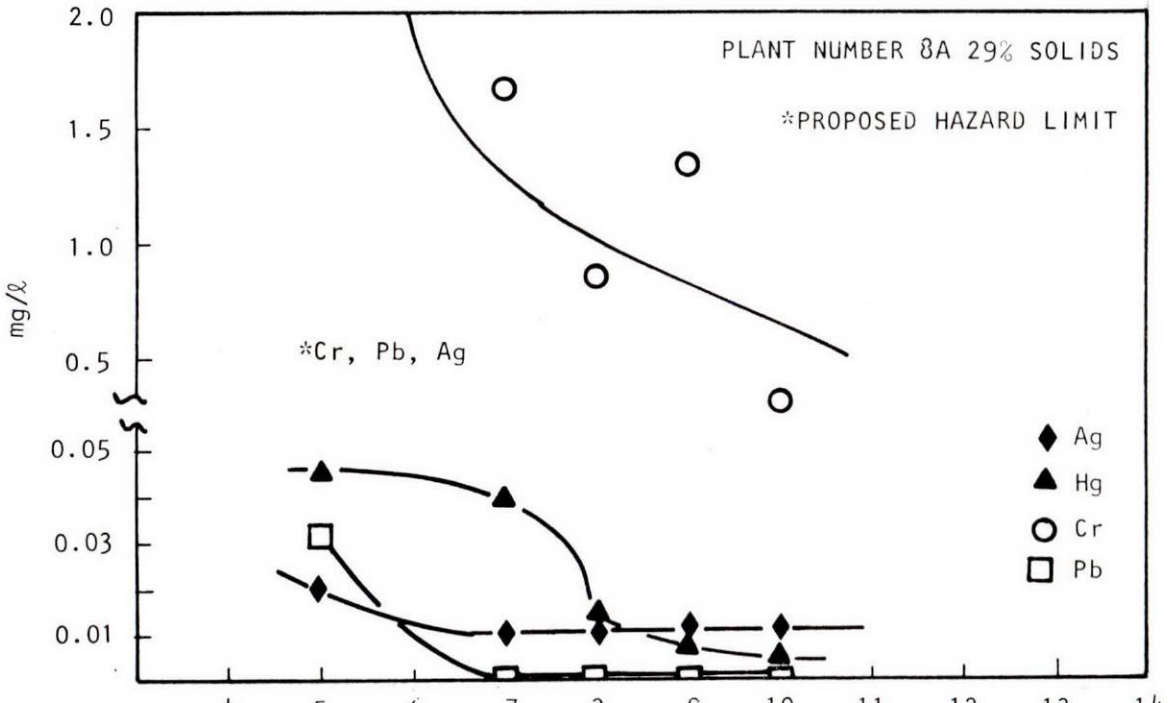

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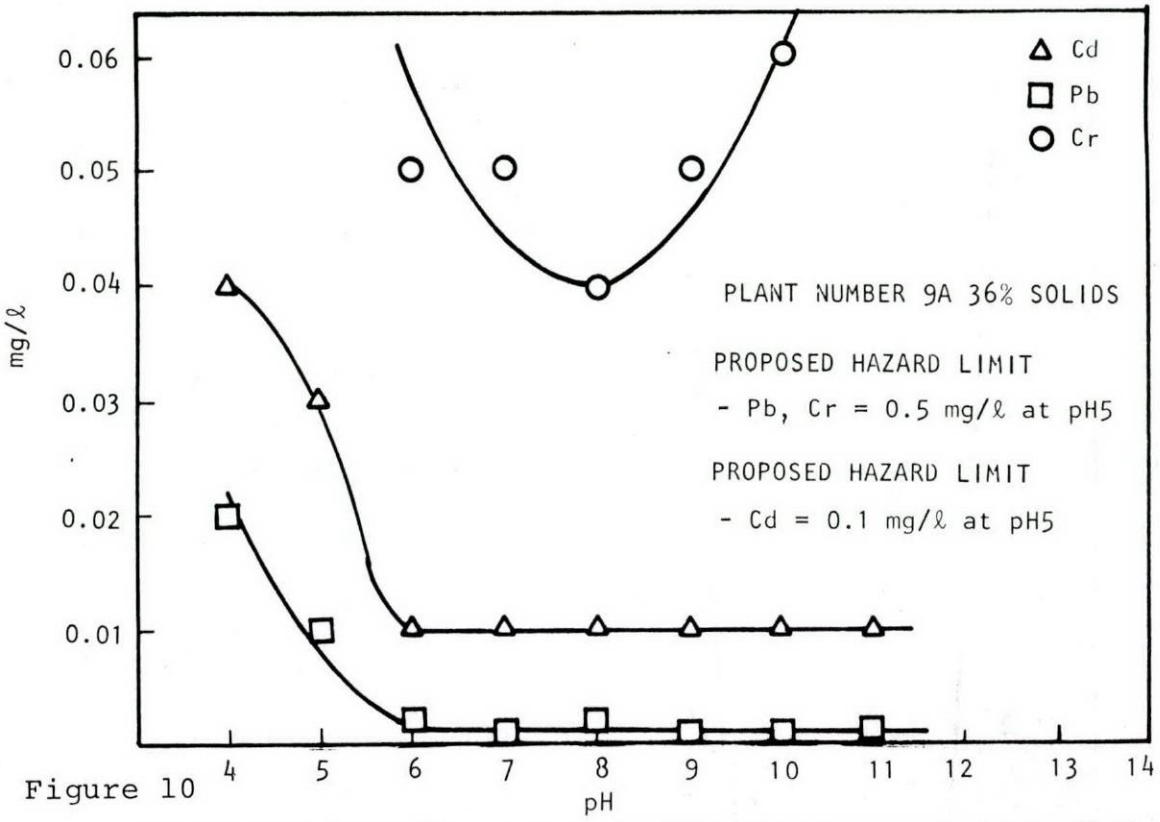
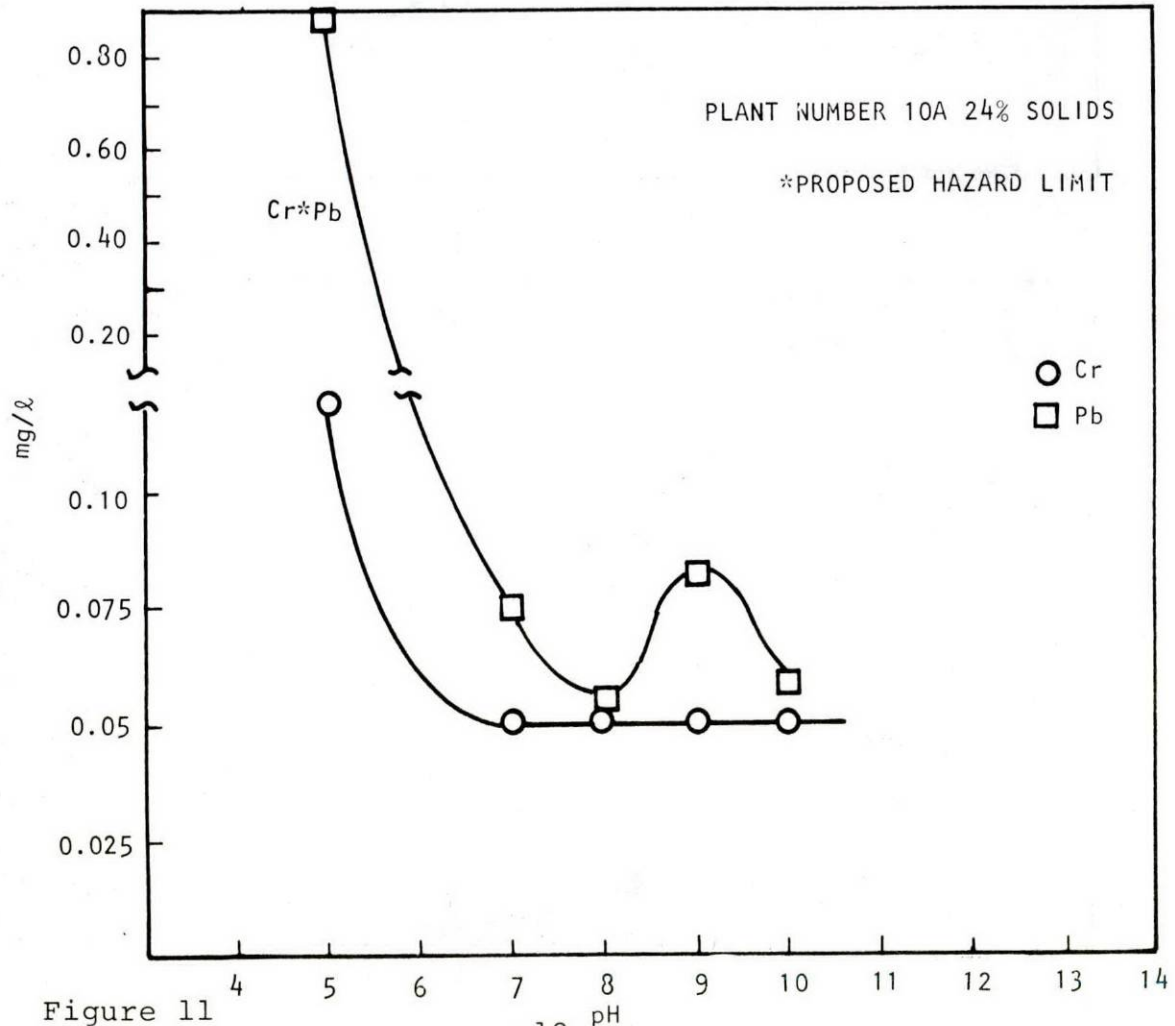


Figure 10



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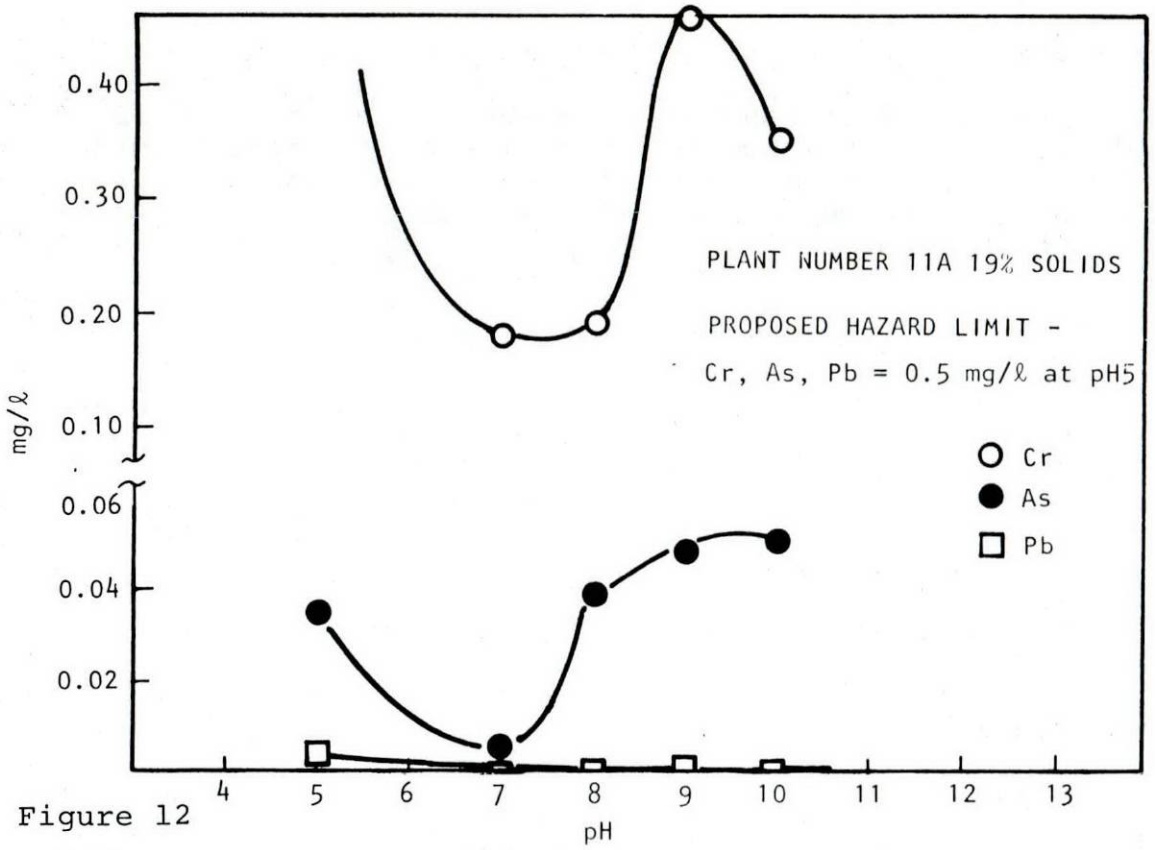

Figure 12

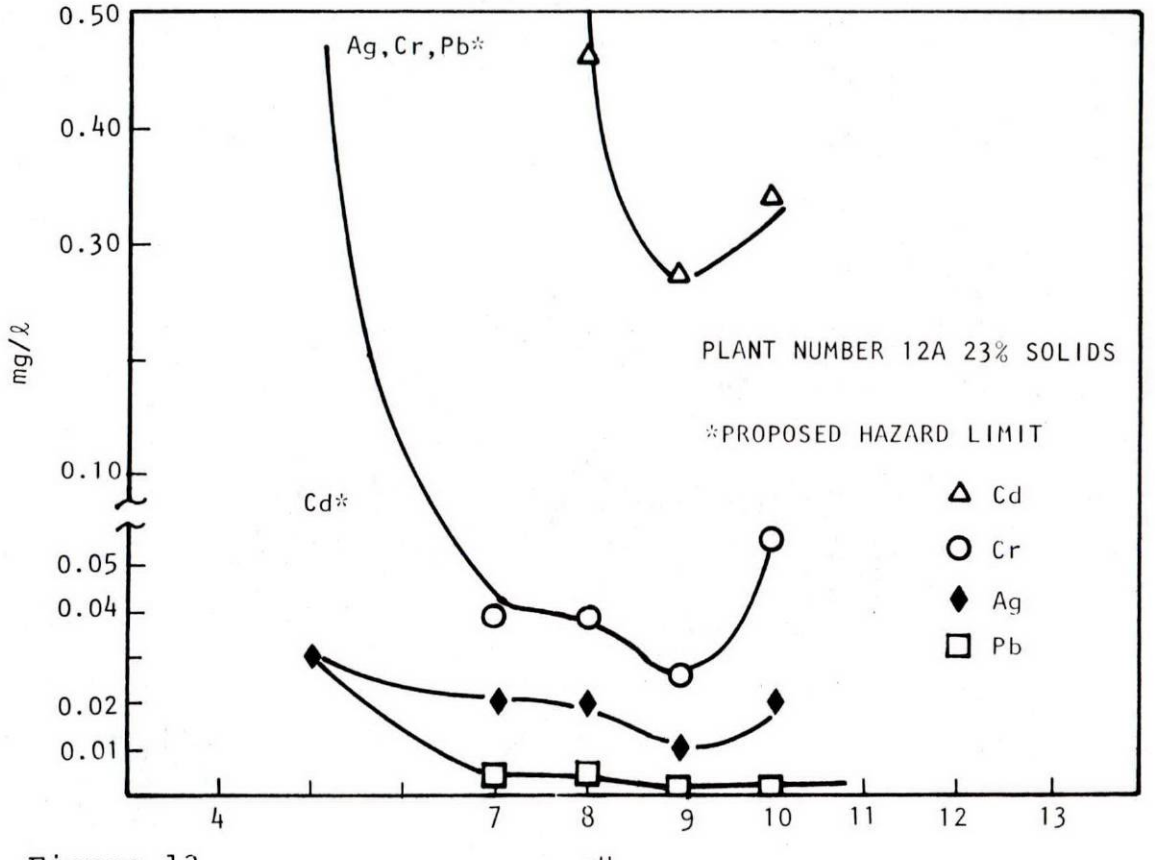

Figure 13

Supernatant and Interstitial Water Analyses

Considerable interest has been expressed as to how much of the soluble toxic metals is contained in the supernatant liquid of the sludge. Experiments were run to determine these metal levels and also to determine the impact of interstitial water quality on EP results.

It was discovered that many of these filtrates have metal levels high enough by themselves to cause the EP extract liquid to have metal concentration over the proposed hazard limits. For example, Plant 2A has 4.08 ppm Cr in its filtrate, and has only 6 percent solids in its sludge. If 75 grams of water are removed before the extraction, leaving 25 grams of "solid" sludge, the extraction liquid would have 500 grams of water. The 75 grams of supernatant water contain 0.306 mg of Cr. When diluted by 575 grams of water (when the filtrate and extract are combined), the EP extract liquid would have a Cr concentration of 0.53 ppm--over the hazard limit-- without anything being extracted from the solid. This would occur any time there is a low solids sludge and a supernatant water with metal concentrations of a few ppm.

Enough Cr was found in the supernatant water of the sludge from Plant 4A to account for the levels of Cr found in the EP extract liquid, indicating that although nothing had been leached from the sludge, it would fail the EP. The distinction is important because in a landfill the liquid portion flushes out with the first portion of the leachate, and inclusion of the supernatant in interstitial waters is not representative of long-term leaching from the sludge.

Dynamic Testing

Figure 14 illustrates typical pH and conductance decay curves for three of the plants tested. Since most sludges are highly buffered, the pH was expected to drop slowly during the tests, and this was the case for all sludges tested. Conductance was expected to start at a maximum, drop off sharply, and then continue at a low level. This was the general case; however, there were a few anomalies at low levels where the conductance would rise after a few days of leaching, then fall off again as in Plant 6A tests.

It was expected that the metal levels would start quite high as the supernatant and interstitial waters were flushed out, and then the levels would taper off. Figure 15 shows the Cr curves for Plants 4A and 12A. Plant 4A sludge was the only sludge which generated a leachate having any metal level as high as 1.0 ppm, and this lasted for only one day. A cadmium leaching curve for Plant 12A, which had an EP result of 268 ppm, is shown

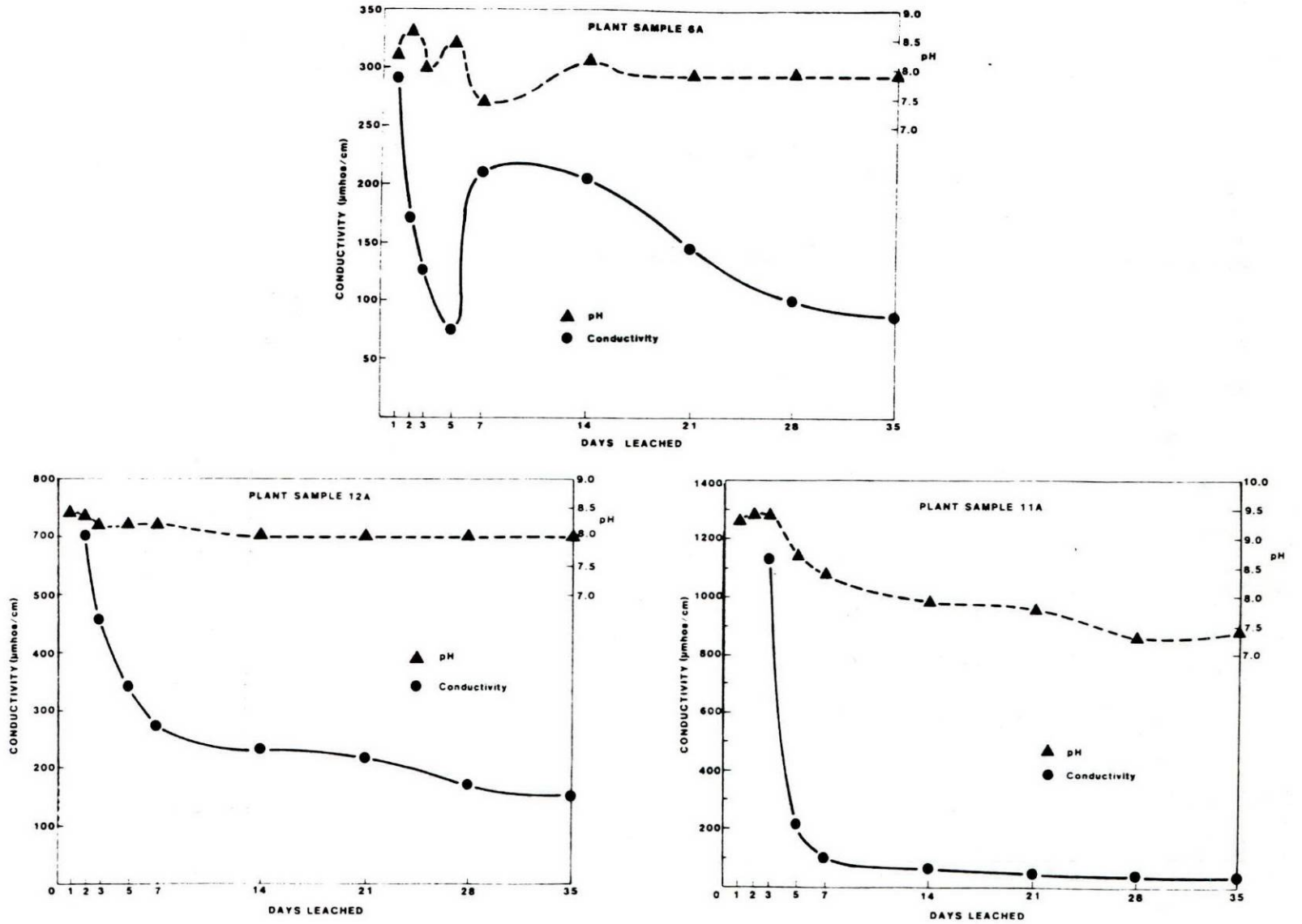

Figure 14. EPA-AES pH and Conductivity versus Days Leached

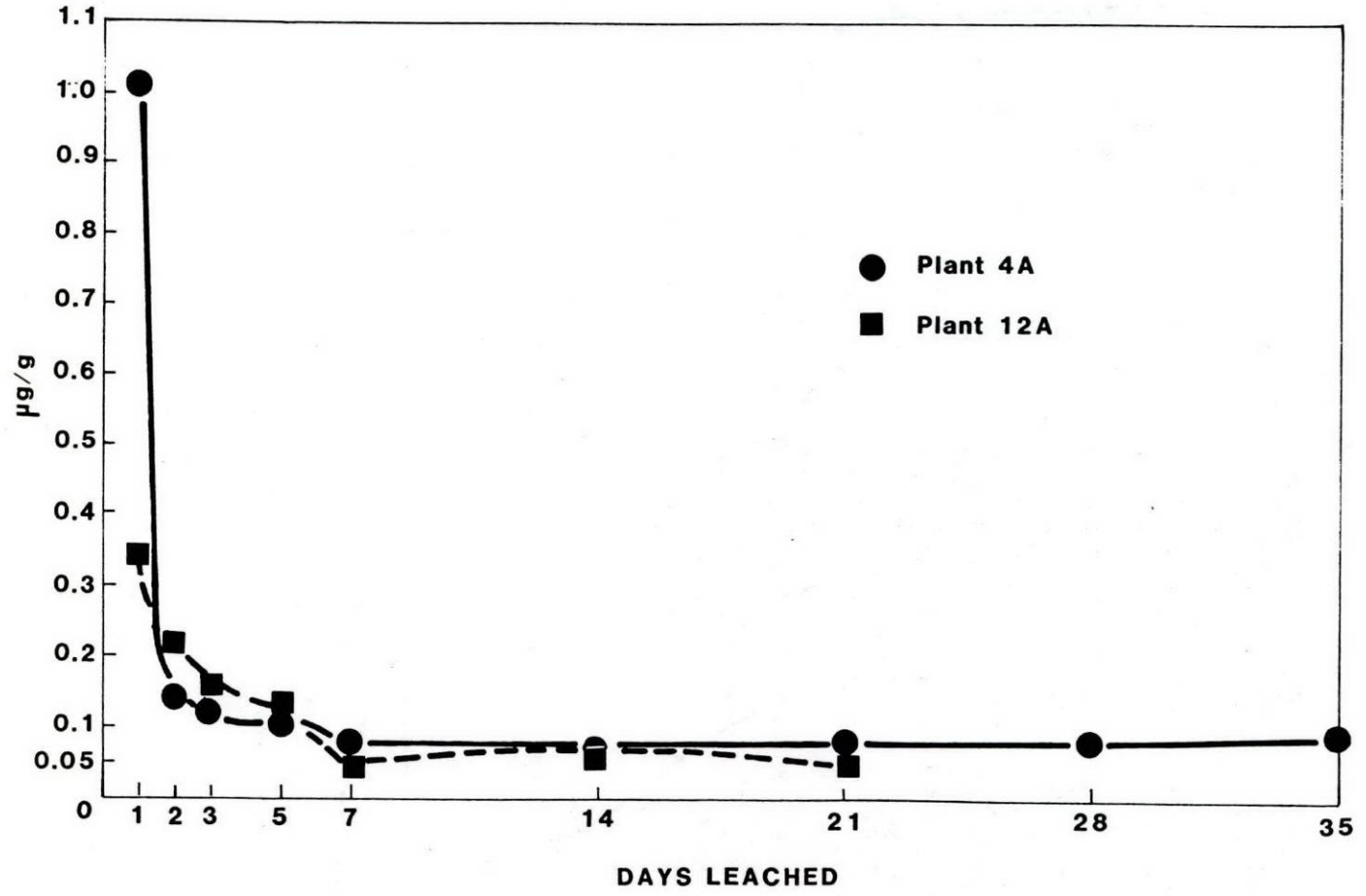

Figure 15. EPA-AES Chromium Leachate versus Days Leached

in Figure 16, and represents the dramatic, yet typical differences between the tests. These dynamic tests indicate that the sludges themselves will not leach high concentrations of toxic metals as long as they are protected from an acid environment. A real-world, segregated landfill would be expected to have even lower metal levels in the leachate due to the natural attenuation of the landfill liner material (clay), plus the fact that water would percolate at a much lower rate.

Field Sampling

Perhaps the most important test result from the field sampling is that the undiluted leachate sample from the landfill currently being utilized showed toxic metal levels well within the EPA interim and proposed drinking water standards. All of the sludges from the older landfill passed the EP easily and showed EP results not significantly different from the background soil sample. While easily meeting all other metal level limits, none of the sludges from the newer landfill could meet the proposed EP limit for chromium. It should be noted that in spite of high EP levels, the leachate from this landfill contained <0.05 ppm chromium. These findings support those of Phase II testing which indicated that electroplating wastewater treatment sludges do not leach significant amounts of heavy metals when protected from an acid environment.

Table VI shows the results from this testing.

SUMMARY AND CONCLUSIONS

Three variables were found to have a major effect on the results obtained by the leaching procedures tested:

- The composition and amount of interstitial wastewater present:

  Many of the tested sludges with low solids concentrations had sufficient interstitial wastewater present at such a concentration to cause them to fail the EP, regardless of the properties of the sludges. Sludges with high solids concentrations consistently performed better in the leaching tests. In addition, dynamic tests showed a radical reduction in metal content of the leachate once the interstitial wastewater had been flushed from the sludge. It is likely that the dewatering of low solids content sludges could greatly improve the results of the leaching test.

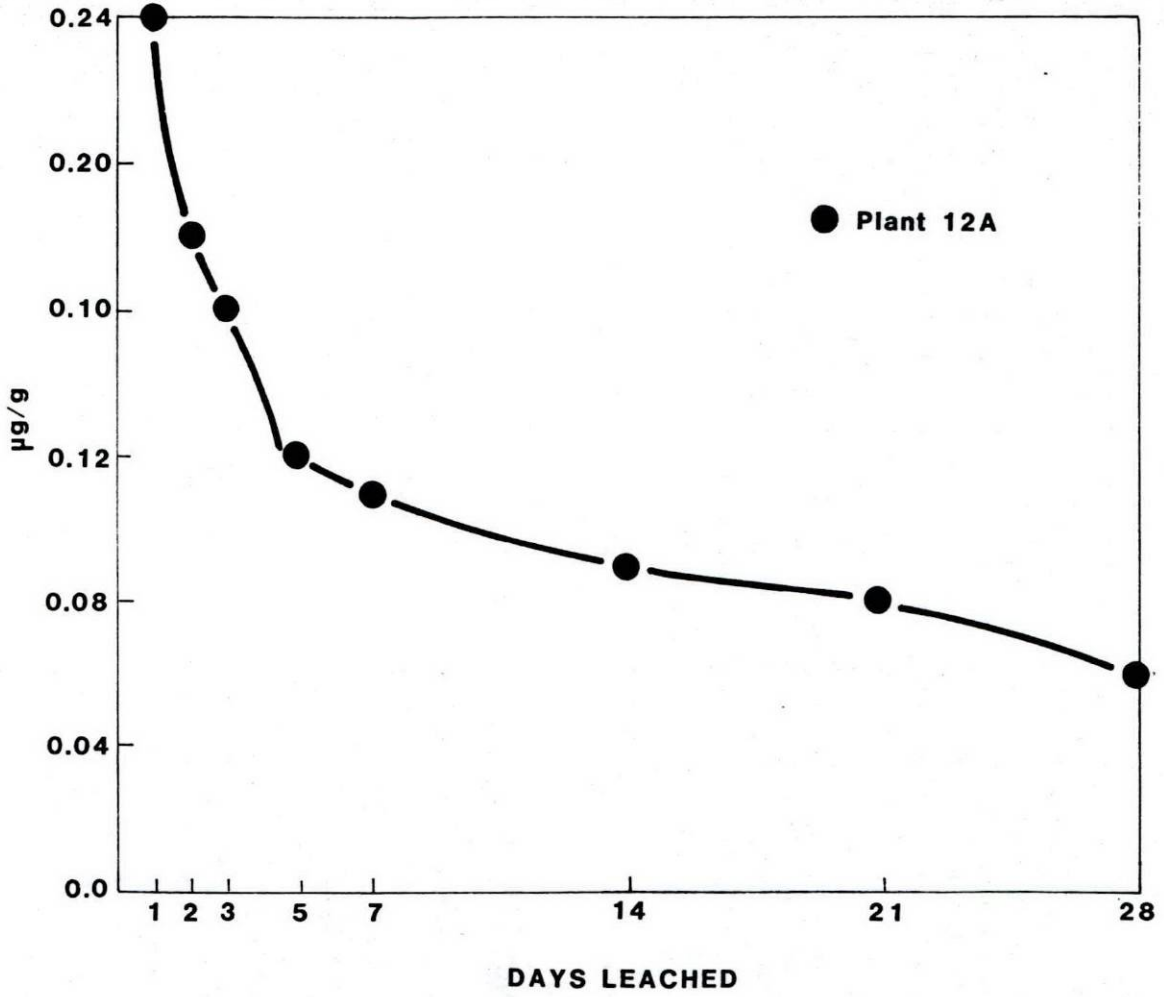

Figure 16. EPA-AES Cadmium Leachate versus Days Leached

Table VI. Phase III Field Testing

EP Results
mg/l

Sample Number	Ag	As	Ba	Cd	Cr	Pb	Se	
11C	.03	.022	<1.0	<.01	<.05	<.001	<.005	
11D	.02	.011	<1.0	<.01	<.05	<.001	<.005	Old Landfill
11E	.19	.002	<1.0	<.01	.09	<.001	<.005	
11H	.02	.006	<1.0	<.01	3.58	<.001	<.005	
11J	.01	.005	<1.0	<.01	4.37	<.001	<.005	New Landfill
11K	<.01	.002	<1.0	<.01	3.35	<.001	<.005	
11F	.01	.004	<1.0	<.01	<.05	<.001	<.005	Leachate
11L	<.01	.004	<1.0	<.01	<.05	.001	<.005	Background Soil

- The pH of the final extract:

  Metal hydroxides follow a generally predictable solubility curve with pH. When the effects of the interstitial water are taken into consideration, the sludges tested generally followed this relationship. Thus, at a continually maintained pH of 5.0 used by the EPA extraction procedure, relatively large amounts of metals are and would be expected to be solubilized; at values closer to neutral or those produced by the natural alkalinity of the sludge, greatly reduced amounts of metal are leached. In a segregated landfill, the alkalinity of the sludges would maintain a pH much higher than the 5.0 used to simulate the conditions in a co-disposal situation. In the two landfills tested, pH's ranged from 7 to 8 in the older landfill and 7 to 10 in the newer one.

  There is limited data to indicate additional factors may be important.

- Age of sludge:

  Different experiments have indicated that older sludges perform better on the EP than fresher sludges, implying that a very slow reaction is taking place which ties up the metal ions, making them unavailable for leaching.

- Mass transfer limitations:

  This effect, which is not measured by any equilibrium type of leaching test, tends to reduce further the amount of metals transferred to leachate in a segregated landfill.

  Dynamic testing has indicated dramatically lower metal values in the leachate than reported by the equilibrium type of test.

RECOMMENDATIONS

Since continued investigation into solubilization phenomena may provide relatively inexpensive but environmentally safe methods for the disposal of metal finishing sludges, specifically through the use of segregated landfills, it is recommended that:

- A laboratory test which would be more appropriate for predicting the behavior of hydroxide sludges in a segregated landfill should be developed.

- A rapid acceptance test suitable for use by generator and disposal site operators is needed.

- The relationship of wastewater treatment and plant operations to sludge floc formation on subsequent leachate/elutriate generation should be investigated.

- A more thorough investigation into why aged sludges perform better on the EP should be conducted.

- Characterization of dewatering of electroplating wastewater sludges should be investigated.

K-2

ENVIRONMENTAL SESSION K

Electrolytic Metals Recovery

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ELECTROLYTIC METALS RECOVERY

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ABSTRACT

Factors previously limiting electrolytic recovery have been poor energy efficiency and handling of low-grade spongy or powdery deposits. New developments allow for high efficiency while generating slabs of pure metal through a unique cell design which minimizes cathode polarization. Some successful applications are discussed along with advantages of electrolytic recovery over other techniques.

Introduction

Electrolytic metals recovery is nearly as old as plating itself. Even before the advent of the energy crisis, and emphasis on material recovery and reuse, many advanced-thinking people realized that it made more sense to recover their metals rather than throw them away or turn them into sludge. To this end, the copper industry long ago began electrolytically regenerating their primary pickle baths and recovering and reusing the metallic copper deposits. Since these early beginnings there have been many attempts to refine the process equipment associated with electrolytic metals recovery, resulting in the issuance of literally hundreds of patents throughout the world.

Cathode Polarization

The bulk of the more recent development efforts are being aimed at the recovery of metals from dilute rinse waters. Companies in the United States, as well as Great Britain, have put considerable effort into the development of systems geared to the recovery of metals from dilute rinse waters and effluents.[1] With this end in mind, it is

immediately apparent that a square tank containing rows of anodes and cathodes is inadequate, and a new breed of recovery equipment began to evolve. These attempts to recover metals from dilute solutions have produced exotic equipment designs. One system incorporates a porous electrode which produces extremely high cathode surface areas.[2] Other systems have employed rotating cathodes or small cathode compartments through which the solution containing the metal to be recovered is rapidly pumped.[3] [4] All these are attempts to solve the same basic problem--cathode polarization. This problem is not unique to electrolytic recovery alone, but rather is common to all of electroplating. The problems caused by cathode polarization, however, become more and more pronounced as the concentration of metal to be plated decreases. As a metal is plated onto a cathode, a film develops next to the cathode surface which is depleted in metal ion concentration. The extent of polarization is determined by the thickness of this depleted layer which in turn directly influences the current efficiency of any plating process. The faster we try to recover a given metal--in other words the higher the current density used--the thicker, more depeleted this film becomes, decreasing plating efficiency. Not only does this cathode film affect current efficiency, but also the quality of deposit that is produced. If the extent of polarization is too great, a powdery, non-adherent deposit can be produced, or a phenomenon known as treeing may occur. As the metal concentration in the plating solution decreases, the current efficiency and the quality of the resulting deposit begin to suffer more and more.

Minimizing Polarization

Fortunately, there are a number of methods at our disposal to combat this problem of cathode polarization. Unfortunately, however, knowing these methods does not guarantee their practical and efficient use. As the concentration of metal in a plating solution decreases, the rate at which the metal is deposited must also be decreased, allowing more time for the metal ions to penetrate the polarization film. In practice, this requires that lower and lower current densities or larger and larger cathode surface areas must be used. This is the basis behind a recently developed recovery system which utilizes high-surface-area porous cathodes.[2] The basic problem with the porous cathode approach is that there is no practical way to remove the deposited metal from the cathode surface.

A second method of reducing cathode film thickness is through rapid agitation. The more rapidly a solution is

agitated, the more often the metal ions will contact the cathode surface and become available for plating. Firms in Great Britain and the United States are developing electrolytic recovery systems based on this principle of rapid agitation. Some claim to be capable of recovering metals from waste waters containing as little as 100 ppm.[1] The water containing the metal to be plated is rapidly pumped through the cathode chamber where the metal deposits as a powder upon a rotating cathode and is swept away by the turbulent flow, to be collected in subsequent solids/liquid separation equipment. The high surface area of this powdery deposit, however, is quite susceptible to surface oxidation, yielding a relatively low-grade product which will not command top dollar on the market, nor will it be suitable for in-house reuse unless additional purification steps are employed.

A third method of controlling cathode polarization is through solution chemistry. As the metal concentration of a plating solution increases, the cathode polarization film decreases due to the increased number of metal ions available to penetrate the film. Addition agents are also often added to control the rate of diffusion through the film, thus producing a uniform deposit. Obviously, however, this method becomes uneconomical and impractical to use for once-through rinse waters and effluents.

Another method of reducing the polarization film thickness is by increasing solution temperature. This imparts a greater mobility to the metal ions, allowing them to more easily penetrate the film. This approach, however, is also impractical when applied to a continuous rinse water or effluent flows containing very low metal concentrations.

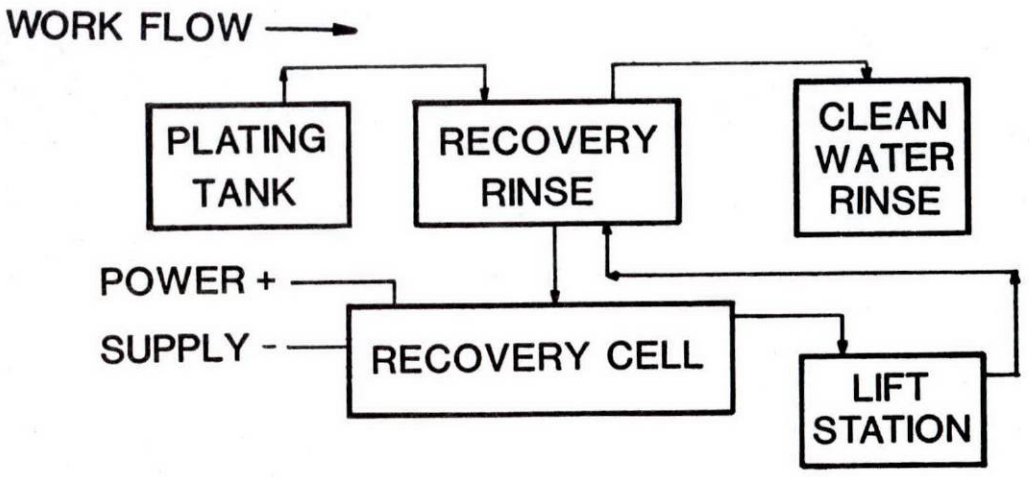
The Combined Approach

If the goal for electrolytic metals recovery is the development of a practical system yielding a high-grade, easily recovered deposit, a combination of the above-mentioned variables must be used. One successful approach to the electrolytic recovery of metals dragged out of various processing baths is to combine the advantages of high agitation and increased temperature, where practical, with a carefully formulated, closed-loop recovery rinse solution. This recovery solution must be located in the production line immediately following the process which contains the metal to be recovered, and functions as a collection station for the bulk of the drag-out. The chemistry of this recovery rinse can then be optimized by incorporating any required addition agents, so as to produce a fine-grained,

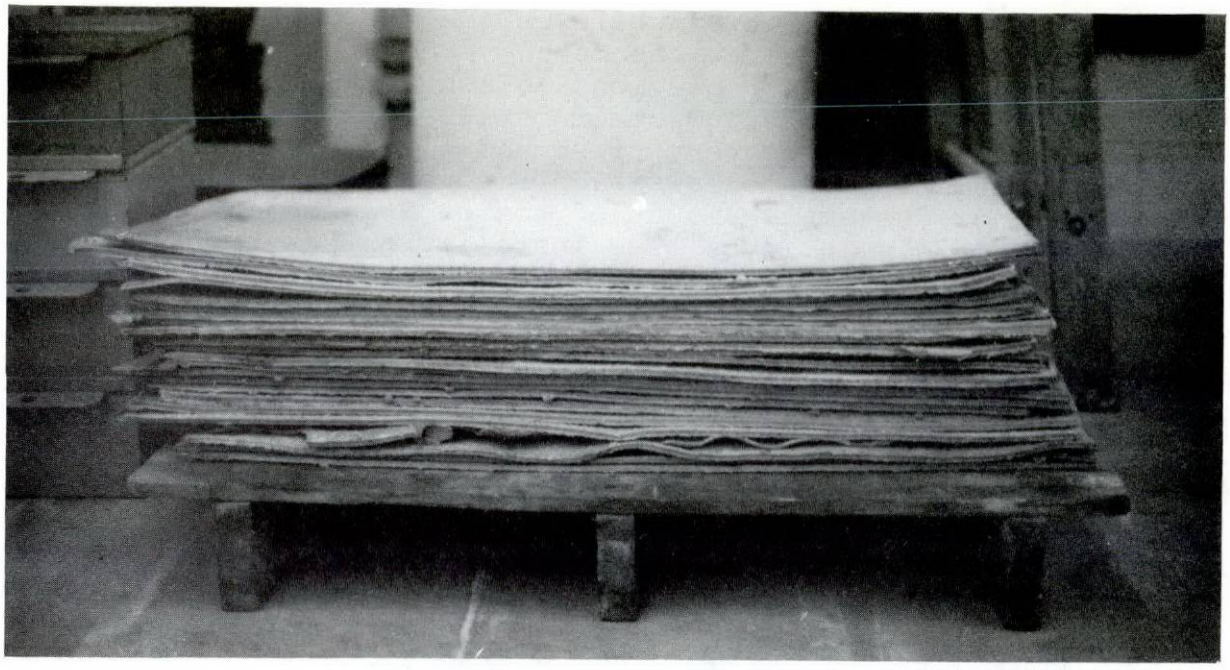
tightly adherent deposit of extremely high quality. This metal may then be reused in-house as anode material, or sold to a refiner for top dollar as electrolytic-grade material. The concentration of metal maintained in this recovery rinse solution can be controlled to produce minimum drag-out. This closed-loop approach, used successfully for many years, is the only method of effectively using the advantages of solution chemistry and temperature to produce a practical, efficient recovery system.

FIGURE 1

TYPICAL CLOSED LOOP RECOVERY APPLICATION



In order to realize maximum benefit from the closed-loop recovery approach, the proper recovery cell design must be used. One patented design[5] uses semi-enclosed, custom-engineered impellers at either end of the recovery cell to achieve flow velocities of 3-5 ft./sec. within the cell. This flow is then directed uniformly over conventional cathode plates by means of horizontal and vertical baffles. This high uniform flow rate effectively decreases the thickness of the cathode diffusion film, allowing higher current densities to be used and reducing recovery equipment size while still maintaining a low metal concentration in the recovery rinse. Since conventional cathode plates of reusable stainless steel are used, the metal can be recovered as high-purity slabs, ready for reuse or sale, with no additional steps required.



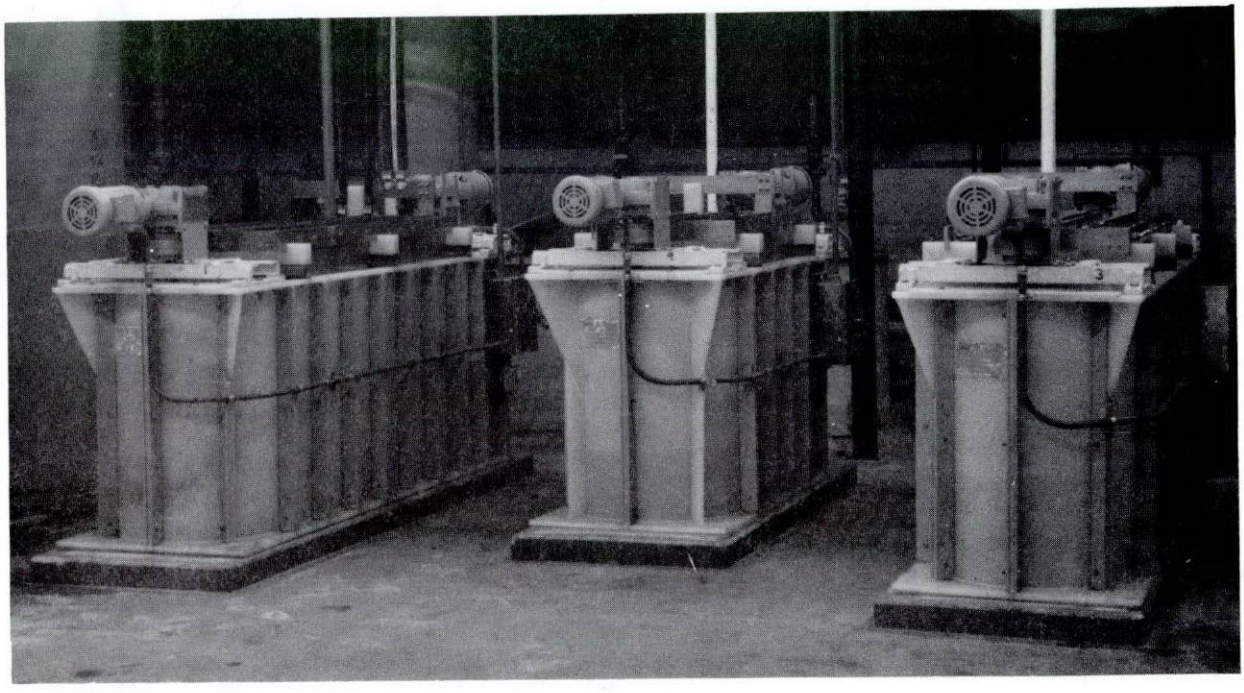
METAL SLABS OF TIN RECOVERED USING THE CLOSED-LOOP RECOVERY RINSE COMBINED WITH HIGH-VELOCITY, UNIFORM-FLOW RECOVERY CELL

Pilot Test

A recent pilot study may serve to illustrate the effectiveness of this combined approach. Tin was to be recovered in a drag-out of a fluoborate plating solution containing about 40 g/liter of the metal. The first of three existing countercurrent rinses was isolated and converted to a closed-loop recirculating recovery rinse. The recovery rinse solution was heated to 130-140° F and predetermined quantities of addition agents were added to produce a fine-grained deposit and prevent the oxidation of stannous tin. Sodium hydroxide was also required to maintain a pH of 1.8-2.5. When enough process solution had been dragged into the recirculating recovery rinse to provide a concentration of 2 g/liter tin, electrolysis was begun. Tests showed that a tin deposit of excellent quality could be obtained at a current density of 10 Amps/sq. ft. with a current efficiency of near 100%. This can be compared to a previously well established maximum current density of 2 Amps/sq. ft. and 65% efficiency for conventionally designed stagnant recovery cells utilizing the same chemistry and metal concentration. Through this closed-loop recovery approach, in combintation with the high-agitation recovery cell, the amount of tin drag-out requiring treatment was reduced by 95% (at an actual drag-out rate of 6 liters/hour).

A Working Installation

A recent installation utilizes six various sized electrolytic cells to recover the metal value dragged out of five different process solutions. Each metal to be recovered is segregated from other metals by its own closed-loop recirculating recovery rinse and electrolytic cell. Waste treatment then follows each recovery system for the treatment of the small amount of toxics dragged out of the recovery rinse solutions. The installation has been operating successfully for about one year during which time approximately $840,000 of metals have been recovered.



THREE OF THE SIX RECOVERY CELLS OPERATING ON CLOSED-LOOP RECOVERY OF COPPER, ACID TIN, AND GOLD

The real significance of this installation does not lie in the dollar value of the recovered metals, but in the conceptual approach to solving this recovery challenge. By utilizing carefully formulated chemistry, high-agitation recovery cells, and through complete segregation, the metals are recovered in the purest form, commanding top dollar with no additional production requirements, and without complicating the production process in any way. All this was accomplished while drastically reducing the total load on the waste treatment system, and producing minimal quantities of sludge.

TABLE I

Metal Recovered	Production Process	Pounds per year	1979 Value
Copper	Acid Sulfate Plating	2,500	$ 1,850
Tin	Alkaline Plating	5,000	32,500
Tin	Acid Sulfate Plating	200	1,300
Silver	Cyanide Plating	50	6,000
Gold	Cyanide Plating	157	800,000
Total		7,907	$ 841,650
Total Recovery equipment Cost			$ 98,700

Other Recovery Techniques

How does electrolytic metals recovery compare with other available recovery methods? Unlike evaporation, reverse osmosis, or simple drag-out stations, the purpose of which is total material return, electrolytic recovery aims at recovery of the most valuable constituent only--the metal. The implications of this conceptual difference should be clearly understood. Many recovery systems are sold on their ability to return very high percentages of process solution drag-out, thereby minimizing waste and showing that the equipment is worth its price. While the economics of total material return look good on paper, there are some serious practical implications.

It is a well appreciated fact that many cyanide plating processes accumulate in carbonate which can cause serious anode polarization problems. As more and more drag-out is returned, the natural equilibrium of the bath is upset and a chain reaction occurs which produces ever increasing amounts of carbonate. This carbonate must then be removed by more frequent crystallization. Since the crystals are small and of large surface area, more solution can be lost on the crystal surface than was returned to drag-out recovery, and nothing but a large production headache and a substantial waste treatment problem have been gained. Other problems associated with high-percentage drag-out return include the breakdown by-products of organic brighteners, as well as inorganic salt build-up. Again, as more and more drag-out is returned, the process bath can eventually become saturated with organics due to their limited solubility. As a result, the plating operator spends hours trying to dissolve some brightener in a bucket, and often doesn't realize why.

The build-up of inorganic salts from preceding natural rinse waters or as a result of solution drag-through from previous processes is a complex problem and affects each plating bath differently. The excessive build-up of contaminants in a plating bath following evaporative recovery, for example, has been well documented.[6] [7] [8] [9] These contaminants must be removed by additional purification steps. This may include periodic solution blowdown, carbon treatment, or treatment using ion exchange resins, all of which create waste. The installation of DI water rinses preceding the process bath in many instances are also necessary. While the need for additional purification is freely admitted, it is often overlooked in the economic considerations of those recovery systems where the aim is high-percentage drag-out return. In the EPA's June, 1979, study on the Economics of Wastewater Treatment Alternatives for the Electroplating Industry,[10] detailed economic analysis sheets were prepared for recovery systems including evaporation, reverse osmosis, ion exchange, and electrodialysis. Nowhere, however, is there a cost included for the solution lost due to increased rate of purification which, as in the case of the carbonate crystals, could well be more than the solution recovered.

Summary

No single recovery method can meet every recovery need. Each system has areas for which it is most practical and best suited. However, an understanding of the true economics and practicality of each of the techniques will often favor electrolytic recovery of the only valuable and sludge-producing constituent--the metal.

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(1) Ricci, Chemical Engineering, December 22, 1975, pages 29-31.

(2) Chemical Engineering, October 13, 1975, pages 73-75.

(3) Schore, Practical Removal and Recovery of Heavy Metals Using Electrochemical Technology, AES, Second Design and Finishing of Printed Wiring and Hybrid Circuits Symposium

(4) Schaer and Krasley, Electroforming Accelerated by Forced Solution Flow, Plating and Surface Finishing, December, 1979, p. 36-38.

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(7) Levin, Jump, McLay, Evaporation of Electroplating Chemicals, Second Pollution Abatement Seminar, presented by the Environmental Committee - American Electroplaters' Society, June, 1979, pages 117, 118.

(8) Hartley, Evaporative Recovery in Electroplating, First Annual Conference on Advanced Pollution Control for the Metal Finishing Industry, EPA Report, 600/8-78-010, May, 1978.

(9) Masarik, Evaporator/Chiller System Recovers Brass Plating Solution, Plating and Surface Finishing, January, 1980, p. 28, 29.

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K-3

ENVIRONMENTAL
SESSION K

High Temperature Treatment of Concentrated Aluminum Finishing Wastes

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HIGH TEMPERATURE TREATMENT OF CONCENTRATED ALUMINUM FINISHING WASTES

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Introduction

Aluminum finishing wastewaters from cleaning, etching, anodizing, painting and other finishing processes contain high levels of soluble aluminum which must be removed prior to wastewater discharge. Aluminum removal is conveniently achieved through precipitation of aluminum hydroxide by pH neutralization of combined rinse, etch and anodize wastewaters at or near ambient temperatures. The aluminum precipitate formed is then removed from suspension by gravity sedimentation. The thickened sludge, however, is not highly concentrated, having a suspended solids concentration which may range from 1% to 2% solids. If the concentration of sludge solids could be increased by a factor of 2 to 4, sludge volumes for subsequent dewatering processes, such as vacuum and pressure filtration, would be reduced by 50 to 75%.

Several processes for conditioning sludges and improving thickening characteristics have been examined including the use of chemical coagulants, freezing, acidification and heat treatment (1). Doe (1) reported that heat treatment or "boiling the sludge under pressure" would result in destruction of the gelatinous nature of alum sludge. Palin (2) found that alum sludge subjected to heat and pressure well below those of the Porteous process (i.e. 140°-200°C and 150-200 psi) had substantially lower sludge volumes than untreated alum sludge. However, he did not report the temperature to which sludge was subjected prior to the settling tests. Therefore, very little is known about the effects of high temperature treatment on aluminum sludges. It is the objective of this study to examine a treatment alternative which results in improved sludge thickening and dewatering properties over those for sludges produced with current wastewater treatment practices in aluminum finishing industries.

An industrial wastewater survey conducted at an aluminum extrusion/anodizing plant, designated Plant I-C herein, indicated that approximately 75% of wastewater aluminum was contained in concentrated caustic etch and acidic anodize wastewaters. In addition, data from numerous other plants indicated that a major portion of waste aluminum is contained in the etch and anodize wastewaters. The research reported herein is an initial investigation of the segregated treatment of concentrated anodize (or hard coat anodize regenerant) and etch wastes to determine the promise of the treatment scheme. As proposed, concentrated sulfuric acid anodize wastes and alkaline etch wastes are to be mixed and neutralized concurrently. Upon mixing these wastes, which may be at an elevated temperature initially, the liberated heat of neutralization and heat of solution results in an increase in suspension temperature. Since an elevated temperature during formation of an aluminum

hydroxide precipitate may result in a decrease in the water content of the precipitate and in the formation of a more crystalline-like sludge particle, high temperature treatment of these major sources of waste aluminum could significantly improve sludge settling and dewatering characteristics. If such improvements are major, the impact on overall waste treatment practice in the aluminum finishing industry could be highly significant. The results reported herein constitute an initial investigation of process feasibility. The primary objective was to examine improvements in sludge settling characteristics at several temperature and pH values.

Materials and Methods

A continuous-flow neutralization system was constructed to generate aluminum hydroxide suspensions by mixing etch and anodize wastewaters (Figure 1). The reaction vessel (liquid volume = 0.7 ℓ) of the neutralization system was stirred with a magnetic stirrer. The content of the reaction vessel was kept at constant temperature of 65°C, 80°C and 90°C with an automatic temperature controller which provided recirculation of heated distilled water through the water jacket around the reactor. Periodic manual measurements of temperature was also conducted to verify the temperature of sludge generation. A pH controller was utilized to control the pH of the generated sludge.

The etch and anodize wastes collected from Plant I-C were diluted by a factor of 10 and the diluted wastes were pumped to the reaction vessel by peristaltic pumps equipped with flow rate controllers. During sludge generation, anodize waste flow was kept constant while the flow of etch waste was regulated with a pH controller to maintain the pH of the suspension at required pH values. Hydraulic retention time in the reaction vessel was approximately 10 min in all runs.

Aluminium hydroxide suspensions were removed from the temperature-controlled reactor by vacuum and transferred to a 20-ℓ glass container held at the temperature of generation in a constant temperature water bath. An experimental run was terminated when approximately 18 ℓ of sludge was collected and held at the temperature of generation until subsequent analysis.

Sulfuric acid anodize and waste caustic etch suspensions were obtained from Plant I-C. The characteristics of the wastes are indicated in Table 1.

Table 1. Characteristics of Caustic Etch and Acidic Anodize Suspensions

Parameter	Waste Etch Suspension	Waste Anodize Suspension
pH	13.3	0.3
Temperature, °C	60	25
Aluminum, g Al^{+3}/ℓ	65	15
Alkalinity, g/ℓ as $CaCO_3$	275	--
Acidity, g/ℓ as $CaCO_3$	--	400
Color	Blue-Green	Light Brown

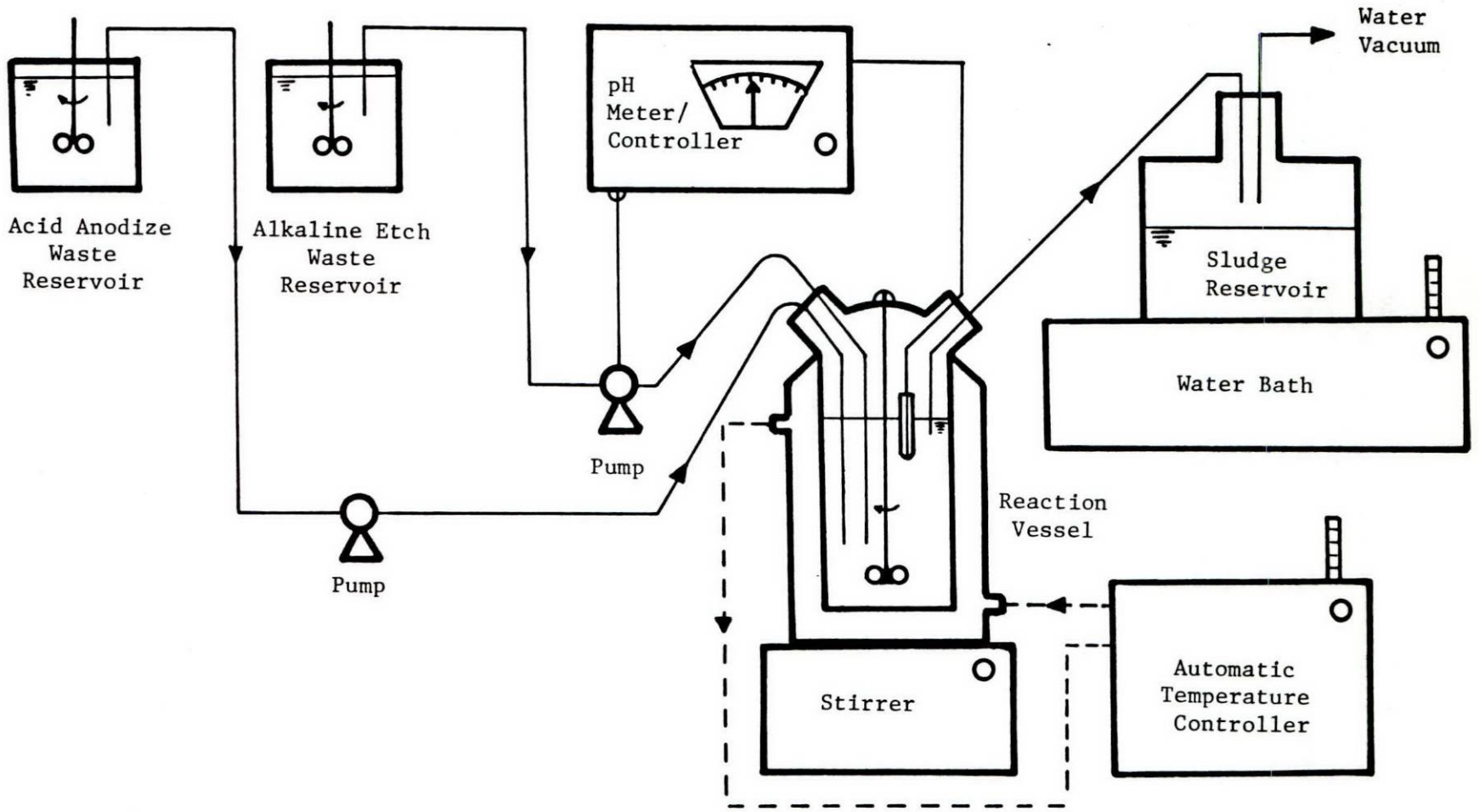


Figure 1. Schematic Diagram of Experimental Unit

Measurements of pH, temperature, alkalinity and acidity were made in accordance to the methods described in Standard Methods (3). For aluminum determinations, acidic anodize waste was acid-digested and alkaline etch waste was alkaline-digested (4). Aluminum content of the wastes was determined by use of a Perkin-Elmer Atomic Absorption Spectrophotometer (Model 303).

Settling tests were conducted with the aluminum hydroxide suspensions using 1-ℓ graduated cylinders (diameter = 6 cm; sludge height = 36 cm) stirred at 1 rpm with a wire stirrer. Prior to the settling tests, aluminum hydroxide sludge collected in a 20-ℓ glass container was allowed to settle and a series of dilutions of the thickened sludge was prepared using clarified supernatant. Settling tests were conducted over a period of 60 min by observing the sludge-liquid interface. Suspended solids of each dilution were determined by filtering a specific amount of the sample in Gooch crucibles and drying at 103°C overnight.

Experimental Results

Five experiments were performed to determine the effect of temperature and pH on settling characteristics of aluminum hydroxide sludges generated at high temperatures. Experimental conditions under which the sludges were generated and examined during the five experimental runs are summarized in Table 2.

Table 2. Sludge Generation and Settling Analysis Conditions for the Five Experimental Runs

	SLUDGE GENERATION			SETTLING TEST TEMPERATURE	
RUN	Temperature °C	pH	Hydraulic Retention Time (min)	Post-Generation °C	Ambient °C
1	65	7.1	9.2	48	22
2	80	7.0	9.2	80	22.5
3	90	7.3	9.2	72	24
4	80	5.5	9.2	80	22.5
5	80	8.5	9.2	80	22.5

For each experimental run, settling tests were conducted at two temperatures (Table 2). For example, in Experiment 1, sludge generation temperature and pH were 65°C and 7.1, respectively. Settling tests for this sludge were conducted at 48°C and at 22°C (18-20 hr after sludge generation).

Variations of zone settling velocity with suspended solids concentration for sludges generated at high temperatures (i.e., 65, 80 and 90°C) and at neutral pH values are presented in Figure 2. In general, only minor variations in zone settling velocities were observed for a single sludge suspension when examined at post-generation (i.e. 48, 80 and 72°C) and ambient temperatures (i.e. 22-24°C). Similar results for variation of zone settling velocities were observed at pH values of 5.5 and 8.5 for sludges generated at 80°C and analyzed at 22.5°C, as shown in Figure 3. With respect to sludges generated

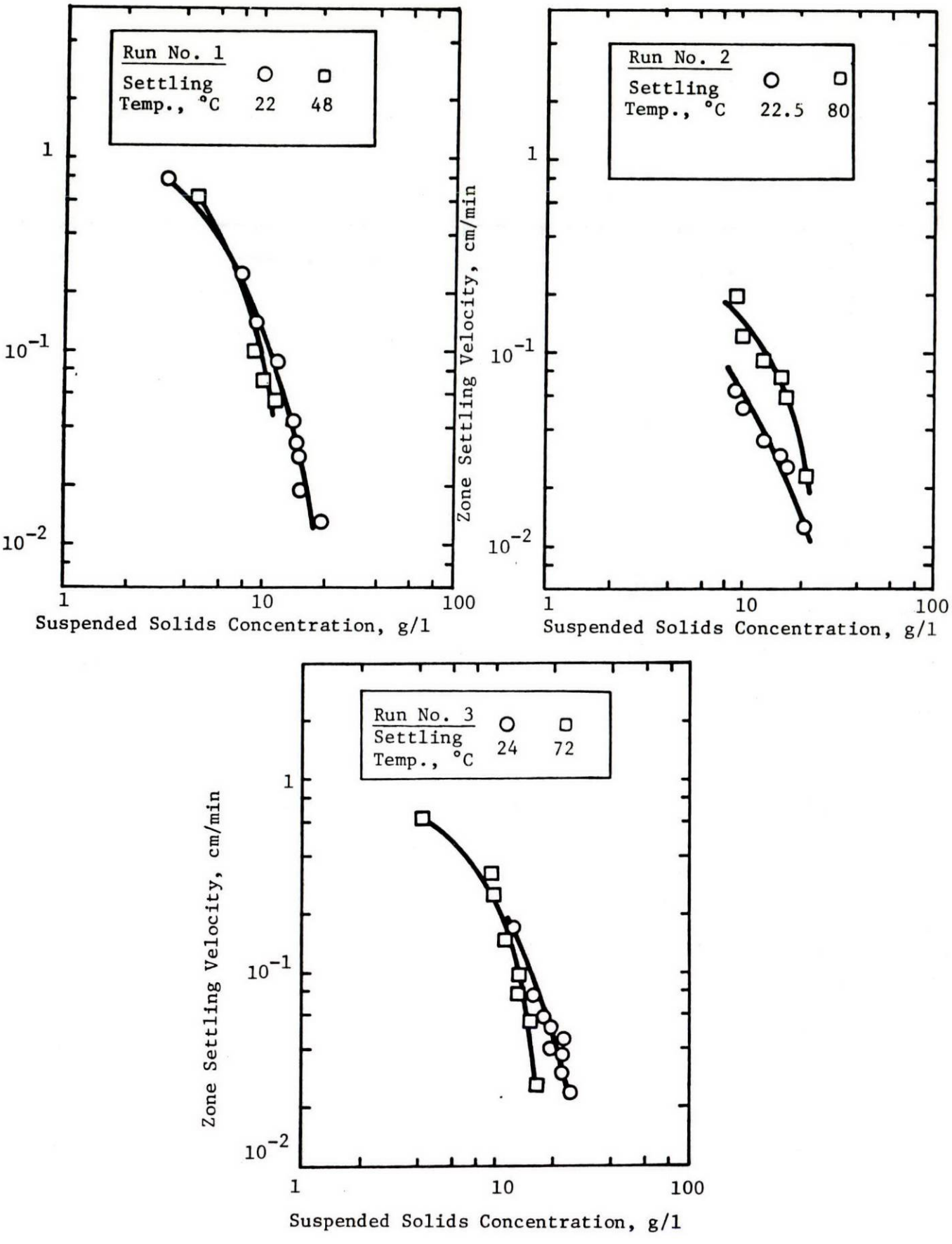
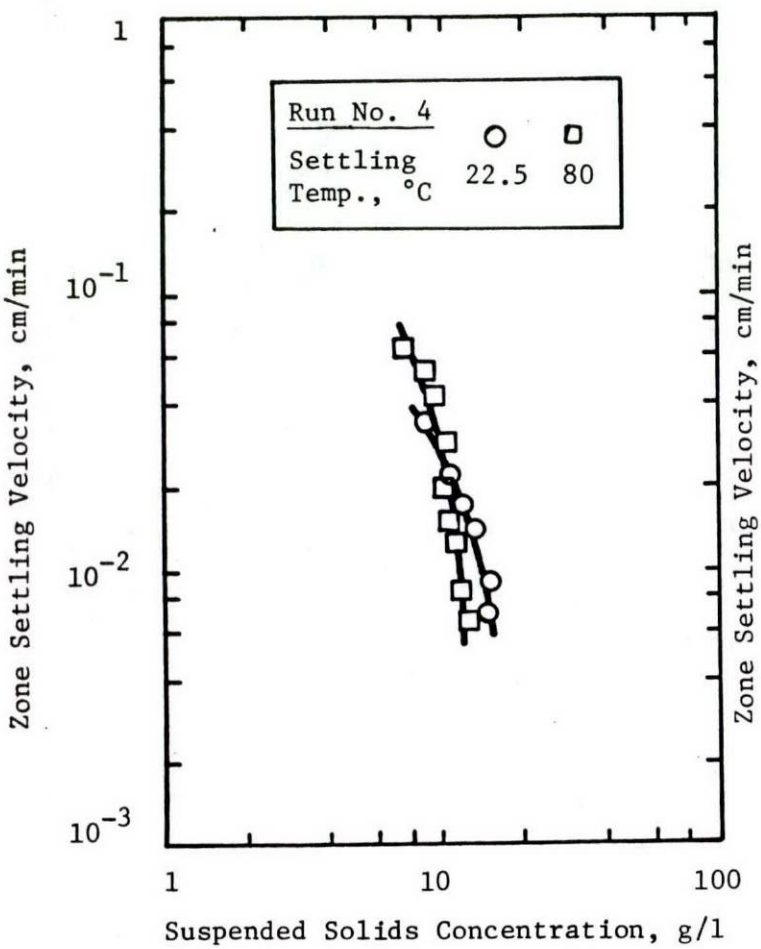


Figure 2: Settling Curves of Sludges Generated at High Temperatures and Neutral pH Values



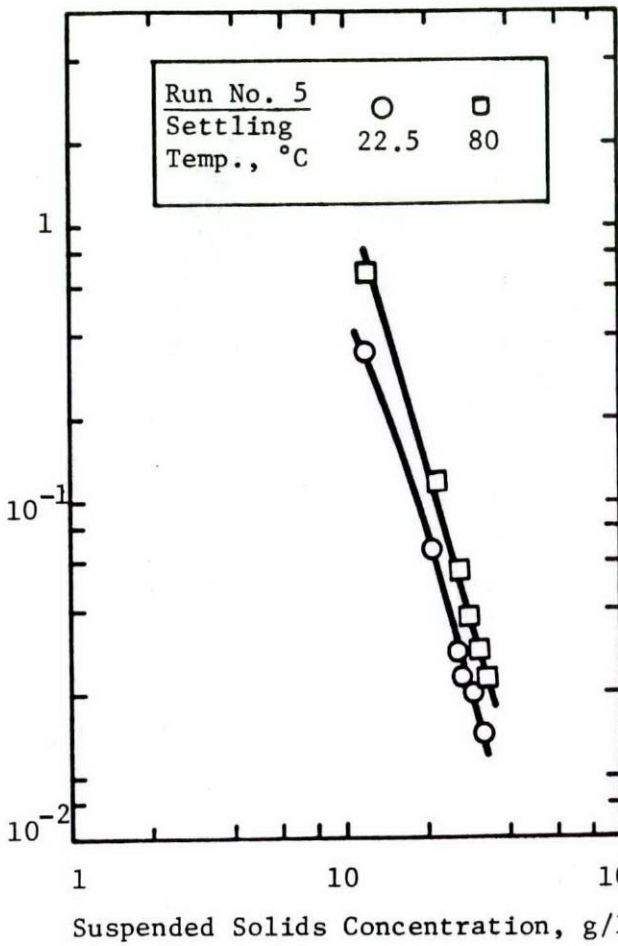


Figure 3: Settling Curves of Sludges Generated at 80°C and at Acidic and Alkaline pH Values

at 65°, 80° and 90°C and at a neutral pH, only minor differences in zone settling characteristics were detected as indicated in Figure 4. Zone settling velocities of the sludges generated at 65, 80 and 90°C and at a neutral pH and analyzed at 22-24°C are presented in Figure 5. Zone settling data for an aluminum sludge from Plant I-C which was generated and analyzed at room temperature and neutral pH (7.2) are also included. It is apparent that there was no relationship between zone settling velocity and generation temperature at neutral pH values.

Further examination of the high-temperature precipitation of aluminum included investigation of the effect of pH on settling characteristics. Since sludges generated and analyzed at 80°C had higher zone settling velocities at higher suspended solids concentrations, this generation temperature was used to examine pH effects. As indicated in Figure 6, an increase in sludge generation pH from pH = 5.5 to pH = 8.5 resulted in significant improvements in sludge settling characteristics. Similar results were obtained with the sludges when settling tests were conducted at room temperature as indicated in Figure 7.

Discussion

Settling characteristics of aluminum hydroxide sludges are influenced by many factors which may include temperature of sludge at the time of settling analysis, age of sludge and type of aluminum hydroxide formed at the time of generation. Temperature may affect the settling rate of a sludge through the influence of liquid viscosity. Liquid viscosity affects particle drag forces during sludge settling. At high suspended solids concentrations, interparticle forces predominate, while at low suspended solids concentrations liquid resistance forces predominate. Therefore, as suspended solids concentrations decrease, changes in analysis temperature would result in diverging settling curves obtained at different temperatures. Such a divergent relationship did not occur for the sludge settling data obtained at the temperatures examined, as indicated in Figures 2, 3 and 4. Therefore, it may be concluded that under the conditions of this study, liquid viscosity did not appreciably influence the zone settling velocity obtained for the sludge examined.

The effects of sludge age and structure on sludge settling properties are dependent on the chemistry of aluminum hydroxide formation during neutralization. Depending upon the pH and temperature of precipitation, numerous forms of aluminum precipitates are formed, i.e. (a) amorphous, (b) pseudoboehmite and (c) trihydroxide forms (4). Amorphous aluminum precipitates, i.e. aluminum hydroxide preparations which are X-ray inactive and contain numerous trihydroxide and oxide hydroxide forms, are hydrophilic, amphoteric forms with low crystalline order (11,13). Precipitation of aluminum at pH values below neutrality (pH<7) results in the formation of these amorphous forms which contain high (e.g. 20%) levels of contaminant anions (e.g., $SO_4^{=}$, Cl^{-}) and have an average water content of 3 moles H_2O/mole Al_2O_3 (13). In addition, Herbillon and Gastuche (8) indicated that only amorphous and pseudoboehmite would be formed in the presence of high concentrations of chloride, nitrate and sulfate anions, regardless of pH. At high concentrations, the amorphous forms are easily coagulated into gels which upon

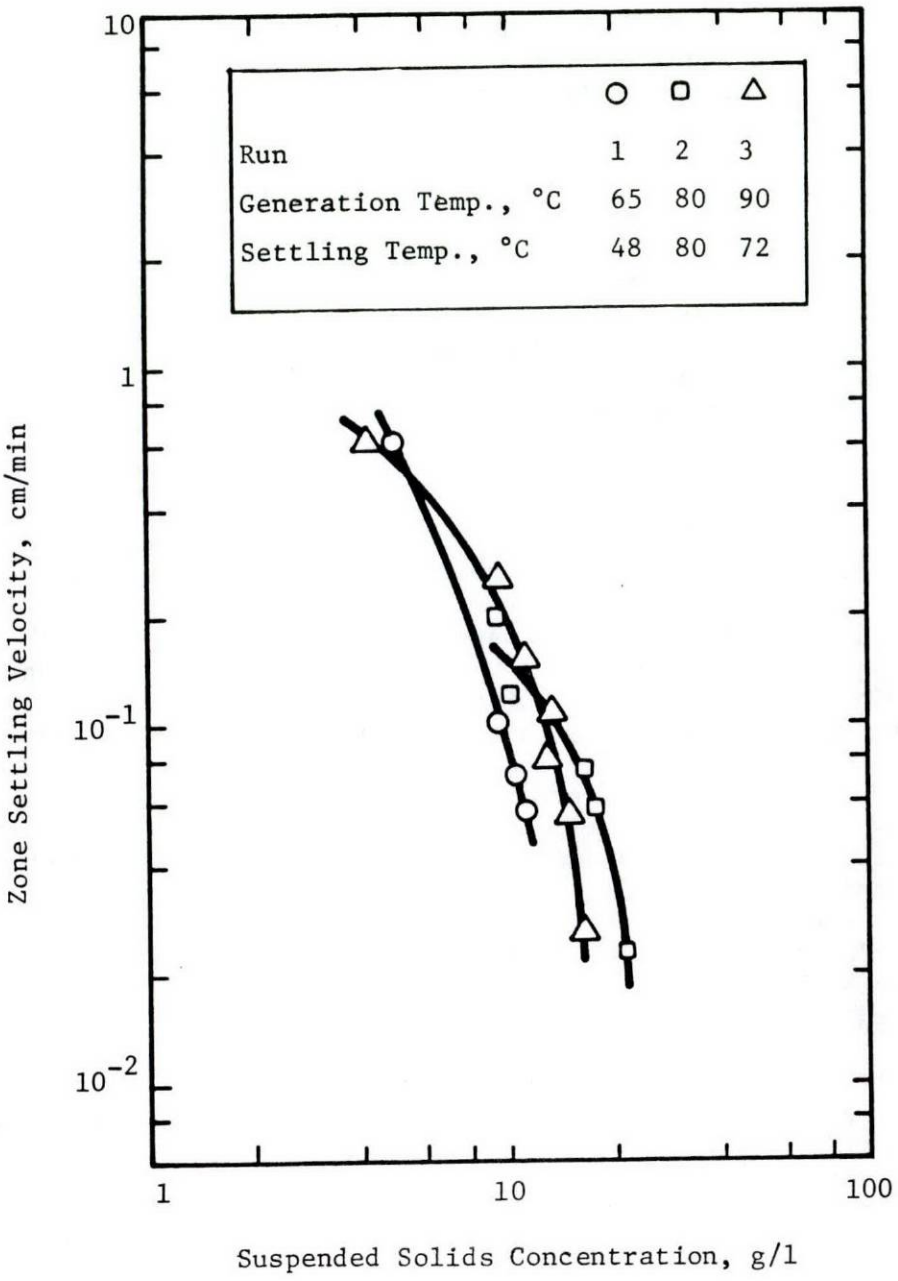


Figure 4: Effect of Settling Test Temperature on Settling Characteristics of Sludges Generated at Elevated Temperatures and Neutral pH Values

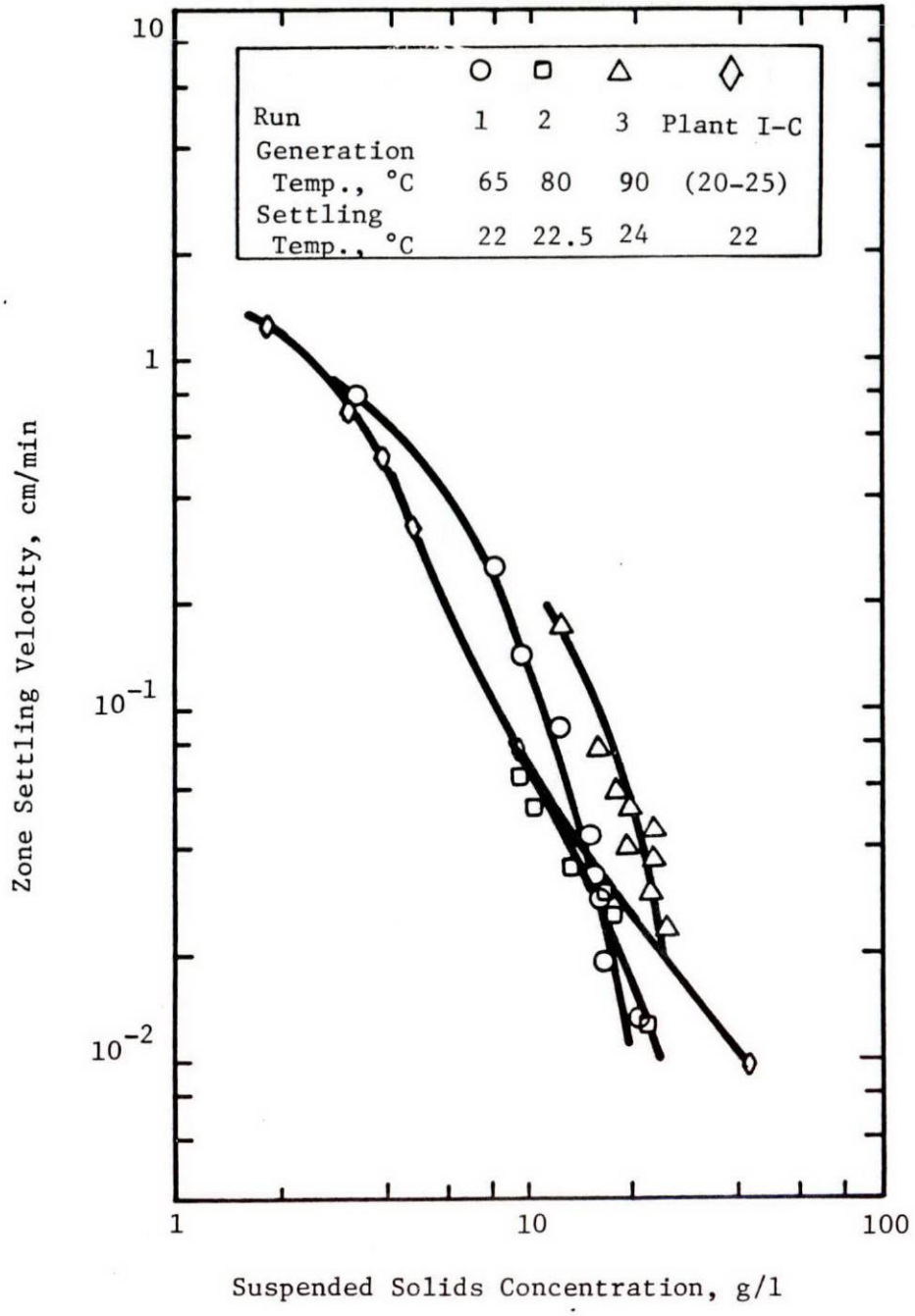


Figure 5: Effect of Sludge Generation Temperature on Settling Characteristics of Aluminum Hydroxide Sludge at Neutral pH Values

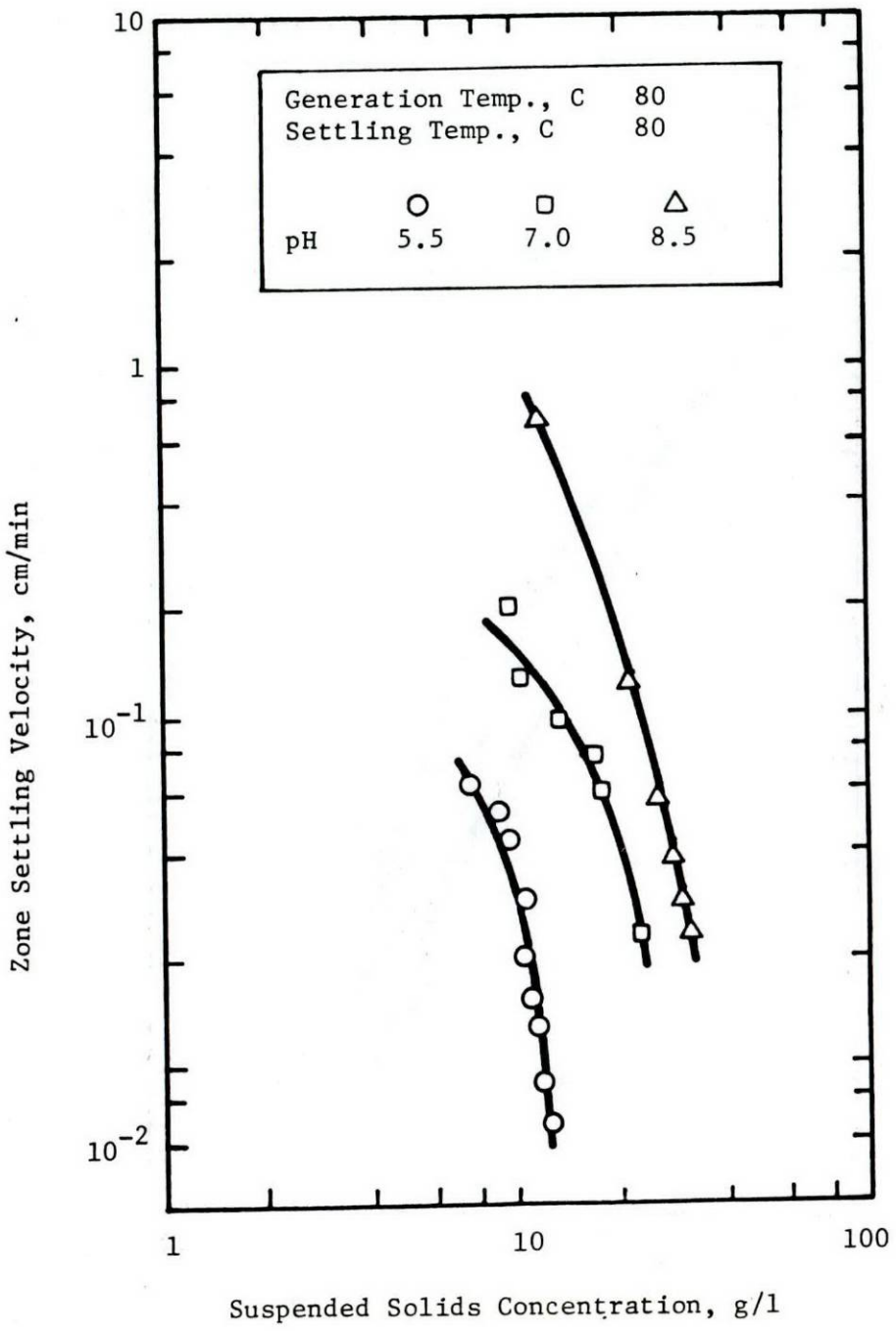


Figure 6: Effect of pH on Settling Characteristics of Sludge Generated at Elevated Temperatures

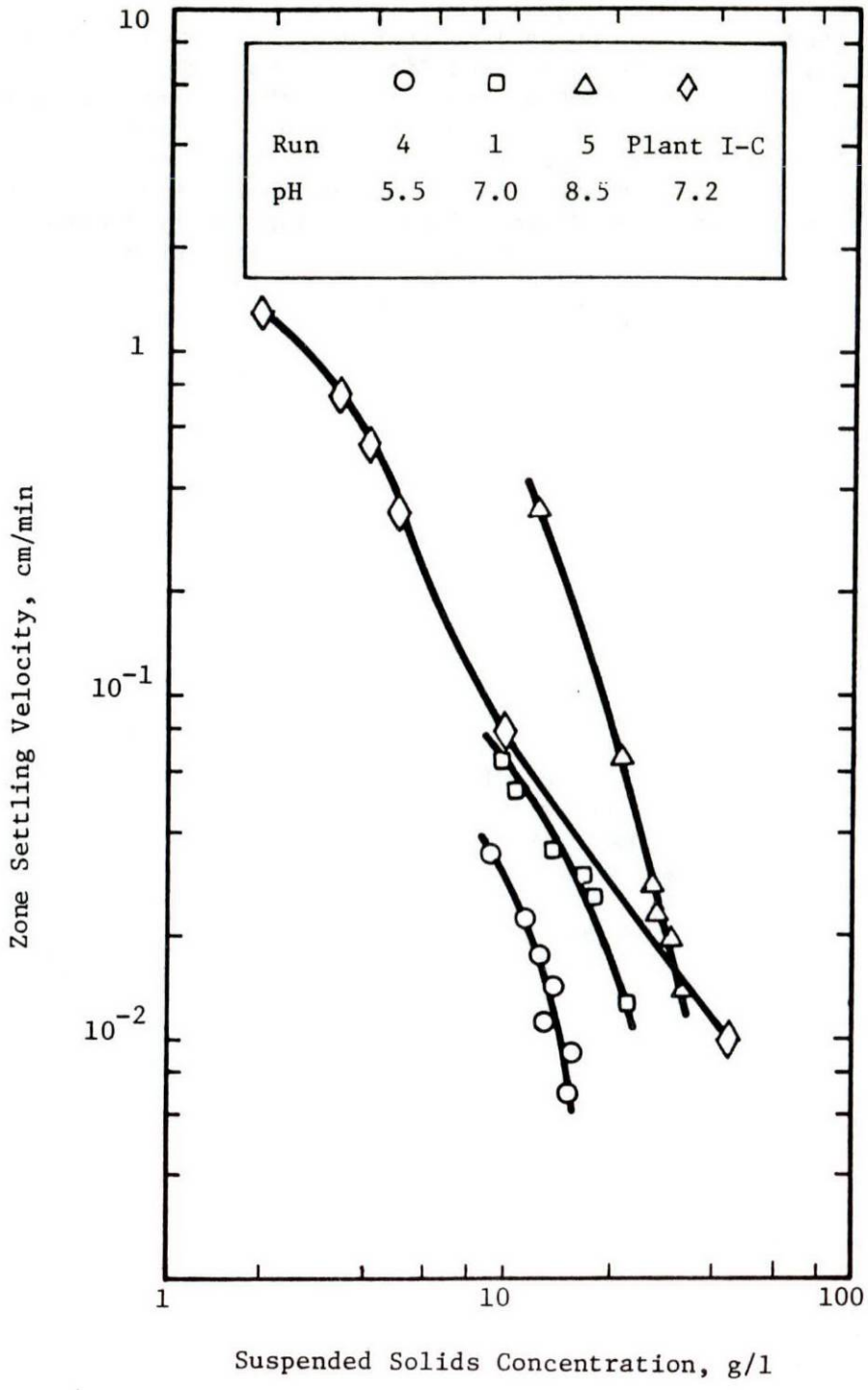


Figure 7. Effect of One Day Aging on Settling Properties of Sludge Generated at 80°C and Examined at 22.5°C and Comparison with Plant I-C Sludge Generated at 20-25°C and Examined at 22°C

aging may be converted into the various trihydroxide forms. With regard to the trihydroxide forms, Barnhisel and Rich (5), Hsu (6), Hem and Roberson (7) and Schoen and Roberson (8) reported that at room temperature, gibbsite is formed in acid solutions, nordstrandite is formed in slightly acid to neutral solutions and bayerite is formed in alkaline solutions. Herbillon and Gastuche (8) observed that when the ionic impurities, especially contaminant anions, were removed from aluminum solutions by dialysis, precipitation of gibbsite occurred at pH 4.6, while precipitation of mixed bayerite and pseudoboehmite occurred at pH 6.5. In addition, mixed gibbsite and bayerite were formed at pH 8 (8). Experiments by Hayden and Rubin (9) using aluminum nitrate solution indicated that, upon heating for five days at 65°C and at low pH values (initial pH = 5.50 and final pH = 4.10), gibbsite was formed. However, when the final pH was 4.42 (initial pH = 5.50), amorphous aluminum hydroxide was formed. Pseudobohmite was observed at a final pH value of 7.25. Papee and Tertian (11) reported that, while amorphous forms were precipitated at pH values below 7, a gel-type boehmite (pseudoboehmite) was formed at a pH of 9 and had a lower water content (i.e. 1.5-2 mole H_2O/mole Al_2O_3) than the amorphous forms. At pH values greater than 10, finely crystallized hydrates (e.g. nordstrandite and gibbsite) were also formed. In addition, as presented in Table 3, the water content of hydrophillic amorphous forms is typically higher than the crystalline trihydroxide forms.

From the above, it is apparent that both generation pH and temperature greatly affect the chemical composition of neutralized aluminum suspensions. Increased temperature tends to reduce the overall water content of aluminum precipitates while increased pH values result in the formation of more crystalline forms, which also have lower water content values. In view of the high sulfate content of neutralized etch/anodize wastes examined herein, it is apparent that amorphous forms of aluminum hydroxide were precipitated during high temperature experimental runs, especially at a pH of 5.5. As pH was increased to neutral (pH = 7.0-7.3) and alkaline (pH = 8.5) values, the crystalline aluminum trihydroxide and aluminum oxide hydroxide forms were produced which would tend to increase sludge density and decrease sludge water content (10).

Aluminum suspensions generated at temperatures ranging from 65 to 90°C and at neutral pH values were apparently composed of similar aluminum forms. That is, the small temperature changes used herein did not significantly affect settling characteristics. Changes in pH, however, had a dramatic effect on sludge composition as indicated by the significant changes in zone settling velocities with increasing pH values. Sludges produced at increasing pH values appeared to contain an increased proportion of crystalline trihydroxide forms (11,13) which would possibly account for the enhancement of sludge settling properties.

From Figures 5, 6 and 7, it is apparent that the sludge suspension generated at 80°C and pH = 8.5 had the best settling characteristics of the suspensions examined. If the process of high temperature precipitation of concentrated etch and anodize wastes at alkaline pH values were implemented in Plant I-C, it is of benefit to evaluate the impact of implementation on sedimentation basin performance. Using a batch flux analysis presented by Vesilind (14), Dick (15) and others, zone settling velocity data can be used to predict

Table 3. Physical Characteristics of Aluminum Hydroxides

Aluminum Hydroxide	Initial Water Content at Room Temperature moles of H_2O/ mole of Al_2O_3	Density* g/cm^3	Reference
Amorphous	3	-	Popée and Tertian (11)
	4		Wefers and Bell (4)
Gibbsite	3	2.42	Newsome et al.(12)
	2.5-3		Popée and Tertian (11)
Bayerite	3.15	2.53	Newsome et al. (12)
	2.5-3		Popée and Tertian (11)
Nordstrandite	2.5-3	-	Popée and Tertian (11)
Boehmite	1.5-2	3.01	Popée and Tertian (11)
	1.15		Newsome et al. (12)
	1.5		Newsome et al. (12)

*Maczura et al. (13)

sedimentation basin performance. Using data for the conventional sludge generated at Plant I-C (generation temperature = 20-25°C, settling temperature = 22°C, pH = 7.2) and the sludge generated at 80°C and pH 8.5 and analyzed at 22.5°C, batch flux data were calculated and are presented in Figure 8. If it is assumed that each suspension were applied to separate, but identical, sedimentation basins at the rate of 1.5 Kg/m^2 hr (i.e., 7.4 lb/ft^2 d), the thickened sludge underflow for the conventional sludge (Curve 2) would be approximately 12 g/l while that for the high temperature sludge (Curve 1) would be 38 g/l, in excess of a 3-fold increase in thickened sludge concentration. The high temperature precipitation process would therefore result in the production of a much thicker sludge for subsequent treatment and would reduce sludge volume by 68%, on an equal mass basis. It is furthermore obvious that sludge application rates below 1.5 Kg/m^2 hr would result in underflow sludge concentrations of 50 to 70 g/l (5 to 7%) for the high temperature sludge.

Since spent etch and anodize wastes may contain from 60 to 80% of the total waste aluminum discharged from an extrusion/anodize facility, segregated treatment of these concentrated acidic and alkaline wastes on a batch or semi-continuous basis should be pursued. Depending on plant operational procedures, it may be possible to only treat dilute rinse waters and spills during operation of a finishing line and store concentrated etch and anodize wastes for later treatment. When finishing operations are not in use and no rinse waters are to be treated, the wastewater treatment system could then be utilized to produce a sludge suspension at a high temperature under alkaline conditions. Sufficient storage space would have to be available to store the large quantity of sludge, however, due to increased sludge concentrations, the required volume would not be as high as that for the conventional sludge. Therefore, the process of alkaline, high-temperature precipitation of spent etch and anodize waste has great promise in the aluminum finishing industry. Immediate implementation of this treatment scheme into many aluminum finishing plants would, furthermore, appear to be feasible. Further investigation of the process of high tempearture precipitation at alkaline pH values over a broad range of temperatures is being pursued in the authors' laboratory, as well as investigations of sludge dewatering properties.

Conclusions

The following conclusions can be drawn from the reported results.

1. Aluminum contained in spent etch and anodize finishing solutions and suspensions can be effectively neutralized and precipitated at high temperatures (i.e. 65 to 90°C) in a reaction vessel with a hydraulic retention time of approximately 10 min.

2. Zone settling velocity data can be used effectively to evaluate settling characteristics of precipitated aluminum sludges.

3. At neutral pH values, the effect of generation temperatures of 65 to 90°C on suspension settling characteristics was minimal.

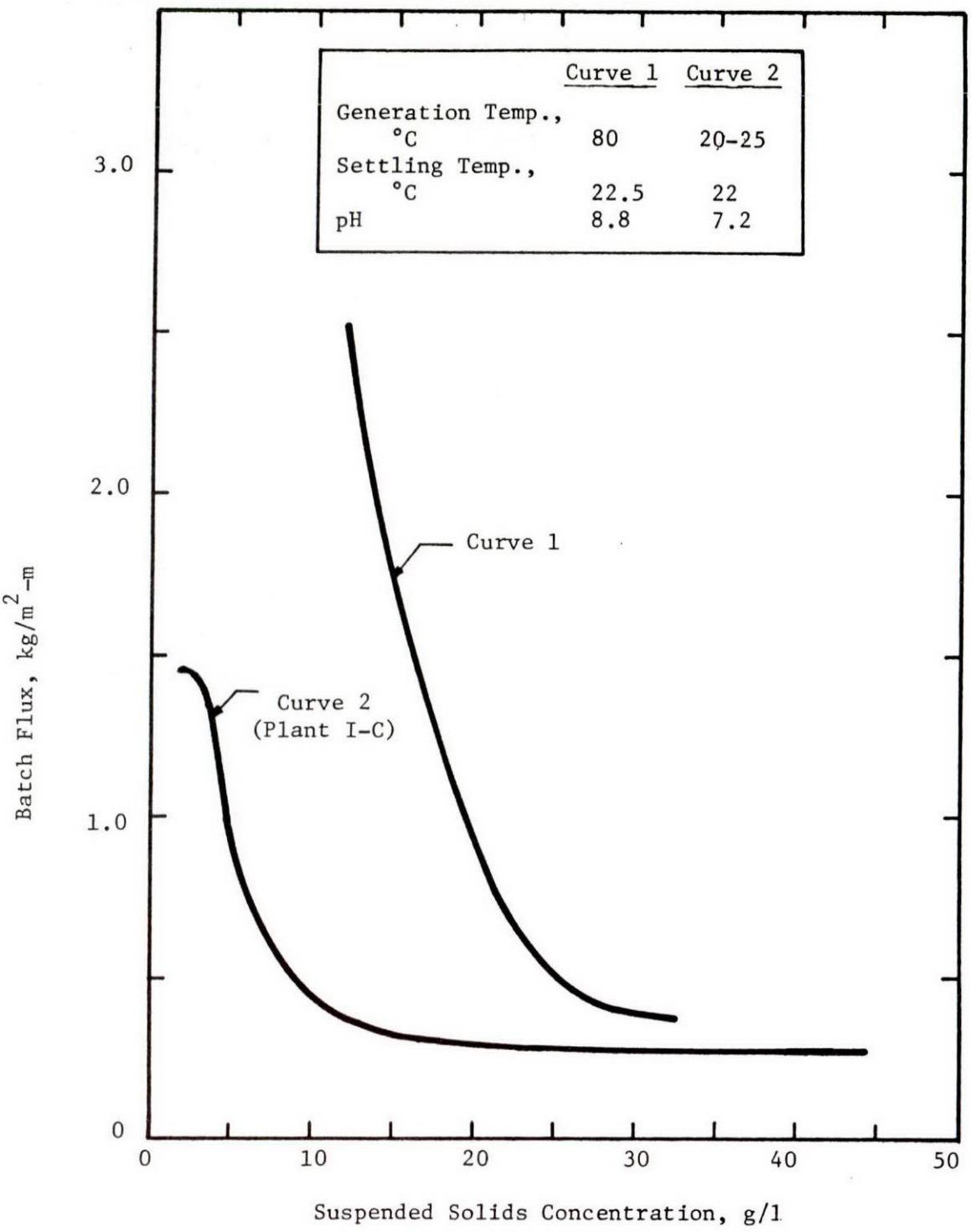


Figure 8: Comparison of Batch Flux Curves of Sludges Generated at High Temperature and at Alkaline pH and at Room Temperature and Neutral pH

4. For the range of suspended solids concentrations examined, the effects of changes in liquid viscosity on suspension settling characteristics were insignificant.

5. Aging of suspensions for 1 day followed by settling analysis at ambient temperatures (e.g. 22°C) indicated that suspension settling characteristics were not altered with respect to those obtained at generation temperatures.

6. Suspension generation pH values significantly altered suspension settling characteristics. Suspensions generated at a pH value of 5.5 (T = 80°C) were the poorest settling suspensions while those generated at a pH value of 8.5 (T = 80°C) were the most improved. Suspensions generated at an alkaline pH (pH = 8.5) had better settling characteristics than suspensions typically generated at extrusion/anodize finishing plants.

7. It was postulated that poor settling sludges generated at a pH of 5.5 contained amorphous aluminum hydroxide, while those generated at higher pH values (pH = 7.0 and 8.5) contained increasing quantities of crystalline aluminum trihydroxides.

8. A comparison was made of zone settling data for suspensions generated at 80°C and pH 8.5 and a sample of a suspension generated at an aluminum finishing plant at ambient temperature. The high-temperature suspension was shown to result in significant improvements in sedimentation basin performance. At solids flux loadings of 1 to 1.5 $Kg/m^2 \cdot hr$ (4.9-7.4 $lb/ft^2 \cdot d$), the high-temperature suspension could be thickened to underflow suspended solids concentrations of 3.8 to 5.0% solids.

9. High temperature neutralization at alkaline pH values of concentrated anodize and etch wastes from aluminum finishing plants can significantly reduce thickened sludge volumes and can be implemented immediately in many plants using existing treatment facilities.

Acknowledgement

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K-4

ENVIRONMENTAL
SESSION K

The Ion Transfer Membrane—A New Technology for the Treatment of Chromium Plating Waste and Recovery of Chromium (VI)

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THE ION TRANSFER MEMBRANE - A NEW TECHNOLOGY FOR THE TREATMENT OF CHROMIUM PLATING WASTE AND RECOVERY OF CHROMIUM (VI)

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ABSTRACT

The technology involves electromigration through an ion permeable membrane. A closed loop chromium rinse water treatment system is described. Rinse water, suppled as catholyte, is maintained at a nearly constant chromium concentration while chromium (VI) and sulfate ion transfer through the membrane, are recovered, and concentrated as anolyte. The membrane is durable and not subject to significant fouling. The system is a simple, modular design, requires no operator and no chemicals. The cost of system operation is less than the replacement cost of the recovered chromic acid.

Introduction

An innovative technology for the treatment of electroplating wastes, the decontamination of electroplating baths, and the recovery of valuable chemicals in reusable form has recently been introduced to the electroplating industry.

A thick membrane composed of capillaries permits separation of ionic species of opposite charge from one another. Upon application of a static electric field across the membrane, migration of ions of like charge through the membrane in a preferred direction occurs. Particular advantages of this membrane technology are:

1. Unlike thin film membranes, the thick membrane is exceptionally durable.

2. Unlike thin film membranes, the thick membrane is not subject to significant fouling.

3. Unlike ion exchange resins, the thick membrane does not require frequent regeneration.

Imagine the possible applications. Water may be softened by removal of all cations and anions. Electroplating baths may be conveniently purified, e.g., the removal of iron and nickel cations from a chromium bath. Rinse water streams may be maintained clean, e.g., the removal of chromium (VI) from a chromium rinse stream. The subject of this paper is a recently commercialized system, depicted in Figure A, which maintains a clean chromium rinse stream.

System Description

The system simply operates on the electroplater's existing rinse stream. A typical installation for an electroplating operation with three rinses is depicted in Figure B. In this installation, the middle rinse is maintained at a daily average chromium concentration of 200-300 ppm Cr. The rinses are operated in counter flow with water being added to the final rinse to make up for evaporation. By this operation, the final rinse is maintained at a chromium concentration 1/5 to 1/10 of the middle rinse chromium concentration, assuming typical drag-in/drag-out factors for the final rinse and a typical daily rate of evaporation. Thus, the chromium concentration of the final rinse is maintained at a daily average of 20-60 ppm Cr.

The system is of modular design in order to be adaptable to the varying sizes of electroplating shops. The basic unit is a tub (4'x2'x2') equipped with a suitable number of membrane modules (to a maximum of eight modules per tub) to handle the daily drag-out of the particular shop's operation. Rinse water is circulated from the rinse stream through the unit(s) and returned to the rinse stream.

The system functions to remove chromic acid and sulfuric acid dragged-out by shop operation on a daily basis. Iron and other metal cations may be precipitated. Thus, the rinse stream is maintained daily at an acceptable average chromium concentration. There need be no routine discharge of rinse water. Water is normally added to the rinse stream only to make up for evaporation. When discharge of rinse water is desired, the system is permitted to reduce the concentration of chromium to safe low levels first; as low as 0.01 ppm Cr is achievable.

A membrane module is shown in Figure C. The module is approximately 0.25 m^2 of membrane (1.25 cm thick) surrounding an inner compartment approximately 3.4 l in volume at normal operating levels of anolyte and catholyte solutions. Platinum plated titanium anodes are inserted through the top of the module into the inner compartment which contains the recovered chromic acid/sulfuric acid anolyte. The outside of the membrane is wrapped with a stainless steel cathode. Rinse water is the catholyte solution.

In operation, under the influence of the electric field applied across the membrane, chromium (VI), primarily as bichromate ion at pH~3 and chromium concentration less than 500 ppm, and sulfate ion migrate from the catholyte to the anolyte. Air agitation of the catholyte prevents formation of a stagnant layer of depleted catholyte solution at the membrane interface and also cools the unit.

Chromic acid/sulfuric acid thus concentrates in the anolyte. Periodically, approximately one-half of the concentrated anolyte is removed. The concentrated anolyte may be either reused by the electroplater in his own shop or it may be sold.

The system requires no monitoring on a routine basis other than to assure daily that circulation pumps and air pumps are operating properly and to initiate periodically the removal of the concentrated anolyte.

As the system operates continuously, it may be elected to reduce the applied voltage on weekends or holidays. The rate of chromium (VI) removal is thus reduced, and the system nearly simulates a typical day's performance over an extended period. If the applied voltage were left unchanged, the system is capable of reducing the chromium concentration of the catholyte to very low levels over a weekend or holiday; as low as 1 ppm Cr.

System maintenance is minimal. Membrane life exceeds two years as determined by laboratory accelerated life tests. At the end of the membrane's life, characterized by greatly diminished performance, an old module is replaced with a rebuilt module.

Periodic cleaning of the system may become necessary when water other than deionized or distilled is routinely used. This cleaning may be best accomplished at those times when it is desired to discharge rinse water. Alternatively, the use of deionized water may be simulated by the installation of a single

module of the system in a reverse configuration in order to scavenge cations from the water used.

Module Performance

Concurrent with commercialization of the system, over the past year extensive laboratory testing of commercial membrane modules has been conducted. These laboratory tests have sought to simulate the environment of an electroplating shop and the electroplater's operation. In many instances more severe conditions were imposed in testing than would be expected in the field.

The ability of a membrane module to remove chromium (VI) is affected by the interplay of a number of factors. The capillaries of the membrane must be small enough to minimize infusion of the anolyte and catholyte, but large enough to provide adequate conductivity at reasonable anolyte and catholyte concentrations. The thickness of the membrane must be large enough to withstand prolonged exposure to corrosive chromic acid, but small enough to provide a sufficiently large electric field at economically applied voltages in order to develop a large ratio of anolyte to catholyte concentrations (gradient) across the membrane. The system's membrane modules are engineered to operate effectively within the ranges noted in Table A. When operated within these ranges a module can remove 55-160 g CrO_3 per day.

TABLE A

TYPICAL OPERATING RANGES

Gradient	10^2 - 10^5	
Voltage	15 - 30	volts
Concentration of:		
Anolyte	20 - 100	g CrO_3/l
Catholyte	50 - 500	ppm Cr
Catholyte pH using:		
Tap water	4 - 7	
Deionized water	2 - 4	
Current	6 - 18	amperes/module
Temperature	< 50^C	C

Consider the following application of the system. The daily drag-out from the initial rinse to the middle rinse is 1500-1600 g CrO_3 per day, i.e., approximately 1/5 of the drag-out from the chromium bath. At a moderate rate of chromium (VI) removal, viz., 100 g CrO_3 per day per module, 15-16 modules (2 units) are required. With the system operating at 25 volts and required to concentrate anolyte to 59-63 g CrO_3/l, at a daily average current of 10-12 amperes per module, the catholyte concentration varies between 100 ppm Cr and 300 ppm Cr daily. The temperature of the system is 32-37° C. Should other conditions of operation be imposed, other daily results are possible. However, the example represents a comfortable operation of the system.

The capital cost of the system, installation, and start-up for the example is $30,000. Power is virtually the only operating expense. At $0.03 per kilowatt hour, the operating cost is $1.90-$2.00 per killogram CrO_3, which is less than the retail cost of CrO_3.

Module performance may be adversely affected by accumulation of iron precipitates and chromium (III) ion in the rinse water. Due to usual drag-in/drag-out of the rinse stream, steady state concentrations of these potential interferents do not pose a severe problem.

At a sufficiently high chromium (III) concentration, the hydroxide precipitates at pH>5. Precipitation may occur both in the rinse stream and within the capillaries of the membrane. Should such fouling of the membrane occur, it is only partial, not complete, and the precipitate redissolves as the chromium concentration in the catholyte increases and its pH decreases. However, module performance is lessened until dissolution of the precipitate is complete. It is to be noted that when tap water is used, the conditions for chromium (III) hydroxide precipitation do not necessarily occur in the rinse stream at chromium concentrations within the typical operating range, but that when deionized or distilled water is used the conditions have never been attained.

Iron precipitates form at pH>2. Precipitation occurs only in the rinse stream. The precipitates readily settle, although in sufficiently large amount they exhibit a tendency to accumulate at the module cathode. Under adverse conditions, i.e., laboratory tests with no drag-out, fouling of the cathode is noticeable after 4-6 weeks of operation. Should such fouling of the cathode occur, remedies short of rinse water discharge and

system cleaning are possible. These are:

1. Either the affected module's cathode may be removed and cleaning accomplished by immersion of the cathode in an acid bath;

2. Or periodically, as necessary, the polarity of the modules may be reversed for a few minutes.

Both remedies remove built-up deposits on the cathode. The iron precipitates have no effect on the membrane itself.

Summary

The system described in this paper is an alternative to already existing technology for the treatment of chrome waste. The system has the following virtues:

1. It is exceptionally durable and relatively free of fouling in normal operation, thus requiring infrequent replacement and maintenance.

2. It is simply operated, requiring no full-time operator or any analysis.

3. It operates without the need for any other chemicals.

4. There is no discharge of water, and water is added only to make up for evaporation.

5. It is non-destructive.

6. It recovers valuable chromic acid for a cost less than the expense of replacement.

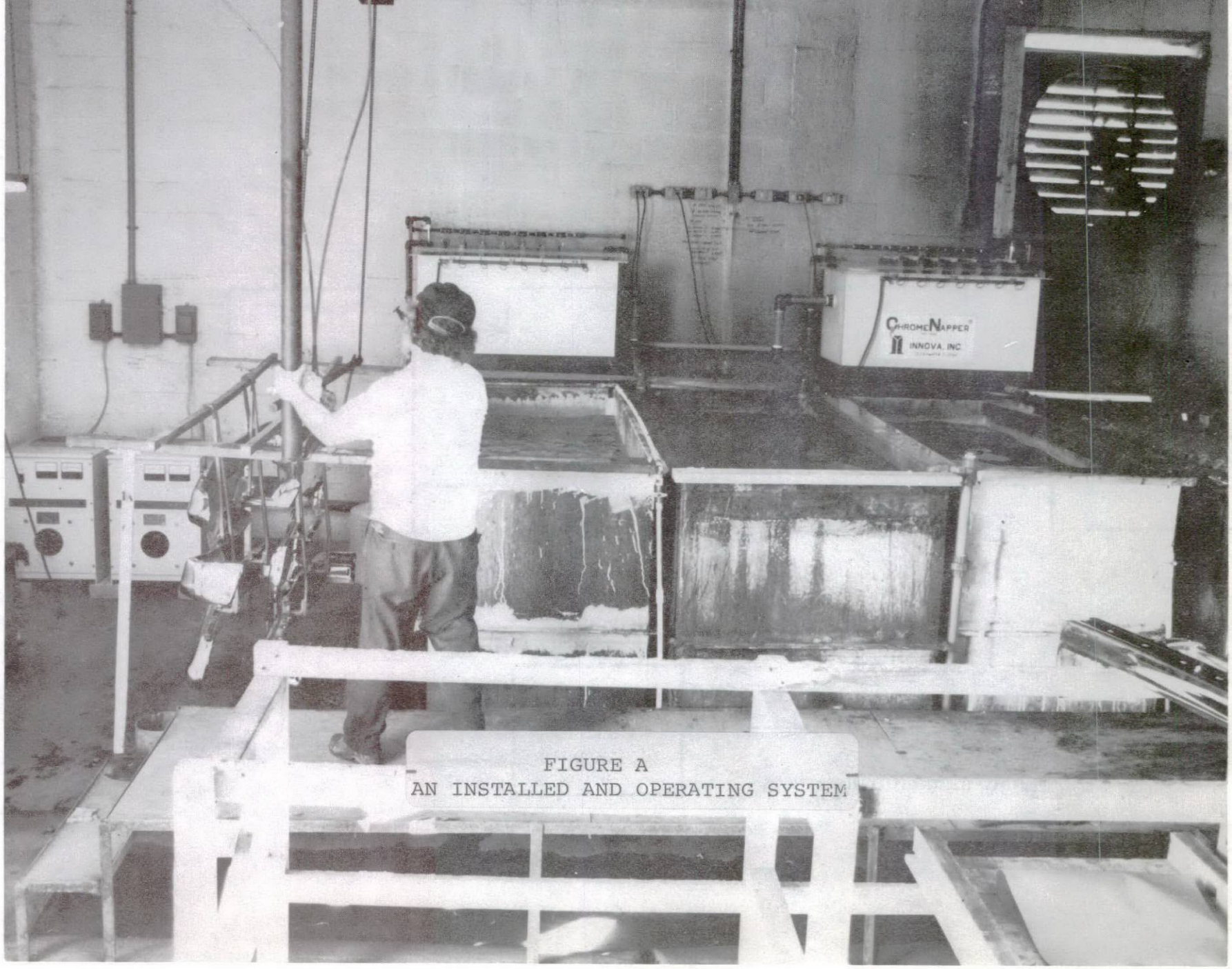

FIGURE A
AN INSTALLED AND OPERATING SYSTEM

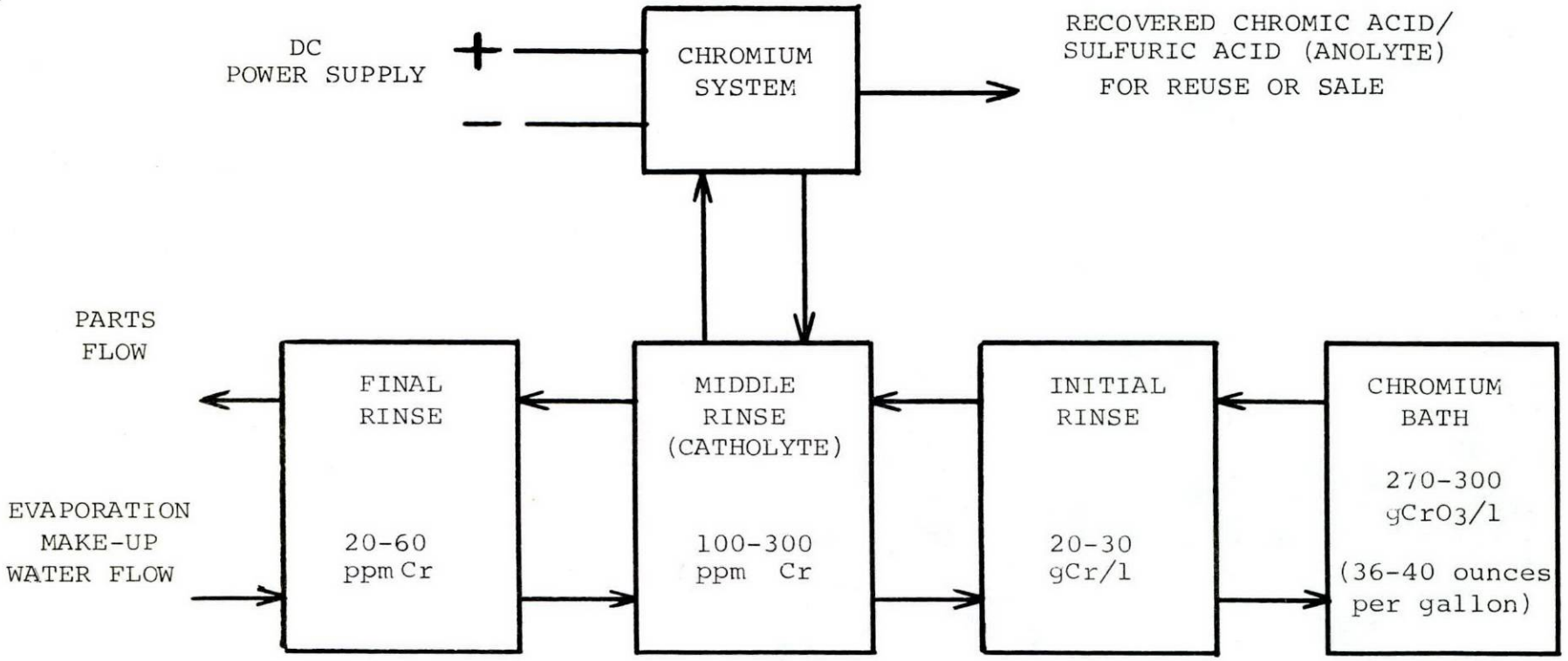

FIGURE B

A THREE RINSE SYSTEM

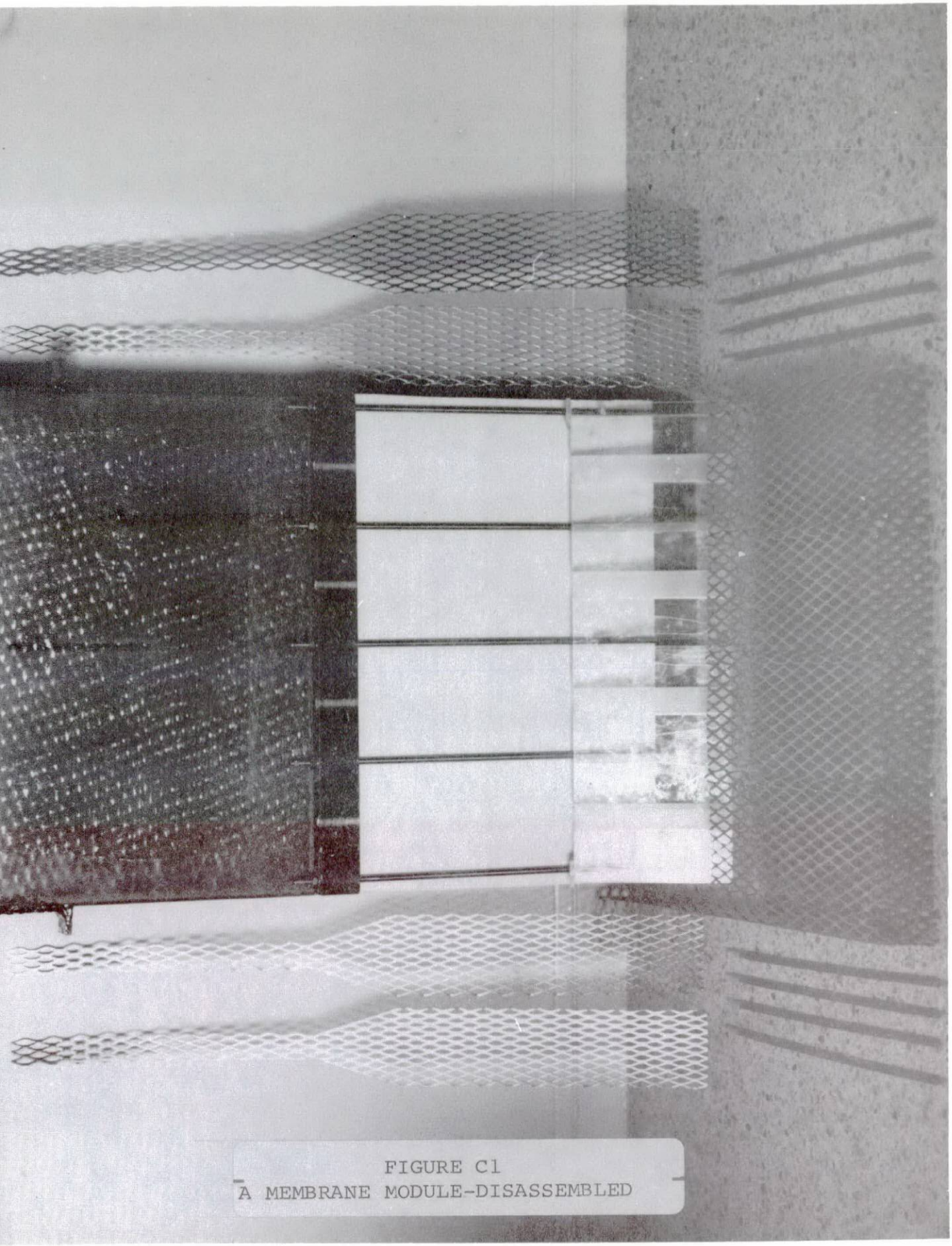

FIGURE C1
A MEMBRANE MODULE-DISASSEMBLED

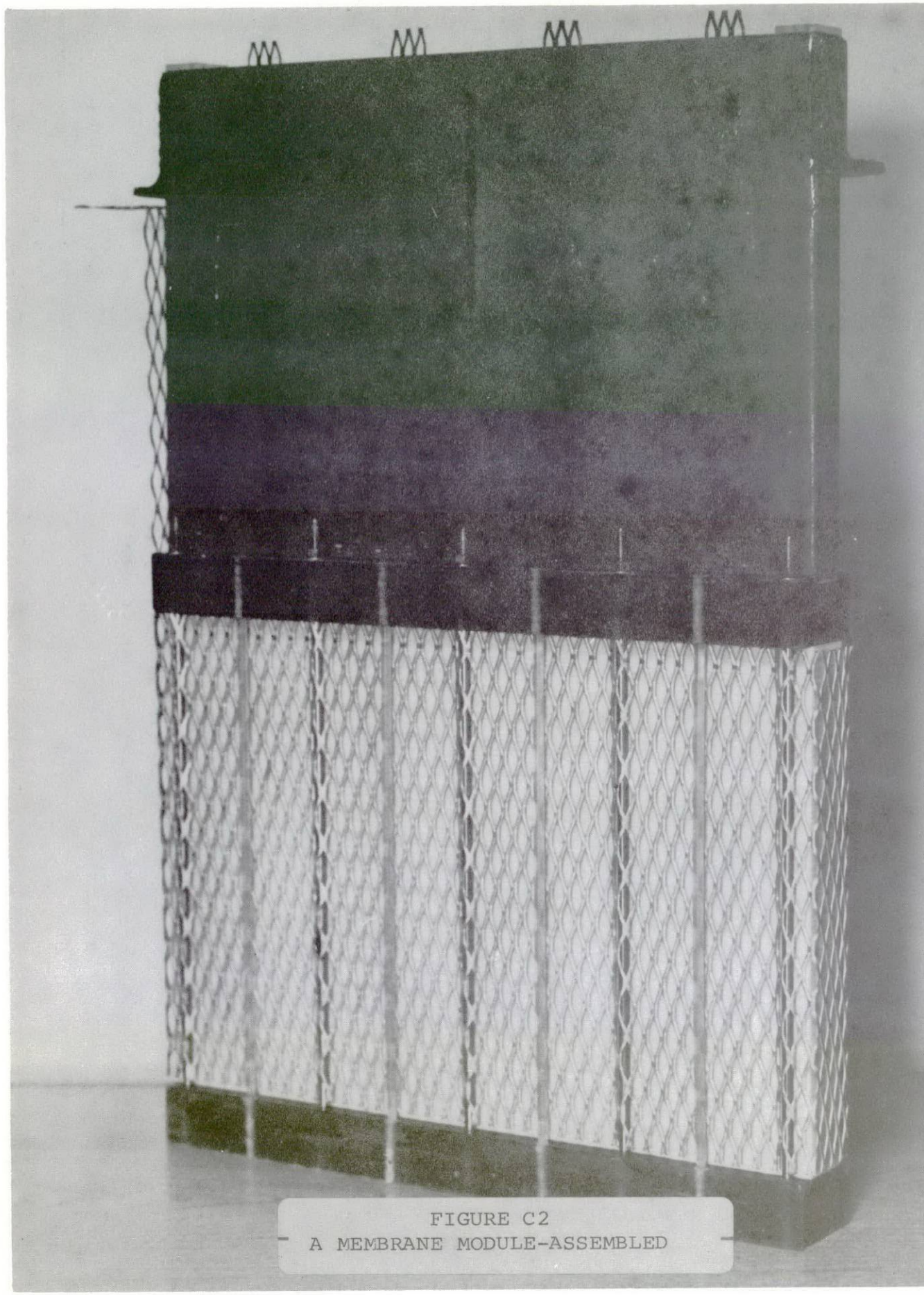

FIGURE C2
A MEMBRANE MODULE-ASSEMBLED

k-5

ENVIRONMENTAL
SESSION K

Wastewater Treatment in a Medium-Sized Metal Finishing Plant—Both Now and in the Future

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WASTE WATER TREATMENT IN A MEDIUM SIZE FASTENER METAL FINISHING PLANT NOW AND IN THE FUTURE

LARRY HAMMOND

STEVE REID

WATER TREATMENT:

In 1972, when the Federal Water Pollution Amendments were passed as a part of Public Law - 92-500, industry was starting to see the handwriting on the wall, in regards, to effluent of all types entering a publicly operated treatment works.

In 1973, the Plant Facilities Department requested a sum of money to research, engineer, purchase, and install a Water Treatment System at our Plant #2 in Rockford, Illinois. At approximately the same time, we purchased a large chloride zinc automatic barrel plater. The Water Treatment Facility and barrel plater were started up in November, 1974. The system was designed for a 100 gpm flow and was to include the treatment of chrome and chromate rinses, also, spent chromate acid concentrates, plus acid and alkali rinses and concentrates, the removal of suspended solids, the reuse of the portion of water flowing into the Treatment Plant, the removal of water from suspended solids thru a vertical leaf filter.

The overall operation is quite sophisticated and is almost all automatic.

The water treatment equipment receives effluent from four separate sources. There are two receiving pits located in the Plating Department. One is known as the Acid-Alkaline Pit, which receives all acid and alkaline rinse water, with the exception of nitric dip and rinse, chromate dip and rinse, and hot water rinse. The second pit is known as the Chrome Rinse Pit which receives the exceptions listed above to the Acid-

Alkaline Pit, and rinse waters from the hand chromate line and dischromate line.

When the waste water in the Acid-Alkaline Pit reaches a certain level, it is sensed by a mercury float switch, which turns on a pump. The solution is then pumped to the Water Treatment Building where it passes a deligating Ph probe, which senses the Ph (acidity or alkalinity). If the solution is acid with a Ph of 0 - 6.5, it will be diverted to the primary acid holding tank by a three way valve. If the solution is alkaline Ph 9.0 - 12.0, it will be diverted to a primary alkaline tank by a three way valve.

Additional alkaline solution is also diverted to the primary alkaline holding tank from four Heat Treat Washers, and a large Parts Washer. These alkaline solutions normally contain a small amount of oil. To eliminate the oil from getting into the Waste Water System, an oil skimmer was installed in the primary alkaline holding tank. The oil skimmed off is drained into a holding tank which is periodically drained into a waste oil tank and burned. If the waste waters Ph is 6.5 - 9.0, it is diverted to the neutral basin tank.

When the waste water in the Chrome Rinse Pit reaches a certain level, a mercury float switch turns on a pump. The solution is then pumped to the nitric-chrome rinse holding tank in the Water Treatment Building. To take care of this solution, we have a chrome reduction system with a pneumatic level control in the tank, which starts the chrome reduction system when the solution reaches a preset level. A sump pump on the chrome reduction system draws the water from the holding tank and pumps it to a tower mixer and thru a sulfur dioxide injector and sulfuric acid injector. The tower mixer stirs the solution and pumps it thru two probes (Ph and ORP (Oxidation Reduction Potential)) before going to the neutral basin. The Ph of the solution is maintained at 2.5. If the solution has a Ph higher than 2.5, sulfuric acid is injected by a meter pump. This is automatically controlled by a controller located beneath the Ph recorder on control panel. The ORP must not raise above 30 on ORP recorder so hexavalent chrome CR^{+6} is reduced to trivalent chrome CR^{+3}. To accomplish this, the ORP probe controls the injection of sulfur dioxide into the solution, which is automatically controlled by an instrument located beneath ORP recorder on the control panel.

A sure way to tell if hexavalent chrome is reduced to trivalent chrome is by the color upon being discharged to neutral basin. A sight glass was installed in the discharge pipe to observe this solution. Hexavalent chrome is yellow to red-yellow in color and trivalent chrome is blue-green to clear in color depending on concentration. If the solution is yellow to yellow green, there is not enough sulfur dioxide being injected or the Ph is too high.

The chromic acid from the plating equipment is pumped directly to a hexavalent chrome holding tank in the Water Treatment Building. A metering pump, pumps the acid from the hexavalent chrome holding tank to the chrome rinse holding tank during the time the chrome reduction is running in order to control the concentration of the chrome (hexavalent chrome).

All waste waters with a Ph of 6.5 to 9 from Acid-Alkaline rinses or concentrate continue to the neutral basin tank, also, all trivalent chrome leaving the Chrome Reduction System is pumped to the neutral basin tank.

The solution in the neutral basin tank is maintained at a Ph of 8.5. This is controlled by a probe in the neutral basin tank, which gives it's indication on a Ph recorder located on the main electrical panel. The system is so designed, that we have a primary and secondary feed adjustment systems, both for acid and alkali. If the Ph rises above 8.5, acid from the primary acid holding tank is pumped to the neutral basin tank to lower the Ph to 8.5. If the solution in the primary tank is weak or the tank is empty, sulphuric acid from the secondary acid tank is pumped to the neutral basin tank. If the Ph drops below 8.5, alkaline solution from the primary alkaline holding tank is pumped to the neutral basin to raise Ph to 8.5. If the solution in the primary tank is weak or the tank is empty, an 11% lime and caustic soda solution is pumped from the secondary alkaline tank to the neutral basin tank. The waste water leaves the neutral basin tank by gravity to the tube settling tank. As the water flows into the tube settling tank, flocculant is injected into the pipe which causes solids to settle and fall to the bottom of the tank. The flocculant is a + ION electrolyte which attracts the - ION's of solids and metals in the waste water, causing them to form large masses which rapidly settle. First on the incline tubes and then to the bottom of the tank. By this method, the water on top of the tube settling tank is clear and overflows into a return trough. These troughs are connected to a pipe line, which contains a conductivity probe which detects the salt dissolved in the water. If the salt content is low, the water flows into a reuse tank, and if it is high, it flows into the sewer.

From the reuse tank, 40% of the water is pumped back to all non-critical rinse tanks on plating equipment. Critical rinse tanks are supplied by recycled fresh water from the Heat Treat Department.

The solids which settle to the bottom of the tube settling tank are pumped into a horizontal leaf filter, which removes solids and metal. After passing through filter, the discharge flows into the reuse tank for consumption. When the filter reaches pressure of 70 PSI or the flow to reuse tank drops to 8 gpm, the filter is taken off the line and blown down into the blow down

tank.

The process of blowing down the filter includes drying the filter cake to approximately 70% moisture. This is done by injecting compressed air to inflate the filter bags to squeeze the water out of the filter cake. The filter is then opened by hydraulic power and cakes are shaken off by air vibrator. After cake is removed, filter is closed and refilled with water from blow down tank. Upon refilling, the filter is then put back into operation.

The sludge from the filter is taken to a special lined landfill where it is dumped. We have approximately 3,000 lbs. of sludge per day. ROCKFORD PRODUCTS uses Waste Hauling Manifests, and a Supplementary Permit to dump this sludge in the landfill.

Alarms were installed on the chrome reduction system to make the operator aware of certain conditions, which are: empty SO_2 cylinders, level and flow rate on the sulfhanator, and condition of sensing probe.

There are also, two high level alarms, one for the hexavalent chrome rinse tank and the other for the hexavalent chrome holding tank. These are usually tripped by large amounts of solution being dumped from plating equipment, or a plugged orifice on the sulfur dioxide injector.

In the Plating Department, alarms were installed in the three pits. These too are controlled by a mercury float switch. If the level in the pits reaches the full limit,a buzzer will go off and a flashing red light will come on. If this occurs, the operator immediately checks the pit pumps, either they have lost their prime or failed electrically or mechanically. This alarm, also, shuts off all waters to the Plating Department, which are connected to the Waste Treatment System.

Though the Waste Treatment System is almost all automatic, there are certain things the operator is responsible for. Listed below are some of these duties:

1. Insuring that proper levels are maintained in all tanks.

2. Blowing down the filter when required.

3. Mixing solutions when needed in:

    a. Flocculant Solution

    b. Lime and Liquid Caustic Soda in the Secondary Tank.

4. Removing and replacing sulfur dioxide cylinders.

5. Insuring there is sulfuric acid in acid drum.

6. Performing some of the preventive maintenance on equipment:

    a. Checking probes for cleanliness or salt.

    b. Cleaning tanks when required.

    c. Periodically checking all pumps for leakage or mechanical problems.

    d. Also, to practice good housekeeping methods on equipment and Water Treatment Building.

All lab analysis are performed by the Plating Department Lab.

The plant effluent is checked daily from samples taken from the sanitary sewer with a composite sampler. They are tested for total suspended solids and metals. The suspended solids are tested with Gravimetric Analysis, and metals are checked with Atomic Absorption Test. Cyanide is tested by the Colormetric Test.

Added equipment necessary to complete our total plating effluent control are: (2) cyanide evaporative systems, with a total capacity of 1,000 gph; (1) cyanide destruction system to neutralize small quantities of cyanide laden rinses and plating concentrates.

The responsibility of plating waste water treatment is that of the Plant Engineering Department - Steve Reid, my Plant Engineer, presently, holds an Illinois Class 7 Waste Water Treatment License and has under him three Pollution Control Technicians. For every hour that our Plating Departments are in operation, a Pollution Control Technician is on duty to monitor, record, and operate all phases of the plating effluent treatment equipment.

The technicians work very closely with the Plating Foreman to make sure that we constantly observe the ordinances and discharge limits as set down by our local POTW Plant.

This is where we are at present, but we all know that by October, 1982, the new Pre-Treatment Guidelines and Standards will compel us to do a more efficient job than under present guidelines. To meet the new Pre-Treatment Regulations, ROCKFORD PRODUCTS CORPORATION has purchased a 150 gpm system for our #3 Plant to control cleaners,cyanides, chromates, acids, and plating baths, which will be in operation (late June) 1980.

This along with the ability to install in both of our systems, polishing filters or other equipment as technologies are improved and perfected, will allow us to meet the 1982 guidelines.

Looking back, ROCKFORD PRODUCTS CORPORATION has been very well satisfied with our Water Treatment Facility that has been in operation for 5 ½ years with only three days of down time over this period.

We feel the experience gained by purchasing, installing, and operating a Water Treatment Facility were dollars well spent and a comfortable feeling that we can meet the more stringent guidelines of the future.

L-1

GENERAL INTEREST SESSION L

Pulse Plating of Nickel Deposits

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PULSE PLATING OF NICKEL DEPOSITS

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ABSTRACT

Pulse plated and conventional nickel deposits have been compared for differences in morphology, mechanical properties, and microstructure. The deposits were obtained from nickel sulfamate, nickel chloride, and Watts nickel plating solutions. No significant differences were found in the direct and pulse current deposits from the sulfamate and chloride solutions; however, significant differences in microstructure, yield strength, and microhardness were observed in deposits from the Watts nickel solution.

Introduction

In the electroplating industry, the choice of an electrodeposit, such as nickel, in a particular application is based on its properties. The main properties that determine the value of a nickel coating applied for decorative purposes are color, reflectivity, hardness, and abrasion resistance. Porosity and certain chemical properties determine corrosion resistance. In the case of heavy nickel deposits for electroforming purposes, different properties are important. Here, the important properties are mechanical, such as internal stress, tensile strength, hardness, ductility, and yield strength. These properties of nickel electrodeposits can be varied over a wide range by changing deposition conditions, by changing the bath formulation, or by introducing chemical additives. Pulsed plating is a new technique used to alter properties of electrodeposits. Avila and Brown[1] found pulse plating eliminated the need for additives to improve nickel deposits from a Watts solution and that the deposit brightness extended over a greater current density range than the additives. In addition, pulse plating inhibits columnar growth and produces a fine grained structure. Raub and Viswanathan[2] found that the nickel structure loses its columnar configuration at low duty cycles and high frequency values. Popov, et al,[3] found that pulse plating of nickel gave smoother, less porous deposits. Leaman and Kownacki[4] found that pulse plating of the nickel diffusion barrier prior to gold plating

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*Operated for the U.S. Department of Energy by The Bendix Corporation, Kansas City Division under Contract No. DE-AC04-76-DP00613.

resulted in a 40 percent decrease in the porosity of the gold deposit.

Pulse plated and conventional nickel deposits were compared for differences in morphology, mechanical properties, and microstructure. Scanning electron microscopy (SEM) was used in the morphology studies; X-ray pole figure analyses and transmission electron microscopy (TEM) were used in the microstructural investigation. The mechanical properties determined were tensile strength and elongation by tension testing and microhardness.

Experimental

The nickel deposits characterized were obtained from nickel sulfamate, nickel chloride, and Watts nickel plating solutions. The composition and operating conditions of these plating solutions are given in Table 1.

The plating cell was a cylindrical glass container which accomodated 2 L of plating solution; the cathode-to-anode spacing was 1 inch (25 mm). Agitation was by means of a magnetic stirrer. Temperature of the plating solutions was kept within ±2°C of the operating temperature, and the pH was controlled to ±0.2 units. The pulse plating power supply was a square wave unit.

Some definitions of terms used in pulse plating are in order. The average current density ($\bar{i}$) is defined as:

$$\bar{i} = i_p \frac{t_{on}}{t_{on} + t_{off}} \qquad (1)$$

where

i_p = peak current density (A/dm^2),

t_{on} = on time (ms), and

t_{off} = off time (ms).

Average current densities are used in this paper. The duty cycle (D), or the percentage of the time the current is on, is defined as

$$D = \frac{t_{on}}{t_{on} + t_{off}} (100) \qquad (2)$$

Results have been reported on duty cycles with an on time of 1 ms and the off time adjusted to obtain duty cycles of 20, 33, and 50 percent.

Table 1. Composition and Operating Conditions of Nickel Plating Solutions

	Watts	Chloride	Sulfamate
Nickel Sulfamate (g/L)			250
Nickel Sulfate (g/L)	330		
Nickel Chloride (g/L)	45	300	
Boric Acid (g/L)	40	40	40
Magnesium Chloride (g/L)			3.5
pH	2.5	2.5	3.8
Temperature (°C)	55	55	60

Concentration of the wetting agent is the same in all the plating solutions.

For the SEM samples, highly polished brass substrates were inserted in a plastic holder with a gasket so the edges and back of the substrate were masked, leaving an area of 0.085 ft^2(8.7 x $10^{-5}m^2$) to be plated. Prior to pulse plating, the substrates were cleaned with a mild alkaline cleaner, treated with a 10 volume percent sulfuric acid solution, and water rinsed after each step. Nickel deposits were obtained from the three plating solutions at current densities of 2 to 12 A/dm^2, and the cathode efficiencies were determined from the weight of the deposit and the ampere-minutes recorded by the integrator of the pulse plating power supply. Thicknesses of these nickel deposits were approximately 2 μm.

Nickel deposits used for the measurement of the mechanical and microstructural properties were plated on 6061 aluminum substrates with one side masked. Prior to nickel plating, the substrates went through a cleaning process, double zincating, and copper deposition from a copper strike solution. Nickel was plated at a current density of 4 A/dm^2 to thicknesses in the 100 to 150 μm range. After removing the maskant, the aluminum was dissolved in a hydrochloric acid solution and the copper in an ammonium persulfate solution. These nickel foils were chemically analyzed using emission spectroscopy and metallurgically cross-sectioned for microhardness and thickness determinations. The cross-sections also were used for grain structure examinations. Tensile strength and elongation of these nickel foils were determined by tension testing using ASTM E345-69. The subsize specimen was used, and the foils were interleaved with hard aluminum sheet during machining. This nickel foil was also used in the microstructural studies.

Results and Discussion

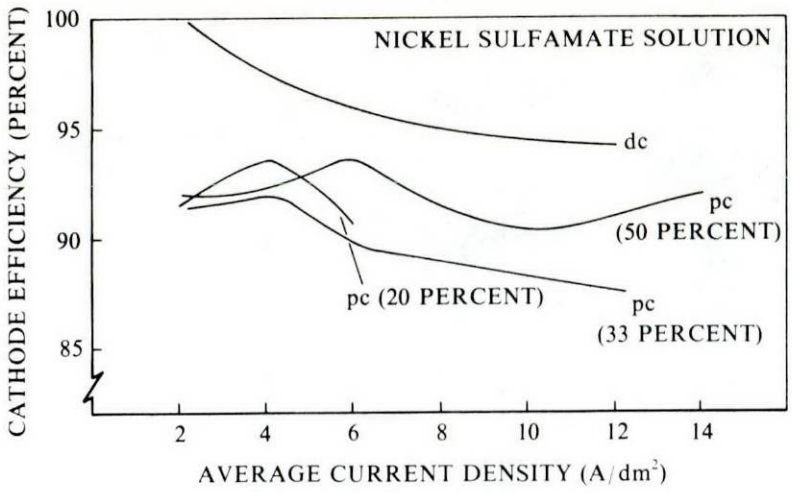
Pulsed and conventional nickel deposits from nickel sulfamate, nickel chloride, and Watts nickel plating solutions were analyzed chemically. The purity of the deposits ranged from 99.22 to 99.82 weight percent; the major contaminant was cobalt, with concentrations from 0.1 to 0.7 weight percent. Cobalt is introduced into these solutions from the nickel salts and nickel anodes. Other contaminants found were copper, iron, silicon, magnesium, and calcium at concentrations of 0.08 weight percent or less. No trends were obvious concerning the influence of pulse plating on the impurity levels in the nickel deposits.

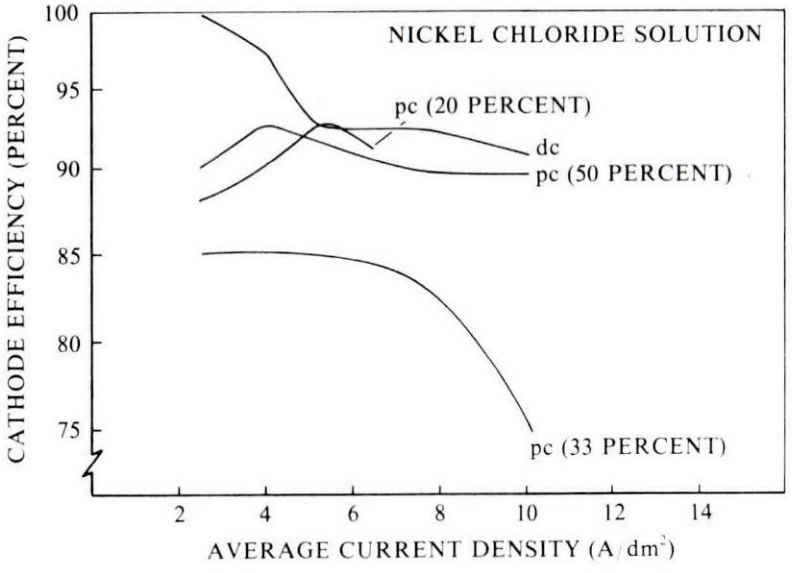
Cathode efficiencies for the pulsed and direct current processes were determined over the current density range of 2 to 12 A/dm^2 for the three nickel plating solutions and are shown in Figure 1. Some trends common to all the plating solutions were observed. In general, the cathode efficiencies using direct current are greater than those using pulsed current. Up to about 4 A/dm^2, the cathode efficiencies for pulsed current processes are about the same (92 to 94 percent), regardless of the duty cycle. With increasing current density and lower duty cycles, the cathode efficiency steadily drops and falls as low as 80 to 85 percent in some cases. With a 50 percent duty cycle, the cathode efficiency parallels the direct current processes and differ by 2 to 8 percent. The greatest difference is at low current densities and the least at high current densities.

Exceptions to these trends are found in the Watts nickel plating solution. Instead of the cathode efficiency gradually decreasing with the current density for the direct current process, a maximum occurs at 5 to 6 A/dm^2. At low current densities with a 50 percent duty cycle, the cathode efficiency exceeds that for direct current plating.

Surface Morphology

The surface morphology of the nickel deposits from the sulfamate, chloride, and Watts nickel plating solutions was investigated using the SEM. In Figure 2, SEM photomicrographs of direct and pulsed current nickel deposits from a sulfamate solution are shown. These rounded and granular appearing deposits are representative of the nickel deposits obtained from various combinations of current density and duty cycle. Finer surface features were not obtained with pulsed current. In Figure 3, SEM photomicrographs of direct and pulsed current deposits from a nickel chloride solution are shown. These deposits have surface features that are pointed and faceted, as opposed to rounded. In general, the pulsed current deposits have finer surface features than the direct current deposit.





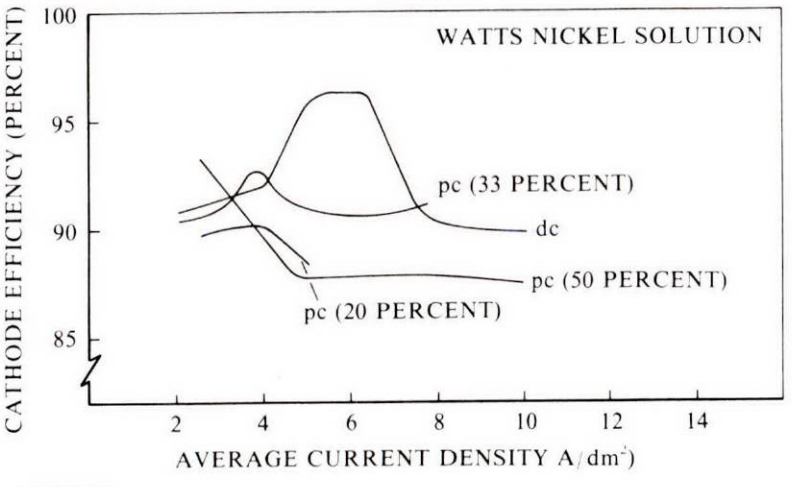


Figure 1. Cathode Efficiencies

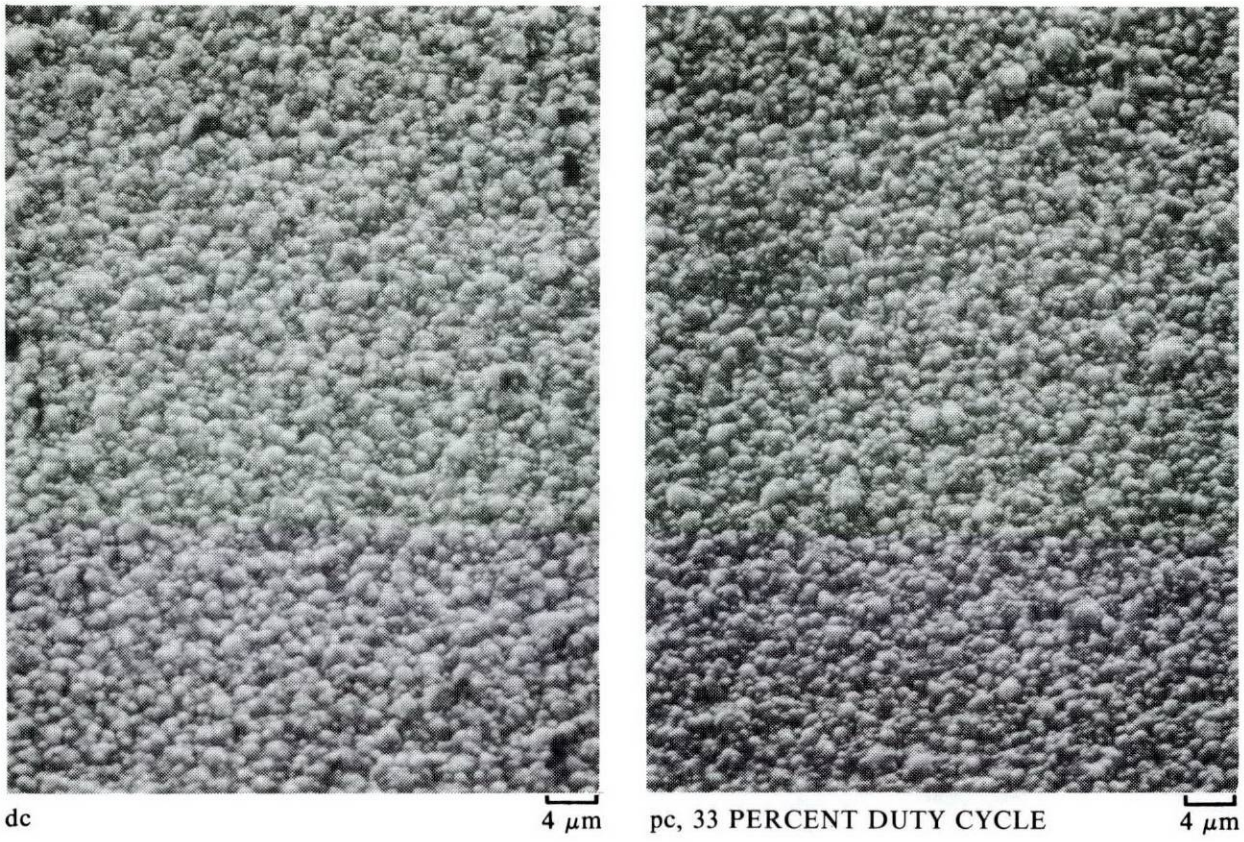


Figure 2. Nickel Deposits From a Sulfamate Electrolyte, 4 A/dm^2

The most prominent changes in surface morphology with pulse plating occurred with the Watts nickel plating solution. In Figure 4, SEM photomicrographs of direct and pulsed current deposits from a Watts nickel solution are shown. The direct current deposit has large granular features and distinct grain boundaries. With a 50 percent duty cycle, the granular features appear to be finer and create a more compact deposit between the fewer observed large granular features. At a 33 percent duty cycle, the granular features of the pulsed nickel deposit are finer and a more homogeneous surface appearance results. With a 20 percent duty cycle, the coarser granular features reappear, but not to the extent of the direct current deposit. The current density of 4 A/dm^2 was used in obtaining these nickel deposits.

Mechanical Properties

The mechanical properties of the pulsed and direct current nickel deposits from the three nickel plating solutions were determined at a current density of 4 A/dm^2. The yield strength and elongation were an average of four determinations. Results were rejected if the sample fractured outside the gage length. The microhardness results were an average of five measurements.

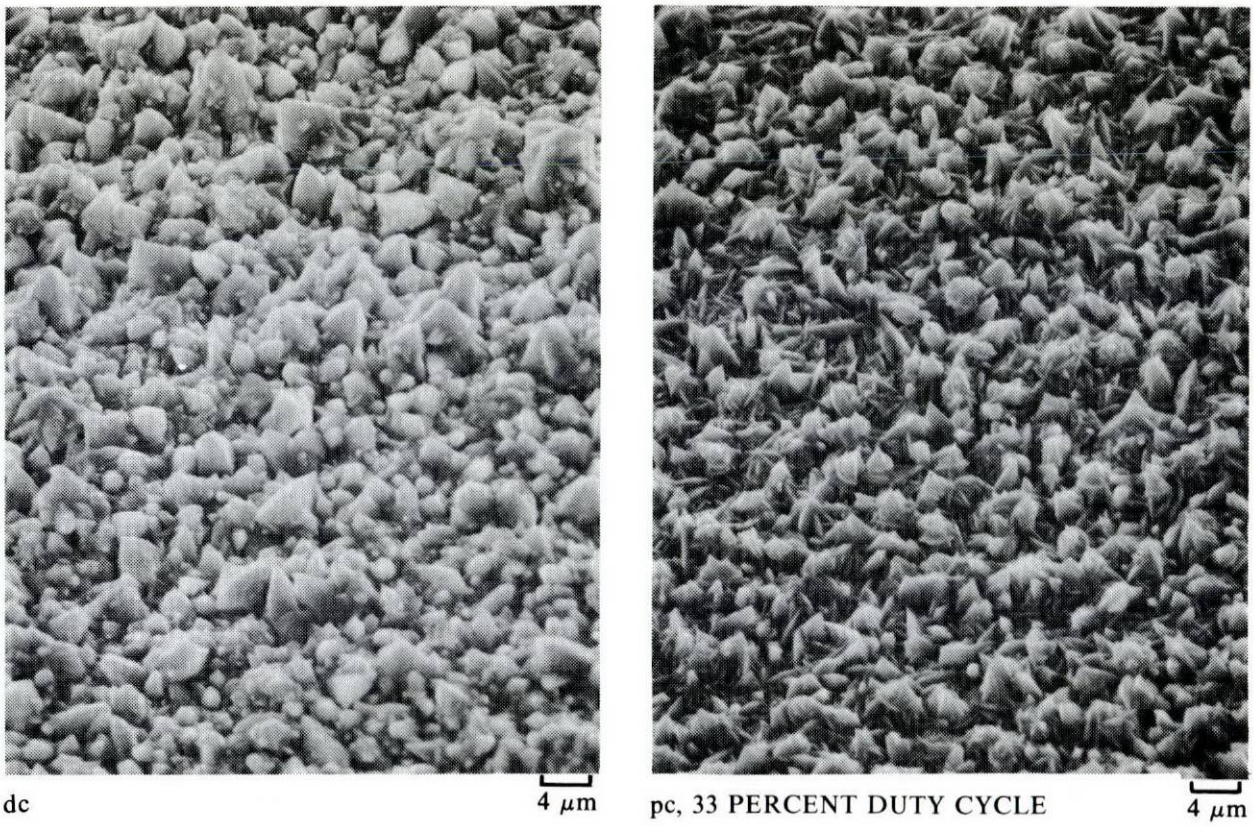
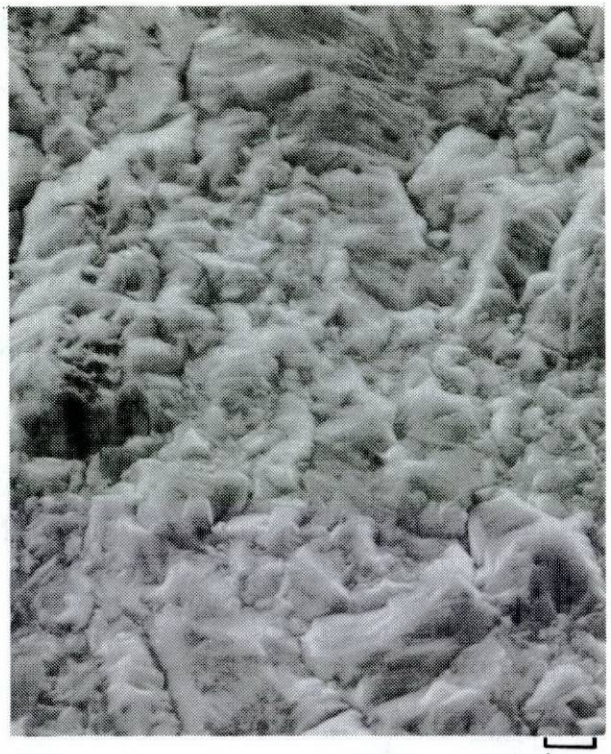


Figure 3. Nickel Deposits From a Chloride Electrolyte, 4 A/dm^2

The mechanical properties of nickel deposits from a nickel sulfamate plating solution are given in Table 2. The yield strengths of the pulse plated deposits for the 20 and 33 percent duty cycles are about 15 percent higher than direct current deposit. The microhardness and elongation for the pulse plated and direct plated nickel deposits are similar. Comparing the yield strength and elongation of these nickel deposits to literature values[5] reveals some discrepancies. Although the yield strengths are in agreement, the elongation test results are significantly lower. The scatter of the results was relatively high for the elongation measurements and could be caused either by intrinsic defects in the nickel deposits or by defects at the machined edges of the samples. The measured values ranged from 1 to 7 percent for the elongation in these samples. The microhardness results are somewhat higher than those reported elsewhere.[6]

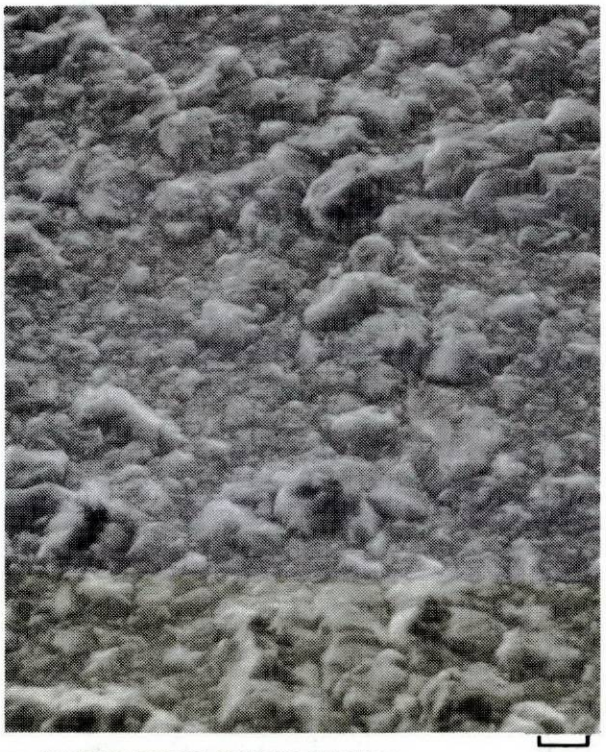
Mechanical properties of nickel deposits from a nickel chloride plating solution are shown in Table 3. No significant difference was found in yield strength, elongation, and microhardness of pulse and direct current nickel deposits. These yield strengths compare well with literature values.[5,7] However, as in the case



dc 4 μm



pc, 50 PERCENT DUTY CYCLE 4 μm



pc, 33 PERCENT DUTY CYCLE 4 μm



pc, 20 PERCENT DUTY CYCLE 4 μm

Figure 4. Nickel Deposits From a Watts Electrolyte, 4 A/dm^2

Table 2. Mechanical Properties of Nickel Deposits From a Sulfamate Electrolyte at 4 A/dm^2

	Yield Strength* (MPa)	Elongation** (Percent)	Microhardness***
dc	606	4.5	368
pc, 50 Percent Duty Cycle	562	5.0	343
pc, 33 Percent Duty Cycle	729	2.3	375
pc, 20 Percent Duty Cycle	703	4.8	380

*At 0.2 percent offset.
**1-inch (25.4 mm) gage.
***Knoop, 100-g load.

Table 3. Mechanical Properties of Nickel Deposits From a Chloride Electrolyte at 4 A/dm^2

	Yield Strength* (MPa)	Elongation** (Percent)	Microhardness***
dc	544	10.7	319
pc, 50 Percent Duty Cycle	589	9.8	326
pc, 33 Percent Duty Cycle	563	6.0	334
pc, 20 Percent Duty Cycle	560	8.3	329

*At 0.2 percent offset.
**1-inch (25.4 mm) gage.
***Knoop, 100-g load.

of the sulfamate nickel deposits, elongation was lower than expected, with a considerable scatter in the results (from 2 to 13 percent). Microhardness was comparable with those reported elsewhere.[7]

The most significant changes in mechanical properties of nickel deposits induced by pulsed plating was observed with a Watts nickel plating solution. These results are given in Table 4. The yield strengths of the pulse plated deposits are an average of 35 percent higher than the direct current deposits. Again, the elongation results were lower than expected,[7] and the high scatter of results prevented making comparisons between pulsed and direct current deposits. Typical scatter was 7 to 19 percent for the elongation of the 20 percent duty cycle deposit. Also, about a 25 percent increase in microhardness was noted for the pulse plated deposits. Yield strength and microhardness results of the conventional nickel deposits compared favorably with some literature values.[5,7]

Microstructure

Grain structures of the nickel deposits from the various plating solutions were obtained from metallurgical cross-sections. A fine grained, laminated structure was observed for nickel deposits from a sulfamate solution. Differences in pulsed and direct current deposits were not distinguished in this case or with the deposits from a nickel chloride solution. The deposits from a nickel chloride solution were fine grained. Changes in the grain structure were observed when comparing pulsed and direct current deposits from a Watts nickel solution. The direct current and pulsed current with a 50 percent duty cycle have a columnar structure with coarse grains. However, with a 20 and 33 percent duty cycle, the nickel deposits are obviously finer grained and appear to lose some columnar structure. Quantitative grain size determination was not possible because of the fine grain size.

With optical microscopy, significant microstructural differences occurred only between the direct and pulse plated Watts nickel deposits. As described previously, changes in surface morphology, yield strength, microhardness, and grain structure also were observed. Because of these changes, further microstructural studies were performed only with the nickel deposits from a Watts nickel solution.

X-ray Pole Figure Analysis

An X-ray pole figure plot is a contour map which graphically displays the scattering efficiency in various directions relative to some specific crystallographic plane. The plane generally is chosen to be the lowest index plane from which diffracted

Table 4. Mechanical Properties of Nickel Deposits From a Watts Electrolyte at 4 A/dm^2

	Yield Strength* (MPa)	Elongation** (Percent)	Microhardness***
dc	364	14.0	225
pc, 50 Percent Duty Cycle	563	5.0	259
pc, 33 Percent Duty Cycle	498	8.5	282
pc, 20 Percent Duty Cycle	436	12.7	290

*At 0.2 percent offset.
**1-inch (25.4 mm) gage.
***Knoop, 100-g load.

intensity is obtained. This plane is the (111) plane for face-centered cubic materials such as nickel. The scattering power is directly proportional to the probability that a grain in the bulk is properly oriented for diffraction. Specific orientations are identified by the use of a series of standard stereographic projections. The high intensity regions of the measured pole figure are matched with the location of the desired diffraction plane (the (111) plane in this case) on the projection. All four nickel foils show a cylindrical symmetry, implying no preferred orientation of the grains relative to a direction on the surface. A preferred orientation is shown in Table 5 for the nickel deposits obtained at 4 A/dm^2 from a Watts nickel solution. These deposits have a fiber texture and also possess dual textures. The primary texture is listed first in Table 5. The texture is a function of many plating variables, principally current density, the electrolyte, temperature of the electrolyte, agitation, and pH. The direct current nickel deposits, which have a principal (100) orientation, exhibit the highest ductility and lowest hardness (Table 4). This relationship of ductility and hardness to (100) oriented nickel deposits has been pointed out by Leidheiser[8] and Evans.[9] Pulse plated deposits with (211) and (111) orientations are inhibited modes of growth for nickel deposits. The appearance of (111) occurs only when all other modes of growth are severely inhibited. This inhibition has been reported[10] to stem from the abundant formation of $Ni(OH)_2$ near the cathode because of a localized pH increase. As the duty cycle is lowered and the pulse current density is increased, more

Table 5. Correlation of Duty Cycle and Preferred Orientation for Nickel Deposits From a Watts Solution at 4 A/dm^2

Duty Cycle (Percent)	Preferred Orientation
dc	(100) + (111)
50	(211) + (311)
33	(220) + (311)
20	(111) + (311)

hydrogen is formed at the cathode surface, favoring this type of inhibition. This same type of change in orientation of nickel deposits occurs when the organic additive, butynediol (but-2-yne 1,4 diol), is used in a Watts nickel solution. Amblard et al,[11] indicate orientation changing from (100) to (211) with the addition of butynediol. At the highest additive concentrations, the orientations further change from (211) to (111).

X-ray diffraction examination also indicates the bulk behavior of each nickel sample is different with respect to each other. The (111) reflection is the basis for comparison and is normally expected to be the most intense line, as is the case for the pulse plated nickel deposits. However, the direct current deposit shows the (200) reflection to be the most intense by far. All the pulse plated deposits show roughly similar overall intensities except the relative intensities of the (200) and (220) reflections. The (331) and (420) reflections are generally less than expected.

Optical and Electron Microscopy

Optical photomicrographs of the nickel deposits from a Watts nickel solution are shown in Figure 5. In all cases, the grain size appears to be very small. The amount of twinning apparently increases with pulse plating. (Arrows in these photomicrographs indicate twinning.) In the pulse plated nickel deposits, twinning increases as the duty cycle decreases. Twinning is an event that takes place with a defined probability during growth of crystallites and depends on the conditions of electrolysis. In general, nickel deposits from a Watts nickel solution have a small amount of twinning. Apparently, pulse plating greatly increases the probability of twinning.

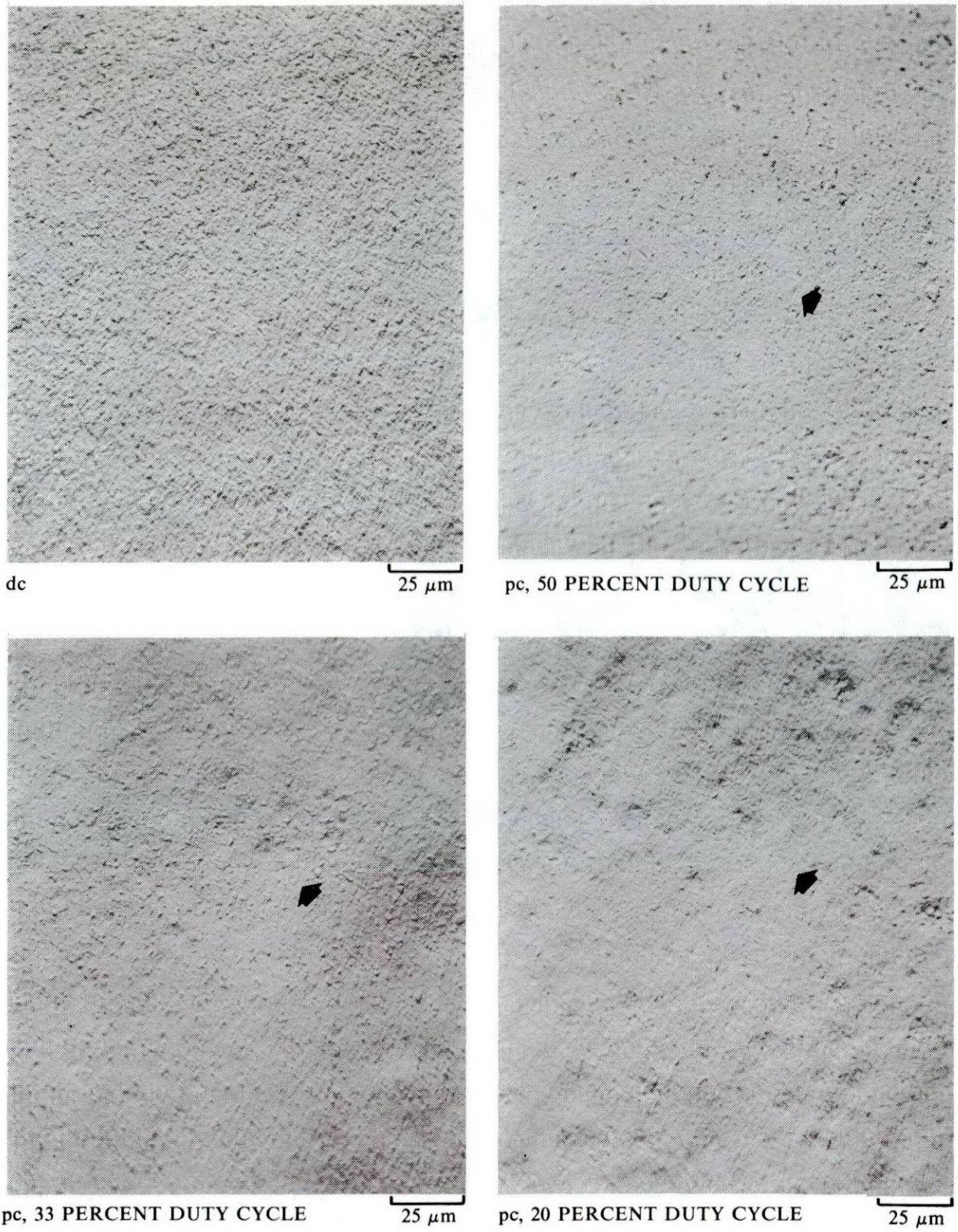
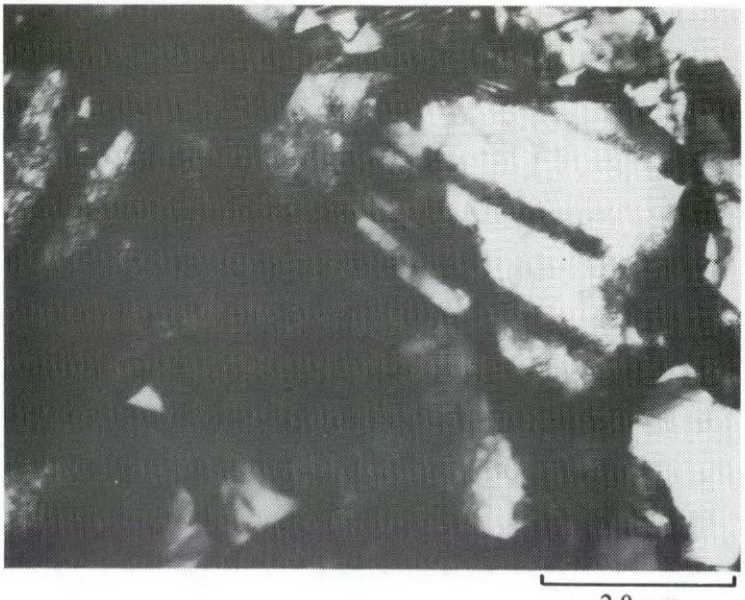
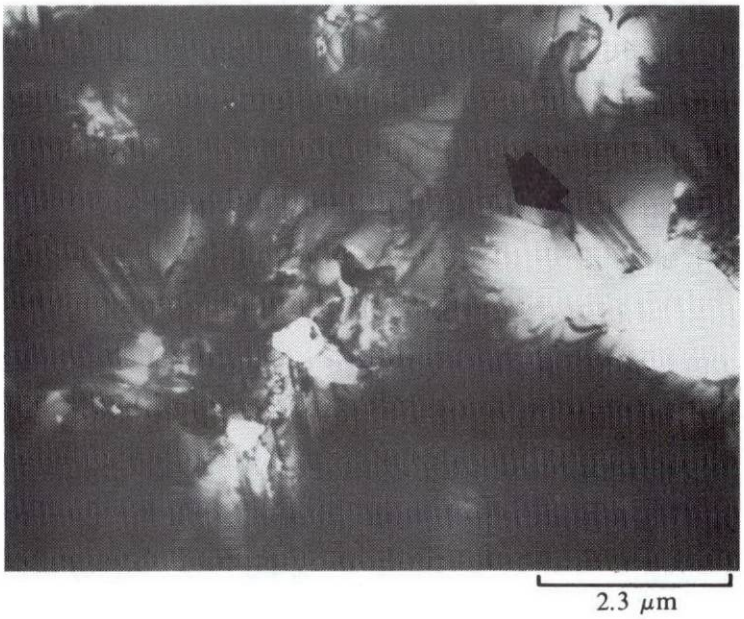


Figure 5. Optical Photomicrographs of Nickel Deposits From a Watts Nickel Solution



dc



pc, 20 PERCENT DUTY CYCLE

Figure 6. Transmission Electron Photomicrographs of Nickel Deposits From a Watts Nickel Solution at 4 A/dm^2

Transmission electron microscopy also verifies the extremely fine grained nature of these nickel deposits as shown in Figure 6. The grain size is roughly the same for the direct current and all pulse plated deposits. Generally, the grains range from 0.4 to 2.5 μm in diameter. The dislocation density, the number of stacking faults, and twinning increase dramatically for pulsed

plated nickel deposits obtained at 33 and 20 percent duty cycles. Again, twinning is by far the dominant feature in all cases and is indicated with an arrow in Figure 6.

Conclusions

In general, no significant differences in direct and pulse current nickel depostis from sulfamate and chloride solutions were found. However, differences were observed in nickel deposits from a Watts nickel solution. These pulse plated nickel deposits had grain sizes ranging from 0.4 to 2.5 μm, a 35 percent increase in yield strength, and a 25 percent increase in microhardness when compared to direct current deposits. Also, the surface morphology of these nickel deposits becomes less pyramidal in character when pulse plating is used. Generally, pulse plating greatly influences the preferred orientation of all the nickel deposits from this solution. Primary and secondary orientations are observed in all the deposits. In addition, pulse plating at low duty cycles dramatically increases the probability of twinning in these nickel deposits.

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L-2

GENERAL INTEREST SESSION L

Electrolytic Stripping - A New Generation of Metal Stripping Processes

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ELECTROLYTIC STRIPPING - A NEW GENERATION OF METAL STRIPPING PROCESSES

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ABSTRACT

Advancements in plating technology, rising production costs and EPA regulations have necessitated a new generation of stripping processes. To comply with these demands advanced electrolytic metal stripping methods have been developed which exhibit far greater solution longevity, are versatile in stripping capabilities, and are highly inhibited against substrate attack.

Introduction

Advancements in plating technology, an emphasis on ecological compatibility and preservation, as well as ever increasing cost factors have exerted a strong impact upon the metal finishing industry. As a direct result of these pressures, the electroplating industry of the eighties must operate at optimum efficiency and safety, and at minimum cost. To achieve these objectives, strong efforts must be made to improve plating procedures as well as to provide methods for the rapid and safe removal of undesirable deposits produced during normal plating operations. This paper is addressed to the removal of undesirable metallic deposits.

In the art of electroplating it is a general practice to support work articles to be plated on jigs or racks which are designed to carry a plurality of parts through a series of electrolytic plating baths. During this process metallic deposits build up on the rack tips or hooks. Due to their small surface area, these contact points are high current density sites and consequently result in a very thick buildup of metallic deposits within a relatively short period of time. Heavy metallic deposits, commonly referred to as trees, impair the performance of the racks, as follows: (1) unnecessary time and labor is spent in racking and unracking of parts, (2) contact points become distorted or broken during racking operations, (3) improper seating of parts results in losses of these parts to production when dropped into the plating solutions, (4) poor contact between parts and contact points results in rejects, (5) the trees act as shields which divert current away from the work, thus resulting in nonuniform distribution of metallic deposits and (6) excessive voltage is required to overcome the resistance imposed by the trees.

Furthermore, racks having poor contact points can result in parts which may be rejected due to peeling, pitting, roughness, staining, misplating, double plating, over and under plating, etc. Today, due to high costs of labor and material, it is no longer feasible to scrap these rejects. These factors and new emphasis on recycling and recovery dictate that

rejects be reprocessed. To effectively recycle these defective parts, the unwanted metal coatings must be removed without deterioration of the substrate. This removal of unsuitable metallic coatings can be accomplished by repolishing, chemical immersion stripping, or by electrolytic stripping.

The same general principles apply to both part and rack stripping processes. Metallic deposits are removed by removal of electrons, thus oxidizing the metal to the ionic form. This can be depicted by: M° ----- $M^{+2} + 2e^{-}$. For this to occur the oxidation potential of the metal must be attained and for effective stripping of metal overlays, it is necessary to maintain this potential.

Oxidation of the metallic overlays to the ionic state can be accomplished either by chemical immersion stripping or by electrolytic (electrochemical) stripping. Regardless of the method employed to oxidize the metal deposits, the ions produced from the dissolved metal must be effectively removed from the solution surrounding the substrate being stripped. Removal of the ions from the metal-solution interface is accomplished by the use of complexing ions and/or suitable chelating agents. The removal of these ions can further be enhanced by movement of the stripping solution by either cathode rod agitation or by a moderate degree of air agitation. Continuous reduction of the metal ion concentration at the metal-solution interface drives the equilibrium reaction toward ion formation, thus insuring a continuous and uniform dissolution of the metal. Though appearing to be a simple procedure, stripping processes in reality are complex by virtue of their selectivity. They require that the metallic overlay be removed quickly and effectively without altering the general appearance of the basis metal. Any attack that occurs must be minimal and uniform; requiring minor, if any, restoration of the base metal by polishing and/or buffing.

A variety of chemical[1,2,3] and electrolytic[4,5,6,7] stripping processes and solutions have heretofore been used, or proposed for use, in removing unwanted metal deposits from substrates, including plated articles as well as contact tips of electroplating apparatus. The following will serve as examples of the above stripping processes:

Chemical Stripping

Nonoxidizing Acid Strippers: The simplest stripping solutions for the removal of unwanted metals consist of nonoxidizing inorganic acids such as hydrochloric and/or sulfuric acid. Dissolution of metals proceeds according to the reaction: $M^{\circ} + 2H^{+}$ ----- $M^{+2} + H_2$.

In this type of solution, the Electromotive Series may be employed to determine the potential difference between metal and hydrogen. Generally, any metal below hydrogen, one that has a more negative potential, will undergo oxidation in nonoxidizing inorganic acids. Though these nonoxidizing acids are economical to use, they do possess the disadvantage of attacking the ferrous basis metal, since a pore-free oxide film cannot develop on the ferrous surface. Furthermore, there are metals which are

exceptions to the oxidation in nonoxidizing acids axiom; among these are nickel, lead and aluminum. Surface oxidation occurs with these metals and a continuous and insoluble film is formed on the passive metal surface that prevents any further attack by the acid.

Nitric Acid Based Strippers: In these strippers, the nonoxidizing acids are replaced with nitric acid. In using nitric acid for the disolution of metals, the metal is oxidized by the action of the concentrated acid, and not by the electron release of hydrogen, as in the case of nonoxidizing acid stripping solutions, according to the reaction: $3M^{\circ} + 2NO_3^- + 8H^+ \text{ --------- } 3M^{+2} + 2NO + 4H_2O$. To increase the rate of metallic dissolution by the nitric acid, activators may be incorporated into the stripping solutions. Examples of the above nitric acid based stripping solutions include a composition containing the acid in conjunction with an activator of chloride or chloride-iodate. Another example of this type of stripping composition includes one containing such additives as copper sulfate, chloride, and to further increase stripping rate, tellurium and selenium salts can be added.

Cyanide Based Stripping Solutions: These chemical stripping baths utilize (1) sodium cyanide to complex metallic ions such as copper, silver, gold and zinc, (2) sodium hydroxide for pH control, and (3) a water soluble aromatic nitro compound such as sodium m-nitrobenzene sulfonate or sodium nitrobenzoate which serve as the oxidants.

Amine and Ammonia Based Strippers: These solutions consist of a water soluble amine to chelate metallic ions; ammonium hydroxide for pH control and complexing of the metallic ions; aromatic nitro compound as oxidants; activators to activate the passive metals; and inhibitors to protect the base metal from attack.

Current chemical immersion stripping processes offer less than adequate methods for the removal of unwanted metallic deposits due to the number of limitations. These solutions are: (1) limited in the variety of metallic deposits each will remove; (2) they become exhausted quickly resulting in the need for frequent disposal of the solutions, thus incurring high waste treatment costs; (3) they cannot be regenerated and (4) stripping rates are slow and nonuniform. Furthermore, the use of nitric acid to strip metal liberates copious amounts of oxides of nitrogen which are extremely toxic. Nitric acid based strippers also affect the adhesion of plastic rack coatings to rack tips due to the oxidation of the plasticizers in the coatings, while the cyanide based strippers are being phased out due to their toxicity and high waste treatment costs.

Electrolytic Stripping

Since the oxidizing characteristics of a stripping solution can be greatly increased through the application of an external power source, electrolytic stripping is often a superior method for the removal of unwanted metallic deposits. The electrochemical stripping process generally operates at 100% anode efficiency. Moreover, making the metal surface to be stripped anodic allows metal deposits, which normally would be more noble than hydrogen, to

be stripped. Thus, electrolytic stripping solutions are generally more suited for stripping a large number of different types of plated metal deposits, singularly, in selective combinations, or in the form of selective alloys.

Electrolytic stripping baths are generally based on aqueous solutions containing ammonium, and/or alkali metal salts of nitric acid. However, stripping formulations employing sulfuric or phosphoric acid also have been proposed.

An example of an ammonium based stripping bath consists of ammonium nitrate, a buffer generally consisting of a water soluble organic carboxylic or polycarboxylic acid, and an accelerator consisting of a halogen compound. Other suggested compositions employ nitric acid salts of amines such as triethanolamine or ethylenediamine. Phosphoric acid based electrolytic stripping baths, containing glycerin as an inhibitor, have also been proposed for stripping of copper, nickel and chromium from steel based substrates; while the sulfuric acid stripping baths containing polycarboxylic acids such as citric, lactic, or tartaric, have been proposed for stripping nickel and/or chromium coatings from nonferrous base metals.

Many of the electrolytic stripping processes now in use exhibit shortcomings which make them no better than chemical immersion stripping solutions. They exhibit slow stripping rates, are prone to attack the basis metal, and are limited in the types of metal deposits they will remove.

Rack Stripping

Unlike its predecessors, new electrolytic stripping processes exhibit properties which meet requirements that are compatible with the industry trend towards rapid removal of unwanted metal deposits and reduction of objectionable effluents. These processes exhibit versatility in the variety of metals they will remove, have fast stripping rates, are highly inhibited against substrate attack, exhibit almost unlimited solution longevity, and contain no chemicals or produce any degradation products which are hazardous.

A typical stripping composition for this new process consists of an activator to accelerate the rate of removal of unwanted metal, an ammonium or alkali metal salt of nitric acid, and a proprietary additive to inhibit the corrosion or etching of the basis metal. A specific example of this type of stripping solution would have the following composition:

TYPICAL STRIPPING SOLUTION

Components	Metric	English
Ammonium nitrate.....	40 - 80 g/l	5.36 - 10.7 oz/gal
Buffer.....	10 - 40 g/l	1.35 - 5.4 oz/gal
Activator.....	5 - 15 g/l	0.67 - 2.0 oz/gal
Proprietary inhibitor.....	5 - 15 g/l	0.67 - 2.0 oz/gal

OPERATING CONDITIONS FOR ELECTROLYTIC RACK STRIPPING

Current Density (Anodic).....	32.4 - 64.8 A/dm^2	300 - 600 ASF
Voltage.....	6 - 12 Volts	6 - 12 Volts
Anode to Cathode Ratio.....	(Minimum) 1:4	(Minimum) 1:4
Anode to Cathode Distance....	10.2 - 25.4 cm	4 - 10 inches
pH.....	6.5 - 7.5	6.5 - 7.5
Temperature.....	49° - 60°C	120° - 140°F
Polarity.....	Work anodic; stainless steel panels cathodic	

This bath is particularly effective in stripping a variety of metal deposits from contact tips. Figure 1 shows stripping rates of this process for a variety of metals.

Studies of amine and amine-free types of electrolytic rack stripping processes, based on the use of new proprietary inhibitors, were conducted and they demonstrate outstanding inhibiting properties of these baths on samples of #301, 304 and 316 stainless steel. Table I shows the conditions employed in this study.

TABLE I

OPERATING CONDITIONS

	Metric	English
Cathode to Anode Ratio.....	8:1	8:1
Cathode to Anode Distance....	6.35 cm_2	2.5 inches
Anodic Current Density.....	54 A/dm^2	500 ASF
Cathodes.....	#316 Stainless Steel	
Anodes.....	#301, 304, 316 Test Coupons	
pH.....	7.5	7.5
Temperature.....	60°C	140°F

An amine type stripping solution employed in the above test had the following composition:

AMINE TYPE STRIPPING SOLUTION

Components	Metric	English
Aliphatic amine.....	52 g/l	7.0 oz/gal
Nitric acid.....	20 g/l	2.6 oz/gal
Buffer.....	20 g/l	2.6 oz/gal
Activator.....	14 g/l	3.2 oz/gal
Proprietary Inhibitor.....	20 g/l	2.7 oz/gal

Table II shows the rate of attack of the above amine type stripping process for different grades of stainless steel.

TABLE II

RATE OF ATTACK ON STAINLESS STEEL - g/hr *

Inhibitor Concentration g/l	Type of Stainless Steel**		
	#301	#304	#316
0	0.087	0.047	0.008
10	0.028	0.013	0.000
20	0.025	0.008	0.000

* g/hr based on 12.9 cm^2 (2 in^2) test coupon
** Refers to Table IV

In contrast, an amine-free electrolytic stripping solution having the following composition,

AMINE-FREE STRIPPING SOLUTION

Components	Metric	English
Ammonium nitrate.....	40 - 80 g/l	5.36 - 10.7 oz/gal
Buffer.....	10 - 40 g/l	1.34 - 5.4 oz/gal
Activator.....	5 - 15 g/l	0.67 - 2.0 oz/gal
Proprietary Inhibitor.....	5 - 15 g/l	0.67 - 2.0 oz/gal

shows, as seen in Table III, a reduced rate of attack on the same type of stainless steel samples.

TABLE III

RATE OF ATTACK ON STAINLESS STEEL - g/hr*

Inhibitor Concentration g/l	Type of Stainless Steel**		
	#301	#304	#316
0	0.070	0.037	0.005
10	0.019	0.010	0.000
20	0.003	0.003	0.000

* g/hr based on 12.9 cm^2 (2 in^2) test coupon
** Refers to Table IV which gives the composition of the stainless steels employed in these tests

TABLE IV

ANALYSIS OF STAINLESS STEEL

Content	Type of Stainless Steel #301	#304	#316
Carbon	0.08 - 0.15 max	0.08 max	0.10 max
Manganese	2.00 max	2.00 max	2.00 max
Silicon	1.00 max	1.00 max	1.00 max
Chromium	16 - 18 max	18 - 20 max	16 - 18 max
Nickel	-----	8 - 11 max	10 - 14 max
Molybdenum	-----	-----	1 - 3 max

Based on this study it becomes obvious that, through the incorporation of the inhibitor in either the amine or amine-free electrolytic stripping bath, these solutions offer protection even to the lower grades of stainless steel. Consequently, substitution of lower grades of stainless steel in rack construction can result in cost reduction for the plater.

To minimize waste treatment procedures and costs, these processes exhibit almost unlimited solution life. This longevity is attributed to the buffer and chelator systems, since these materials provide an environment in which a steady state of metal ion concentration is reached in the range of 12.0 - 16.5 grams per liter (1.6 - 2.2 oz/gal). Concentration of metal in excess of this range produces insoluble metallic salts which precipitate out as a sludge of short chain, aliphatic acid, and metal hydroxides. This sludge settles to the bottom of the stripping tank and can be removed periodically.

A typical installation operating at 0.36 amperes per gallon of stripping solution, 24 hours a day, 5 days a week, will require desludging in 3 - 4 months of service. This desludging of 1,500 gallons of stripping solution will produce between 1.5 and 4 drums of sludge, resulting in a solution volume loss of between 10 and 15%. After the desludging, the solution can be adjusted to its original volume with additional new stripping solution.

When properly maintained, this process will operate trouble free almost indefinitely. Waste treatment of the concentrated stripping solution is not necessary; it is, therefore, primarily directed towards the rinse waters which are used in conjunction with the stripping solution.

An analysis of rinse waters for ammonia and heavy metal ions was made prior to and following treatment. Results indicate that the rinse water from rack stripping solutions shows an initial ammonia ion concentration of 0.17 g/l; after treatment with 0.3% by volume of sodium hypochlorite at a pH of 12 for 3 hours, the ammonia ion concentration is reduced to 0.05 g/l, a reduction of 70.6%. The treated effluent shows a nickel, iron and copper ion concentration of less than 1 mg/l each, and 0.0026 mg/l of chromium, showing reductions of 96.5% for iron, 98.7% for nickel, 98.8% for copper and 99% for chromium.

As of this writing, there are no Federal Regulations[8] controlling the concentration of ammonium ions in discharged rinse waters. However, there are regulations in effect controlling the heavy metal ion concentration in daily effluent discharge. The regulations provide that a maximum allowable concentration of 1.4 mg/l of nickel, 1.4 mg/l of copper, and 0.25 mg/l of chromium per 10,000 gallons per day may be present in rinse water.

These stripping processes are applicable to hand operated as well as to fully automated installations. In automated installations, rack-stripping processes are incorporated into the plating cycle, and the time can be adjusted to the cycle on the machine. Hand operated installations are preferred where rack contact tips receive minimal metal deposition during the plating cycle. In such installations stripping may take place either after each plating cycle, or after accumulated plating cycles when sufficient metal buildup has taken place to require a prolonged stripping time. The advantage of a hand operated line is that the stripping time is flexible.

Electrolytic Part Stripping

Current electrolytic part stripping processes do not always meet today's stringent government and industry requirements. Response to the demands of the plating industry has prompted development of new processes which more adequately meet the stripping requirements for parts. The objectives set for developing an electrolytic part stripping solution were very similar to those for the rack stripping process. However, these were much more difficult to achieve due to the intricacy of design of the parts and to the relatively small difference in potentials existing between the metal or alloys being stripped and the metal substrate. Unlike racks which have a limited variation of design, parts offer an infinite possibility of configurations. This complexity in design becomes a decisive factor in the current density distribution of part stripping operations. The current densities on a single article may vary from 10 to 200 ASF, and the time of stripping will vary accordingly. The problem imposed by current density distribution is further compounded by having to strip many parts mounted on a single rack.

The problems encountered were resolved by developing a stripping bath consisting of an electrolyte which contains nitrates together with a blend of activators to increase the rate of stripping, buffers, and a blend of inhibitors which offer excellent protection against attack of mild as well as high carbon steels. Parts stripped in this bath require only minimal activation, prior to plating, to remove the protective film which is formed in the stripping solution. Proper maintenance of this solution offers very long solution life, thus minimizing waste disposal problems. Table V shows a specific example of a parts stripping solution.

TABLE V

ELECTROLYTIC PART STRIPPING SOLUTION

Components	Metric	English
Ammonium nitrate.....	120 - 480 g/l	16 - 64.3 oz/gal
Blend of Activators.....	1 - 10 g/l	0.13 - 1.34 oz/gal
Blend of Proprietary Inhibitors	1 - 10 g/l	0.13 - 1.34 oz/gal

The operating conditions for this bath are given in Table VI.

TABLE VI

OPERATING CONDITIONS
FOR ELECTROLYTIC PART STRIPPING

	Metric	English
Current Density-Anodic.....	1.08 - 21.6 A/dm^2	10 - 200 ASF
Voltage.....	3 - 6 Volts	3 - 6 Volts
Anode to Cathode Ratio.....	(Minimum) 1:4	(Minimum) 1:4
Anode to Cathode Distance....	5.1 - 25.4 cm	4 - 10 inches
pH.....	4.5 - 6.5	4.5 - 6.5
Temperature.....	21.1° - 37.8°C	70° - 100°F
Cathode Rod Agitation		

Figures IIa and IIb give stripping rates for a selection of metals stripped in the above bath under optimum conditions of 100°F (38°C) at an anodic current density range of 10 - 200 ASF (1.08 - 21.6 A/dm^2) from mild carbon steel base metal. This solution has the versatility to strip a variety of shapes, forms, and alloys as illustrated in Figures III - VI.

During the stripping operation, areas receiving maximum currents will be stripped first, leaving their base metal exposed to attack by the stripping environment; therefore, these exposed areas must be adequately protected. This protection is realized through the addition of a proprietary inhibitor. This film provides maximum protection to the base metal even upon prolonged exposure to the stripping solution. This unique property is illustrated in Figures III and IV.

Figure VII illustrates further advantages obtained from the presence of the proprietary inhibitor in the stripping solution. Parts which are accidently dropped into the stripping solution were found not to be significantly attacked and thus can be salvaged for replating.

As is evident from Figure VIIb, the part reclaimed from a stripping solution containing no inhibitor shows severe attack by the stripping solution. The surface appearance of this part cannot be made acceptable with a significant amount of buffing or polishing. The article retrieved from the solution containing the proprietary inhibitor, Figure VIIa, shows no apparent visible change in the general appearance of the base metal. It can be activated quite simply and replated producing a very acceptable finish.

In the presence of the inhibitor, a film forms during the stripping operation which is indicated by the gradual decrease of anode efficiency as the metallic deposits are oxidized, exposing the metal substrate. As this film forms, the base metal becomes passive and gassing occurs.

The process is further characterized by an almost unlimited solution life. The longevity of this bath is attributed to its complex buffer-chelator system. The buffer-chelator system is the key factor determining the success of the process. It must provide a balance which allows for almost unlimited life of the solution. To accomplish this, it must be able to chelate large quantities of metallic ion; however, the metal-chelate must not be so strong as to limit the life of the stripping solution through increases in metal content until it reaches saturation, nor must it be so weak that it will form voluminous amounts of sludge thus making the process impractical to maintain. The metal chelate must be strong enough to complex the metals yet weak enough so that it can release them to form a controlled precipitation of metallic salt-sludge. The buffer-chelate system chosen for this anodic stripping system permits a total metal ion concentration in the range of 26 to 30 g/l (3 to 4 oz/gal) at a pH of 5.5 to 6.2. At a concentration exceeding this range, the metal ions are removed from the solution in two reactions. Metallic ions may migrate to the cathode and plate out loosely on the stainless steel cathodes. As the metal content increases on the cathode it sluffs off, due to its poor metal to cathode bond, forming a metallic sludge at the bottom of the tank. The metallic ions which do not migrate to the stainless steel cathode interact with the anions of the stripping solution to form insoluble metallic salts which also find their way to the bottom of the tank. The total sludge, containing metal hydroxides, sulfides, free metals and degraded organic materials, settles at the bottom and can be removed periodically. By virtue of its long life, the waste treatment of this stripping operation requires minimum attention. Under normal conditions, this process requires no batch treatment. Waste treatment is primarily restricted to the treatment of the rinse waters following the stripping solution. The quantities of the chelator material reaching the treatment plant are minimal, due to the dilution factor of one to one hundred. They pose no adverse effect on the overall treatment of the plating operations effluent.

Analysis of the treated rinse waters show that the pollutants are within the range of EPA regulations set for the metal finishing industry appearing in the September 7, 1979 Federal Register, Table VII.

TABLE VII

ACCEPTABLE EPA EFFLUENT POLLUTANT CONC. VS.
STRIPPER EFFLUENT POLLUTANT CONC.

(EPA Regulations for Plants Discharging 10,000 gal/day or more)[9]

Pollutants	Regulations Final (mg/l)		Stripper Effluents (mg/l)
	Daily Max.	30 Day Average	Treated with 0.3% NaClO at pH of 12.0
Cu	4.5	1.8	1.0
Ni	4.1	1.8	1.0
Fe	--	--	1.0
Total	10.5	5.0	3.0

Conclusion

Unlike the nitric acid base strippers, the new generation of anodic strippers do not produce copious, noxious, toxic oxides of nitrogen, which require elaborate and costly ventilation and exhaust systems to meet EPA and OSHA requirements. They do not contain amines which may produce carcinogenic nitrosamines upon electrolysis. They eliminate costly waste treatment of concentrated solutions, since they are regenerated by additives added on an ampere-hour basis. Furthermore, they reduce cost to the plater by minimizing and completely eliminating the necessity of polishing and/or buffing operations before replating.

Therefore, through recent technical developments, there has emerged a new generation of processes for the effective removal of a wide variety of unwanted metallic deposits. These processes not only offer maximum protection to the metal substrate, and meet the stringent requirements established by industry and government, but also help in the preservation of our environment.

Acknowledgement

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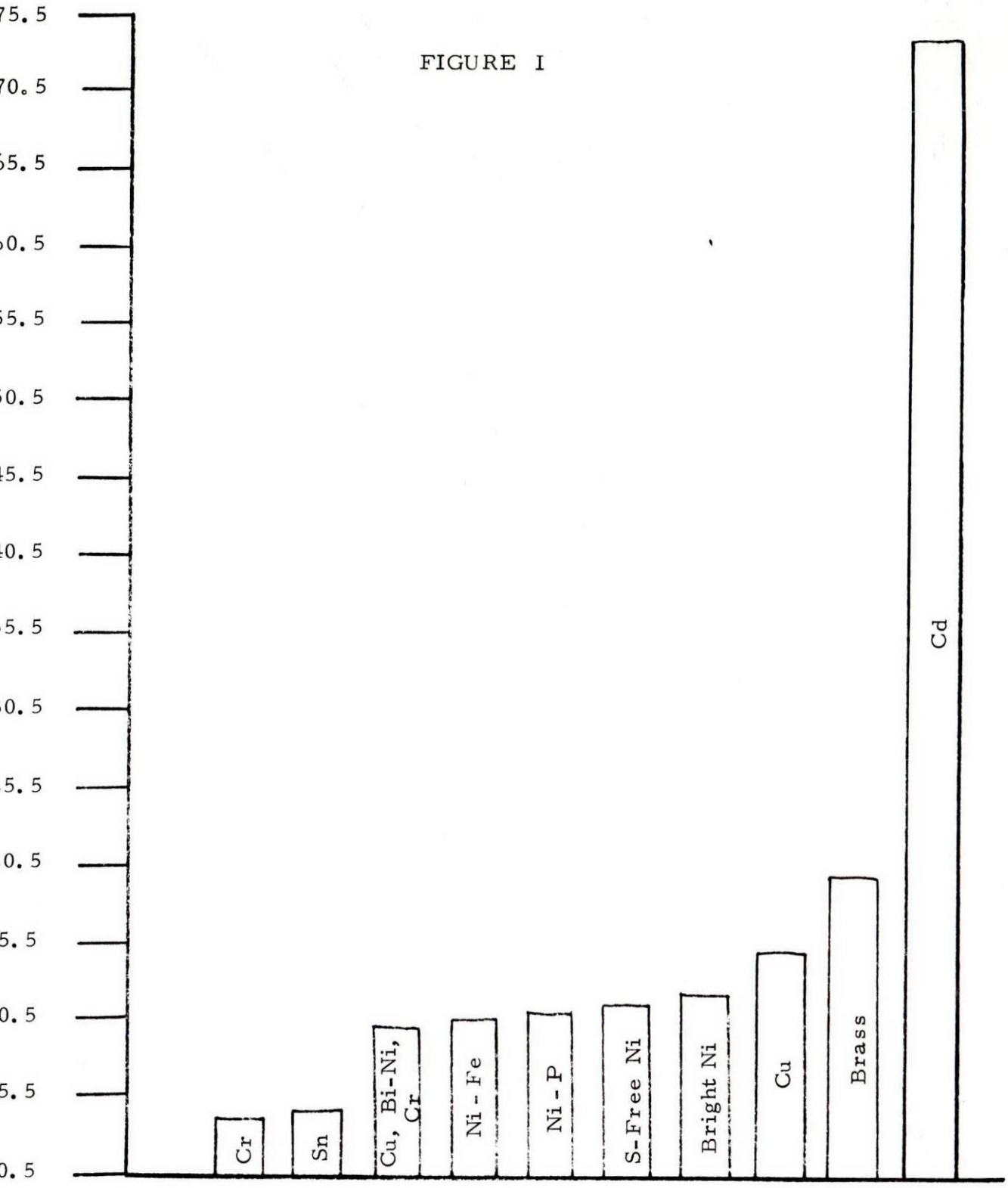
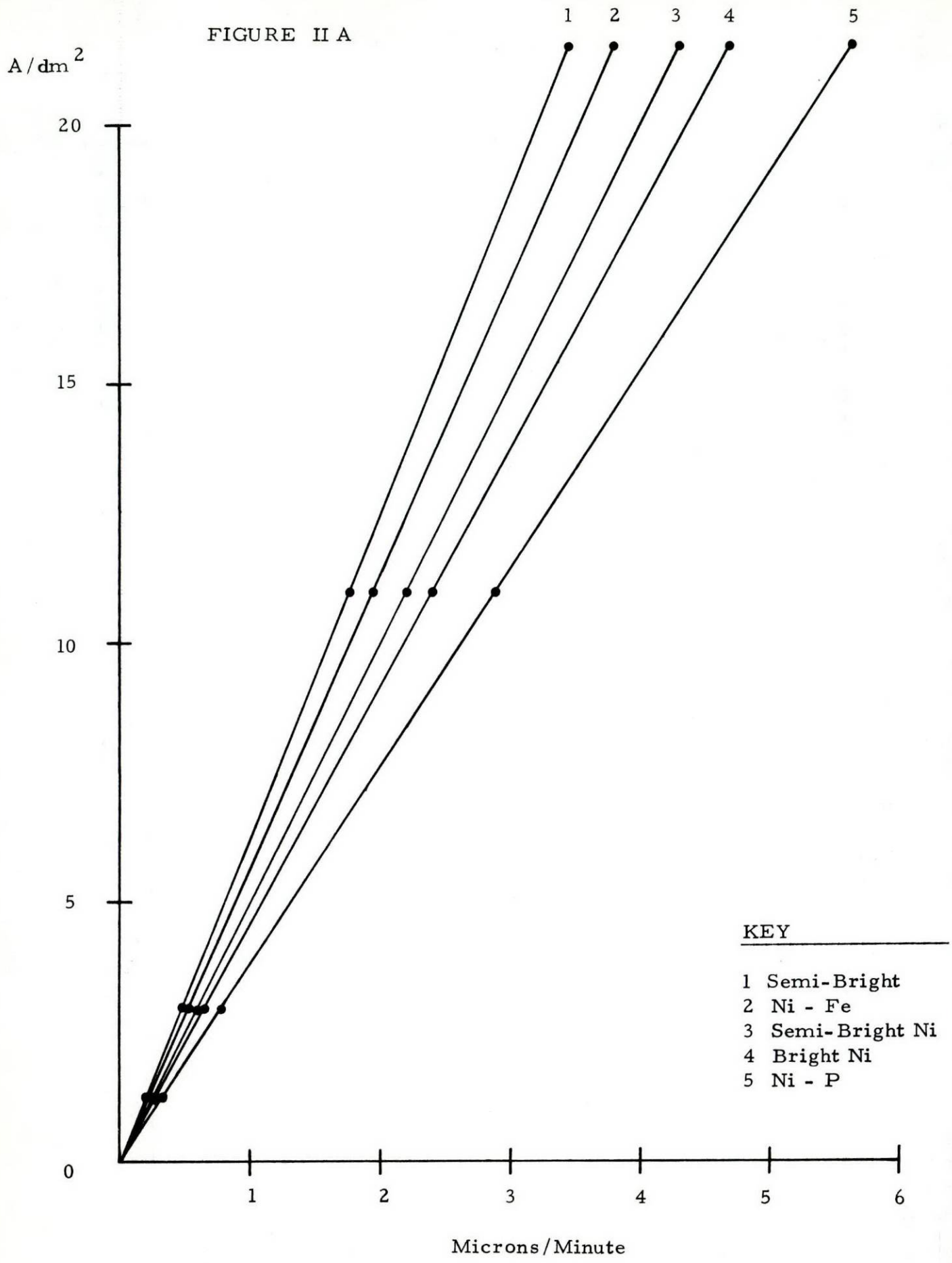
FIGURE I



Stripping Rates of Various Metals

At Anode C. D. of 54 A/dm^2

FIGURE II A



STRIPPING RATES OF VARIOUS METALS AT VARIED ANODE CURRENT DENSITI

STRIPPING RATES OF VARIOUS METALS

AT VARIED ANODE CURRENT DENSITIES

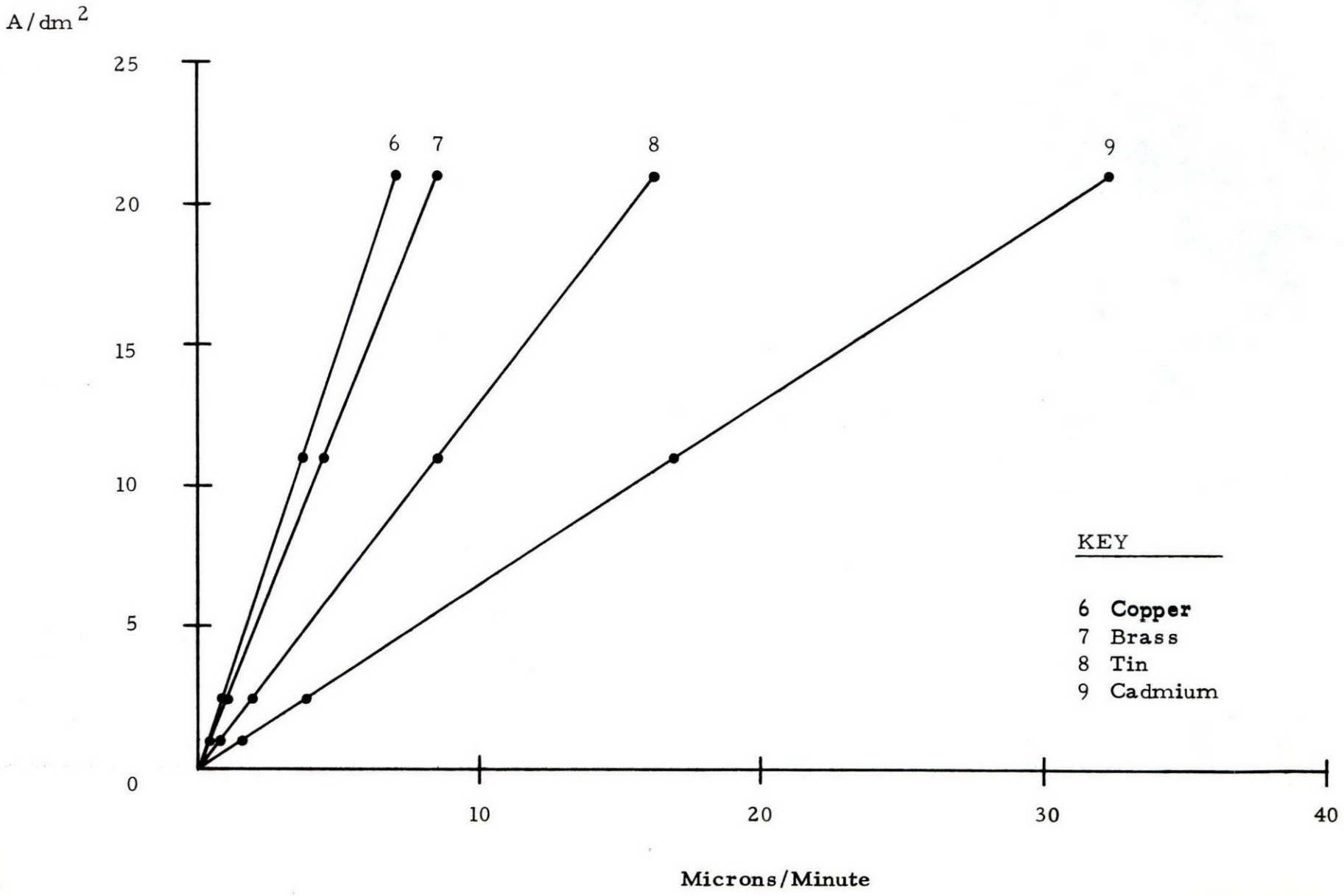




FIG III

THIS BUMPER GUARD WAS STRIPPED OF ITS BRIGHT AND SEMI-BRIGHT NICKEL DEPOSIT AT 100 ASF.

The original polishing lines, in the base metal are still visible after the stripping operation. This article can be replated without refinishing of the base metal.

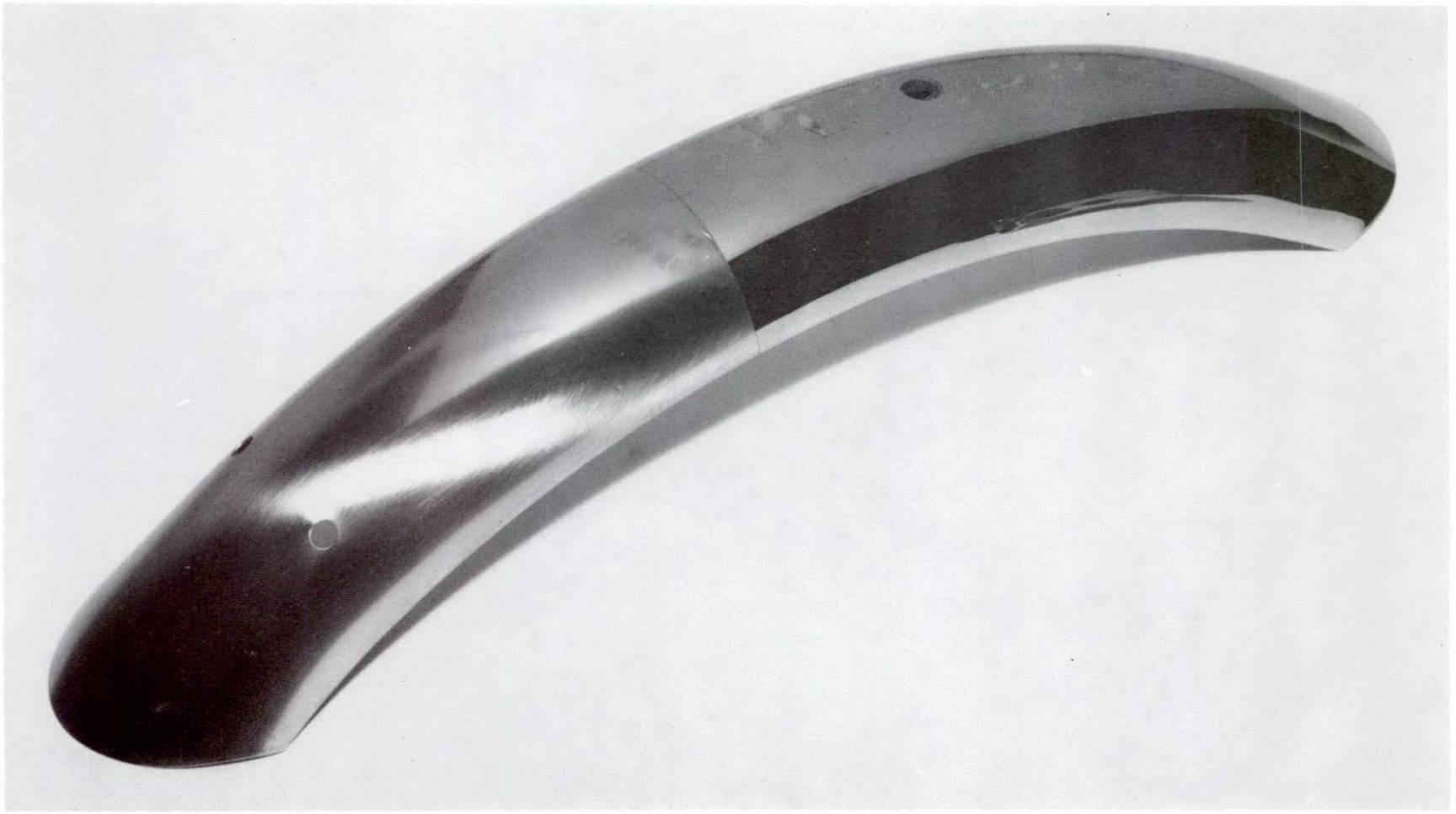


FIG IV

BICYCLE FENDER STRIPPED OF BRIGHT NICKEL AT 100 ASF.

The original polishing lines are clearly visible, thus showing no visible degradation of the base metal during stripping operation.



FIG V

TYPICAL ASH TRAY DESIGN STRIPPED OF Ni-Fe AT 100 ASF.



FIG VI

WRENCH STRIPPED OF BRIGHT NICKEL DEPOSIT AT 100 ASF

(HIGH CARBON STEEL)

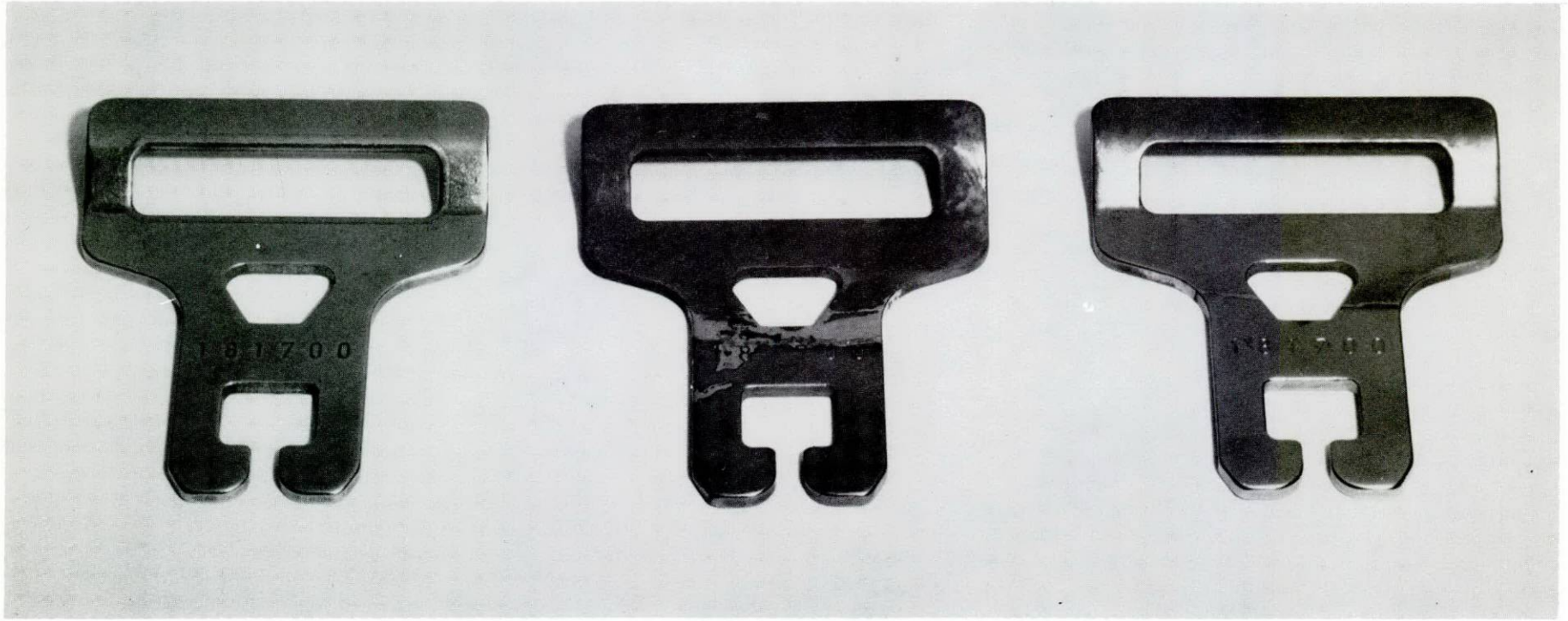


FIGURE VII

Comparison of stripped plated parts with unplated part. Left, this article was stripped in a solution containing an inhibitor, it was then submerged in the stripping solution for an additional 48 hours at 24 °C (75 °F). Center, this article was stripped in a solution containing no inhibitor, it was then submerged in the stripping solution for an additional 48 hours at 24 °C (75 °F). Right, unplated article.

L-3

GENERAL INTEREST SESSION L

Simplified Electrochemical Deburring—Versatile New Tool

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SIMPLIFIED ELECTROCHEMICAL DEBURRING -- VERSATILE NEW TOOL

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ABSTRACT

In the USA, ECD has largely developed from ECM and has resulted in some highly sophisticated and expensive equipment with limited application, primarily for very high production within the automotive industry. This paper will introduce a simple, economical and versatile approach to ECD, one that can be utilized by most deburring departments having two or more people doing manual deburring. There are substantial opportunities to improve deburring in product areas inaccessible to most methods--even for fairly low production quantities.

INTRODUCTION

Both electrochemical machining and electrochemical deburring are comparatively new production methods. Perhaps it's somewhat unfortunate that ECM preceded ECD; that is, the simpler system was developed from the more complex. Many of the early applications for electrochemical machining did not prove satisfactory and much of the earlier equipment did not achieve the expected results. Some of the early ECD equipment was developed from first generation ECM machines, incorporating some of the problems and limitations of that equipment. Such machines were very expensive, special-purpose units.

While there are a number of very efficient, sophisticated and high-production ECD machines available, they are still somewhat special purpose and too expensive for all but the major problem applications. It is only very recently that there has been a fresh look at ECD; to develop the process and the equipment in its own right, not as an offshoot of ECM. This is resulting in equipment of much lower initial cost and far greater versatility. ECD is now providing a simple, economical approach to selectively removing burrs from inaccessible areas, with consistent results and absolute uniformity.

Since deburring and edge finishing are still amoung the greatest problems facing industry today, new tools available to overcome or minimize the problems should be given serious consideration. Simplified ECD does offer a fresh answer to many of the problems, but does have distinct limitations. It is a selective deburring tool, requiring components to be fixtured, and so is inherently more expensive for general purpose deburring and finishing than mass finishing, blasting and buff, brush and polish processes.



Figure 1. 500 Amp ECD Machine

The Simplified Approach to ECD

Electrochemical deburring is basically the reverse of electroplating. Burrs are dissolved from the component by passing a direct current from the burr area (the anode) to the tool (cathode) through the medium of an electrolyte. The part to be deburred is generally fixtured and the cathode is designed to insulate all areas of the part, except adjacent to the burr. Electrolyte flow is away from the burr area so that the base material of the component is taken back to the electrolyte reservoir, not plated onto the cathode.

The most important applications for ECD are for removal of burrs in inaccessible areas such as intersecting holes, or complex-shaped components where other edges and corners must not have any action. A real benefit is that deburring capability and speed is independent of workpiece hardness. Usually the more exotic the material, the more metallurgically cleaner it will be and, therefore, the better the process. There will be no stresses induced during the deburring operation, nor any metallurgical or physical change to the material of the part being deburred. Simplified ECD equipment is compact,

easy, clean and comfortable to operate, requiring very little maintenance or process control. Equipment is made to withstand the corrosive atmosphere of the electrolyte, but does not require the very expensive and difficult-to-handle materials used in ECM. Nor does such equipment need to operate at the electrolyte temperatures and pressures of ECM.

Simplified ECD equipment normally operates at 12 to 24 volts DC with output up to 500 amps being ample for most applications. A sound rule of thumb is to have 20 amp supply available for every inch of burr. The machine shown in Figure 1 is a 500 amp unit, taking up floor space of only 6 ft. by 4 ft., and is completely self-contained with its electrolyte tank, rectifier, electrolyte heater, all controls and pumps. Basic construction is of reinforced Fiberglas.

This description should make the difference between ECD, ECM and electropolish apparent. Electropolish action is on all exposed edges and surfaces and has very little capability for removing burrs. With ECD, the cathode is static; in ECM it must feed into the workpiece and requirements for removal of metal are greatly in excess of those needed with ECD.

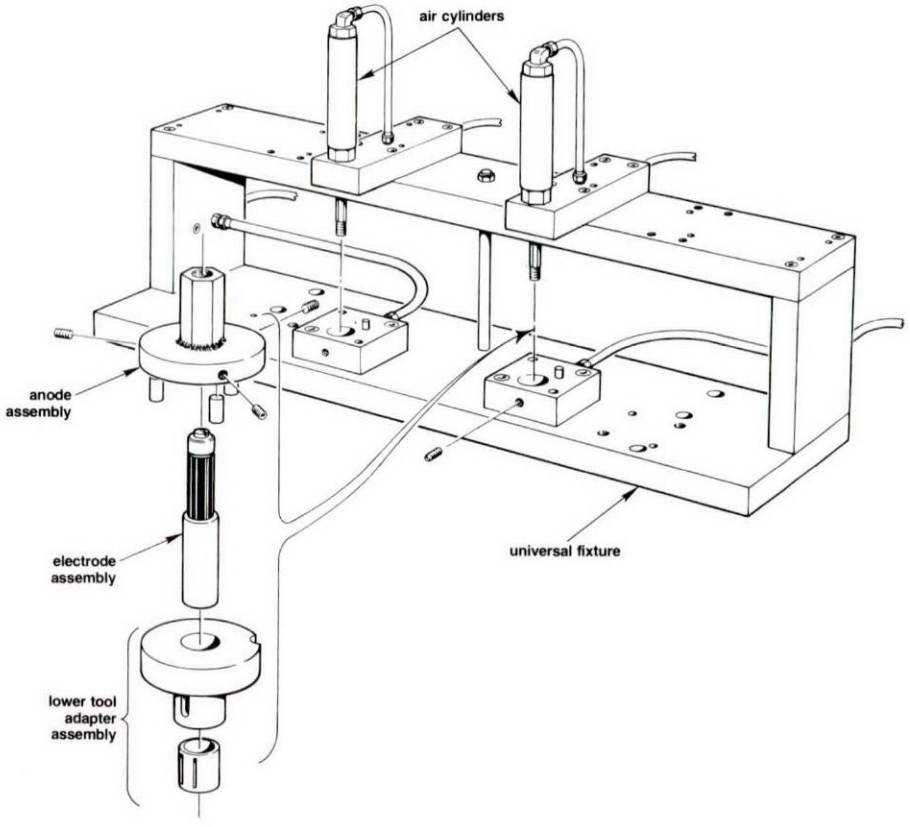


Figure 2. Universal Fixturing Technique

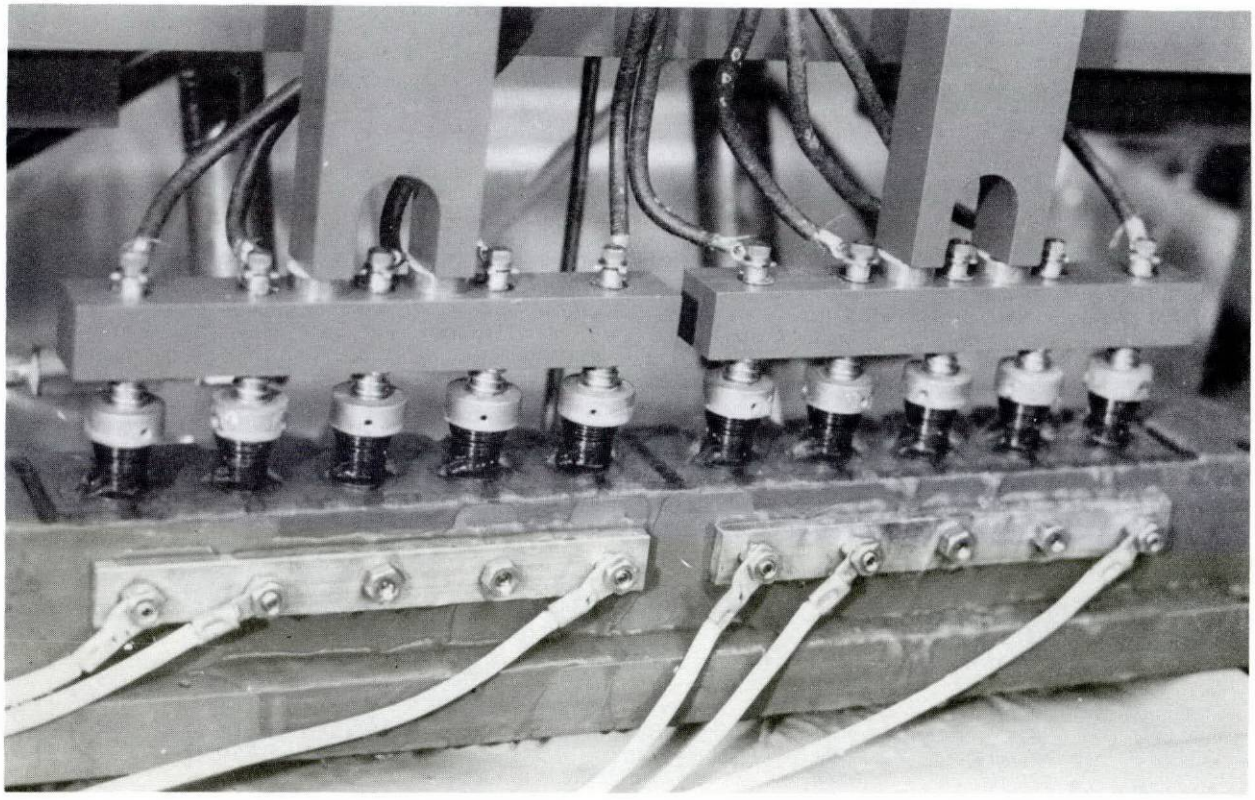
Fixturing and Tooling for ECD

The most important part of the ECD process is design and manufacture of tooling and fixturing. Simplified ECD utilizes in many cases materials superior to those used in ECM, yet is of low initial cost and very low maintenance cost. The design is based upon a universal fixturing concept, featuring standard components. An immense variety of different parts can be deburred on the same basic fixture, changing only the component adapters--simply taking a common sense approach to tooling and fixturing in general manufacturing and applying it to ECD machines. This tooling concept, an example being shown in Figure 2, has enabled ECD to become a versatile and economical process for deburring.

While G10 Fiberglas is necessarily used for fixturing ECM to meet process parameters such as high temperature, it is too expensive and too difficult to machine for ECD. The universal fixture components are made of PVC, because of excellent insulating and wear characteristics. PVC is strong and completely stable when temperatures are less than 160°, and far less expensive and easier to machine than G10 Fiberglas.

Beryllium copper, copper tungsten, titanium, and sometimes platinum are common cathode materials in ECM. All of these materials are expensive and fairly difficult to machine. For ECD, brass is frequently just as satisfactory and much more economical. Occassionally stainless steel and titanium tubing is used. Acrylic can normally be used for insulating with ECD equipment, more satisfactory and economical than Teflon which must be used with ECM.

Figure 3. Standard 2-Station ECD Fixture



The anodes for ECD fixturing are, as with ECM, the major wear point of tooling because they are of positive polarity and are therefore being de-plated while parts are being deburred. With good design, it is frequently possible to have the anodes serve in component clamping, and also arranged to keep the anode out of contact with the electrolyte, avoiding fast erosion. There the anode necessarily comes into contact with the electrolyte, then simplified ECD will use standard stainless steel pins, easily replaceable and of low cost.

Typically, the universal fixture for simplified ECD will deburr a number of small parts simultaneously. Figure 3 shows a standard two-station fixture where parts are being deburred at one station while a second station is being reloaded. Such a fixture can be adapted to four stations by addition of two more air cylinders and adapters. Such tooling can be readily adapted, with standard components, to accept substantially larger components, or applications requiring indexing tables, rotary tables or continually moving strip material. A hand probe is available which will accept standard cathodes and may be used where part design is such that fixturing would become extremely complex or where quantities are so small that it is not economical. An example is a manifold which has all the holes in a horizontal or vertical plane except for one or two which have an angular relationship. It can frequently be more economical to handle those one or two holes with the hand probe rather than re-fixture the part.

Applications for Simplified ECD

For components to be suitable for deburring by the electrochemical process, they must be made of conductive material and they must be manufactured to tolerances such that they can be fixtured and cathode can be properly located adjacent to the burr to be removed. Position of the burr must be considered here, because it is normally necessary for the cathode to enter the part in the same direction as that component was machined. That is, cathode and burr will be parallel to one another. As with all deburring operations, it is highly desirable that the method of burr removal be considered at the design stage of the component and given a priority similar to the establishment of the basic forming methods.

The application of simplified ECD in one organization will probably best indicate how the process may be used, its benefits and limitations.

Cox Hobbies Inc., of Santa Ana, CA, is the world's largest manufacturer of engine powered model airplanes. Although these are "only" models, the engines are machined to specifications that match today's most advanced jet engines, with tolerances within the piston chamber of 50 millionths of an inch. And also like jet engines, burrs are the single largest cause of problems.

The company had found that approximately 90% of the rejects for malfuntioning engines were due to burr-related problems in the cylinder.

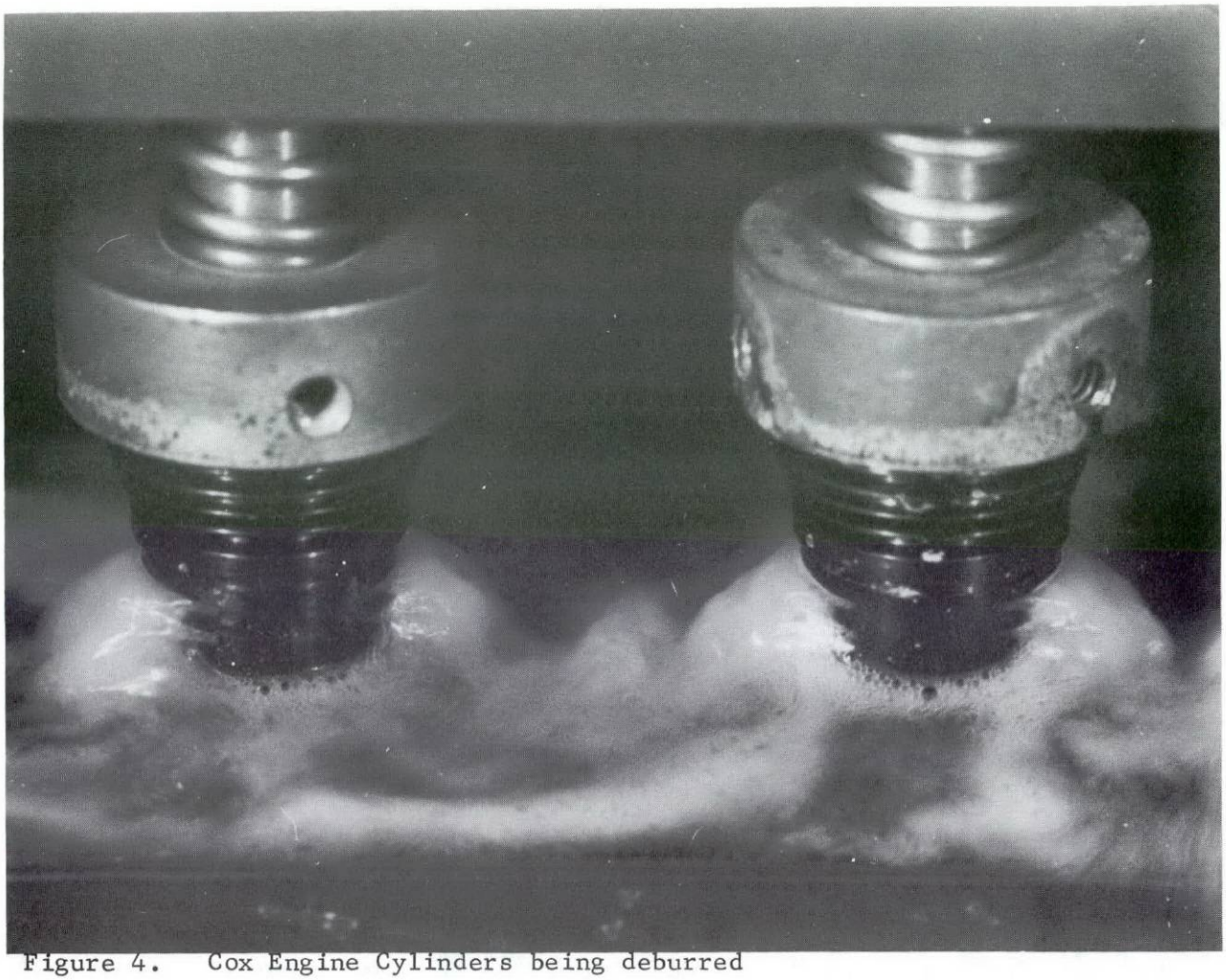


Figure 4. Cox Engine Cylinders being deburred

The cylinders are manufactured from ledloy B11-12, and go through seven machining and honing operations before reaching deburring, so the investment in each is high. The burrs form on the internal edges of tiny slots on the cylinder wall (see photo), a place very difficult to reach. Cox Hobbies was removing these burrs by hand, employing five women. The procedure allowed little room for error--taking off too much material caused problems, as did leaving too much in place. The women were able to deburr 5,600 to 6,500 cylinders per day, but with an average 20% return rate. With the loss of time, plus scrap and rework costs, the company realized the little burrs were a big problem.

The company selected a Harper ECD machine manufactured by The Harper Buffing Machine Co., E. Hartford, Ct. With one full-time operator, Cox Hobbies can now deburr 10 engine cylinders every 36 seconds (floor to floor time), for approximately 7,000 parts per day--more than the output of the five women, who have been shifted to more productive jobs. The return rate has been cut drastically, and the close, high-technology tolerances can be better maintained.

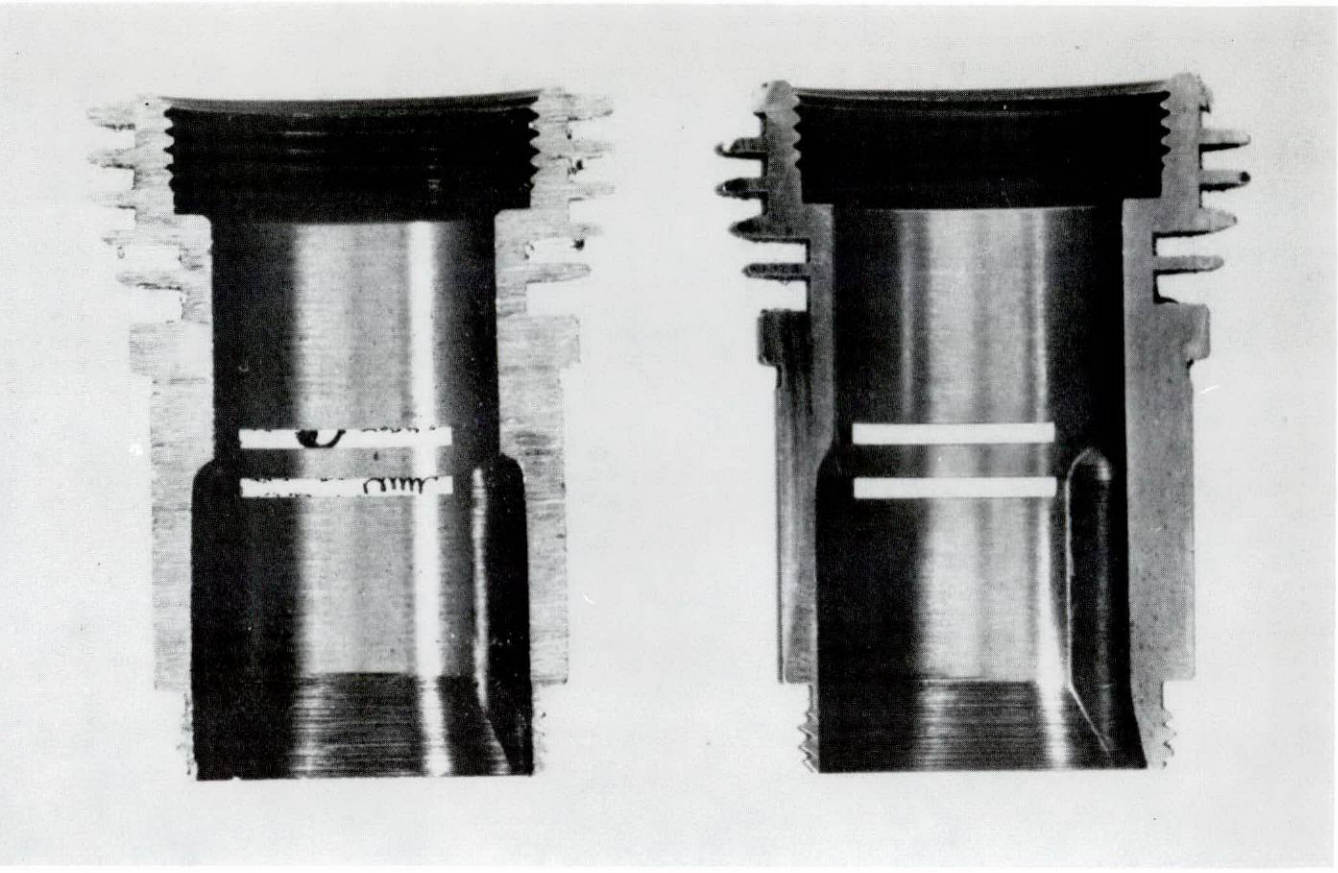


Figure 5. Cox cylinder parts which are deburred by ECD

Conclusion

ECD is not a cure-all and is normally not competitive with mass finishing, blasting buffing or brushing. Most simplified ECD applications are replacing manual deburring, scraping or filing. It is the hard-to-reach internal areas where benefits are most likely to be greatest, but there are cases where the quality requirement or difficulty of uniform deburring is such that ECD is used economically for removing external burrs. Where ECD is applicable and where it can replace the present manual deburring techniques, it will almost certainly be substantially faster and more economical and will have the major additional asset of being absolutely uniform and consistent. There are no consumable materials of significance, and the cost of electricity and water is minimal.

L-4

GENERAL INTEREST SESSION L

The Microstructural and Property Changes of Laser Treated Electrodeposits

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THE MICROSTRUCTURAL AND PROPERTY CHANGES OF LASER TREATED ELECTRODEPOSITS

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ABSTRACT

The use of the LASER as a tool to improve the properties of electrodeposits for wear and erosion resistance is introduced. The microstructures and microhardness of LASER treated electrodeposits of chromium and duplex coatings of Cr/Co on steel are shown. Cobalt as an underlay is shown to produce superior surface structures compared to chromium directly on steel which suffers from the formation of brittle phases at the chromium-steel interface.

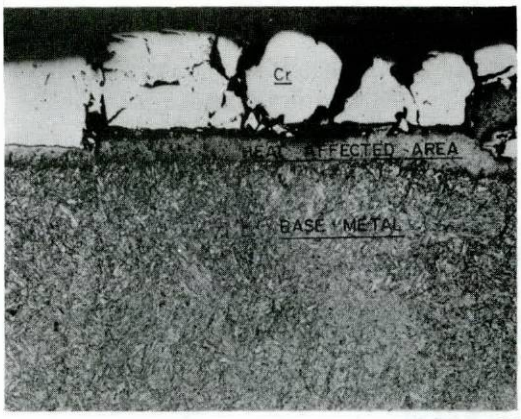
Introduction

For the surface protection of high strength steels against severe high temperature gases, attention has often been directed towards the use of refractory metal coatings. Electrodeposition would be an economical way for depositing refractory metals but is limited to rhenium[1-3] which is a brittle and costly metal. Amongst the successful metals that can be electrodeposited is high contractile (HC) or hard chrome. This has shown the ability to withstand severe wear and high temperature environments. In spite of its success however, chromium is also brittle and possesses an inherent crack pattern which leads to excessive spalling or flaking when subjected to high stresses. Evidence of the latter can be seen in Figure 1.

Low contractile (LC) chromium[4-6] is a more ductile coating and is less susceptable to spalling. It however, lacks some of the mechanical properties that one requires under high loads.

Attempts to improve the properties of electrodeposited chromium or refractory metals by alloying with iron group metals have also fell far short of the ideal coating. In such cases, the deposits were found to be brittle, and non-adherent to steel substrates.[7-10]

Heating chromium plated high strength structural steels to an elevated temperature for diffusing the chromium with the substrate to produce suitable alloying at the surface has also been attempted. The major disadvantages of this approach are the formation of brittle diffusion layers[11], the decrease in the mechanical properties of the bulk structure, and the distortion which may occur.



x250

FIGURE 1. CROSS-SECTIONED CHROMIUM PLATED STEEL SEGMENT TAKEN FROM THE BORE OF A GUN TUBE WHICH FIRED HYPERVELOCITY ROUNDS.

In view of the above, recent attention has been given to a new approach for altering the properties of a metal deposit, which involves the heat treatment of the plated surface using LASERS. This present investigation is basically a preliminary study which advances the efforts of a previous investigation on the behavior of LASER treated chromium deposits on steel substrates.

During the past two decades the LASER (Light Amplification by S timulated Emission of Radiation) has advanced from a laboratory curiosity to a precious tool promoting numerous advances in metal processes. The LASER has attracted the metallurgists, primarily because it can focus vast amounts of energy very rapidly and with pinpoint accuracy upon a metal surface.

The introduction of the LASER in the 1950's and the development of high power gas LASERS in the 1960-70's have led to rapid advancement in industrial applications for the processing of metals. Due to these advances, LASERS are being successively applied in the field of cutting, drilling, welding, and surface heat treating of metals and alloys.

Solid LASERS were the first to be employed but are limited since they can only function in a pulsed rather than continuous mode and due to their melting point could absorb only a limited power input. In 1965, the concept of the gas LASER was introduced whereby high energy could be radiated in the continuous mode as well as in pulses. Because of the high power capability, the gas LASER was employed for this present study.

A LASER technique[12] developed in recent years for the thermal treatment of a metal surface is called Laserglazing*. Such a technique involves the melting of thin surface layers (e.g. steels) at a high melting efficiency, resulting in rapid solidification and cooling to achieve a variety of microstructures and properties without affecting the bulk substrate. This is accomplished by rapidly traversing the surface of a material with a LASER beam focused to a power density range of 10^4 - 10^7 W/cm^2.

In order to compare Laserglazing with other material processes using LASERS, a spectrum for operational boundaries is shown in Figure 2 in which LASER power densities are related to interaction time.

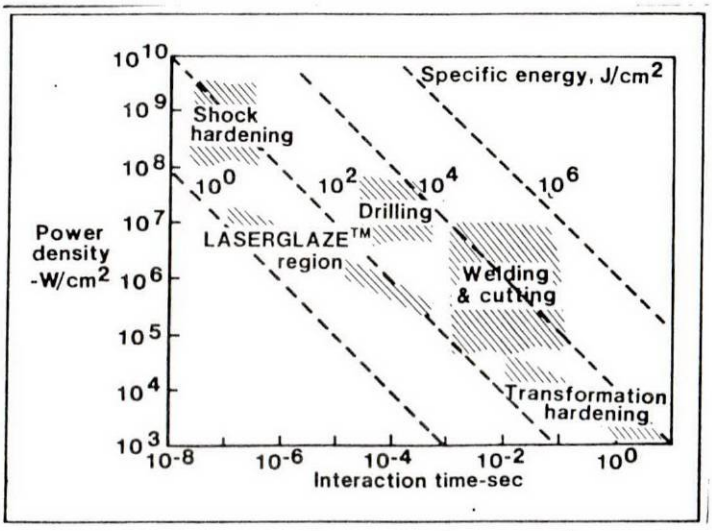


FIGURE 2. OPERATIONAL BOUNDARIES FOR LASER BEAM-MATERIAL INTERACTION FOR VARIOUS PROCESSES.[12] THE DIAGONALS ARE LINES OF CONSTANT SPECIFIC ENERGY WITH THE VALUES SHOWN.

The significant difference which results in the structure of a Laserglazed surface can be clearly realized when comparison is made with the structure obtained in conventional casting of an alloy. In the casting of a bulk alloy, the phases with high melting points are difficult to melt and phase separation occur. Such structures provide non-uniform properties. In the case of a Laserglazed surface, the melted layer is thin and since the substrate remains cold, rapid solidification occurs thus reducing those problems associated with slow cooling.[12]

*LASERGLAZE - Trade Mark by United Technologies Corporation.

This technique of achieving homogeneous phase transformations in the surface with sufficient control of surface depth has formed the basis of this present investigation. Also the ease of automating the process for a variety of geometrical shapes offers a number of economic advantages.

The work of Montgomery[13] appears to be the first study dealing with the LASER treatment of electrodeposited chrome to improve properties and adhesion. This work involved LASER heating of the plated surface with transformation of the steel substrate approaching depths of 80-100 mils. The coating thicknesses ranged from 1-12.5 mils and the speeds of LASER beam travel (which controls interaction time) were 10-40 in/min. Results of the above study revealed suitable Fe-Cr alloying but some undesirable embrittlement of the softened unalloyed portions of the deposit and indications of the formation of intermetallic compounds of Cr-Fe carbide. The latter deposits resulted in premature failure in wear tests.

In this present investigation, the effects of intermediate layers of LC chromium and cobalt are investigated as a function of exposure time as a means of optimizing structural and interfacial characteristics.

Experimental Procedure

Electrodeposition

All test coatings were plated on flat steel strips (cold rolled SAE 4340*) which measured approximately 1.9 cm wide, 15 cm long and 0.16 cm thick (0.75 x 6 x 1/16 in.). The test panels were first cleaned by soaking in a hot caustic solution and scrubbing, followed by a hot water rinse. After rinse the panels were electropolished to remove 1-2 mils of the surface. Without delay the panels were immediately rinsed and plated on one side to produce deposits of:

(a) 3.4 mils of Cr on steel (1.7 mils of HC chromium over 1.7 mils LC chromium).
(b) 3.4 mils of Cr on 3.75 mils of Co on steel.

Laser Treatment

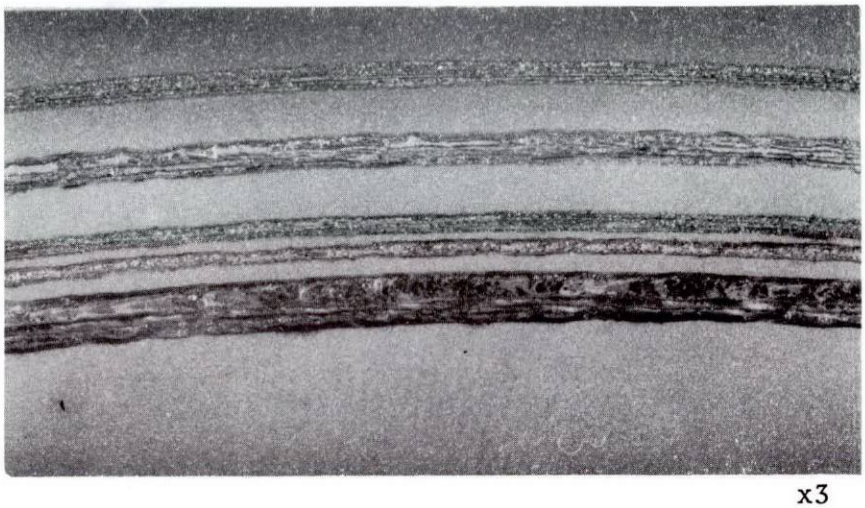
A high-power electric discharge cross beam CO_2 LASER operated as an unstable resonator (with a constant power setting of 6 KW) was employed in a continuous mode to heat the plated specimens for the present study with the following parameters:

*No concern was given to the tempering of the test coupons prior to plating, in view of the altering of the underlying steel during LASER heating and quenching.

Total energy applied to specimen surface	4.7 KW max
Power density	2.3×10^6 W/cm^2
Wavelength	10.6 um
Focal length of beam	18 3/4 in.
Diameter of focal spot	20 mils
Scanning speed (linear)	10-188 ft/min
Shielding (100% He)	100 ft^3/hr
Focusing Mirror	Copper, off-axis parabola

The LASER treatment was carried out by mounting the plated specimens on a large aluminum rotating horizontal disk so that the LASER beam (mounted in a stationary position) would make contact with the surface along the length of the specimen during various preset speeds. The speed of the rotating disk and the number of revolutions (or passes) controlled the interaction time (i.e., time specimen was exposed to the LASER beam). In order to prevent oxidation of the plated surfaces during the LASER treatment, a helium environment was utilized.

Nominal exposure times, calculated from specimen speeds were 0.5, 10, and 50 ms, resulting in the surface patterns shown in Figure 3. The width of the affected trails were increased by displacing the specimens a small distance laterally from the fixed focal point of the LASER beam before each pass.



x3

FIGURE 3. SURFACE VIEW OF LASER TREATED CHROMIUM PLATED SPECIMEN SHOWING THE ALTERED TRAILS CAUSED BY THE LASER BEAM DURING SPECIMEN TRAVEL.

Specimen Evaluation

Examination of the samples consisted of metallographic, microhardness, and microprobe analysis.

Results and Discussion

As-Plated Chromium/Cobalt/Steel

A cross-section of the as-plated duplex structure of electrodeposited chromium over cobalt on steel is shown in Figure 4. The etched layers of chromium reveals the coarser grained columnar structure of the LC versus the HC deposit (see top inset). The microstructure of the cobalt is also typically columnar and shown in the lower inset. The steel is shown to be a spheroidal structure.

The hardness and characteristics of chromium deposits directly onto steel substrates were found to be approximately the same as those with the cobalt underlay.

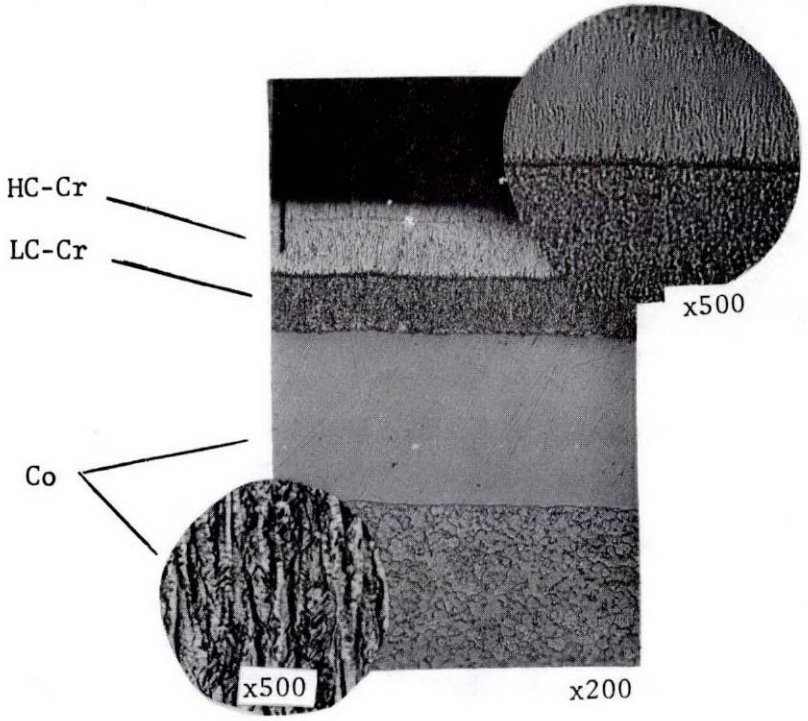


FIGURE 4. CROSS-SECTION OF AN AS-PLATED DUPLEX STRUCTURE OF ELECTRODEPOSITED CHROMIUM OVER COBALT ONTO STEEL.

LASER Treated Cr/Steel and Cr/Co/Steel

A. Exposure Time of 0.500 ms - This test run was accomplished by a single pass across the LASER beam with a specimen travel speed of 95.5 cm/sec (188 ft/min).

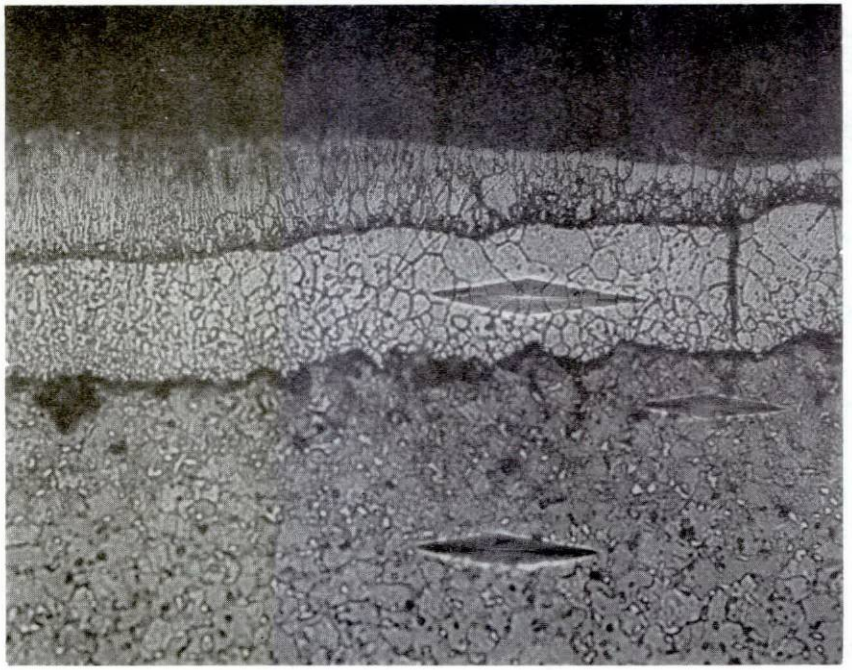
Chromium/Steel - The LASER beam affect on the microstructure of this trial run is shown in Figure 5(a). As can be seen, the microstructure of the LC chromium is no longer columnar but has been transformed (through recrystalization and grain growth) to a somewhat equiaxed structure with the grains progressively coarser towards the edge of the LASER path. The HC chromium top layer which obviously experienced higher temperatures, still reveals some columnar structure, but has significantly coarsened. The underlying steel substrate reveals some early signs of phase reaction. The substrate exhibits an increase and the chromium a decrease in hardness as shown in Figures 6 and 7.

Chromium/Cobalt/Steel - The microstructural changes of the chromium layers over the cobalt are approximately the same as the chromium/steel specimens (Figure 5(b)) with a corresponding decrease in hardness. An interesting observation is the widening of the initial cracks in the chromium. The cobalt and underlying steel revealed no changes in microstructure although the hardness profiles (Figures 6 and 7) revealed a slight hardness decrease for cobalt and slight increase in the steel just beneath the cobalt.

B. Exposure Times of 10 ms - This LASER treatment was performed with a specimen linear speed of 25.9 cm/sec (51 ft/min) and the specimen passing across the LASER beam five times for a total interaction time of 10 ms.

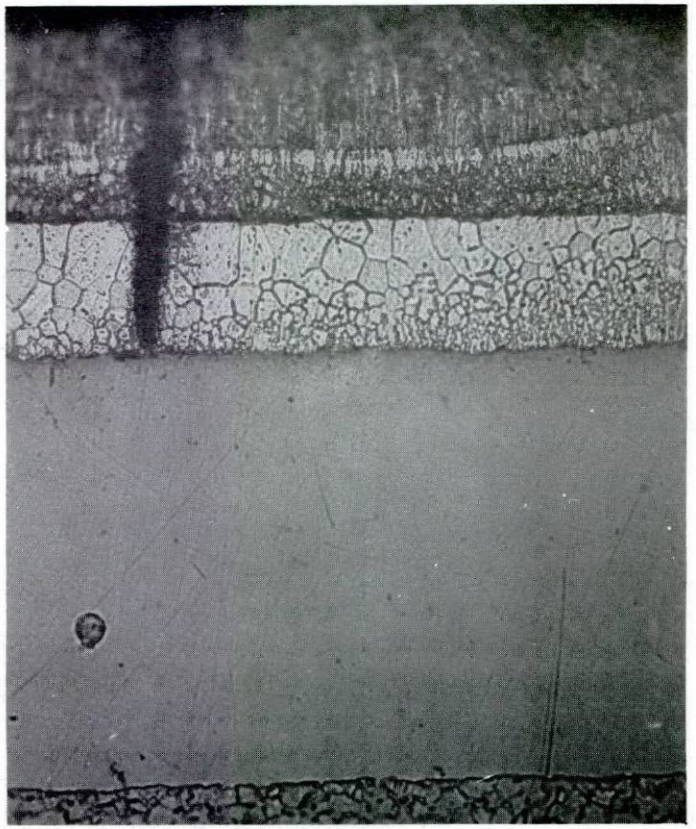
The specimen was moved 10 mils laterally prior to each overlapping pass in order to widen the heat affected zone. The total lateral displacement for the four succeeding passes was approximately 60 mils.

Chromium/Steel - Figure 8(a) shows extensive changes in microstructure of the chromium and underlying steel with no visibility of the HC-LC interface. In addition, the coating did not respond to microetching indicating changes in chemical resistance. Microprobe analysis has shown indications of varying concentrations of iron in the chromium. One can see a heat affected zone (HAZ) in the underlying steel with significant nonhomogeneity at the Cr/steel interface. Another significant observation is the existence of internal cracks in the chromium coatings (possibly related to the high quenching rates or shrinkage during cooling). Figure 8(b) is a cross-section of an area adjacent to the LASER beam path which reveals the thermal alterations due to edge affects. Material from the substrate appears to be partially drawn up through the cracks in the chromium. This indicates that the substrate could possibly approach the melting temperature at the bottom of pre-existing cracks. The entry of material into the cracks was observed to a greater extent in the previous study.[13]



x500

(a) Cr/Steel



x500

(b) Cr/Co/Steel

FIGURE 5. CROSS-SECTION OF HEAT AFFECTED ELECTRODEPOSITED STEEL SPECIMENS AFTER LASER INTERACTION TIMES OF 0.500 ms. NOTE THE RECRYSTALLIZED GRAIN STRUCTURE OF THE CHROMIUM LAYERS.

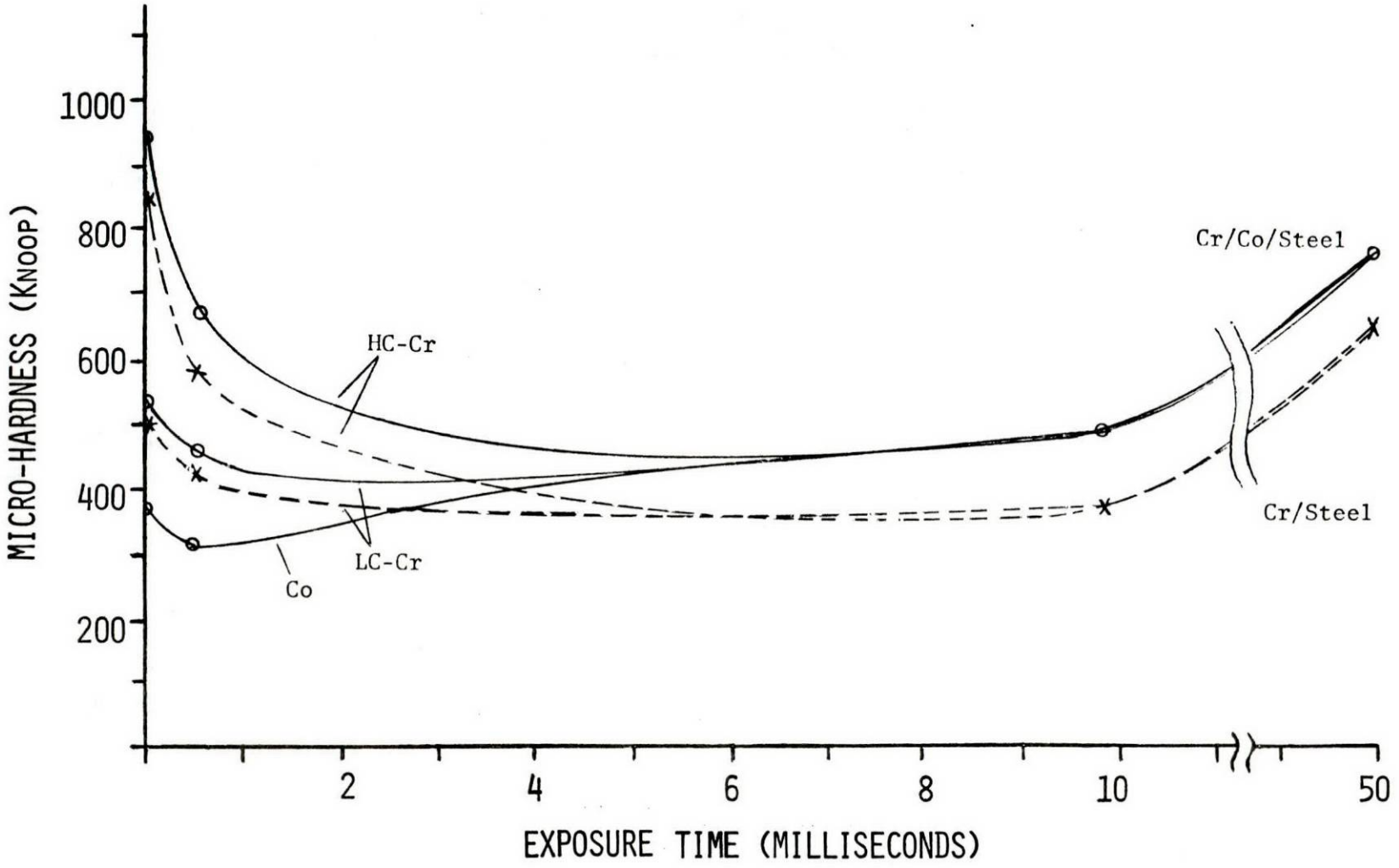


Figure 6. Relation of hardness to interaction time for chromium and cobalt coatings.

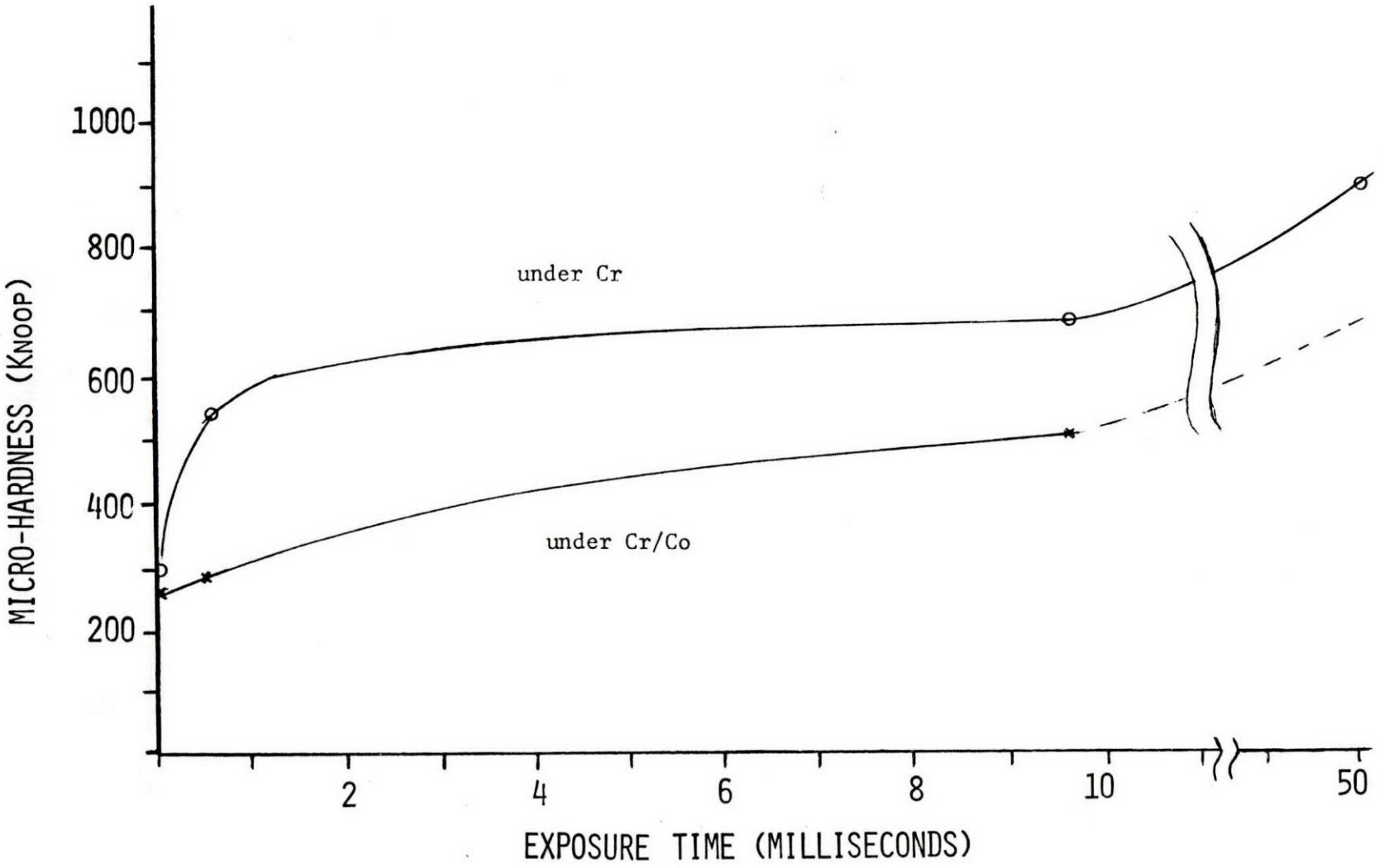
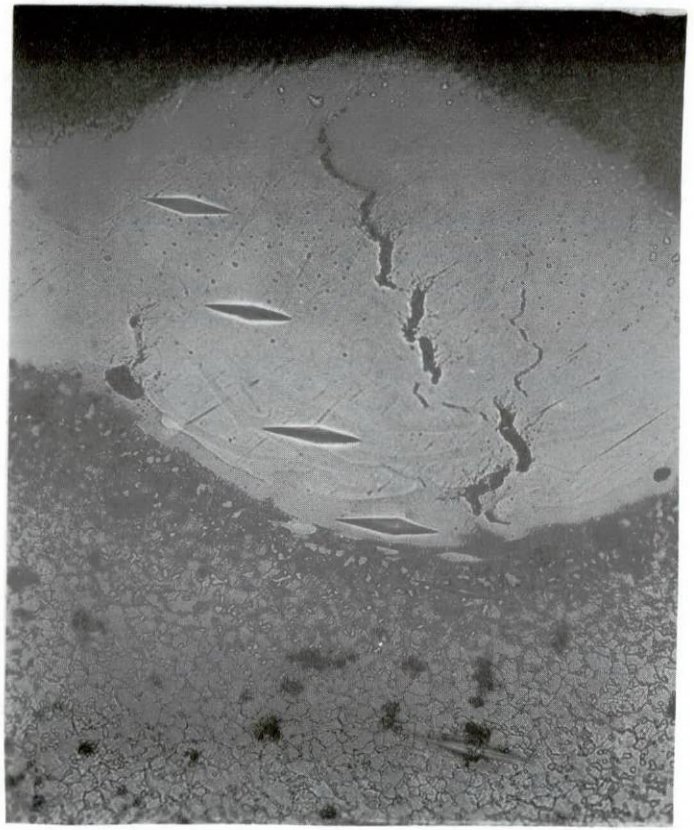
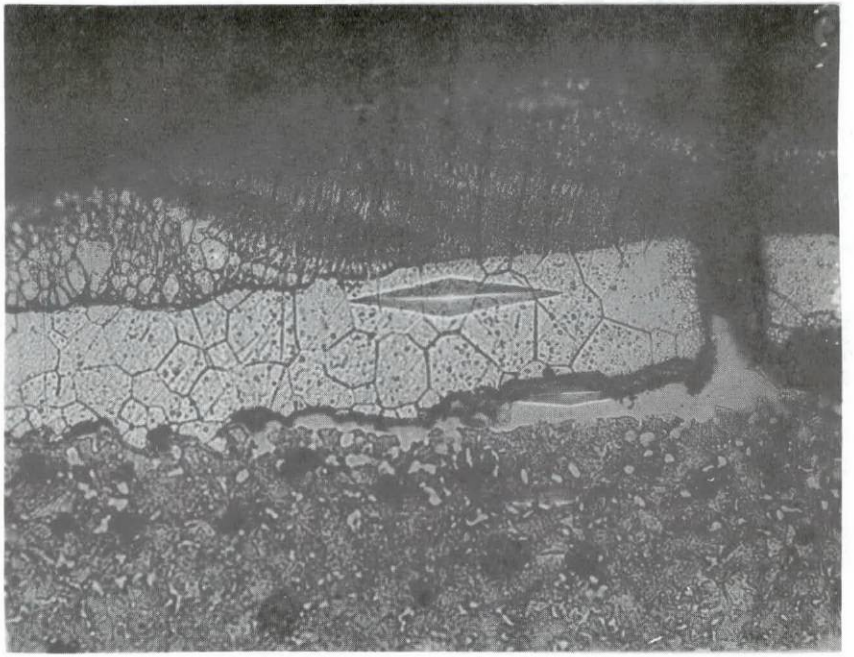


Figure 7. Relation of hardness to interaction time of the underlying steel substrate (HAZ).



x300

(a) Transformed Cr-Fe coating which lies in the center of LASER beam path. Note internal cracks.



(b) Edge of LASER beam path where layers are still distinguishable due to partial heating. Note the nonhomogeneity of the thermally altered underlying steel.

FIGURE 8. CROSS-SECTIONS OF HEAT AFFECTED ELECTRODEPOSITED Cr/STEEL SPECIMENS AFTER LASER INTERACTION TIMES OF 10 ms.

Chromium/Cobalt/Steel - Figure 9 clearly depicts the significant phase changes in the Cr/Co/steel system for the same interaction time (10 ms). The extreme left of the view (a) represents the center of the narrow LASER beam path where the coatings appear to have transformed into a single and homogeneous layer which again did not respond to etching. However, the section on the right side of the photomicrograph (i.e., less heat input) clearly reveals the chromium and cobalt layers. The chromium is shown to be progressively recrystallized as it approaches the beam path. The interface between these two zones reveals a number of voids and disarranged structure due to the end effects of the LASER beam where temperature gradients are extremely high.

Figure 9(b) shows the overall view of the transformed coating which corresponds to the center of the LASER beam path.

Examination of the underlying steel reveals a transformation which appears to be untempered martensite. These microstructural changes of the coatings and substrate, again are shown to correlate with the corresponding hardness changes in Figures 6 and 7.

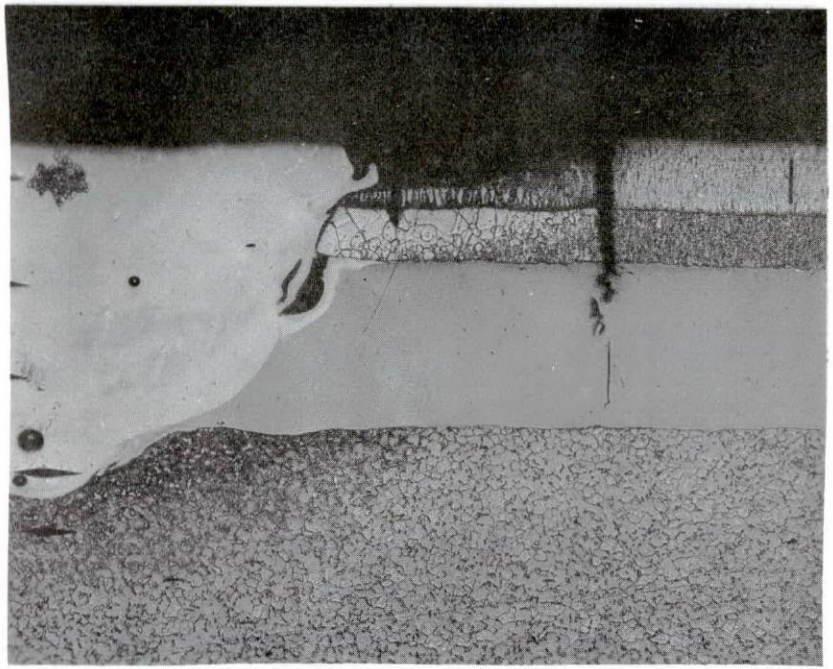
C. Exposure Time of 50 ms - This LASER treatment involved a specimen linear speed of 5.08 cm/sec (10 ft/min). Again, the specimens were passed across the LASER beam five times for a total interaction time of 50 ms. The specimen lateral displacements for these trial runs were 20 mils for each succeeding pass for a total displacement of 100 mils.

Chromium/Steel - The results from this LASER treatment shown in Figure 10 reveals phase transformations which extend through the complete thickness of the specimen. Again, neither the affected coatings or the steel responded to microetching confirming that significant phase changes have taken place. The structural changes as a result of this treatment was accompanied with an increase in microhardness (as shown in Figure 6). This could be due to solid solution strengthening of the Cr-Fe formation which was identified by microprobe analysis. A hardness plot extending through the full thickness (62 mils) of the specimen reveals a relatively uniform level as shown in Figure 11.

Chromium/Cobalt/Steel - The LASER treatment of the Cr/Co/steel system appears to have experienced the same extensive phase transformations and the metallographic view appeared identical to the Cr/steel as shown in Figure 10. The change, was again, accompanied by an increase in hardness which was comparatively greater than the Cr/steel specimens (see Figures 6 and 11).

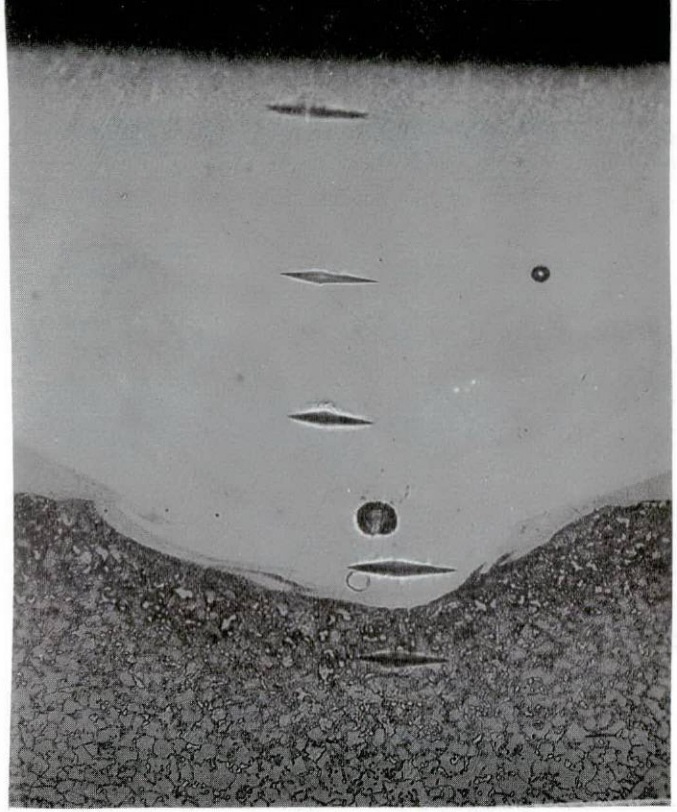
Conclusions

(a) The Laserglaze technique was shown to affectively confine the heating of the surface to controllable depths. At an exposure time of .5 ms, grain growth in the chrome occurred with a decrease in hardness and negligible interfacial effects. At an exposure time of 10 ms, total recrystallization of the chrome occurred. In the chrome-cobalt duplex coating,



x200

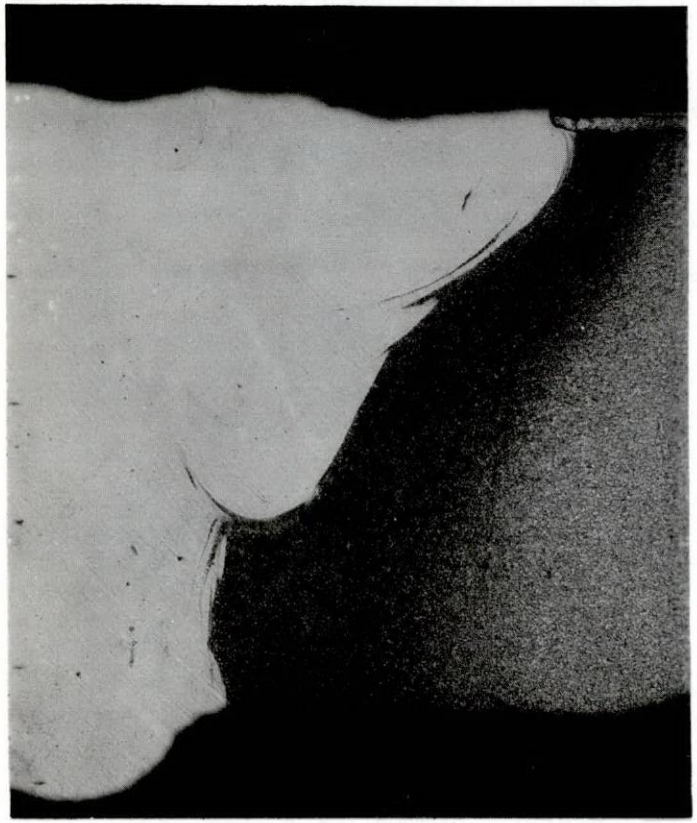
(a) Showing half of LASER beam path where layers are transformed into a single coating. Note the edge affects due to partial heating where layers are distinguishable.



x300

(b) Showing center view of the transformed coating path. Note HAZ of the underlying steel.

FIGURE 9. CROSS-SECTION OF HEAT AFFECTED ELECTRODEPOSITED Cr/Co/STEEL SPECIMEN AFTER LASER INTERACTION TIME OF 10 ms.



x50

FIGURE 10. CROSS-SECTION OF HEAT AFFECTED ELECTRODEPOSITED Cr/STEEL SPECIMEN AFTER LASER INTERACTION TIME OF 50 ms. PHASE TRANSFORMATIONS HAVE ADVANCED THROUGH THE COMPLETE THICKNESS OF THE SPECIMEN.

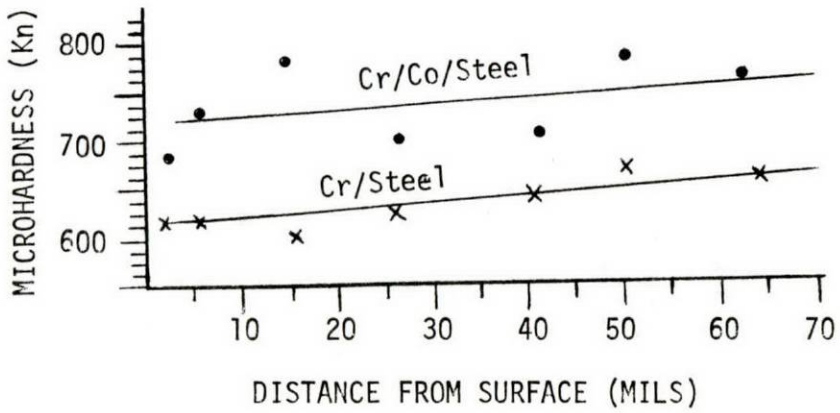


FIGURE 11. HARDNESS PLOT THROUGH SPECIMEN THICKNESS FOR THE INTERACTION TIME OF 50 ms.

complete alloying occurred. At 50 ms, alloying through the total 0.062 specimen thickness occurred.

(b) The introduction of cobalt as an underlay for chromium was found to be beneficial in eliminating phase reactions at the Cr/steel interface. Also the Cr/Co/steel system exhibited less cracking and porosity and possessed greater hardness after treatment than the Cr/steel system.

(c) The LC chromium layers exhibited less cracking and porosity than the HC chromium following the 0.5 ms and 10 ms LASER treatments. After the 50 ms treatment, no differences could be observed.

Acknowlegements

Special gratitude is extended to Dr. David Snow (United Technologies Research Center) who LASER treated the specimens. Indebtedness is also expressed to T. Brassard for her metallographic efforts and J. Cox for the microprobe analysis, who are all associated with the Benet Weapons Laboratory of ARRADCOM.

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M-1

RESEARCH SESSION M

The Cross-Sectional Structures of Thick Electrodeposits and Their Relationship to the Properties (AES Research Project #38A)

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Stevens Institute of Technology
Hoboken, NJ

AES Research Project 38A

THE CROSS-SECTIONAL STRUCTURES OF THICK ELECTRODEPOSITS AND THEIR RELATIONSHIP TO THE PROPERTIES

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Stevens Institute of Technology
Hoboken, NJ

Last year in Atlanta, our report on AES Research Project 38 dealt with the relationship of the structure in the first 100 nm (4 millionth of an inch) of deposit to its properties. This presentation is concerned with the structures of electrodeposits of practically used thicknesses and their implications about the properties.

As we reported last year, the initial electrodeposit of nickel on copper consists of very tiny crystallites about 50 atomic distances across. If the substrate surface is clean of soils and oxides and its structure is not distorted as would result, e.g., from buffing, polishing, or other mechanical finishing, the crystallites grow epitaxially. Epitaxial growth occurs when the deposit copies the atomic arrangement of the substrate. Thus, all the crystallites which form on one substrate grain have the same plane of atoms parallel to their surfaces.

Epitaxial growth generally continues beyond the layer of deposit which just covers the substrate. A purified plating solution, a low current density, an elevated temperature and certain orientations, i.e., the crystal planes parallel to the surface, favor a thick epitaxial deposit. We now have evidence that the crystal-growth mechanism observed in the initial deposit is prevalent throughout the epitaxial layer.

It seems appropriate to briefly discuss why the observed crystal-growth mechanism is prevalent. The mechanism consists of the formation of tiny, three-dimensional crystallites which then join together into a layer of deposit. The reason why extended two-dimensional layers do not spread over the substrate, as is often postulated, apparently lies in the nature of nickel electrodeposition. It seems that when nickel is plated, only about 50 rows of atoms can spread laterally, i.e., parallel to the substrate surface, before they are stopped. We have found that lateral spreading was so stopped even in the most highly purified plating solution; and even when deposition occurred under an argon atmosphere so that oxides could not form, lateral spreading was impeded. Therefore, the agents primarily responsible for stopping lateral growth must be produced as a result of the nickel-deposition reactions. It is very likely that basic compounds form because of the higher pH in the solution adjacent to the deposit. This high pH results from hydrogen evolution. The basic substances are the most likely lateral-growth stoppers. In less pure plating solutions or when addition agents are present, other foreign materials can also impede lateral spreading.

When atom layers cannot spread laterally, new ones form on top of the existing ones and three-dimensional crystallites develop. New crystallites also form between those already present; they then join until a deposit layer has developed. As the lateral-growth-impeding substances continue to be

present as plating proceeds, it would be expected that the formation and joining of tiny crystallites is a general growth mechanism in epitaxial nickel deposition, as we experimentally found.

We have also studied the transition from epitaxial to non-epitaxial growth. These studies were conducted in highly purified and conventionally purified plating solutions and also when addition agents such as saccharin were present. In the conventionally purified plating solutions and when saccharin was present, the transition to non-epitaxial growth occurred after the formation of hillocks. Figure 1 shows a number of hillocks, i.e., the dark dots. A large number of hillocks are seen on the white background in the middle of Figure 1. There are fewer on the gray background. The area of preferential hillock growth, i.e., the white one had a different grain orientation from the gray one. The first small, non-epitaxial crystallites subsequently form on the hillocks. Figure 2 shows the cross section of a deposit at a much higher magnification than Figure 1. The saw-tooth shape of the epitaxial layer and the very tiny, non-epitaxial crystallites on top of it are evident. The properties of epitaxial and non-epitaxial deposit layers differ considerably. This difference is currently under investigation.

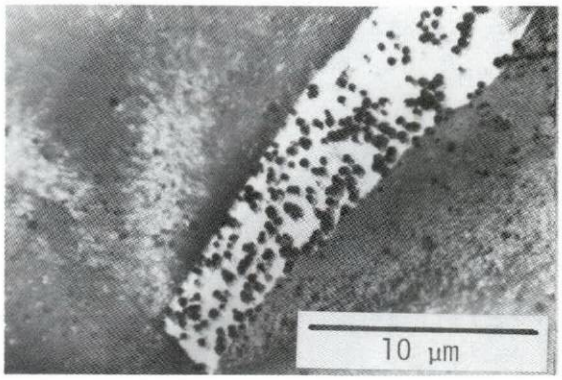

Figure 1. Electron Micrograph of Surface of Nickel Electrodeposits Showing Hillocks

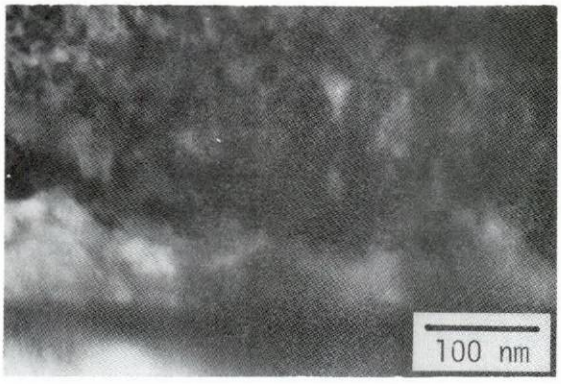

Figure 2. Electron Micrograph of Cross Section of Deposit From Saccharin-Containing Plating Solution

If the substrate has a surface structure which cannot be copied, even the first deposit grows non-epitaxially. Non-epitaxial growth at the start of plating also occurs if the current density is high. Then, the atoms arrive in so great a number that they cannot be incorporated into the existing orientation. Figure 3 shows the cross section of nickel from a sulfamate solution containing additives, on an amorphous electroless-nickel substrate. As the substrate has thus no crystal structure, it naturally cannot be copied. A very small grain size adjacent to the substrate can be seen. Here, there are misorientations between neighboring crystals which are much greater than in an epitaxial deposit on one substrate grain. In Figure 3, it can also be seen that a few favorably oriented crystallites, such as the one indicated by an arrow, grew outward, i.e., perpendicular to the substrate surface. These favorably oriented crystallites have a columnar shape. It was not known previously

that such a very fine-grained deposit was columnar in nature. In fact, the structure in Figure 3 resembles that of large-grained sulfamate nickel deposits as observed with an ordinary microscope. The grains in Figure 2 are also columnar. There are more pronounced misorientations within each column in the direction perpendicular to the surface than there are in Figure 3.

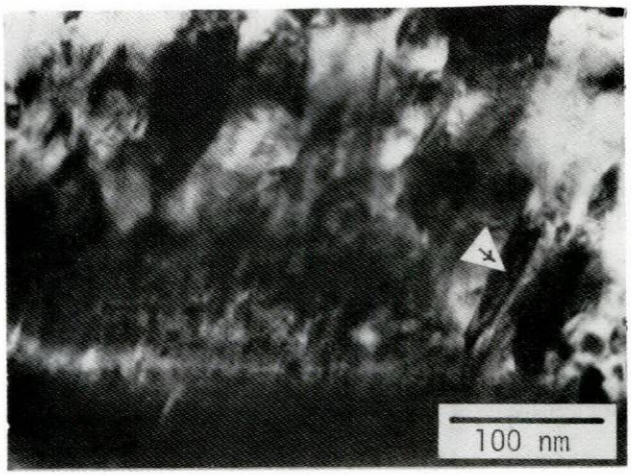

Figure 3. Electron Micrograph of Cross Section of Sulfamate Nickel Deposited on Electroless Nickel Substrate

The non-epitaxial grains also appear to develop by the formation of much smaller crystallites and their subsequent joining as was the case in the epitaxial deposits. The basic compounds, which probably impede lateral spreading of atom planes, are still present. Therefore, the small crystallites should also form when growth is non-epitaxial. Because boundaries between crystallites within the columnar grains in the direction perpendicular to the substrate are more widely spaced in Figure 3, it appears that the foreign materials permitted more atom planes to grow parallelly on top of each other. In Figure 2, the additive, saccharin only permitted a few atom planes to grow parallelly on top of each other before causing them to become misoriented. It is apparent that the growth mechanism of crystallite formation and joining may be quite general when metals like nickel are plated.

Several ways in which addition agents or other foreign substances in the plating solution affect the structure of the electrodeposits and, in turn their properties have now been elucidated as a result of AES Research Project 38. The results can be applied to deposits of practically used thicknesses. Addition agents have little effect on the lateral size of the three-dimensional crystallites in epitaxial deposits because it is apparently determined by basic compounds. However additives have considerable influence on the way the crystallites join and thereby on the properties of the deposit. If the crystallites join before the spaces between them are filled in, tensile stresses develop. Small misorientations between joining crystallites can also lead to the formation of dislocations, which have a dominating influence on the mechanical properties. Voids, which have been observed between improperly joined crystallites, can lead to poor protection of the substrate against corrosion. Foreign substances influence the formation of hillocks and thus the transition to a non-epitaxial structure. In the non-epitaxial structure, the difference between the structures shown in Figures 2 and 3 is attributable to the influence of foreign substances in the plating solutions. As the joining of crystallites is also prevalent in non-epitaxial deposition, which is the case in most practical applications, the effect of the additives and other foreign substances, previously discussed, should also be applicable here. The details of these studies are expected to be published in the near

future. The main purpose of this presentation was to show that a much better understanding is being gained of the ways by which electrodeposition occurs which should lead to a more scientific, i.e., less empirical method of controlling the properties of deposits and the formulation of the plating solutions.

Acknowledgements

The advice of the Project Committee consisting of W. Cochran, A. Damjanovic, G. Fisher, D. Hardesty, J. Horkans, F. Koch and D. Shanefield and the support of the AES Research Board and the sustaining membership is gratefully acknowledged. The TEM was obtained under a matching grant DMR-7716339 from the National Science Foundation.

M-1

RESEARCH SESSION M

The Cross-Sectional Structures of Thick Electrodeposits and Their Relationship to the Properties (AES Research Project #38A)

R. Weil
Stevens Institute of Technology
Hoboken, NJ

M-2

RESEARCH SESSION M

The Effect of Electroplating Wastewater Sludge as an Admixture of the Physical Properties of Concrete (AES Research Project #49A)

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ABSTRACT

*THE EFFECT OF ELECTROPLATING WASTEWATER SLUDGE

AS AN ADMIXTURE ON THE PHYSICAL PROPERTIES OF CONCRETE -

PHASE II
PRELIMINARY REPORT

Robert J. Spinna, P.E. - Principal Investigator
Walter P. Saukin, Ph.D. - Assistant Investigator
John D. Mahony, Ph.D. - Assistant Investigator

The electroplating industry has a major environmental problem with the sludge which results from treatment of wastewater from their various chemical processes. The sludge consists, to a large extent, of heavy metal hydroxides, silicates and phosphates. It is a difficult material to dispose of in a manner which does not seriously contaminate the environment.

It has been suggested that the sludge, which is 20% to 30% by weight solids, might react favorably in a concrete mix to produce insoluble compounds similar to many natural materials. If this can be done in a manner which does not lower the quality of the resulting concrete and which does not permit subsequent leaching of the sludge constituents into the environment, large amounts of the sludge could be disposed of at concrete batching plants located in many places through the country.

Research conducted under a grant from the American Electroplaters' Society during the Spring of 1979 has demonstrated the feasibility of using electroplating wastewater sludge as a concrete admixture as was reported in a paper presented at the Society's 1979 National Convention. It is possible to enhance the strength of the concrete and alter setting time while replacing as much as 2% of the mixing water with heavy metal elements in the sludge without significant leaching of the metals.

Wastewater sludge was collected from electroplating plants in the New York area and then these sludges were added in varying amounts to standard concrete mixes. The resulting concrete was subjected to a number of tests to evaluate the effect of the sludge on the physical properties of the resulting concrete.

Among the concrete tests were: compression (standard cylinder tests), plasticity (slump), leaching (solubility during curing and after) and bar pull-out tests; exposure tests were also conducted by allowing the samples to weather.

In addition to these tests on the concrete mixes, tests of the chemical composition of the sludge and resulting concrete were performed. X-ray diffraction patterns of the sludge were obtained. Analysis of these patterns indicates the presence of crystallinity in the sludge and its composition in terms of such compounds. It also indicates the formation of compounds between

*AES Research Project #49A

the concrete and the metalic constituents of the sludge. Any variation of the diffraction pattern of normal concrete helps to elucidate the nature, durability and resistance to deterioration. Shifts were so slight that firm conclusions concerning the nature of the resulting compounds could not be drawn.

Radio chemical techniques were also employed to elucidate the extent of the leaching of the sludge constituents into the curing water and, after curing, into water in which concrete samples had been submerged.

This paper presents the results of a continuing study which incorporates aluminum-bearing sludges in addition to the previously used cobalt, nickel, zinc, and manganese-bearing sludges in a variety of concrete mixes. Also, cadmium and chromium were added to the study to determine the leaching rates of these metals from the concrete generally in accordance with the Toxicant Extraction Procedures established by the Resource Conservation and Recovery Act. High early strength cement was used in addition to Type I Portland Cement. In addition, year-long leaching and weather exposure studies were performed.

The research data leads to tentative conclusions concerning the feasibility of disposing of electroplating wastewater sludges by admixing with concrete and supports the conclusion that the physical properties of the concrete were not adversely affected and the resulting compounds appear insoluble. It was observed that setting rates for the concrete could be varied widely by varying sludge content and strength variations from slight strength decreases to increases of as much as 50% could be achieved. The use of high early strength cement appears to enhance the ability of the concrete to bind the metal ions into insoluble compounds although even with Type I cement leaching rates of only a few parts per billion were observed. Additional extensive testing is required to confirm the results of this preliminary study and develop design criteria.

At this time testing has not been completed and results will not b fully available until June 1980 when they will be presented at the 1980 SUR/FIN conference. However, results from Phase I testing and available results from Phase II are presented herewith.

LEACHING STUDIES

TABLE I. SLUDGE COMPOSITION

WHYCO (1.5% SOLIDS)		NEP (5.33% SOLIDS)	
	ppm		ppm
Cr	500	Cr	1600
Cu	present but not determined	Zn	1520
Co	500	Ni	1360
Fe	present but not determined	Fe	1840
Mn	300	Cu	350
Na	present but not determined		
pH = 8.2		pH = 8.6	

WHYCO - WHYCO Chromium Corp.
Thomaston, Conn.

NEP - New England Plating Corp.
Worcester, Mass.

TABLE II NUCLIDE PROPERTIES

Nuclide	Radiation	Half-Life	Energy	Quantity
$^{60}_{27}Co$	γ	5.27 y	1.332 MeV 1.173 MeV	5μCi*
$^{54}_{25}Mn$	γ	312.5 d	0.8348 MeV	5μCi
$^{65}_{30}Zn$	γ	245 d	1.115 MeV	10μCi
$^{45}_{20}Ca$	β^-	165 d	0.254 MeV max	10μCi
$^{63}_{28}Ni$	β^-	125 y	0.067 MeV max	100μCi

* 1μCi is equivalent to 2.22×10^6 disintegrations per minute.

TABLE III SOLUBLE RADIOACTIVITY IN LEACH WATER AND CONCENTRATION EQUIVALENT

Immersion Time (Days)	Ni		Co		Zn		Mn		Ca	
	μCi	ppb	μCi	ppb	μCi	ppb	μCi	ppb	μCi	ppm
3	4.6×10^{-3}	1.3	2.3×10^{-5}	0.25	nil	0*	nil	0	3.1×10^{-2}	235
6	4.8×10^{-3}	1.4	8.8×10^{-5}	0.94	nil	0	nil	0	3.5×10^{-2}	270
9					nil	0	nil	0		
10	5.0×10^{-3}	1.5							4.6×10^{-2}	350
12			1.6×10^{-4}	1.7	nil	0	nil	0	5.4×10^{-2}	420
13.5	4.7×10^{-3}	1.4								
15			1.9×10^{-4}	2.0	nil	0	nil	0	7.3×10^{-2}	560
18	4.7×10^{-3}	1.4	1.5×10^{-4}	1.6	nil	0	nil	0	5.4×10^{-2}	420
21			2.0×10^{-4}	2.1	nil	0	nil	0		
22.5	1.0×10^{-2}	3.0							7.0×10^{-2}	540
24			1.5×10^{-4}	1.6	nil	0	nil	0		
25.5			2.7×10^{-4}	2.8						
27					nil	0	nil	0	8.0×10^{-2}	610
29.5	1.1×10^{-2}	3.1								
32					nil	0	nil	0	6.8×10^{-2}	520
34.5			3.7×10^{-4}	3.7						
37	1.0×10^{-2}	3.0			nil	0	nil	0	6.8×10^{-2}	520

Immersion Time (Days)	Ni μCi	Ni ppb	Co μCi	Co ppb	Zn μCi	Zn ppb	Mn μCi	Mn ppb	Ca μCi	Ca ppb
42			3.1×10^{-4}	3.2	nil	0	nil	0		
45.5	1.6×10^{-2}	4.7								
47			3.0×10^{-4}	3.1	nil	0	nil	0		
49										
52			2.8×10^{-4}	2.9	nil	0	nil	0		
57			2.9×10^{-4}	3.0	nil	0	nil	0		
60	1.3×10^{-2}	3.9								
62			3.4×10^{-4}	3.5	nil	0	nil	0		

TABLE IV TOTAL RADIOACTIVITY IN AGITATED LEACH WATER AND CONCENTRATION EQUIVALENT

Immersion Time (Days)	Ni μCi	Ni ppb	Co μCi	Co ppb	Zn μCi	Zn ppb	Mn μCi	Mn ppb
76	6.7×10^{-2}	20	1.9×10^{-3}	20	5.7×10^{-3}	18	5.0×10^{-3}	31
90	4.7×10^{-2}	14	1.0×10^{-3}	11	6.9×10^{-3}	22	6.9×10^{-3}	44

μCi = microcurie (2.22×10^{6} disintegrations per minute)

ppb = parts per billion

ppm = parts per million

*lower limit of detection is 0.04 ppb

The study of samples cured for 100 days and then reimmersed has been continued. The results are given below (ppb in leach water).

TABLE V

Days Leaching	7	21	48	113	143
Co	1.0	2.2	6.0	Results not yet available due to analyzer mal-function	
Mn	31	37	24		
Zn	6.1	3.2	0.7		
Ni	18	11	5.6	3.5	4.2

The results of the leaching studies on the new Ni, Cd, and Al systems are summarized below. The regular concrete was cured for 72 hours (longer than in the previous work because the bleed water was entirely retained). The high early concrete with NEPsludge had to be cured for a week for it to step up. Radioactivity includes both dissolved and undissolved metal ions.

TABLE VI

Metal	days leaching	ppb in leach water (approximate)
Al	3	trace
	13	trace
	27	nil
	45	1-2
	66	nil
Cd(reg)	3	7
	10	2
	17	5
Cd(HE)	6	1
Ni(reg)	5	3
	10	1
	16	7
Ni(HE)	6	3

PHYSICAL TESTS ON CONCRETE

TABLE VII - FOUR WEEK RE-BAR PULL-OUT STRENGTH

WHYCO SLUDGE CONTENT (1.5%) % WT. OF MIX WATER	0	25	50	75	100
AVERAGE LOAD (LB.)	15,400	15,600	15,000	15,100	15,300
NEP SLUDGE CONTENT (6.5) % WT. OF MIX WATER	0	5	10	15	20
AVERAGE LOAD (LB.)	15,150	15,200	15,700	15,350	14,700

SLUMP TESTS

Sludge-concrete mixes having high sludge solids contents had lower slumps than mixes with low solids contents. It was further observed that high solids contents also increased the setting time. In the case of the 100% NEP sludge-concrete, the curing time was five days. However, the strength did develop as the concrete cured.

TABLE VIII- CONCRETE COMPRESSION STRENGTH -

28-DAY RESULTS

SLUDGE	% SLUDGE SOLIDS TO MIXING WATER	ULTIMATE COMPRESSION STRENGTH (psi)
WHYCO (Coarse)	0	1925
	.375	2150
	.750	2100
	1.125	2000
	1.500	1900
NEP	0	3050
	.325	3350
	.650	3150
	.975	3250
	1.300	3200
WHYCO (Dense)	0	3075
	.375	3150
	.750	3050
	1.125	3150
	1.500	3075

M-3

RESEARCH SESSION M

Recrystallization Kinetics of Several Nickel Electrodeposits (AES Research Project #50)

J. D. Katz, H. W. Pickering and W. R. Bitler
Pennsylvania State University
University, PA

RECRYSTALLIZATION KINETICS OF SEVERAL NICKEL ELECTRODEPOSITS*

by
J. D. Katz, H. W. Pickering and W. R. Bitler

ABSTRACT

Samples prepared by electrodeposition of nickel from Watts, All-Chloride and Chloride-Free baths onto a copper substrate were annealed for various times and temperatures. They were subsequently examined by optical and scanning electron microscopy. The extent of recrystallization and grain growth of the electrodeposits was observed and recrystallization curves were constructed. Activation energies for recrystallization of Watts, All-Chloride and Chloride-Free electrodeposits were also determined. Recrystallization appeared to have begun at the copper-nickel interface. Kirkendall porosity was also observed.

INTRODUCTION

The problems which result from the interdiffusion of an electrodeposit and its substrate are of special importance to the electronics industry. Gold electrodeposited on substrates such as copper and kovar is used extensively for electrical contacts. Gold has many properties which are desirable for an electrical contact. However, the attribute which precludes the replacement of gold as the primary electrical contact coating material, is that, of all the metals, it alone has no thermodynamically stable oxides at ambient temperatures. Since the resistance of any oxide is several orders of magnitude larger than any metal, the ability to remain free of oxide is an essential consideration when designing a low voltage contact.

Because of the constantly increasing price of gold, it is very desirable to minimize the amount used by decreasing the thickness of the electrodeposit. Unfortunately, decreasing the thickness also decreases the service life. Failure results from the diffusion of copper (or any other substrate material) through the gold electrodeposit to the surface where it forms a high resistance oxide. Frant[1] illustrated this phenomenon by growing copper oxides on gold which had been electrodeposited onto a copper substrate.

To retard diffusion and thereby prolong service life, a barrier layer may be inserted between the substrate and the electrodeposit. To date, a large amount of experimental work on the effectiveness of specific barriers has been performed. All of these studies concerned the effectiveness of as-plated barriers. No attempt was made to modify the structure of the barrier to make it more effective.

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*This paper is condensed from the final report on AES Project 50.

Most electrical contacts see service at or near ambient temperatures and grain boundary diffusion, not bulk diffusion, is the dominant diffusion mode. The grain boundary diffusional flux through a recrystallized large grained electrodeposit will be much less than through an unrecrystallized smaller grained one. Therefore, a recrystallized electrodeposit should be a more effective barrier than an unrecrystallized one. In this study, methods by which the structure of a barrier may be optimized through the process of recrystallization have been looked at.

The effects of recrystallization can be dramatic. Marx et. al.[2] found that samples annealed at 175°C resulted in a lower diffusivity than similar samples annealed at 100°C. These results seem anomalous but can be understood by considering the effects of recrystallization. Samples annealed at 175°C recrystallized early in the anneal, while the samples annealed at 100°C recrystallized much later in their anneal. Hence, the flux through the recrystallized, large-grained electrodeposit was much smaller even though it was annealed at a higher temperature.

The work reported on here concerns the recrystallization kinetics of nickel electrodeposits. Three types of nickel electrodeposits, Watts, All-Chloride and Chloride-Free, were studied. The recrystallization information presented here will be combined with diffusion data to gauge the effectiveness of recrystallized barriers. Knowledge of the recrystallization kinetics is essential before a comparison of recrystallized and unrecrystallized barriers can be made.

EXPERIMENTAL PROCEDURE

All samples were prepared by electroplating onto a copper substrate. The copper was obtained as 1/2 inch diameter hard drawn bar and met the specifications of ASTM-187. The bar was sectioned into three-inch lengths with an abrasive cutoff wheel. Each section was center drilled, drilled and tapped to a 1/2 inch depth while mounted in a lathe. During plating, electrical contact was made by screwing a threaded conducting rod into the copper bar.

Each three-inch section was abrasively cleaned with steel wool before the pretreatment procedure. Pretreatment prior to electrodeposition was in accordance with the procedure detailed in Table #1. The plating baths are standard and their compositions were obtained from the Metal Finishing Guidebook and Directory[3]. Three nickel baths were used: Watts, All-Chloride and Chloride-Free. Their compositions and plating variables are listed in Table #2.

All electroplating was performed in the presence of mechanical agitation. A propeller type stirrer driven by an electric motor provided agitation. A breaker containing the plating bath was immersed in a constant temperature bath so that electroplating could be performed at a constant and specific temperature. The anode consisted of commercial nickel bagged in canvas. For the Watts and All-Chloride baths, pH was adjusted with either hydrochloric and boric acids or nickel carbonate. The pH was adjusted with either boric or nickel carbonate for the Chloride-Free bath.

Those samples which were annealed for 1 hour were electroplated at 1.5 amps (30 asf) for 40 minutes. All other samples were plated at 1.5 amps (30 asf) for 1 hour.

The as-plated samples were sectioned into 1/8 inch thick discs with an abrasive cutoff wheel and then encapsulated in pyrex or vycor under vacuum. Each disc was separated from its neighbor in the capsule by either a pyrex or alumina spacer. Samples from each of the three respective baths were annealed for one, ten and one hundred hours at 300, 400, 500, 600, 700 and 800°C in laboratory muffle furnaces. After completion of its anneal, each capsule was air cooled.

Upon cooling to room temperature, the capsules were broken and the samples were rinsed in acetone. Those samples which were annealed for 1 hour were mounted in bakelite. For edge protection, the remaining samples were plated with copper from an Acid-Copper bath and then mounted in Buehler's copper-filled diallylphalate. The mounted samples were successively ground with 240, 320, 400 and 600 grit silicon carbide paper. Alumina powders of 0.3 and 0.05 microns were used successively for polishing. All samples were etched with a solution of 50% nitric acid-50% acetic acid for various lengths of time either by dipping or swabbing.

A Zeiss Ultraphot microscope was used for optical examination. An International Scientific Instruments model Super III-A scanning electron microscope (SEM) was used for SEM examination.

RESULTS AND DISCUSSION

SEM or optical microscopy was used to determine the extent of recrystallization of each sample. Electrodeposits were viewed sequentially according to annealing temperature. This served to exemplify the change from unrecrystallized to recrystallized. The transformation from unrecrystallized to completely recrystallized was sudden, always within one annealing period. Because of the abrupt character of the transformation, detailed information concerning the shape of the recrystallization curve was not obtained. However, since recrystallization is a nucleation and growth transformation, a sigmoidal curve can be expected.

Both optical and SEM examination of as-plated Watts electrodeposits revealed a columnar-lenticular type structure. Figure 1 is a micrograph typical of the as-plated Watts microstructure. The structure appears to be an artifact of the electrodeposit process. The features which were resolved are not individual grains but clusters or groups of grains. By using replica TEM, Weil and Paquin[4] became the first to correctly identify these structural features as grain clusters or colonies. More recently, thin film TEM has been utilized to provide explicit views of individual as-plated grains (6,7,8). As-plated grains have been observed to range in size from submicron to several microns. Figure 2 is a micrograph typical of a recrystallized Watts electrodeposit.

After analysis of the annealed samples, recrystallization curves were constructed. Figure 3 is such a curve; it illustrates the recrystallization

characteristics of Watts electrodeposits.

As-plated All-Chloride electrodeposits produced for this study have a fine columnar-lenticular structure. Figure 4 is a micrograph typical of the as-plated structure. Again, the features which are resolved are not individual grains but clusters. Kirkendall porosity is evident on the copper side of the substrate-electrodeposit interface. The grains are largest in the region closest to the copper-nickel interface. It is probable that the nickel adjoining the substrate-electrodeposit interface was the first to recrystallize. The electroplate is coherent with the substrate here and more highly stressed because of extrinsic or misfit stress. This observation is very well supported by the recent work of Feigenbaum and Weil[9]. They measured the stress in nickel electrodeposits on copper substrates as a function of thickness. Stresses in the region of the substrate-electrodeposit interface were found to be as much as four times greater than the value measured in the bulk. The recrystallization characteristics of All-Chloride electrodeposits are illustrated in Figure 6.

As-plated Chloride-Free nickel, shown in Figure 7, has a concentrically layered or banded structure. This structure is drastically different from the previously observed structures of Watts and All-Chloride electrodeposits. Banded structures can be caused by several variables[10]. Among them are current density and chloride or ammonia ion content.

The surfaces of the nickel electrodeposit and the copper substrate are not level. The height differential is caused by accelerated attack by the etchant of the substrate adjacent to the electroplate. The nickel electroplate is cathodic to the copper substrate. The galvanic effect is large near the interface where the IR drop is small. The galvanic effect is opportune since it permits observation parallel as well as perpendicular to the specimen surface.

Figure 8 is a micrograph typical of a recrystallized Chloride-Free electrodeposit. A wide distribution of grain sizes are visible. The recrystallization characteristics of Chloride-Free electrodeposits are illustrated by Figure 9.

Activation energies for recrystallization were determined and are presented in Table 3. Activation energies for deformed nickel, from the work of Wensch and Walker[5], are included in Table 1 for comparison. All of the activation energies determined are much smaller than the literature values for deformed nickel. The value obtained for Chloride-Free electrodeposits was extremely low.

Several other investigators have studied the microstructural changes of nickel electrodeposits as a function of temperature (6-8, 10-16). However, there is no general agreement on recrystallization temperatures or if recrystallization occurs at all. Several workers have observed only grain growth without recrystallization (6,7). The type of deposit, plating variables and substrate material all affect the recrystallization behavior. These factors are probably responsible for the experimental variance.

To better illustrate the dramatic difference in the recrystallization characteristics of nickel electrodeposits and deformed nickel, Table 2 was constructed. Since the activation energies are known, it is possible to predict the time at a certain temperature to achieve complete recrystallization. For example, from Table 4, at 300°C we can expect both Chloride-Free and Watts electrodeposits to recrystallize during what could be considered a typical service life for an electrical contact. An All-Chloride electrodeposit or deformed nickel would not recrystallize at this temperature for practical purposes.

CONCLUSIONS

Activation energies for recrystallization of electrodeposited nickel are much lower than for conventionally fabricated deformed nickel. The large intrinsic stress stored in electrodeposits via the deposition process is responsible for the low activation energies. Because of these low activation energies the recrystallization and grain growth behavior of electrodeposited nickel is very much different from conventional nickel. Electrodeposited nickel begins to recrystallize at much lower temperatures and after shorter times than conventional nickel. Chloride-Free nickel was observed to recrystallize at the lowest temperatures and after the shortest times, followed by Watts and All-Chloride respectively.

Because of extrinsic stress, recrystallization starts at the electrodeposit-substrate interface. Recrystallization was always observed to begin at this interface. The grains adjacent to it were always the largest viewed.

Optical or scanning electron microscopy is not capable of resolving individual as-plated grains. The features which were resolved are grain clusters and phenomenon such as deformation twins. Recrystallized electrodeposits are resolvable into individual grains.

The flux of copper into the electrodeposit is greater than the flux of nickel into the substrate. Kirkendall porosity was observed on the copper side of the substrate-electrodeposit interface. While it has been previously proven that the high temperature diffusivity of copper into nickel is larger than the reverse, these studies were concerned with nearly pure conventionally fabricated metals. This observation is important because it concerns diffusion in electrodeposits.

ACKNOWLEDGEMENTS

The authors wish to thank the members of the Project 50 Committee for their help and guidance. In addition, the support of the American Electroplaters' Society and it's Research Board is gratefully appreciated.

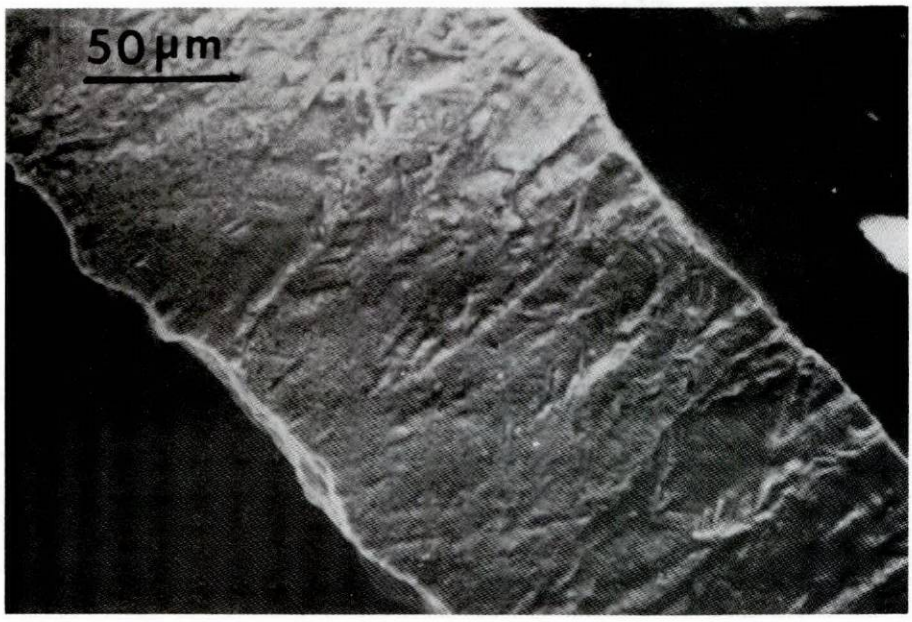

Figure 1. As-plated Watts electrodeposit (SEM, mag. 400x, etch: 50% nitric acid-50% acetic acid).

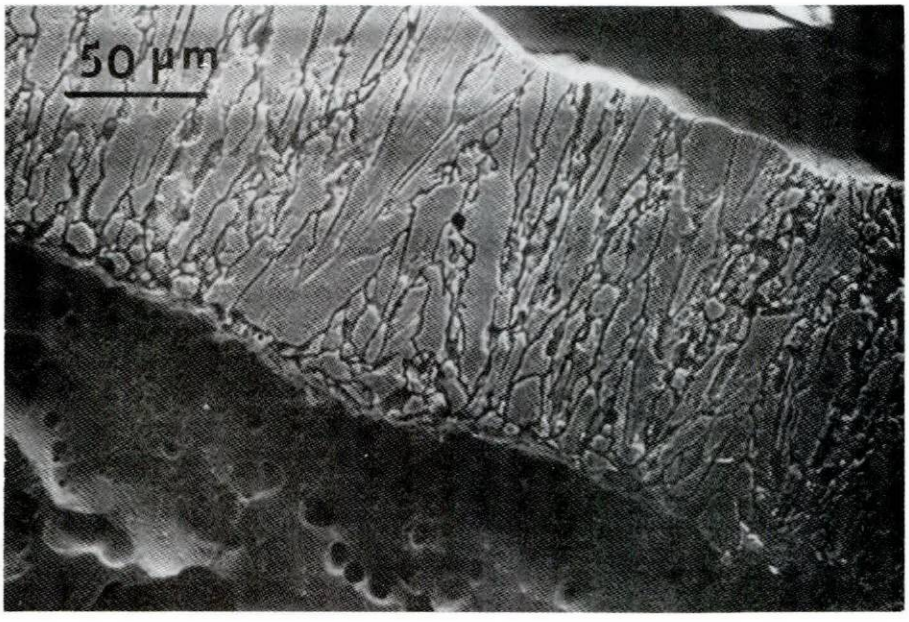

Figure 2. Recrystallized Watts electrodeposit, (annealed at 600°C for 10 hours. SEM, mag. 360x, etch: 50% nitric acid-50% acetic acid).

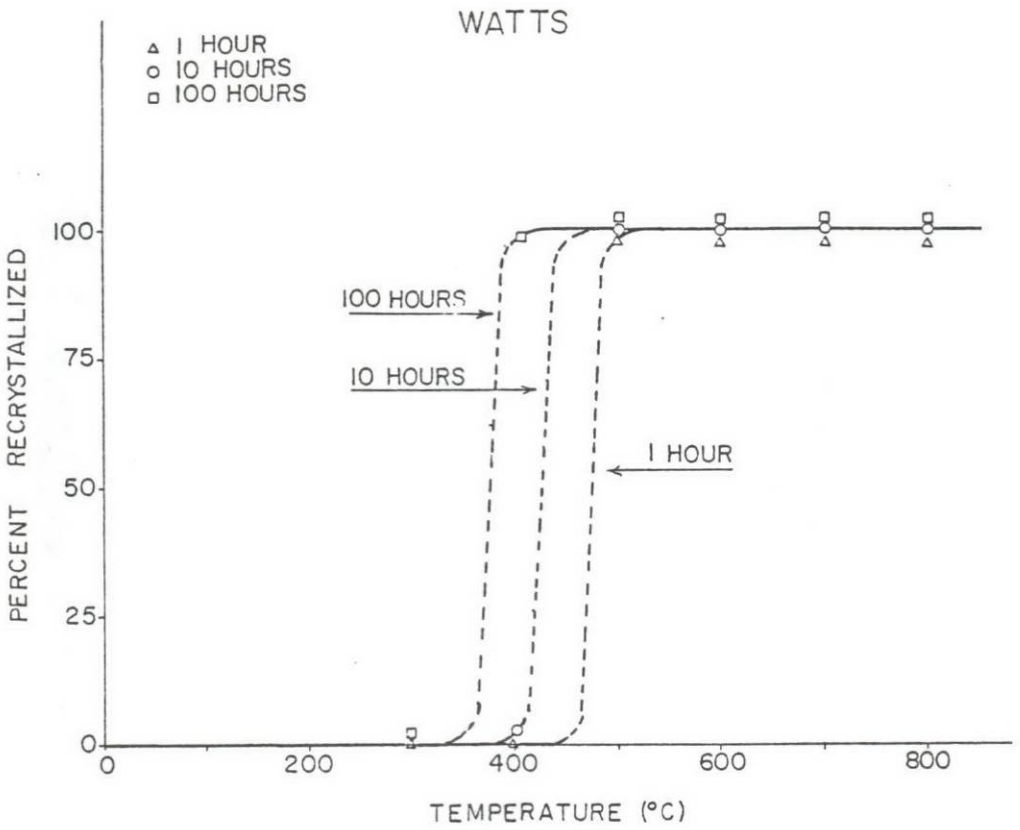

Figure 3. Watts Electrodeposit Recrystallization Curves.

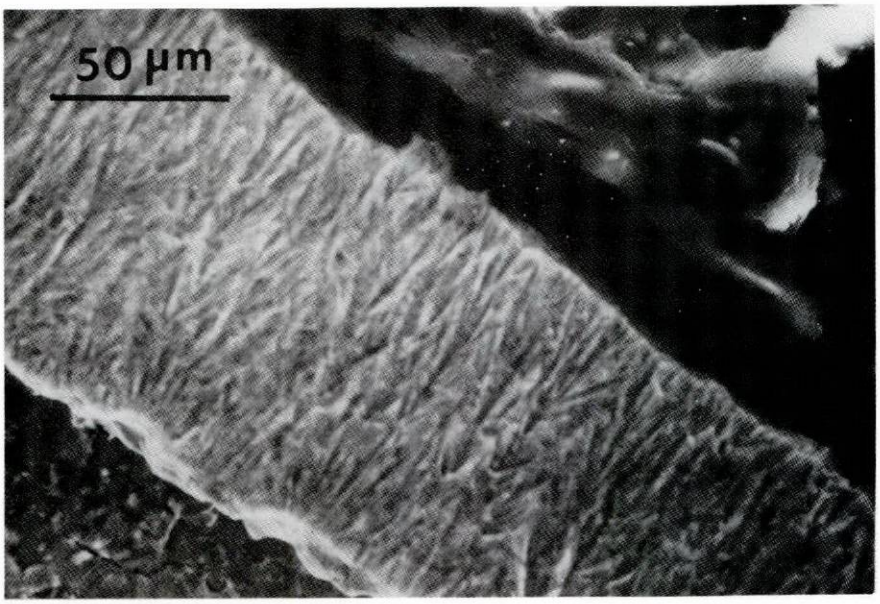

Figure 4. As-plated All-Chloride electrodeposit (SEM, mag. 460x, etch: 50% nitric acid-50% acetic acid).

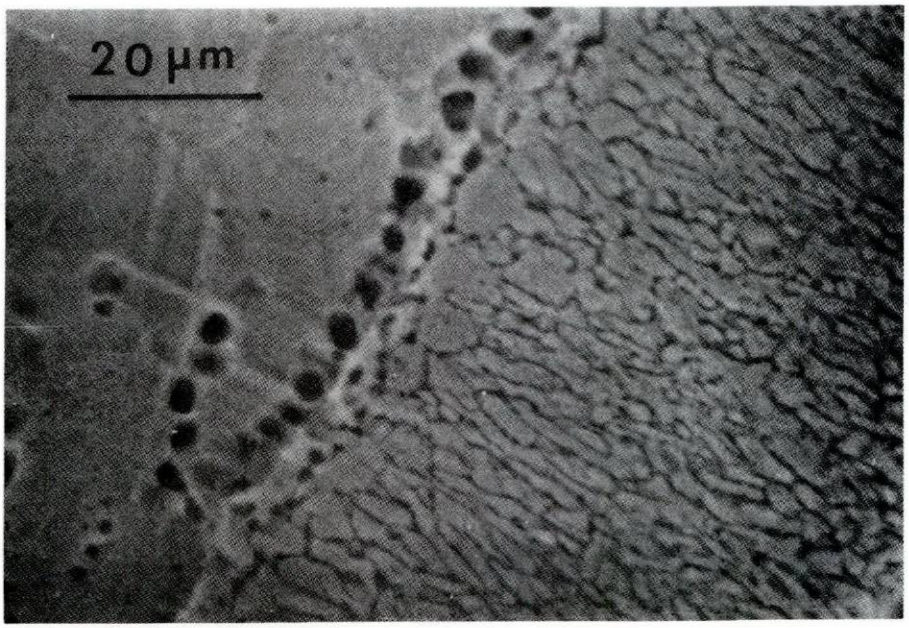

Figure 5. Recrystallized All-Chloride electrodeposit, (annealed at 700°C for 1 hour. SEM mag. 1260X, etch: 50% nitric acid-50% acetic acid).

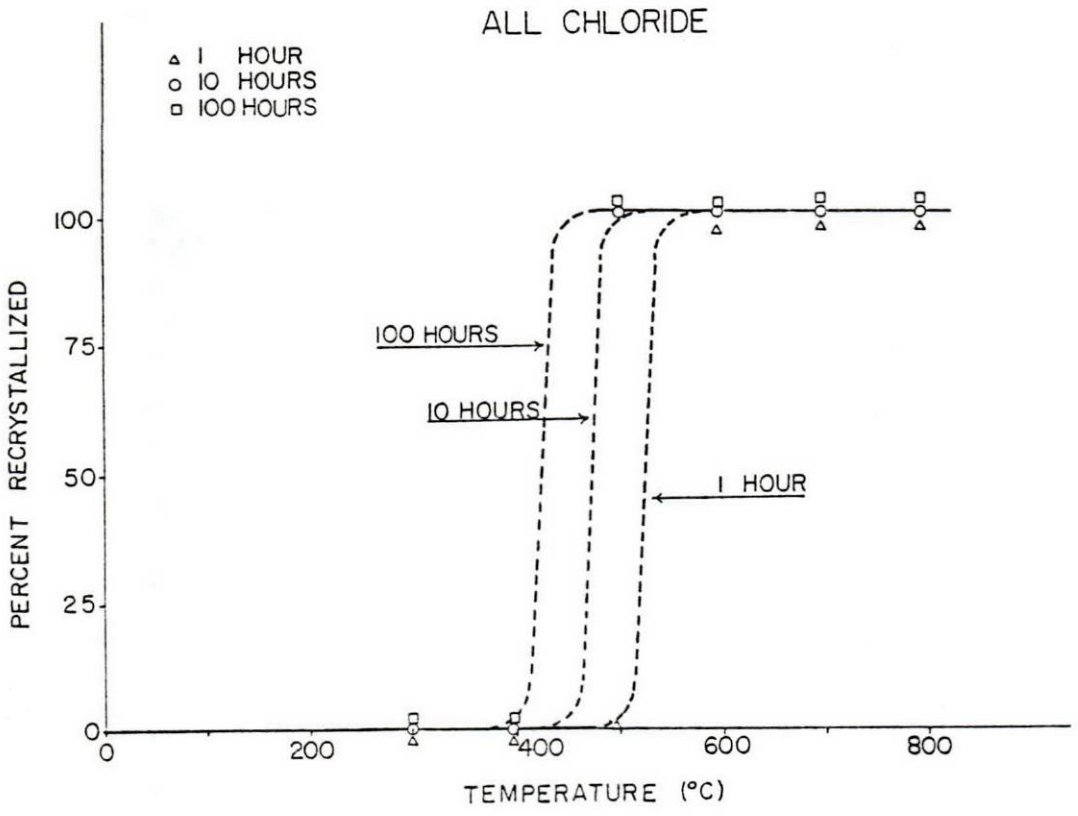

Figure 6. All-Chloride Electrodeposit Recrystallization Curves.

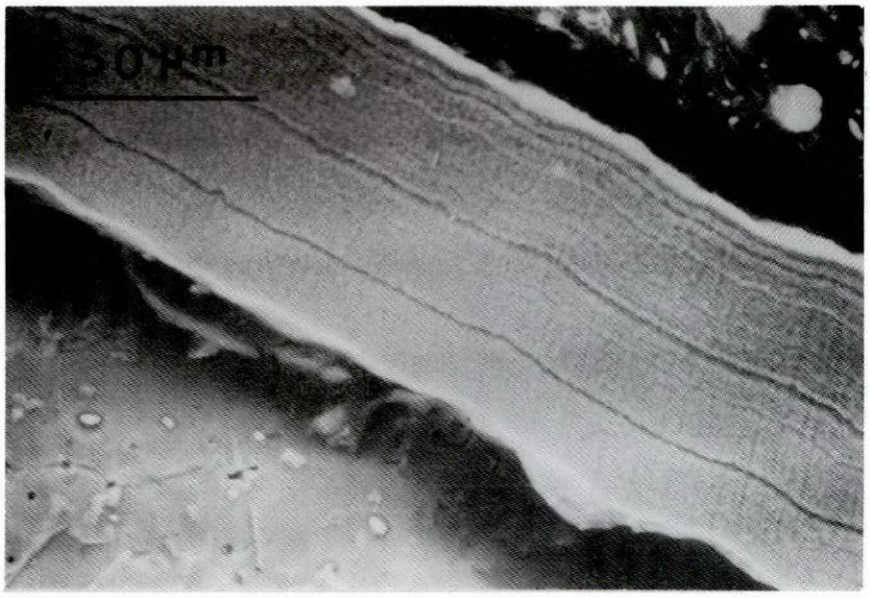

Figure 7. As-plated Chloride-Free electrodeposit. (SEM, mag. 500x, etch: 50% nitric acid-50% acetic acid).

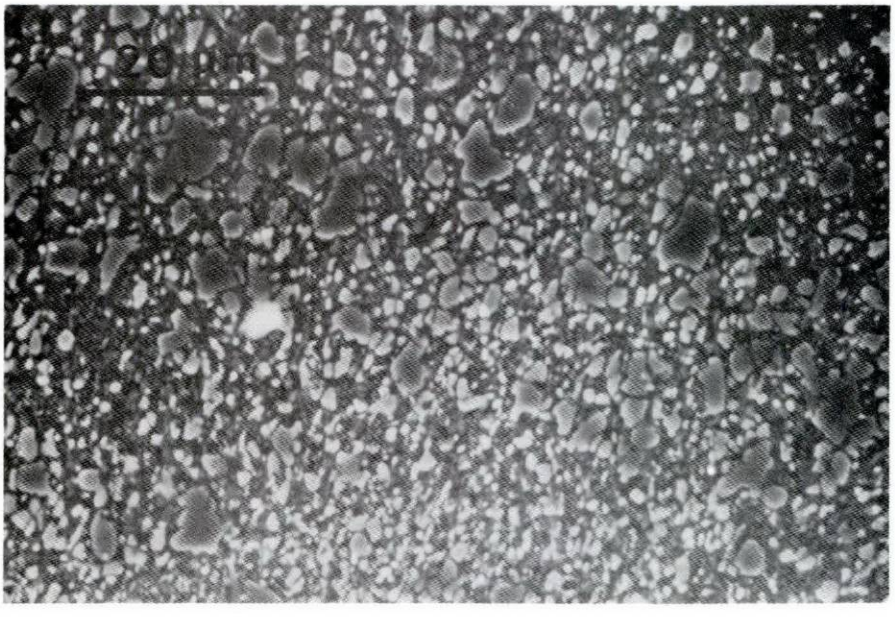

Figure 8. Recrystallized Chloride-Free electrodeposit, (annealed at 500°C for 100 hours, SEM, mag. 1200x, etch: nitric acid-50% acetic acid).

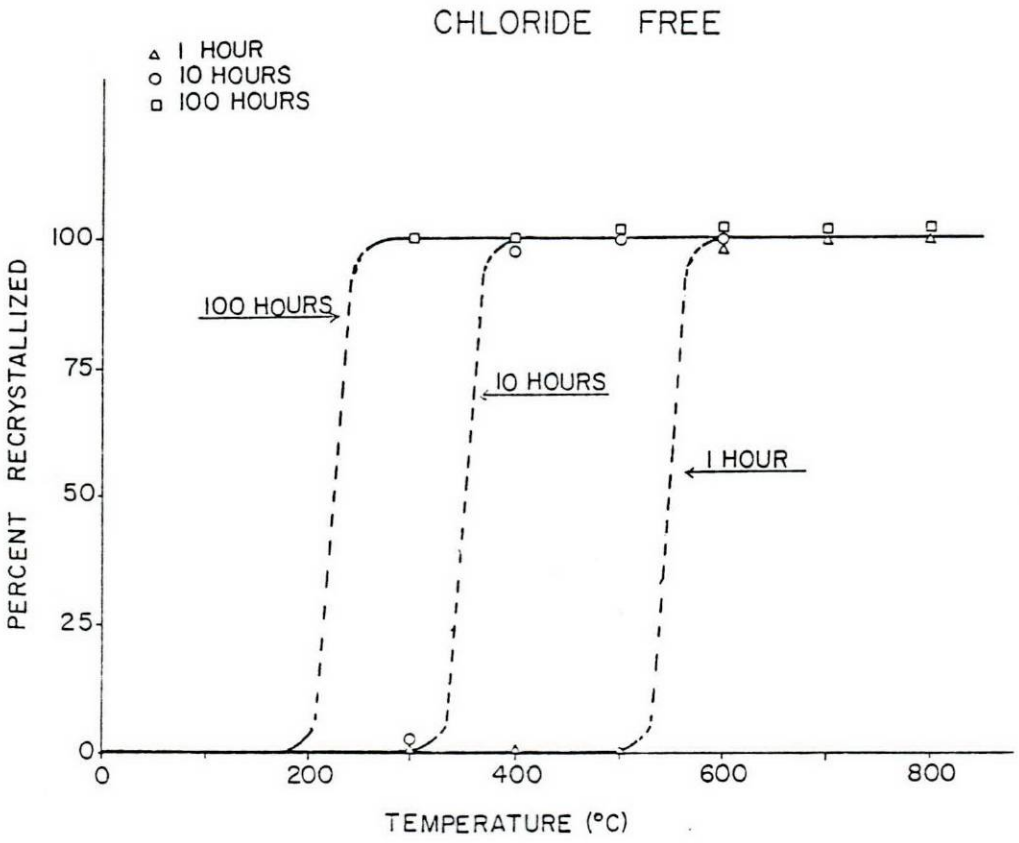

Figure 9. Chloride-Free Electrodeposit Recrystallization Curves.

Table #1

Pretreatment Procedure for Copper

1. Alkaline Soak Cleaner at 80°C

30g/l	Na_2CO_3
30g/l	$Na_2P_4O_7$
1g/l	Dupanol ME

2. Distilled H_2O Rinse

3. Bright Dip at Room Temperature

45.0%	H_2SO_4
22.0%	HNO_3
0.09%	HCl
32.9%	H_2O

4. Distilled H_2O Rinse

5. Surface Activation

   Direct current

   45g/l KCN

   6v for 20 sec

6. Distilled H_2O Rinse

7. Dilute H_2SO_4 Dip

8. Distilled H_2O Rinse

Table #2

Watts Bath	
Composition	
Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	300 g/l
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	45 g/l
Boric Acid (H_3BO_3)	35 g/l
Temperature	65°C
pH	3·1-4·1
Current density	30 amps/ft^2
Agitation	

Chloride-Free Bath	
Composition	
Nickel sulfamate ($Ni(NH_2SO_3)_2$)	450 g/l
Boric Acid (H_3BO_3)	30 g/l
Sodium Lauryl Sulfate	0.375 g/l
Temperature	50°C
pH	4·1-4·4
Current density	30 amps/ft^2
Agitation	

All-Chloride Bath

Composition	
Nickel Chloride ($NiCl_2 \cdot 6H_2O$)	300 g/l
Boric Acid (H_3BO_3)	30 g/l
Temperature	65°C
pH	1·6-1·9
Current density	30 amps/ft^2
Agitation	

Table 3

ACTIVATION ENERGIES (Kcal/mole)

Chloride-Free	13.40	$(^{+0}_{-3})$
Watts	47.70	$(^{+0}_{-12})$
All-Chloride	58.20	$(^{+4}_{-10})$
Nickel-60% deformation	69.50	
Nickel-40% deformation	73.30	
Nickel-20% deformation	75.80	

Table 4

Time at 300°C For Complete Recrystallization

Chloride-Free	58 hours
Watts	5.089×10^{4} hours (6 years)
All-Chloride	5.509×10^{6} hours (629 years)
Nickel-60% deformation	7.370×10^{46} hours (8.4×10^{43} years)

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M-4

RESEARCH SESSION M

Adhesion of Electroplating to Problem ABS Substrates (AES Research Project #42A)

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AES PROJECT 42A - ADHESION OF ELECTROPLATING TO COMPLEX ABS SUBSTRATES

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Introduction

This study was undertaken to investigate the effects of the common etchant chemicals on ABS substrates. The test piece was a 2-1/2" diameter x 2" high cylinder closed at one end; it consists of two relatively simple surfaces with a well-defined problem area at the intersection of the two surfaces. The problem area extends approximately 2" around the rim of the part, and, when necessary for the preparation of test samples, it could be located precisely. The effects of the chemicals were studied by means of thermal cycle, porosity and mini-peel tests.

Experimental

The etchants investigated were:

A	Chromic Acid	1140 gr/1
	CR^{+3}	69 gr/1
B	Chromic Acid	420 gr/1
	Adjusted to 7.7 normal with sulfuric acid	
C	Sulfuric Acid	790 mls/1
	Chromic Acid	27 gr/1
	D.I. Water	219 ml/1
O	Organic Conditioning Solution[1]	

A number of the test parts were processed utilizing one or more of these etchants. Half the parts were electroplated with copper, nickel and chromium and were put through three thermal cycles of 180°F to -20°F. The remaining parts were electroplated with approximately 2.5 mils of Bright Acid Copper and were peel tested utilizing the mini-peel test developed in Phase I. The results are summarized in Tables I and II. The peel test values listed are pounds for a one-sixteenth inch strip.

Cycle Test: Cycle test failures with the test part are generally experienced in or about the area covered by Band 5. The symbols in the cycle test column have the following meaning:

Pass: No evidence of failure.

[1]A proprietary product manufactured by Shipley Company and marketed under the trade name "PM 920"

VSF: Very slight failure. A hairline lifting of the electroplate where the two significant surfaces meet at an angle of approximately 270°. The raised area extended for approximately 1" around the circumference. The failure was so slight as to be almost unnoticeable.

SF: Slight failure. Same area as above, but the width of the raised band was between 1/32" and 1/16". The defect was more noticeable than that defined under VSF.

Fail: A noticeable failure 1/16" to 1/8" wide.

MF: Massive failure. One or more blisters 1/8" x 1/4" extended down from the 1/8" wide raised area.

SEM: A standard 3" x 5" EP 3510 plaque was etched with each group of tests. A one-inch-square section was cut from the center of each plaque, and the sample was examined by means of a Scanning Electron Microscope. A typical area was photographed. For comparison purposes, a representative section from each photograph is reproduced in either Fig. 1 or 2. The photographs represent the degree of porosity developed by the individual etchants under optimum conditions--an uncontaminated etch solution working on an ideal substrate.

When the test pieces for cycle and peel testing had been processed through the solutions, a number of additional test pieces were etched in them and prepared for SEM analysis. Figure 3 is a striking presentation of the variable response of the surface of the test piece to one of the etchants; note particularly that the porosity developed falls off as we approach the problem area. Figures 4 through 7 present some similar data for the other etchants. The micrographs labeled "a" represent the porosity developed by each etchant under optimum conditions--a fresh etchant solution on an optimized plaque molding; the micrographs labeled "b" are of areas 1/2" below the defective section of the test piece; and those labeled "c" are of areas in the defective section--the processing was with slightly used etching solutions.

Skin Condition: Close inspection of the sections of the peel-tested samples adjoining the peeled Band 5 strip revealed traces of a loose, overlapping skin projecting from the lip of the test pieces in the problem section. Only those parts processed with etchants O and C as the initial treatment appeared to be free of the defect. Inspection of the peeled metal strip on these parts, however, revealed that a heavy film of plastic had been removed from the part at the significant section and remained attached to the peeled metal strip. This suggested that these etchants were sufficiently aggressive to degrade the skin leading to its removal in the subsequent processing.

In an attempt to elucidate the skin problem, a series of short shots were molded. The condition is formed at the very initial stages of injection at the point where the flat area is filled and the plastic flows over the lip into the cylindrical portion of the part. At the problem area, the flow of the plastic lags slightly behind the general front and does not appear to pack tightly against the wall of the cavity; the outer skin may well set or

chill at that point; when the cavity is subsequently filled and packed, the skin may be stretched and forced flush against the surface.

To test this theory, we are planning on modifying one cavity; it is hoped that the proposed modification will improve the flow characteristics. Parts molded in the modified cavity will be processed and tested side by side with parts molded in the unmodified cavity. It will be interesting to determine if we can eliminate the adhesion problem in the area.

Control Test: The scanning electron microscope is an expensive item of equipment and is not readily available in the plating shop. For the test piece, the results of the following simple tests have been found to correlate closely with the results of the SEM evaluation.

a. Appearance of the electroless copper preplated part. Areas of poor etch porosity have a distinctly shiny appearance which stand out dramatically against the overall mat appearance of the part.

b. The area becomes whitened and crazed in an acetic acid test.

Conclusion

The parts processed with Solution C were heavily pitted and were virtually unuseable from an appearance standpoint.

While organic pre-etching followed by chromic acid etching can develop sufficient adhesion in the area to pass the thermal cycle test, the root cause of the problem appears to be stress in the molding. It is probable that the stress would later result in field failure. Field performance could best be assured by eliminating or at least minimizing the stress in the area.

TABLE I

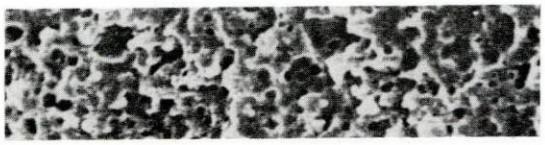
DATA FOR CAVITY A

Test No.	Etch Treatment						Peel Test							
	First			Second			Band 3			Band 5			Cycle Test	Skin Condition
	Solution	Time Mns	Temp °F	Solution	Time Mns	Temp °F	Range Min.	Range Max.	Av.	Range Min.	Range Max.	Av.		
1	A	10	150	-	-	-	0.705	0.800	0.720	0.102	1.019	0.701	Pass	Yes
2	A	20	150	-	-	-	0.700	0.906	0.769	0.268	0.978	0.752	VSF	No
3	B	10	150	-	-	-	0.356	0.748	0.597	0.000	0.920	0.545	SF	Yes
4	C	3	135	-	-	-	0.120	0.281	0.173	0.000	0.174	0.000	Pass	No
5	O	1	94	A	10	150	1.229	1.328	1.310	0.877	1.074	0.780	Pass	No
6	O	1	94	B	10	150	0.235	0.658	0.465	0.238	0.948	0.644	VSF	Yes
7	O	1	94	C	3	135	0.084	0.199	0.113	0.000	0.000	0.000	Pass	No
8	B	3	150	A	10	150	0.541	0.680	0.586	0.000	1.084	0.735	SF	Yes
9	B	10	150	A	10	150	0.619	0.815	0.621	0.000	0.866	0.495	Fail	Yes
10	C	1	135	A	10	150	0.292	0.544	0.376	0.000	0.291	0.115	SF	S1
11	C	3	135	A	10	150	-	-	-	-	-	-	MF	No
12	B	10	150	C	3	135	0.169	0.325	0.205	0.068	0.279	0.097	MF	No
13	C	1	135	B	10	150	0.190	0.403	0.281	0.004	0.361	0.182	-	No
14	C	3	135	B	10	150	0.209	0.347	0.243	0.000	0.268	0.083	MF	No

TABLE II

DATA FOR CAVITY B

Test No.	Etch Treatment						Peel Test							
	First			Second			Band 3			Band 5			Cycle Test	Skin Condition
	Solution	Time Mns	Temp °F	Solution	Time Mns	Temp °F	Range		Av.	Range		Av.		
							Min.	Max.		Min.	Max.			
1	A	10	150	-	-	-	0.776	0.882	0.841	-	-	-	VSF	-
2	A	20	150	-	-	-	0.597	0.769	0.711	0.234	0.887	0.654	VSF	S1
3	B	10	150	-	-	-	0.498	0.798	0.595	0.060	0.993	0.642	SF	Yes
4	C	3	135	-	-	-	0.094	0.271	0.165	0.000	0.289	0.077	VSF	No
5	O	1	94	A	10	150	0.648	0.919	0.793	0.548	1.041	0.796	Pass	No
6	O	1	94	B	10	150	0.187	0.477	0.348	0.024	0.921	0.625	Pass	Yes
7	O	1	94	C	3	135	0.066	0.160	0.155	0.000	0.135	0.048	VSF	No
8	B	3	150	A	10	150	0.531	0.682	0.568	0.000	0.890	0.534	VSF	Yes
9	B	10	150	A	10	150	0.658	0.752	0.615	0.176	0.958	0.696	Fail	Yes
10	C	1	135	A	10	150	0.085	0.756	0.365	-	-	-	Pass	-
11	C	3	135	A	10	150	0.102	0.328	0.258	0.000	0.494	0.175	MF	No
12	B	10	150	C	3	135	0.138	0.192	0.161	0.014	0.227	0.107	MF	No
13	C	1	135	B	10	150	0.180	0.660	0.297	0.009	0.324	0.215	Pass	Yes
14	C	3	135	B	10	150	0.192	0.381	0.246	0.040	0.236	0.118	MF	No



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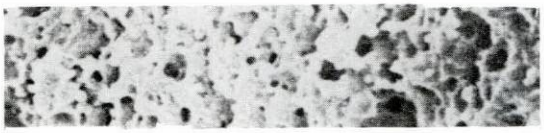

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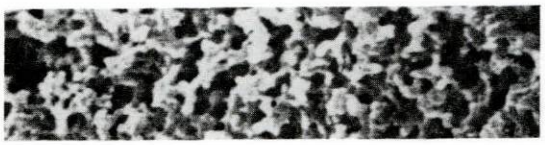

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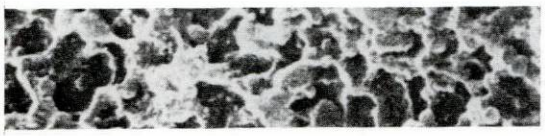

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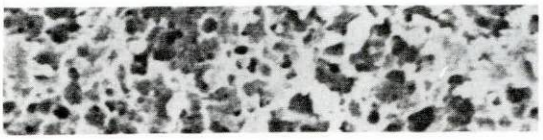

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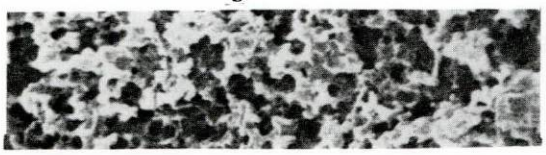

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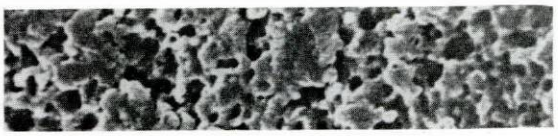

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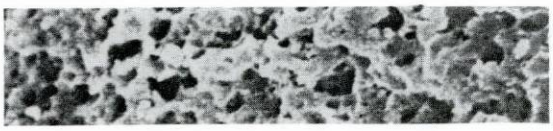

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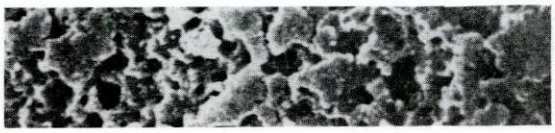

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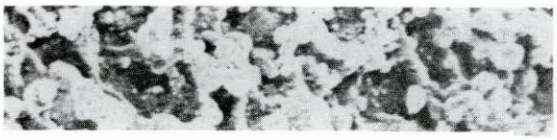

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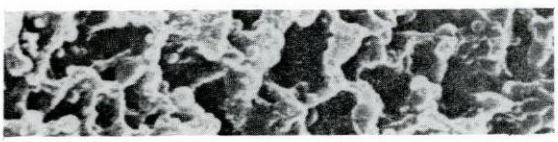

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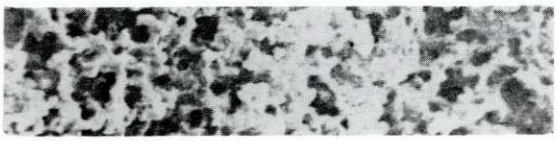

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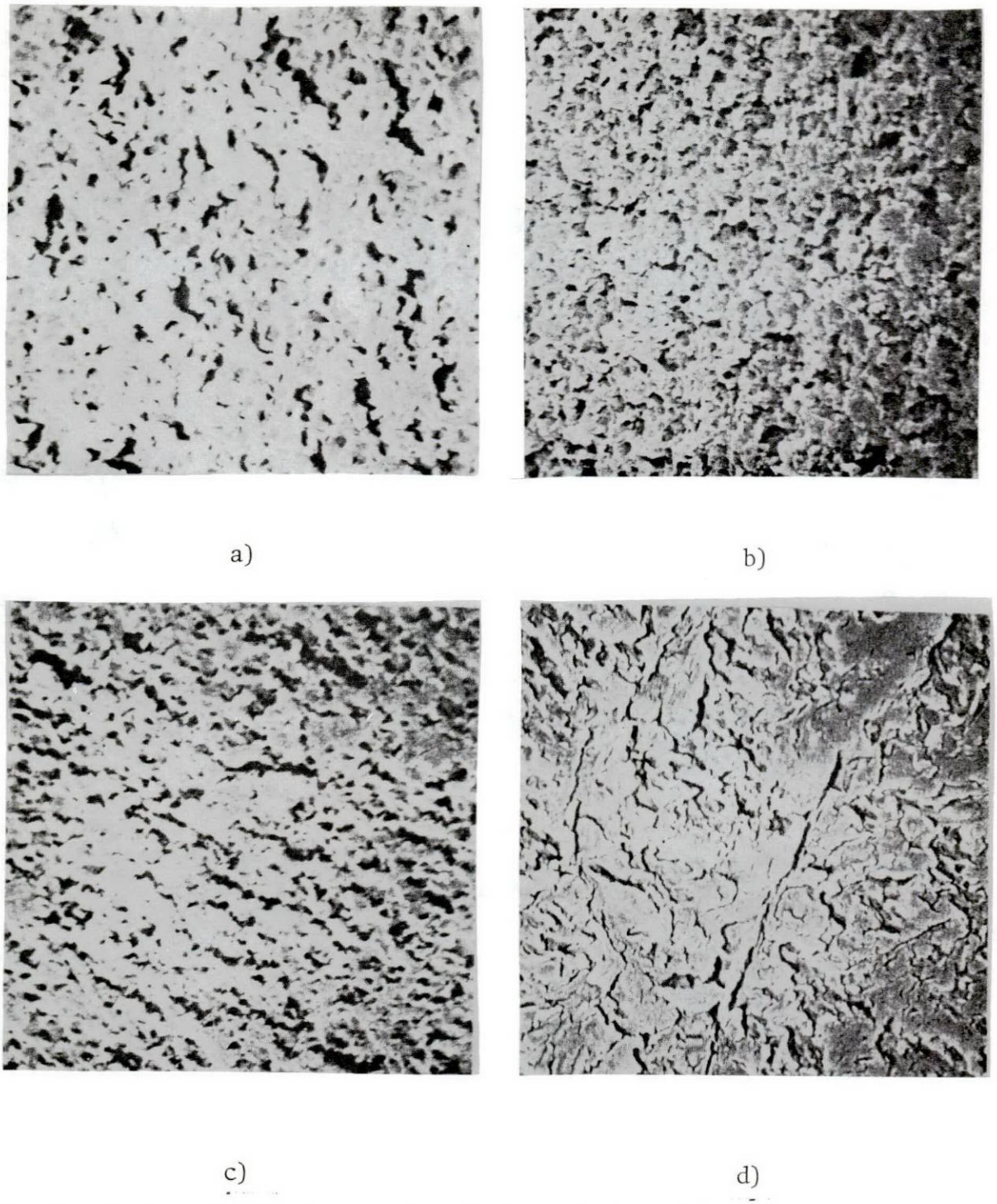
Fig. 1. SEM micrographs of the etched surface of Standard Cycolac EP 3510 plaques processed as in Tests 1 through 7, Table I. Original magnification 3500X. .

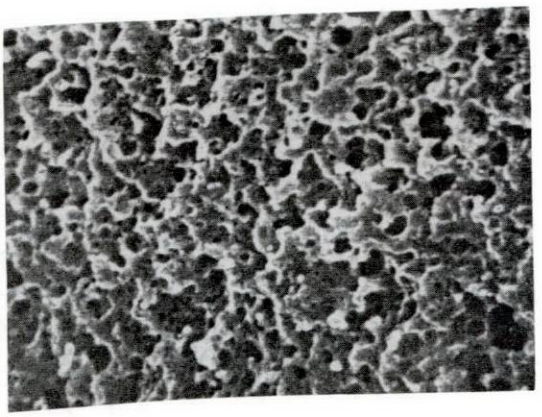
Fig. 2. SEM micrographs of the etched surface of Standard Cycolac EP 3510 plaques processed as in Tests 8 through 14, Table I. Original magnification 3500X.



a) b)

c) d)

Fig. 3. Series of SEM micrographs of the etched surface of the test piece processed as in Test 4, Table I. a) is of an area in the vicinity of Band 3; b) is of an area approximately 1/2" below the defective section; c) in the defective section; and d) on the upper lip of the defective section. Original magnification 3500X.



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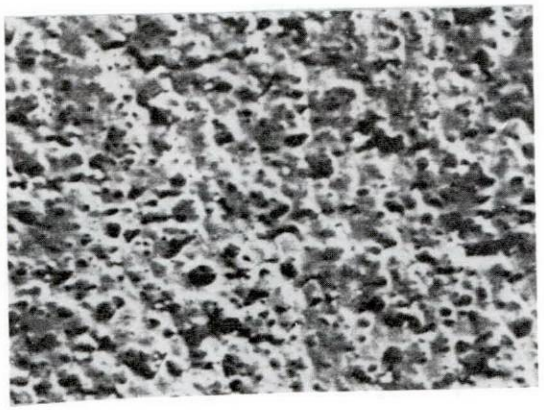

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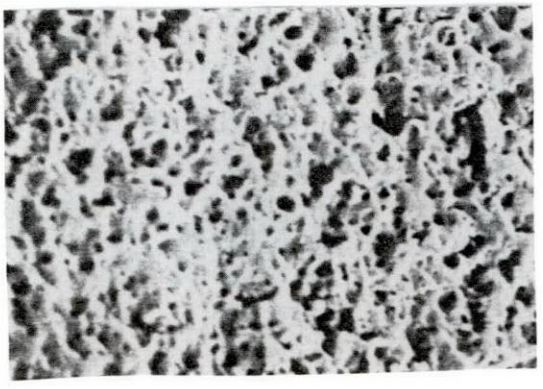
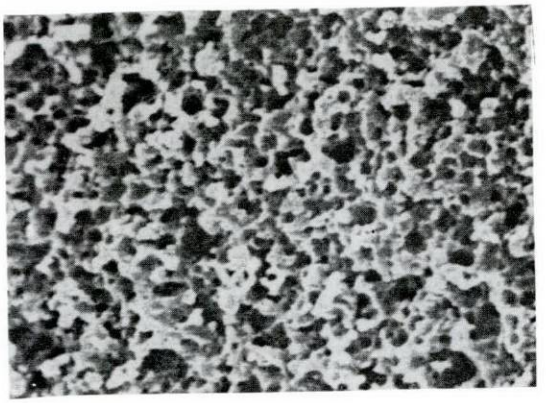


c

Fig. 4. Processing as in Test 1, Table I.



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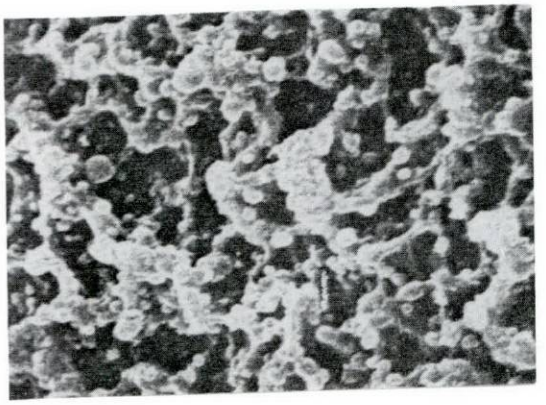

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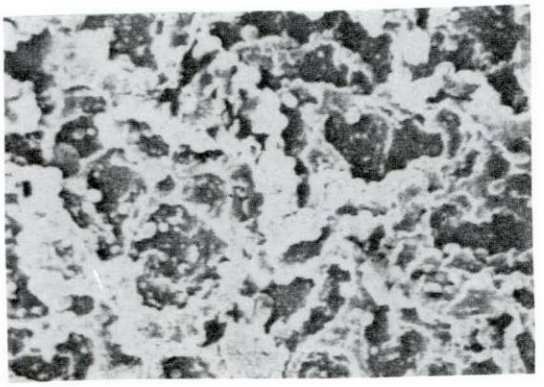

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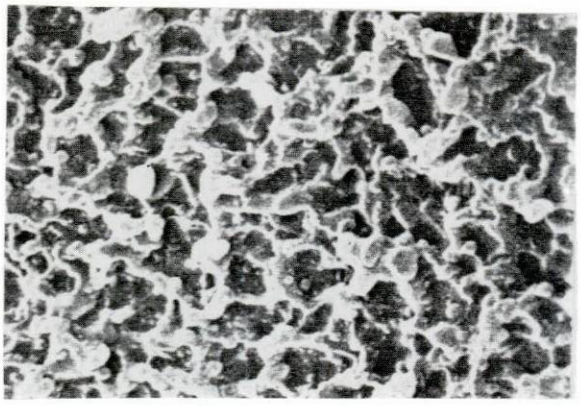
Fig. 5. Processing as in Test 3, Table I.



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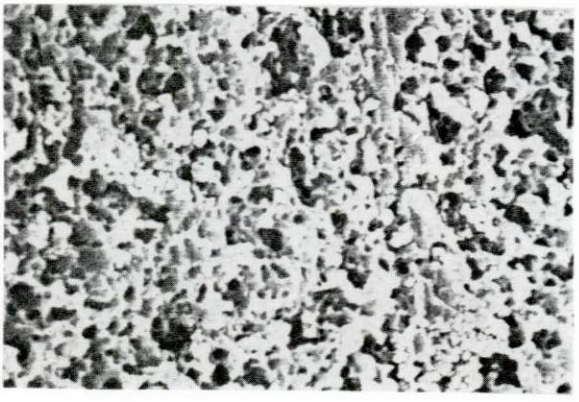

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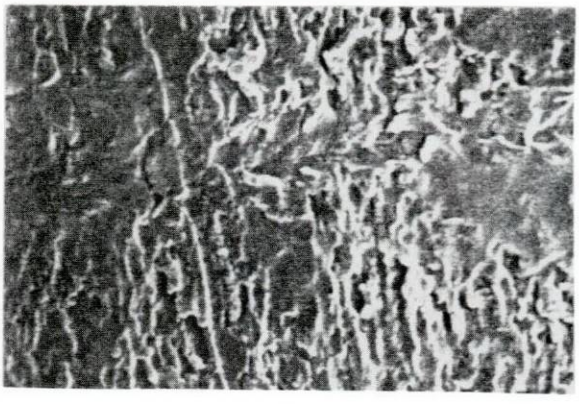

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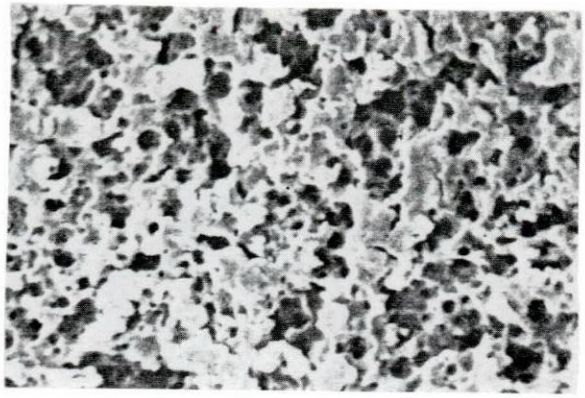
Fig. 6. Processing as in Test 4, Table I.



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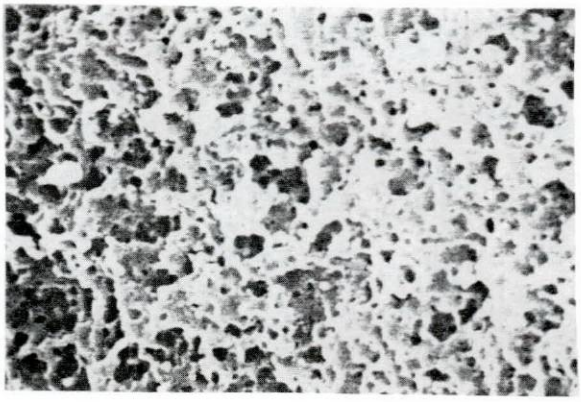

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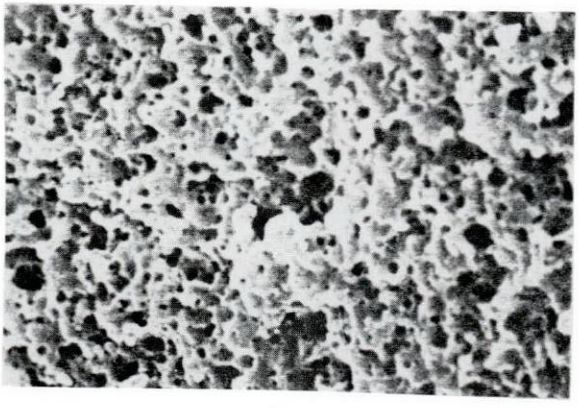

c

Fig. 7. Processing as in Test 5, Table I.

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RESEARCH SESSION M

Development of A Reactor to Eliminate Cyanide in Electroplating Effluents (AES Research Project #53)

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DEVELOPMENT OF A REACTOR TO ELIMINATE CYANIDE IN ELECTROPLATING EFFLUENTS

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ABSTRACT

AES Research Project 53 was initiated to determine the technical and economic feasibility of a new process for the treatment of cyanide wastes. This process, based on the hydrolysis of cyanide to ammonia and formic acid, was tested on sodium, zinc, cadmium, iron, nickel and copper cyanides at the batch scale. The results indicated that cyanide removals of greater than 99.9% could be achieved on all of the solutions tested at temperatures of 150°C to 250°C in less than 90 minutes. Larger scale (e.g. 1 gallon) batch and continuous-flow tests are planned to confirm the process performance and the design variables. The results of these tests, although unavailable at the time of writing, will be presented at the conference.

Background

Alkaline cyanide baths have found favour in the electroplating of metals, especially copper, zinc and cadmium, because of their relatively low cost, ease of operation, superior plating ability and excellent throwing power. The wastes generated, however, pose a severe environmental hazard and strict government regulations have been established to restrict the discharge of these wastes.

A variety of processes have been developed for the treatment of cyanide-containing wastes. Alkaline chlorination of cyanide-bearing wastes has been the accepted method of cyanide destruction for about twenty years. In this process, cyanides are first oxidized to cyanates and then to carbon dioxide and water. More recently, processes have been described using ozone[1]; a combination of a peroxide and formalin[2]; a packed-bed electrode[3]; and a catalytic conversion process[4]. Drawbacks to these methods may include high capital outlay, incomplete cyanide destruction or expensive operating costs for treatment chemicals.

In late 1977, the Ontario Research Foundation (ORF) conducted a series of tests on the hydrolysis of cyanides to ammonia and formate as a method for complete cyanide destruction without the use of expensive chemicals. Heisse and Foote[5] reported 65% conversion of cyanide to formate at up to 150°C, ∿ 93% conversion at 150°C to 200°C and essentially complete conversion at temperatures in excess of 200°C. The hydrolysis reaction proceeded as follows:

$$CN^- + 2\,H_2O \rightarrow NH_3 + HCOO^-$$

Similarly, R. M. Wick(6) reported that at temperatures in excess of 45°C, potassium cyanide is hydrolyzed to ammonia and potassium formate. Batch, semi-batch and continuous-flow pilot plant tests were performed at ORF on sodium cyanide, cadmium plate tank waste, copper cyanide plate tank waste and copper stripping solution at temperatures of from 188°C to 250°C. The minimum destruction of cyanide achieved in 60 minutes was 98.75%. In almost all of the tests at 200°C or greater, removals of greater than 99.99% were obtained in 60 minutes.

AES Research Project 53 was initiated to confirm the findings of these tests and to determine the economic viability of the process.

Batch Test Results

Batch tests were performed in a 2-litre autoclave on:

- sodium cyanide solutions
- copper plating solution
- cadmium plating solution
- nickel stripping solution
- potassium ferrocyanide solution

Tests were performed at from 150°C to 250°C on diluted samples to provide initial cyanide concentrations of from 200 mg/L to 20,000 mg/L.

The results of the 36 batch tests are summarized in Figures 1, 2, 3 and 4. Tests were performed on the test equipment to establish the total error in each test at approximately 0.1% of the feed cyanide concentration. Since the majority of tests were performed at 300 to 1,000 mg/L cyanide, this represents an overall error of 0.3 to 1.0 mg/L. For this reason, the Figures indicate removals of up to only 99.9%. It is anticipated that larger-scale testing will enable the accurate identification of the final effluent concentration. The reactions at all of the conditions tested proceeded according to first order kinetics. Sodium, zinc and cadmium cyanides were hydrolyzed at the same rate at all of the temperatures studied. One test was performed on potassium ferrocyanide at 230°C and the results obtained were the same as for sodium, cadmium and zinc cyanides. The rates of hydrolysis for nickel and copper cyanides were substantially lower at all of the temperatures studied (see Figures 3 and 4) than those achieved for sodium, cadmium and zinc cyanides. Since the reactions proceeded according to first order kinetics, a semi-logarithmic plot of the reaction rate constant versus the inverse of the reaction temperature yields a straight line, as shown in Figure 5. The differences in the rates of hydrolysis for the cyanides can be clearly seen in this Figure. In order to achieve removals of greater than 99.9% in cyanide in 60 minutes or less, the operating temperatures required are summarized below:

- for sodium, cadmium, zinc and ferricyanides - 160°C
- for nickel cyanides - 200°C
- for copper cyanides - 240°C

The same performance can be achieved at lower temperatures with longer residence times.

The treated nickel strip solution contained a small amount of red-brown precipitate which was analyzed via semi-quantitative X-ray spectroscopy. The results, presented in Table 1, indicate that the solids are largely comprised of iron and nickel.

There was no evidence in the batch tests of any refractory metal-cyanide complexes in the effluents.

Future Work

The initial batch tests described in the present paper were conducted to establish the optimum process conditions for the final series of tests, as described below:

- larger-volume (1 gallon) batch tests on concentrated (i.e. 1% to 7% cyanide) cyanide solutions
- continuous-flow pilot-plant tests on dilute (i.e. 200 mg/L to 5,000 mg/L) cyanide solutions

The results of these final tests will be presented at the conference.

Process Description

The process involves simply heating the cyanide-containing solution to the required temperature (i.e. 150°C to 250°C) and maintaining the solution at that temperature for a sufficient length of time to ensure that the hydrolysis is complete. Since the hydrolysis is performed above the boiling point of water, the solution must be contained under pressure to maintain an aqueous phase. There is no process limitation with respect to the cyanide concentration which can be treated. No chemicals are added to the solution.

The energy required to heat the solution to the required temperature represents the major operating cost for the process. The hydrolysis process can be operated in a continuous or batch manner. In general, the continuous system will involve a higher capital investment than a batch system of similar capacity. Continuous systems, employing a counter-current heat exchange of the hot effluent with the cold influent, will, however, be more energy efficient and, therefore, will result in lower operating costs. Low-volume, high-strength cyanide wastes would, therefore, be most economically treated in a batch manner whereas high-volume, low-strength wastes would be most economically treated in a continuous-flow manner.

The batch system would involve an electrically heated tank designed for operation at from 200 to 500 psig. The waste is transferred into and out of the vessel at ambient conditions.

The continuous-flow system would be comprised of a pump to deliver the solution at 200 to 500 psig, a small heat exchanger, an electrically heated pipe (i.e. reactor) and a pressure control valve (see Figure 6).

Process Economics

A literature review was undertaken to establish the approximate costs of alternative processes used for cyanide waste disposal. All of the costs, including all capital and operating costs, were standardized (e.g. operator labour at $12.00 per hour) and the treatment costs developed for 1980. The total treatment costs for alkaline chlorination, electrochlorination, ozone, ultra-violet light and ozone, hydrogen peroxide, reverse osmosis and evaporation, etc., are all of the same order of magnitude, as outlined below:

- For waste streams containing less than 100 mg/L cyanide in greater than 40,000 gallons per day, the total cost is ∿ $25.00 per kilogram cyanide.
- For waste streams containing from 100 to 1,000 mg/L cyanide in flowrates of ∿ 3,000 gallons per day, the total cost is ∿ $15.00 per kilogram cyanide.
- For waste streams containing greater than 50,000 mg/L cyanide in less than 1,000 gallons per day, the total cost is ∿ $5.00 per kilogram cyanide.

Since the major cost item for the hydrolysis process is for energy, a preliminary assessment of the economical viability of the system can be determined from these costs, as outlined below:

Concentration of Cyanide in the Waste	Total Energy Cost Based on $5.00/$10^6$ Btu (dollars/kilogram cyanide)	
	Batch System with No Energy Recovery	Continuous System with Heat Exchange of the Hot Effluent and Cold Influent
30 mg/L	$150.00	$40.00
300 mg/L	15.00	4.00
600 mg/L	7.50	2.00
3,000 mg/L	1.50	0.50
10,000 mg/L	0.45	0.15
100,000 mg/L	0.04	0.01

For waste streams containing less than about 100 mg/L cyanide, conventional processes would be the most economical. As the cyanide concentration increases, the hydrolysis process cost advantage over alternative processes increases. Two examples, as outlined below, clarify the comparison of process costs.

Example 1

+ Design Basis: 3,000 gallons per day of waste containing 300 mg/L cyanide.

+ Conventional Systems: The total cost would be $50.00/day.

+ Hydrolysis System: This would be a continuous-flow system. The heat exchanger could be a tube-in-tube unit comprised of 6.35 mm (0.25 inch) internal pipe and 12.70 mm (0.5 inch) outside pipe. The reactor would be an ∿ 400 mm (16 inch) diameter pipe of about 2.4 meters (∿ 8 feet) in length. Based on all wetted process parts of 316 SS, the total installed cost would be $15,000.00 to $20,000.00. The total disposal cost would, therefore, be $18.00/day.

Example 2

+ Design Basis: 200 gallons per day of waste containing 70,000 mg/L cyanide.

+ Conventional Systems: The total cost would be $270.00/day.

+ Hydrolysis System: This would be a batch system consisting of one tank of about 0.6 meters (∿ 2 feet) in diameter by about 1.5 meters (∿ 5 feet) high to process two batches per day. The total installed cost of the process, at about $10,000.00, and the energy costs, at ∿ $3.50 per day, represent relatively minor costs in comparison to the operator labour. Assuming approximately 1-1/2 man-hours per day to load and unload the vessel (e.g. @ $12.00 per hour), the total cost would be ∿ $25.00/day.

Summary

Preliminary batch tests have confirmed the technical feasibility of the hydrolysis process for the disposal of cyanide wastes. For waste streams containing greater than 100 mg/L cyanide, the hydrolysis system would appear to offer economic advantages over conventional cyanide disposal processes. The process, whether batch or continuous, would be simple, easy to operate and require very little plant space.

It is expected that details of the final batch and continuous-flow tests will be presented at the conference and that the final process costs will be available.

References

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(3) Chen, D. T., and Eckert, B., "Destruction of Cyanide Wastes with a Packed Bed Electrode". Plating and Surface Finishing 63 (10), 38 (1976).

(4) Jola, M., "Destruction of Cyanides by the Cyan-Cat Process". Plating and Surface Finishing 63 (9), 42 (1976).

(5) Heise, G. W., and Foote, H. E., "The Production of Ammonia and Formates from Cyanides, Ferrocyanides, and Cyanized Briquets". The Journal of Industrial and Engineering Chemistry 12 (4), 331 (1920).

(6) Wick, R. M., "The Decomposition of Cyanide Solutions". Quarterly Review of the American Electroplaters' Society 19 (10), 20 (1933).

TABLE 1

Analysis of Solids in Nickel Strip Solution
After Hydrolysis

Element	Percent of Solids by Weight
Sodium	0.19
Magnesium	-
Aluminum	0.28
Silicon	0.08
Phosphorus	0.06
Sulphur	0.17
Chlorine	0.02
Potassium	Trace
Calcium	0.16
Titanium	0.86
Vanadium	-
Chromium	0.17
Manganese	0.13
Iron	High
Cobalt	0.46
Nickel	High
Copper	0.32
Zinc	0.23
Tin	Trace
Lead	Trace

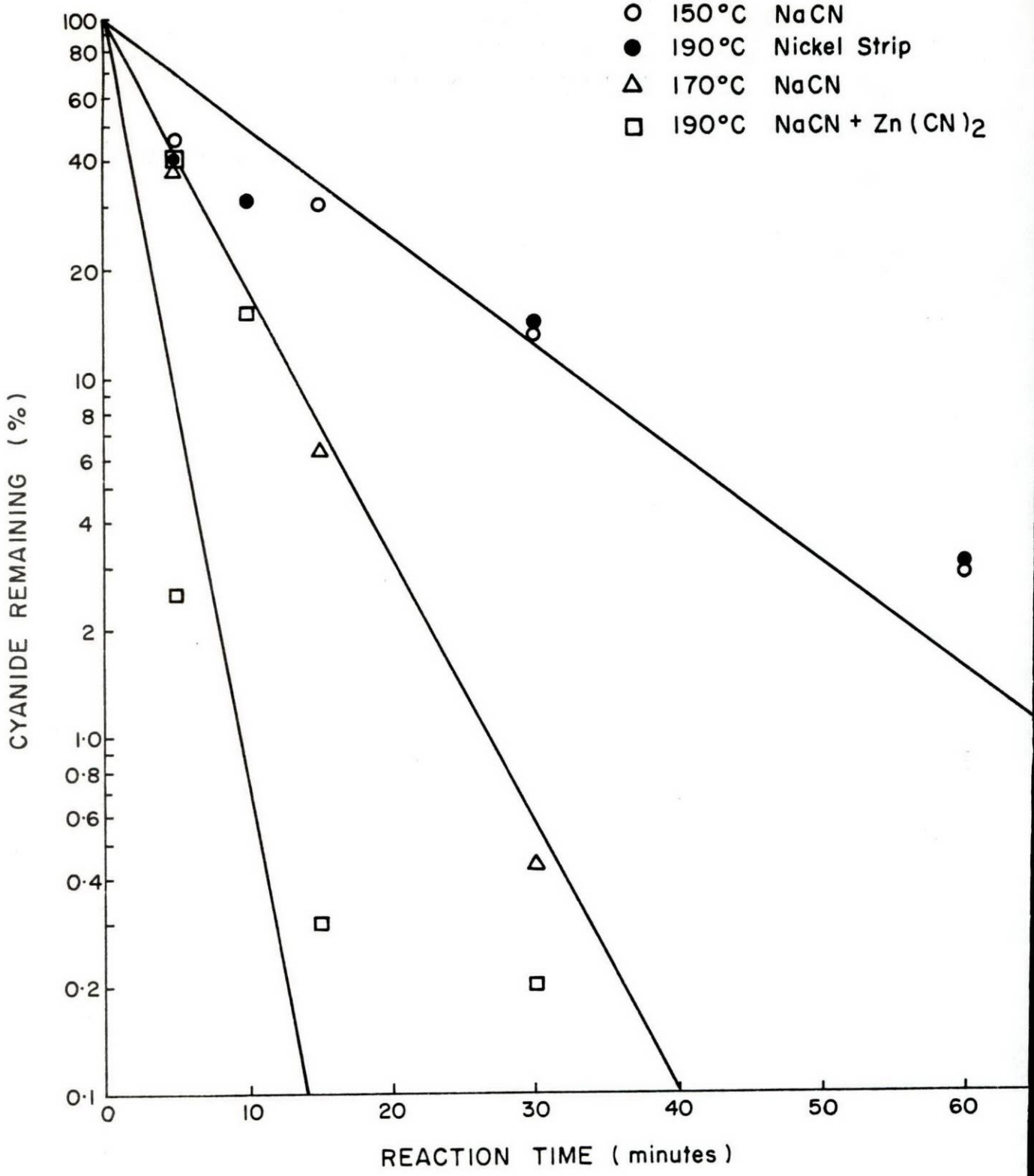

FIGURE 1. CYANIDE HYDROLYSIS TEST RESULTS AT 150°C to 190°C

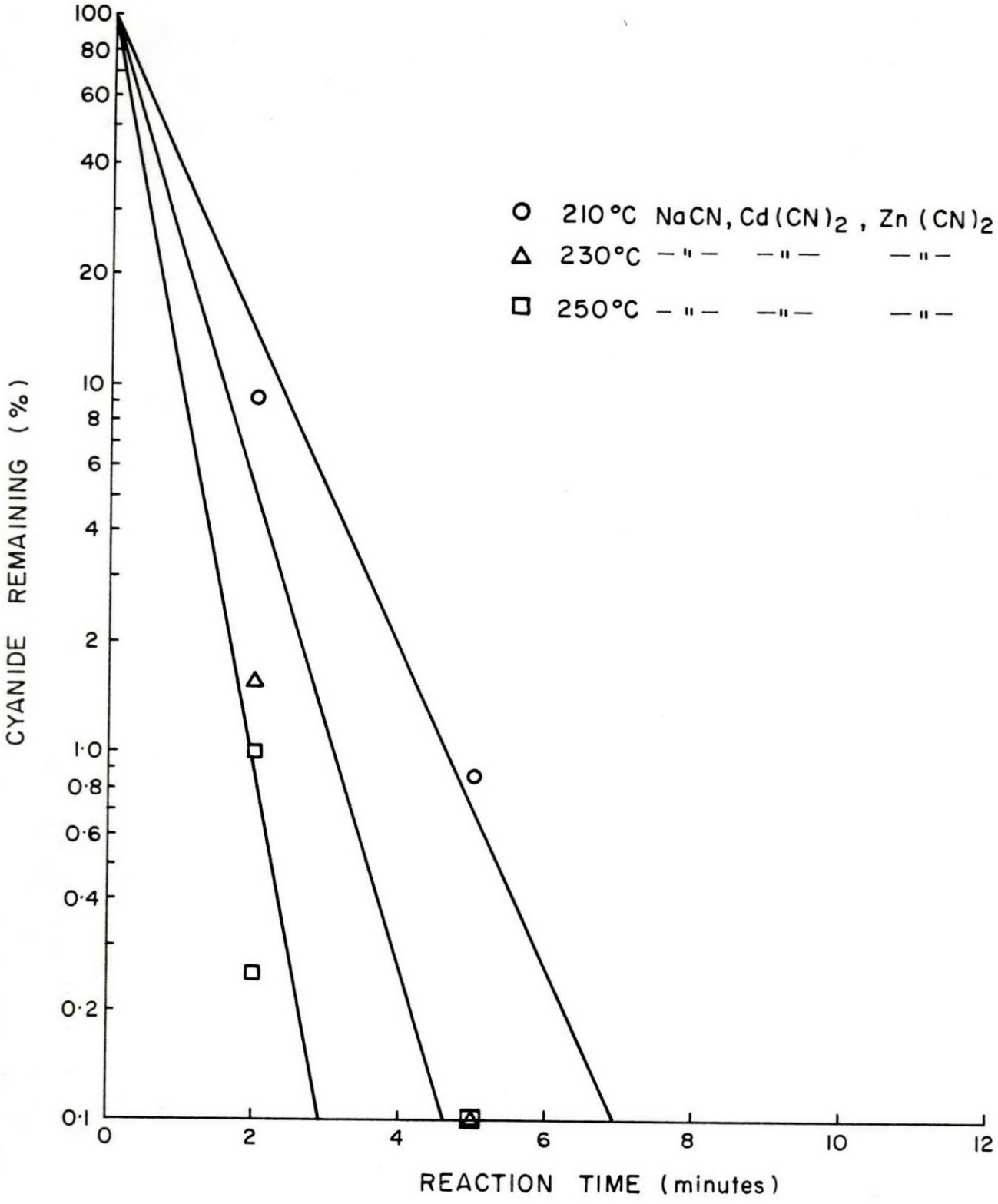

FIGURE 2. CYANIDE HYDROLYSIS TEST RESULTS AT 210°, 230° & 250°C.
($NaCN$, $Cd(CN)_2$ and $Zn(CN)_2$)

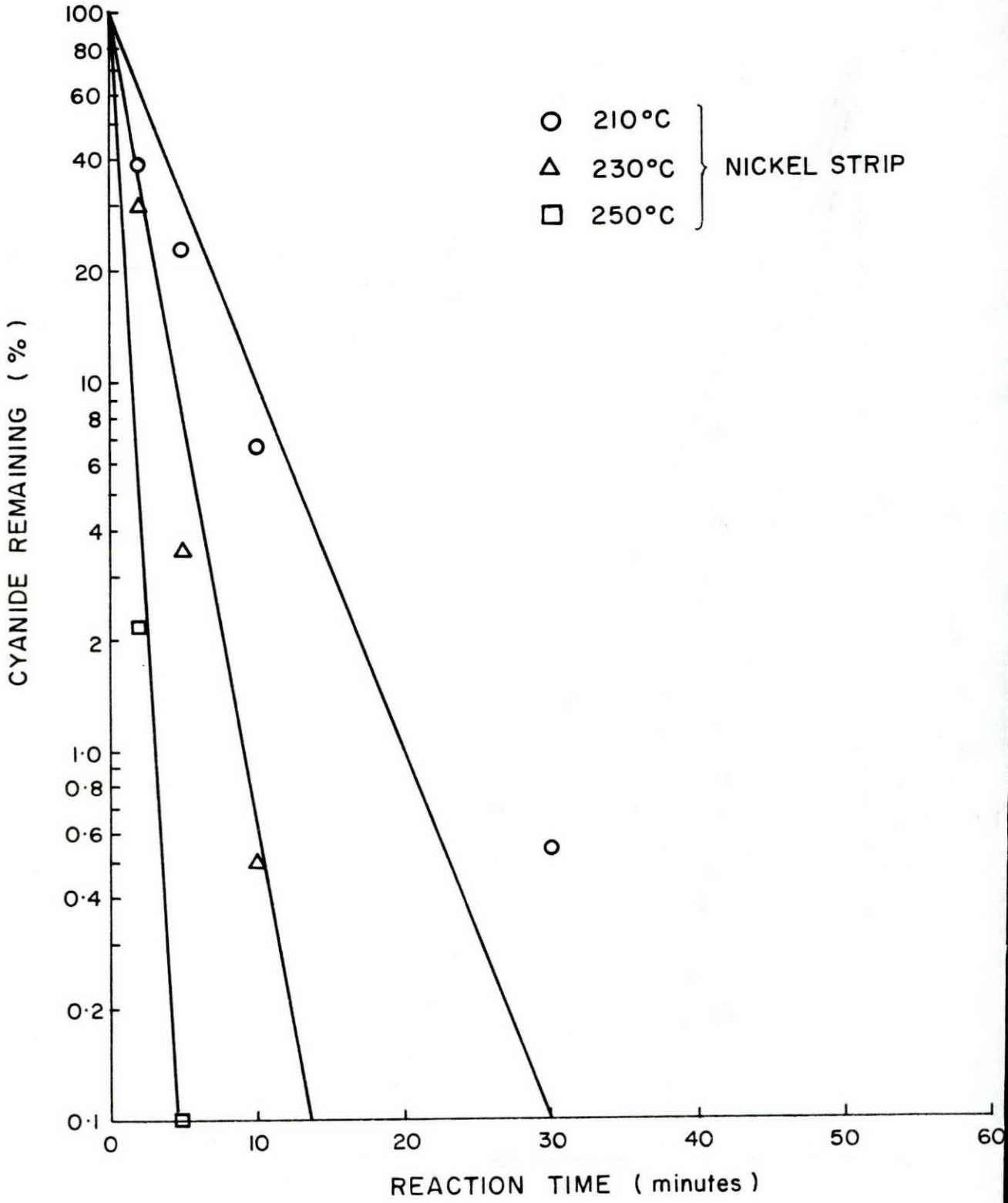

FIGURE 3. CYANIDE HYDROLYSIS TEST RESULTS AT 210°, 230° & 250°
(NICKEL STRIP)

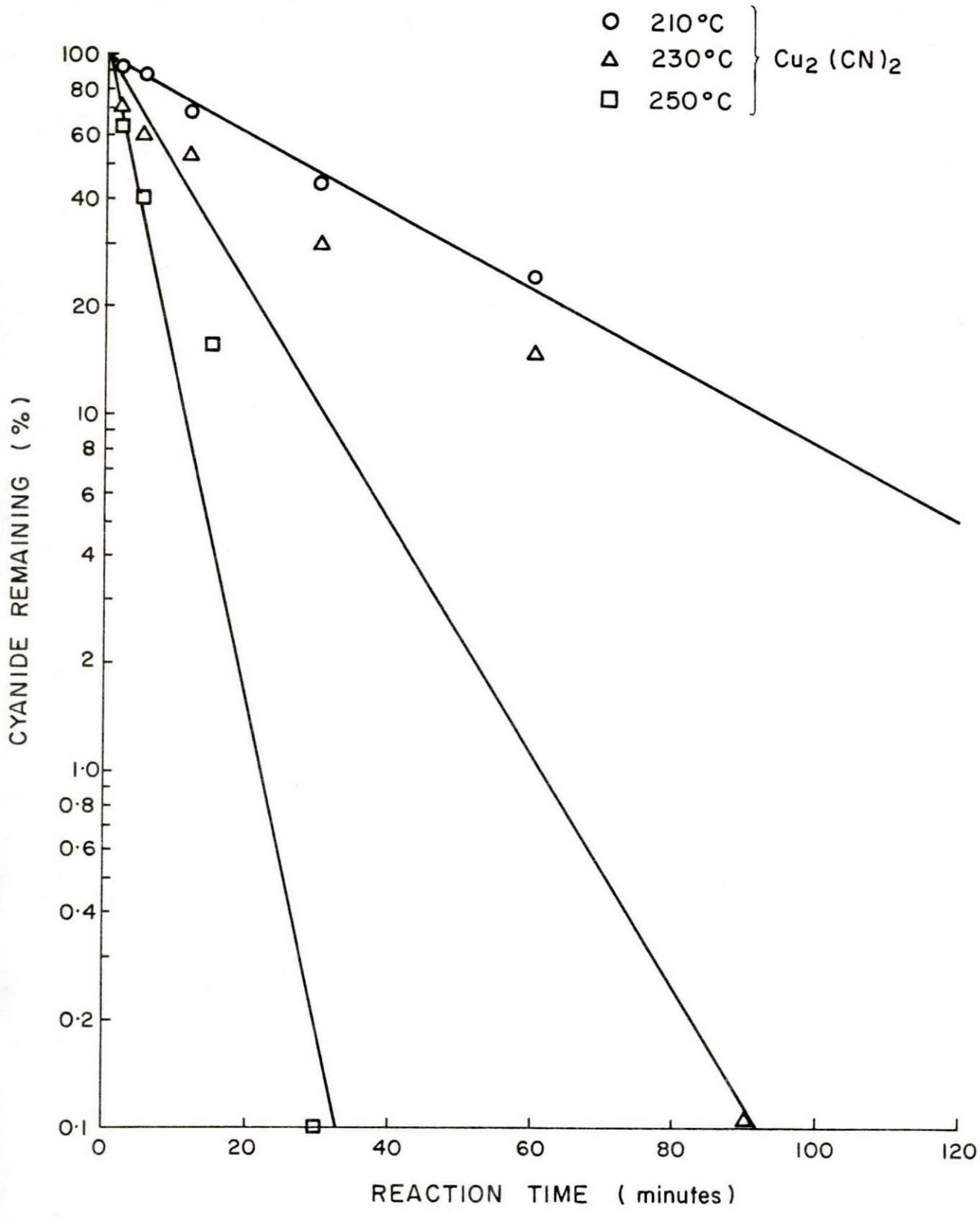

FIGURE 4: CYANIDE HYDROLYSIS TEST RESULTS AT 210°, 230° & 250°C ($Cu_2(CN)_2$)

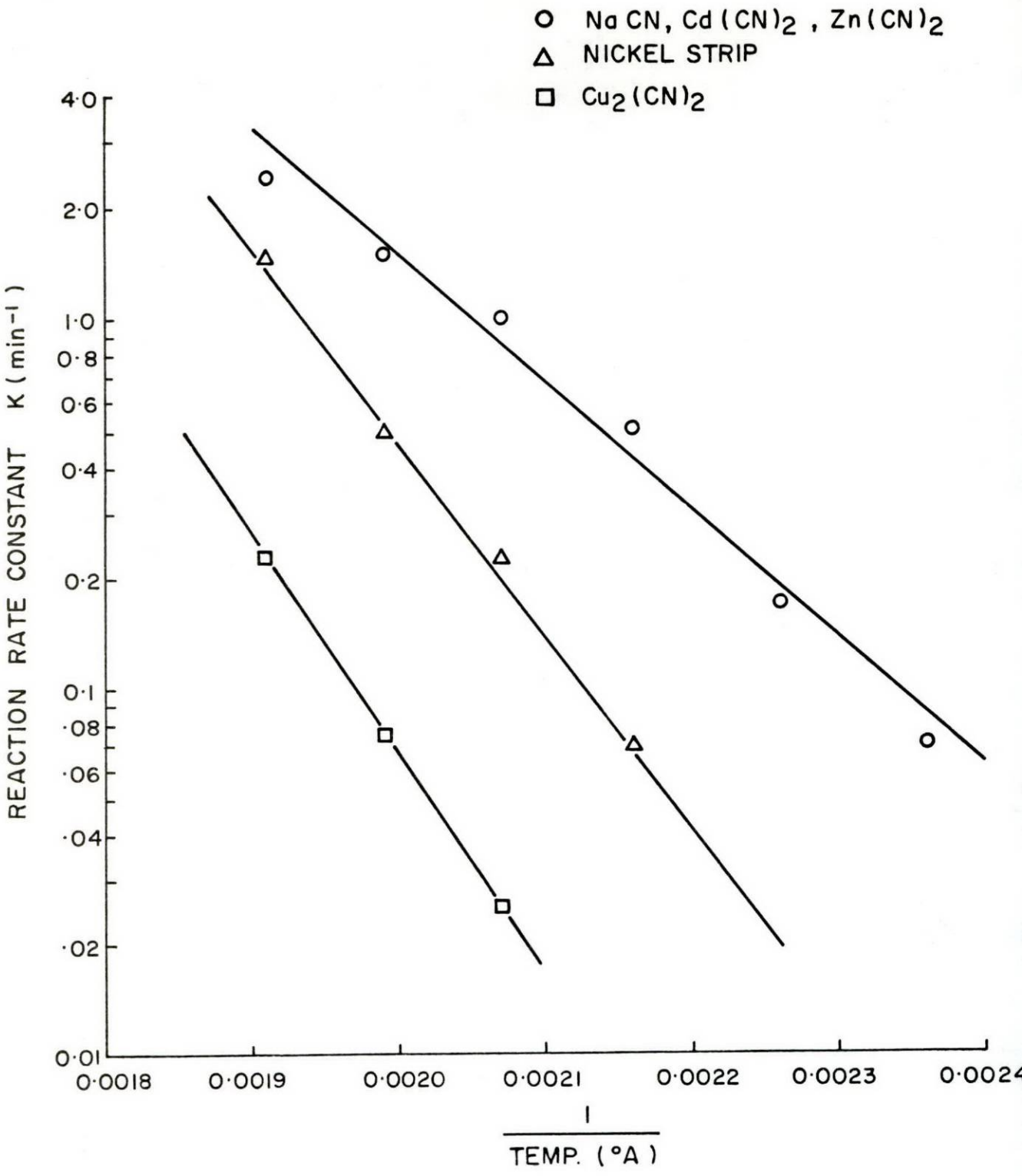

FIGURE 5. EFFECT OF TEMPERATURE ON REACTION RATE CONSTANT FOR CYANIDE HYDROLYSIS.

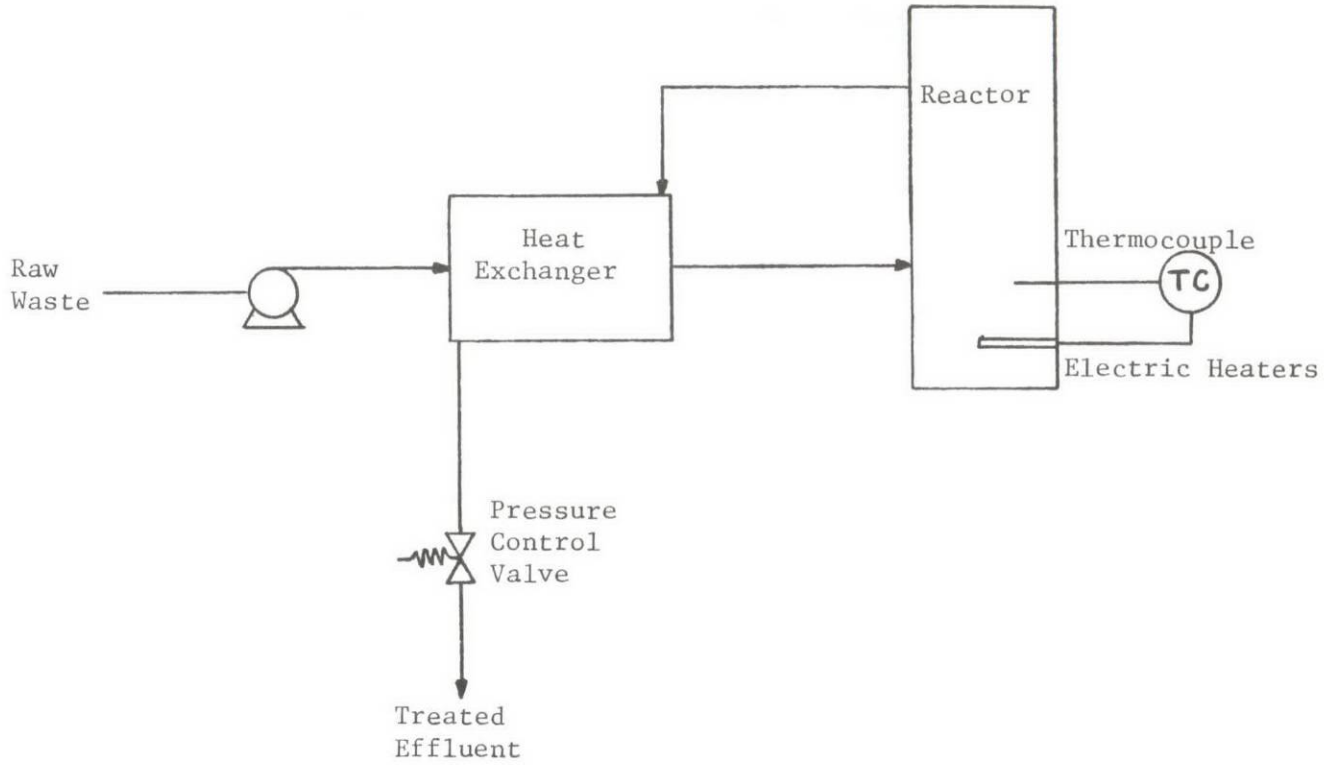

FIGURE 6 - Continuous Process Flowsheet

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ORGANIC FINISHING SESSION N

Emerging Technologies in the Chemical Coatings Industry

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EMERGING TECHNOLOGIES IN THE CHEMICAL COATINGS INDUSTRY

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ABSTRACT

The use of organic solvents in organic coatings must be reduced significantly over the next two years. Organic solvent is that part of the chemical coating that volatilizes into the atmosphere, thus contributing to the air pollution that we hear so much about today. In addition to contributing to air pollution, the excessive use of organic solvent is costly to the coatings users and a waste of petrochemicals. Replacing conventional low solids solvent-borne coatings with HIGHER SOLIDS LIQUID, WATER-BORNE and DRY POWDER coatings is the challenge facing the manufacturers and users of organic coatings.

Introduction

The chemical coatings industry is currently undergoing the most dramatic technological change in its history. It would be no exaggeration to view this change as a "mandated technical revolution". Mandated by whom? Certainly, of significance, are the legislative controls designed to clean our air through the reduction of hydrocarbon emissions. Organic solvent is that part of a chemical coating that volatilizes into the atmosphere, thus contributing to air pollution. Of increasing importance, is the increased cost and potential lack of availability of organic solvents. In an attempt to satisfy the environmentalists, lessen the impact of rising solvent costs on the applied cost of organic finishes and reduce the potential risk of the lack of availability of organic solvents, the challenge to our industry is to REDUCE, REPLACE or REMOVE organic solvents as a chemical coatings carrier. Towards this end, we see three technologies emerging as replacements for conventional, low solids, organic solvent-borne coatings. These technologies are:

1. HIGHER SOLIDS solvent-borne coatings - REDUCE the organic solvent content.

2. WATER-BORNE coatings - REPLACE organic solvents with water.

3. DRY POWDER coatings - REMOVE organic solvent.

A description of these technologies and the advantages and disadvantages when compared to conventional solids organic solvent-borne coatings is the subject of this presentation.

First, let us define "conventional solids solvent-borne coatings". Over 70% of the organic coatings used today are organic solvent-borne. They are supplied to the user at 40% to 50% solids and further reduced by the user to 25% to 30% solids for application. For purposes of this presentation, we will consider volume solids rather than weight solids. It is the more meaningful measure when comparing economics. Solids are the non-volatile, or actual film forming portions of the coating. The remainder is the volatile, or non-film forming portion of the coating commonly referred to as reducers, solvent or diluent. The primary function of the solvent is to reduce the viscosity of the coating to a point where it is fluid enough to be circulated to and atomized by the application equipment. In reality, it acts as the fluid which carries the film forming paint solids to the object being coated and then, volitalizes off as a waste or by product of the painting operation. Let's dwell a moment on the word WASTE. After the solvent performs the function of carrying the paint solids to the part being painted, it serves no other purpose and must be disposed of as a waste. In most of the conventional coatings used today, 70%-75% of the liquid paint applied is solvent waste. This solvent waste is what the Environmental Protection Agency (E.P.A.) refers to as V.O.C., or the volatile organic compounds that contribute to air pollution. The E.P.A. is mandating that this 70%-75% organic solvent content be reduced to 35%-45% as the coating is applied or that any solvents used beyond that level be incinerated or mechanically captured before they enter the atmosphere. The latter two alternatives are options, but costly ones when compared to REDUCING, REPLACING, or REMOVING organic solvents from the coating. The cost of the solvent alone has recently become a significant factor. As little as ten years ago, when common solvents were $.25 per gallon, the cost of the waste (solvent) to coat one million square feet of surface at one mil film thickness was around $470.00, but today, with solvent costs in excess of $1.35 per gallon, the cost of the waste is in excess of $2,500.00 for every million square feet coated. Therefore, it makes good economic sense, as well as environmental sense, to REDUCE, REPLACE or REMOVE organic solvents wherever and whenever possible.

HIGHER SOLIDS, obtained by simply reducing the organic solvent content of existing coatings, would appear to be the most expedient solution. Just remove solvent and apply the coating at higher viscosity. Unfortunately, most of the conventional coatings in use today have a viscosity profile that prohibits the removal of any significant amount of solvent without rendering the coatings too viscous for application. This necessitated the development of new resins that have high solids, low viscosity profiles. Not an easy task, but, fortunately, research in this technology began several years ago; today there are coatings that can be applied at 45%-55% volume solids on conventional application equipment. This still falls short of the E.P.A. guidelines for many industries but does result in a considerable reduction in the emissions of volatile organic compound. For example, converting from a coating applied at 25% solids to one applied at 50% solids will reduce the emission of volatile organic compounds by 67%. There is also a favorable economic impact. Using the

example of coating one million square feet at one mil film thickness, we would reduce solvent consumption from 1875 gallons, with a 25% solids coating to 625 gallons with a 50% solids coating. A savings of 1,250 gallons of solvent at over $1.35 per gallon.

To get back to the E.P.A. guidelines for a moment. Research is continuing on the development of higher solids - lower viscosity coatings. We feel confident that we will develop coatings that will apply at between 60% and 70% solids on conventional application equipment. In the meantime, however, the equipment manufacturers have developed new equipment that will apply higher viscosities. We know from experience that today's higher solids coatings can be applied at or above E.P.A. compliance levels with this new equipment.

With all of these advantages, then, why isn't everyone converting to higher solids? Many are, but certainly not a majority. Many manufacturers are hesitant to make any change until they can be assured that the change will comply to the appropriate clean air regulations of their state or location within their state. Other cannot afford the capital expenditure for application equipment necessary to gain clean air compliance. Higher solids is not necessarily the best option for everyone; there are limitations and disadvantages.

Higher solids coatings, as we know them today, require heat for curing; they do not air dry. Film thickness control can be a problem if the automatic application equipment and/or conveyor speed is not regulated. High solids coatings will coat more square feet of surface per given unit of paint. Controlling film thickness on complex parts, where manual or hand spray equipment is used, can be difficult, if not impossible. Higher solids coatings have not been used successfully for dipping or flow coating. Higher solids coatings remain tacky until they are partially cured. This means that painted parts are subject to dirt pick-up until they are in the curing oven. The overspray also remains tacky, which may require additional booth clean-up, or a change in the clean-up procedures.

HIGHER SOLIDS coatings are not always the best option for all applications, but it is safe to say that they are probably the best choice to replace conventional solvent-borne coatings where the application is automatic spray and heat is used for curing.

WATER-BORNE coatings, where water REPLACES organic solvents, have been commercial for over two decades. Water-borne coatings can be broadly described as liquid coatings whose volatile portion is predominantly water. Most water-borne coatings do contain some organic solvent. In most instances, organic solvent makes up 20% to 30% of the volatile portion, with water making up the balance. As a result, most water-borne coatings will comply with clean air standards, while, at the same time, providing the obvious economic advantage of REPLACING costly organic solvents with water. Qualities are available that will satisfy most end use performance requirements. The two major drawbacks of water-borne coatings are:

1. The ability to control the release of the water from the film. In situations where air drying is required, it is essential to provide an atmosphere that will permit rapid evaporation of water. For example, in an atmosphere of 60° to 65°F, and a relative humidity of 90%, water will not evaporate from the film and the film will remain wet. Using the one million square feet of surface to be coated at one mil film thickness, provisions would have to be made to evaporate between 1000 and 1500 gallons of water if you use a 30% solids water-borne coating. Mother Nature will not always, or at least not consistantly, provide such an atmosphere. With baked, or heat-cured water-borne coatings, the problem can be getting the water out in the proper time intervals. At 212°F, the water will boil, resulting in blistering or spattering. Therefore, it is essential to dehydrate the film before actual curing. This can be done by zoning the oven so that the first stage will dehydrate the film. This can be difficult where heavy film thicknesses are required.

2. Because water is so highly conductive, it can be difficult to use electrostatically without shorting out the electrostatic equipment. This can be remedied by isolating the entire painting system, including circulation lines. Some advances have been made in equipment design to alleviate this problem, but commercial use at this time is limited.

In spite of these drawbacks, water-borne coatings have found a place in the coatings industry, and will continue to gain market share at the expense of conventional solvent-borne coatings. They are being successfully employed in dip and flow-coat operations as primers and in some instances topcoats. The construction and farm implement industries are using water-borne coatings for dipping and flowcoating component parts and hand spraying assembled units. The beer and beverage can industry is using water-borne spray applied coatings for lining the interior of cans.

A discussion of water-borne coatings would not be complete if we did not touch on ELECTROCOAT. This is a process whereby an organic coating is electroplated onto a part from a water bath. There are two types of electrocoat systems; anodic and cathodic. In the anodic process, the part to be coated is the anode. In the cathodic process, the part to be coated is the cathode. Both processes involve dipping the part to be coated in a liquid water paint bath and applying voltage which results in the paint solids being plated out on the part. The important advantages of this process are:

1. There is virtually no waste. The coating on a part is over 95% solids as it exits the dip tank. Very little water is retained in the film after the plating process.

2. It is possible to achieve a uniform film on all surfaces, regardless of configuration.

3. Electrocoat systems are completely automated.

Electrocoat technology has been commercial for over twenty years, and has proven itself to be one of the most economical coating processes because of its high efficiency and automation. It is also accepted by all environmental agencies as a coating process that meets all existing and future clean air guidelines. The most recent technical advances in electrocoating have been in the cathodic technology. The cathodic process does result in better overall film performance from the standpoint of corrosion. There are several theories as to why better performance results, but suffice to say that in a production situation, where the metal and metal pretreatment are usually less than laboratory quality, cathodic electrocoat will out-perform anodic electrocoat in corrosion protection. As with all coating processes, electrocoat too, has certain limitations. Because it is a dip process, a separate tank is required for each color. Therefore, in situations where more than one or two colors are required, electrocoat is probably not the best choice. In general, electrocoat requires a high bake for curing, however, there has been recent progress in developing an air dry and forced dry anodic electrocoat. There is one forced dry electrocoat tank in operation, and several companies are testing the product. Initial capital expenditure for electrocoat equipment can be higher than equipment for other coating processes but is usually justified through labor savings. Electrocoat will continue to be one of the fastest growing water-borne technologies.

DRY POWDER COATING technology is the technology where all organic solvent is REMOVED from the coating. The coating is applied in a dry powder state. The carrier or vehicle that transports the powder from the application equipment to the part to be coated is air. Air is certainly less expensive than either organic solvent or water, is abundant and does not have to be disposed of. Powder is the chemical coatings industry's answer to a cleaner environment and the necessary conservation of petrochemicals. In addition to these benefits, powder coatings offer better performance properties than their liquid solvent-borne or water-borne counterparts. One of the reasons for the higher performance levels is the fact that dry powder formulations can emply higher molecular weight resin backbones. In general, higher molecular weight provides higher performance levels. With higher molecular weight, however, we usually find significantly higher viscosities. Many are so high in viscosity that they will not lend themselves to liquid coating formulations because they are too viscous to apply by methods available to us today. With powder being a solid, its application is not adversely affected by high viscosity. As stated previously, powder is transported by air to the

product being coated in what resembles a dust cloud. The paint particles are electrically charged and cling to the part in a dusty form until they reach the curing oven. At that point, the particles melt, flow and fuse together as a continuous paint film. This brings us to the first limiting factor of dry powder coatings as compared to liquid coatings. All dry powder coating must be heat cured at temperatures ranging from 250°F to 400°F. Another limiting factor is that liquid application equipment cannot be modified to handle powder. Therefore, converting from a conventional liquid coating to dry powder will require a capital expenditure. In situations where new production lines are being installed, whether for purposes of expansion or obsolescence of existing equipment, powder must be a consideration. The total system economics of powder is competitive with other technologies. It is safe to say that coating efficiency with powder is over 95% because all overspray is recovered, recirculated and reused. The ability to recover, recirculate and reuse powder overspray can limit the number of colors used in a single recovery system and/or application system, but equipment manufacturers are aware of the problem and are making progress toward minimizing it.

Conclusion

It is our opinion that the three technologies covered, HIGHER SOLIDS liquid coatings, WATER-BORNE coatings and DRY POWDER coatings will become the dominant technologies of the future. In 1978, according to our marketing research, 75% of all coatings supplied were based on low solids, solvent-borne technology. We predict, that by 1988, this will drop to below 20%, with HIGHER SOLIDS, WATER-BORNE and DRY POWDER making up the majority of the difference. This revolution is, and will continue to be, mandated by our need for a cleaner environment; the necessity of conserving petrochemicals and most important, the cost savings associated with the REDUCTION, REPLACEMENT and REMOVAL of organic solvents from chemical coatings.

N-2

ORGANIC FINISHING SESSION N

Everything You Have Always Wanted to Know About Powder Coating, But Were Afraid to Ask!

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EVERYTHING YOU HAVE ALWAYS WANTED TO KNOW ABOUT POWDER COATING, BUT WERE AFRAID TO ASK!

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There are many questions frequently asked about powder coating. A few of them have to do with the very basics of the subject and it is surprising how many people are not familiar with even these basics. Most of these people come from the upper management areas.

QUESTION: What is powder coating?
ANSWER: Powder coating is the electrostatic spraying of your clean metal part or substrate with a dry powdery material having the consistancy very much like that of flour. The part is then introduced to a curing oven where the powder material melts, then cures. This covers the surface with a smooth continuous coating designed to protect, enhance, and further exemplify the beauty of your finished product.

Q. What colors are available?
A. Other than the normal spectrum of colors found in a rainbow, there are metallics, veined colors, spatter effects, dead flats, and even one that when cured looks like denim, and is called "blue denim".

Q. Is powder coating expensive?
A. Compared with what? If it is compared on an "apples to apples" basis with liquid coatings from the same family, it is not. The important thing is, do you need the kind of a finish powder will give you, or don't you care how long or how well the finish lasts.

Q. Isn't a powder finishing area dusty?
A. No. The reclaim systems used with powder systems are designed to keep a slightly negative pressure in your finishing enclosure, thereby removing any accumulations of excess powder and/or dust to the reclaim containers. These accumulations are then recycled and eventually sprayed onto your substrates, thereby giving about 95% usage of each pound of powder purchased.

Q. Is powder dangerous?
A. I wouldn't suggest that you sprinkle it on an ice cream sundae, or use it to color a milkshake. A lighted match dropped onto a pile of powder will not cause an explosion or a fire. The powder will simply melt and form a solid continuous cover for the powder laying underneath it. While we are discussing dangers, I would like to mention that a few people have openly talked about powder explosions. High concentrations of dust can cause problems if not removed from the confines of an enclosure. In my home state of Minnesota we have had grain terminal explosions. I have noticed that now during the rebuilding process, they are installing high efficiency cyclones. These are designed to remove the dust problem.

I have heard people condemn powder and expound on other coatings, with equal vigor. I have also heard powder people condemn wet coatings and high volatile solvents. Equipment people have designed safety into both wet and powder systems. When the safety systems are "overridden" anything can happen. When you smoke while spraying lacquer you help make this happen.

Q. Is it difficult to educate employees to use a powder system?
A. No. Normally two or three hours is time enough. Remember, if they do make a mistake, take the part off of the line before it gets into the oven, blow the powder off within the confines of the booth, rehang, and try it again. No sags or drips, and you get to reuse the powder.

Q. Our company uses seven colors. Won't this mean we will need seven booths?
A. No. Depending upon your frequency of change, one or two booths should be enough. Color change can be made "on the fly" or by leaving a wide, empty spot on your conveyor line. We know of two companies who have conveyor line speeds of from 17 to 20 F.P.M. One sprays seven colors, and the other sprays sixteen. They both change colors with no more than seven to ten minutes change over time.

Q. We just want the coating to stay on until it gets to the distributors warehouse. Why should we bother with powder?
A. Put yourself into the distributors position. It's difficult to sell a potential customer a product with a finish that has started to rust, chip, has dried sags or tears. Your best and most economical sales tool is a good looking finished product. Competition in most industries is very keen. When shopping for most products, tell me the truth - doesn't the looks of a product have an effect on your decision, provided all other points are pretty close to being equal?

Q. My product is so large. How could we possibly powder coat it?
A. Our company is in the process of installing phase one of a system that will be coating an agricultural product that is 15 feet long, 8 feet wide, and weighs 950 pounds. Automobiles are being powder coated on a production line in the U.K. and Italy. Combines, truck frames and busses are being powder coated.

Q. What about the so called Faraday cage effect?
A. The effect is no different than the effect created when electrostatics are used with wet coatings. Reductions in current, a different angle of attack with the gun, various diffusers or probes all lead to success. Actually, a Faraday cage is a retirement home for old painters.

Q. I am presently dipping 40,000 to 50,000 pieces every day. How can you compete with that?
A. That would be hard to do. If you're dipping you are probably dripping some of your profits away. Don't cry when you see the tear at the bottom of your finished part. Non-dripping powder, when applied properly with some intelligent thought being given as to the method used, will do an

economical job for you without solvents or thinners and their high costs.

Q. I usually supply my distributors with spray cans of touch up paint so they can repair equipment damaged in shipment. If I convert to powder what do I do? Send a can of powder and a powder puff?
A. Not unless you want a punch in the nose. Talk to your powder supplier, and equipment people. A powder film properly applied and cured on a clean substrate is not as likely to ship off as some coatings. However, should you need touch up, it can be done.

ANALYZING YOUR PRODUCT LINE

Why are you thinking about powder? (a) you are setting up a new finishing line, or are going to upgrade your present one (b) you want your end product to have a better finish for some reason or another (c) you are setting up a complete new product line (d) a governmental agency has told you to clean up your act or close it (e) you have never done in plant finishing, but have decided you want better control and therefore want to bring finishing into your plant.

What qualities do you need in a finish? (a) exposure to indoor conditions, outdoor conditions (b) there are special requirements such as 1000 hour salt spray, corrosives, FDA approval, electrical insulation (c) anything special at all.

What is your volume? (a) onesy and twosy (b) a steady or seasonal high volume (c) a constant flow, increasing each year.

What size is your end product or products? (a) can it be handled on a conveyorized system (b) if the sizes do vary, is it feasible that they all be handled on the same conveyor line.

How many colors do you spray? (a) one (b) a few (c) a custom coater with a limited few (d) one who is a satisfier of any architectural whim, with a veritable rainbow color chart.

You should be able to answer these questions and some others that get more complex. You will have to answer them to your accountant, banker, management, and your equipment supplier. Other questions will be about original cost, operating cost, pay back period, operational labor, ecology, environment, etc.

A DRY BUT NOT BORING COMPARISON OF POWDER VERSIS WET COATINGS
(in dollars and sense)

This paper is about powder coating, but we must compare "apples to apples" when we shop. I will attempt to give equal billing to both wet and powder coatings.

Let us agree for a minute we are trying to compare equipment and coating prices and we draw some parameters to work with.
(a) we want to spray it automatically (b) our production rates and wage rates deem we do as much as possible automatically (c) our part is a 36" by 36" flat sheet, a lawn mower deck, a bicycle frame, or a 36" by 36" square hanging fixture with many small parts (d) our line speed is 10 FPM (we need that to handle our production).
What is the logical way to go? Powder or wet coatings?

We naturally face our work or product with the automatic coating equipment. The wet coating equipment would amount to: two automatic coating units, enclosures or booths for them, and an air make up unit. You might say we could index halfway through and eliminate one half of the system. That is not too practical at 10 FPM.

Two water wash, dry filter, or other type of enclosures.....	$8000.00
Two wet coating units.....	$20000.00
At least one pumping unit.....	$1500.00
One air make up unit.....	$5000.00
TOTAL	$34500.00

Powder equipment would amount to an automatic coating unit, a cyclone, and final filter. The guns to coat both sides would be in the same enclosure..... $30000.00

	$34500.00	wet equipment
-	$30000.00	powder equipment
	$ 4500.00	(as of 2/79)

A mere drop in the bucket, and not a paint bucket.

Coating material costs should of course be taken into consideration, because wet coatings don't work in powder guns.

How about some epoxy? Epoxy can be expounded upon for hours and will give a good durable finish to most products.

Wet epoxies start at about $13.00 a gallon on the retail market and are usually thinned with about a quart of thinner (about $1.50 per gallon) for a total cost of about $13.38 per gallon.

With a wet epoxy we normally spray about 400 sq. ft. per gallon plus the quart of thinner sprayed, for a total of about 500 sq. ft. sprayed. Remember, the thinner evaporates so we still get only about 400 sq. ft. coated. However, a percentage of sprayed wet coating will miss the product and wind up in your filter or water wash. Without offending anyone, let us say that 80% strikes the part. This gives us a 20% loss. We now have 320 sq. ft. of surface covered at one mil thick. This means $13.38 divided by 320 sq. ft. for $0.042 per sq. ft.

Being dry, powder sells by the pound. An average powder epoxy cost would be $2.00 per pound. One pound will usually cover about 125 sq. ft. at one mil thick. We don't use solvents and oversprayed powder is reclaimed

so we get to use about 95% of each pound.

So we have 125 sq. ft. X 95% of 119 sq. ft. $2.00 a pound divided by 119 sq. ft. is $0.017 per square foot. Taking the aforementioned 36" X 36" sheets and hanging them on a conveyor, one every 42", running at 10 FPM, and spraying both sides with about 2 mil average for a seven hour work shift, we have: 3' X 3' X 2 sides X 2 mils = 36 sq. ft. of material per part. 10 FPM, 3.5 ft. spacing, and 7 hour shifts, five days a week for a fifty week year is: 10 FPM X 60 min. divided by 3.5 X 7 hours X 5 days X 50 weeks X 36 sq. ft. is a lot of production or 10,800,000 square feet.

The wet epoxy @ .042 X 10,800,000.....$ 453,600.00
The powder epoxy @ .017 X 10,800,000.....$ 183,600.00

Potential Savings.....$ 270,000.00

There will be numerous variations and exceptions, fudge factors, coating rates, variations of coverage, but the basic numbers are close. You could go so far as to say, subtract 25% from the wet cost and add it to the powder cost. It still works out. The important fact is POWDER will prevail.

The above is based on using one color. We can go multiple colors. Wet equipment requires solvents to clear lines, and probably some additional pumping, valving and piping. Powder equipment requires a little more. An additional automatic system (the coating unit) would cost about $20,000. and would let you change colors in about ten minutes. You could pay for it out of your first years savings.

I am confident any good wet or powder coating salesman could come up with a set of figures close to the ones you have just seen. The numbers I have not added to the "wet" side of the ledger, but must be added are:

Annual dry filter replacement costs for filter booths.....$_____
or
Annual chemical costs for wet booths.....$_____
Annual booth coating costs for wet and dry booths.....$_____
Solvents for clean up.....$_____
The higher cost of epoxy.....$270,000.00
These added together should give you some good costing.

On the powder side of the ledger we will need a good vacuum cleaner for about $700.00.

By the way, are there any solvent restrictions (emissions) in your part of the country? Can you drain your water wash booth into your sewer system? What does sludge removal cost? What is your annual labor cost for all of the above items and how much non-production time is required to do it?

FAMILIES IN POWDER

Two basic families make up the powder field:

Thermoplastic materials
Thermosetting materials

The thermoplastic family branches off into polypropolene, nylon, P.V.C. polyethylene. Most of these products require a primer which must be cured prior to the application of the top coating.

The application of the top coat is normally done to a preheated part and frequently a fluidized bed is used. This then helps give the ability of applying a heavy coating to the substrate. The product is then post cured. Temperatures generally run in the 400°F to 500°F range. Some of the areas of use are: lawn mower and snow blower handles, dishwasher baskets, freezer shelving, and parts requiring insulation. Mil thicknesses of 10 to 40 mils can be achieved.

The thermosetting family branches off into the following types, many of which are totally designed for your particular needs. They are generally sprayed on your phosphatized substrate which is at ambient temperature, and without a primer coating. They are usually sprayed at from 1.2 to 4 mils.

EPOXY is the most popular and least expensive of all coatings. Presently, the bulk of all powder coating is done in epoxy.
Advantages: chemical resistance, electrical insulation value, impact resistance, hardness, flexibility are but a few of its virtues.
Disadvantages: outdoor resistance to U/V is poor. It tends to chalk and does have problems with color retention.

POLYESTER is more costly than epoxy and the second most popular material.
Advantages: excellent outdoor exposure and durability.
Disadvantages: chemical resistance is lower than that of epoxy.

HYBRIDS are more or less a combination of epoxy and polyester giving some of the good points of both.

I will summarize by saying that thermosetting and thermoplastic materials each have their respective areas of use. Your end product use, total material, equipment, and energy costs must be evaluated when considering either family. I must say the bulk of powder coating as we know it is done with thermosetting products.

POWDER COATING IN THE U.K. AND EUROPE

The application of powders by electrostatic spraying methods was introduced in Europe in about 1962. Since then it has grown substantially with the development of automatic coating equipment, high efficiency reclaim systems and solid state electronics.

I was fortunate to attend a seminar in Brighton, England in 1979. One of the papers was given by a Professor from Southhampton University. It was on the second generation or the new breed of powder equipment. I saw some of this equipment in operation in the U.K. It is interesting to see that we are scratching the surface with powder equipment.

It was also interesting to see the direction of powder sales in Europe. About 600 tons is devoted to automotive chassis, axles and bumpers in the U.K. alone. Presently powder is being used to coat phenolics and wood.

Sales are most popular in the area of epoxies. Second goes to the epoxy/polyester hybrids, and the remainder to polyesters, acrylics and polyurethanes.

SUMMARY

Powder can be a very valuable tool to your manufacturing operation. There are many areas where it will excel over wet coatings. It's application and ancillary pieces of equipment are excellent examples of simplicity in finishing.

I know of no restrictions by any governmental regulations with regards to powder spraying or curing.

Powder storage and use is simple and requires no expert handling. Accidental powder spillages require the services of a vacuum cleaner.

There are no rapidly escalating solvent costs to contend with. No solvent or thinner blends to change with changes in the weather.

If powder can be an asset for your particular finished product, it is truly a clean, simple solution to economical and ecological survival.

N-3

ORGANIC FINISHING SESSION N

Robots in Spray Finishing

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ROBOTS IN SPRAY FINISHING

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Despite the obvious advantages to robotic finishing, United States industry has been slow to adopt. This was particularly true up through 1978; however, some strides are now being made toward implementation of robotics. There are numerous reasons for the hesitancy. Such as, initial investment, worker/union reaction, reliability, availability of labor, etc. However, the favorable points for robot implementation seem to outnumber the unfavorable. Such circumstances as international success, EPA, OSHA, energy shortages, low profits, inflation, competition and declining employee productivity are forcing the change.

The main topic of this paper will be to discuss the correct way to implement a robotic spray finishing system. Most of the points will also hold true for other robotic applications such as welding, part handling, etc.

The beginning step is to choose the correct application. The first consideration should be an application that has a predictable success level. You certainly do not want to choose a job which is the most difficult in your plant and is destined to failure.

The application should be economically feasible; however, it is also up to you to sell the applications' economic justification to your management. Therefore, economic justification becomes extremely important in the implementation of a spray finishing robot.

Economic savings can be realized from a robotic spray painting installation in many ways. Labor savings, paint savings, energy reduction, reduced rejects, reduced spray booth maintenance, quality assurance and, of course, OSHA, EPA and other governmental agencies.

The next step in implementation is to consider the entire system. A robot can not be just added to a syystem with no thought being given to such items as conveyor interface, spray booth modifications, color change, product identification, etc. All these factors must be integrated with the robot to achieve a successful production type system.

The next step, of course, is purchasing the unit. The ideal way is to contact a vendor that indeed can supply you with the total system. Also work with a vendor that has the right unit for you. In other words, talking with part handling or welding robot vendors will not be any help on a spray painting application and visa versa.

Training of your people is the next important step. If the project is to be a success, your in-plant people are going to have to service the unit. Servicing a robot is no mystical problem. Granted, it is a little more sophisticated than other machinery, however, it can be and is being done

everyday in U.S. industry. The largest hurdle in training is to educate your maintenance department not only in the electrical and mechanical functions, but in the machines' capabilities. The battle you have to fight here is the connotation of the word robot. Once the maintenance personnel think of the robot as any other piece of machinery, your maintenance problems seem to decrease.

The next area of concern is installation and start-up. Firm schedules are what all managers want to work with; however, robot installations, especially spray painting, are a little different. We suggest sufficient time be allowed for installation and the job be done carefully and correctly. Incorrect installation or "short-cuts" can cause monumental problems in trouble shooting during start-up.

The start-up period should be well thought out. The laborer the machine is replacing should not be removed from his job immediately. There must be a transfer of work from the operator to the machine, especially in spray finishing. The machine must be taught an efficient manner in which to paint a part and this is not done in one (1) eight (8) hour day. Also most robot controls are micro processor or computer based and a pre-production burn-in time should be allowed.

In conclusion, spray finishing robots are indeed the painters of the future; and if implemented properly, can begin saving your company money in a very short time after installation.

N-4

ORGANIC FINISHING SESSION N

Improving the Corrosion Resistance of Automotive Fasteners

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IMPROVING THE CORROSION RESISTANCE OF AUTOMOTIVE FASTENERS

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ABSTRACT

Increasing corrosion resistance requirements of automotive fasteners have required chemical treatment suppliers to upgrade the treatment process. Oil finishes, long the standard final finish after heavy immersion zinc phosphating, have given way to organic coatings which substantially increase the salt spray resistance of treated parts. Discussed are improvements to the zinc phosphate conversion coating process, the coating parameters found to influence such salt spray resistance, and the technical approaches used to develop organic coatings, which are demonstrably superior to conventional oils.

Introduction

Approximately 200 billion nuts, bolts, screws, and clips, items which are generally known as fasteners, are consumed annually in the United States. While these are used in many industries for many different purposes, some 27 billion alone are used by the automotive industry[1] and a substantial number of them are used in under-the-hood assembly of automotive components. Over the years, a number of pretreatment processes have been developed that materially improve the corrosion resistance of these fasteners. As measured by such accelerated tests as neutral salt spray (ASTM B-117), the improvement in corrosion resistance can range from just a few to several hundred hours.[2] Even so, as the trend to upgrade the corrosion resistance of the entire automobile body continues, we've recognized that further improvements are being sought even with the smallest of the components.

Corrosion resistance of fasteners, as measured by salt spray, can be upgraded by a variety of pretreatment processes ranging from zinc plating to "heavy" zinc phosphating with supplementary oils and waxes. To better understand the degree of corrosion resistance which can be achieved by both processes, a comparison of previously observed results would be desirable.
For example, Skimin, et al, described the corrosion characteristics of chromated and unchromated zinc electrodeposits from

acid, high cyanide, and alkaline non-cyanide plating baths[3] and observed that all the clear chromated zinc deposits exhibited white stained areas during the first eight hour test cycle, but that the first observation of white stained areas on irridescent chromated deposits did not occur until between fifty-six and sixty-four hours of neutral salt spray. Depending on the thickness of the electrodeposit and the type of chromate conversion coating applied, red rust did not appear until between some 100 hours up to about 900 hours. Pearlstein also observed[4] that the salt spray corrosion resistance of zinc plate to white product formation could range from about eight to 172 hours, depending on the type of chromate coating applied.

In contrast to electroplated deposits, "heavy" zinc phosphates are immersion applied conversion coating processes that can develop from one to several thousand milligrams of mixed tertiary zinc and iron phosphate per square foot. These are to be distinguished from so called paint-base phosphate coatings which are substantially thinner and which can be applied by either spray or immersion. Even with a final chromic seal, though, only about two hours of exposure to salt spray can be expected before the first signs of red rust are visible. With a supplementary oil or wax applied, however, several hundred hours of salt spray can be achieved. In one laboratory study[5], corrosion resistance was found to depend largely on the supplementary oil used. Depending on the particular pretreatment, fasteners or test panels were observed to go from less than 168 hours to 504 hours before failure. However, our experience has been that production treated fasteners typically achieve no more than 100 hours salt spray before failure occurs.

The requirements established by automotive manufacturers for the salt spray test on fasteners has increased over the past forty years. From an initial requirement of twenty-four hours in 1940, the requirement had increased to thirty-six hours in the late 1940's, to forty-eight hours in the 1950's, to seventy-two to ninety-six hours in the 1960's, to 120 to 168 hours in the early 1970's.[5] In 1977, one automotive manufacturer, taking advantage of new finishing technology, increased the requirement to 240 hours.[6] This new technology, the development of organic coatings usable over heavy zinc phosphate conversion coatings, has represented a substantial departure from previous commercial practice. In the paragraphs below, some of the parameters we have found important in the development of such organic coatings are examined and their application techniques in commercial practice are described:

Fastener Coating Requirements

The basic requirements for the fastener coating are detailed in an automotive specification.[6] What is required is a black

corrosion protective coating which is produced in a process consisting of zinc phosphate treatment, optional chromic acid rinse or seal, organic coating, oven bake, water and oil emulsion post treatment, and air dry. The coating should have a uniform, black appearance, be free from tears or sags, and not be oily or tacky to the touch after curing. Moreover, the coating which deposits in the threads cannot adversely affect normal installation and removal practice.

A number of accelerated tests must be met by the zinc phosphate conversion coated, organic coated part. Among these are adhesion, weathering, flexibility, humidity, and salt spray. In particular, the parts must pass a 1000 hour weathering test (ASTM G-23) in which parts are exposed to a daily schedule of twenty cyclic periods (twenty hours) with each period consisting of light only at 60±3°C for 51 minutes and light with spray at 7±3°C for 9 minutes. No loss of adhesion, discoloration, or red rust should be evident. As for flexibilty and chip resistance, the coating must withstand the normal flexing encountered by springs and clips without evidence of flaking or loss of adhesion, as well as withstanding normal handling and storage conditions. In order to meet the humidity requirement, parts should show no evidence of blistering or other appearance changes after a ninety-six hour minimum exposure to 100% relative humidity at 38°C and should show no more than 3.0mm peel back from the intersection of lines scribed and tape tested immediately after a 10 minute recovery period following exposure.

Salt spray testing of bolts or screws differs from testing of other parts or test panels with respect to two preliminary preparation steps. First, the bolts are washed in a room temperature, tap water solution of commercial car wash concentrate, agitated for thirty seconds, rinsed in tap water, and dried with a forced air blow-off. Then the bolts are driven into a nut or tapped hole in such a way so as to simulate a production assembly situation in which the head of the fastener turns tight against a flat surface. The amount of torque applied depends on the size of the bolts or screws used and in general simulates production assembly. For example, 5/16 inch bolts are torqued at 15-22 foot-pounds (20-30 Newton-meters). The torqued bolts are then mounted in a fixture-rack and tested in the usual manner. The simulated car wash removes oils that might otherwise provide an extra margin of corrosion inhibition and of lubricity during torquing. These washing and torquing steps make the salt spray test much more severe.

Development of Solvent-Borne Fastener Coatings

Our investigation was begun by surveying the organic resin materials that could be expected to have the flexibility,

toughness, and corrosion resistance in thin films to meet the specified requirements. It was observed that while many resin systems had the necessary corrosion resistance to meet the salt spray requirement if the parts were not torqued, only phenolic and epoxy resins with and without additional crosslinking agents would have the necessary performance to successfully pass the test if the parts were torqued.

In order to speed the evaluation process, a large number of fasteners were obtained which were treated in a commercial zinc phosphate converison coating bath, rinsed and dried. These parts were not post treated in a chromic acid final seal, however. With these parts on hand, solvent-borne coating formulations were first evaluated using the following method:

1. Dip fasteners into coating and centrifuge off the excess.
2. Air dry for 30 minutes.
3. Bake for 30 minutes at 350°F.
4. Repeat steps 1, 2, and 3.
5. Dip coated fasteners into a commercial emulsion of oil and water for 1 minute at 140°F.
6. Allow to dry for at least 24 hours, preferably 72 hours.
7. Wash with detergent, rinse, and dry.

Following this, the fasteners were torqued to twenty, thirty, or fifty foot-pounds using a calibrated torque wrench and subjected to the salt spray test.

Five examples of epoxy and phenolic based formulations that were first evaluated are shown in Table 1.

Table 1. Experimental Solvent-Borne Fastener Formulations

	Formulation (Weight Percent)				
Component	1	2	3	4	5
Phenolic resin "A"	-	-	40	-	-
Epoxy resin "A"	34	34	-	26	26
Epoxy resin "B"	-	-	-	5	5
Aminoplast "A"	14	14	-	14	14
Methyl isobutyl ketone	20	-	-	-	-
Toluene	20	-	-	-	-
Methoxypropanol	-	5	5	5	5
Cyclohexanone	-	35	43	36	36
Graphite	-	-	5	-	5
Flow additives	-	-	-	2	2
Black pigment dispersion	12	12	7	12	7

These formulations were evaluated using the procedure described earlier. Two or three fasteners, coated in each of these formulations, were tested after torquing to twenty foot-pounds in salt spray. The results that were obtained are shown in Table 2. Ratings for these tests were based on a system of values of 5 to 10, where 10 represents no rust and 5 represents 50% or more rust. No values below 5 were used.

Table 2. Torqued Salt Spray Ratings

Formulation	Hours Salt Spray		
	120	240	360
1	9,9,9	8.5,7.5,9	-
2	9.5,10,9.5	8.5,9.5,9.5	-
3	10,10	10,10	10,10
4	9.5,9.5	9,9.5	9,8.5
5	10,10	10,10	10,9.5

The best performance was given by formulation three. Despite superior salt spray results which were repeated several times, fasteners coated in a commercial heavy zinc phosphate, sealed with a chromic acid rinse, and treated with the phenolic based formulation (#3) failed the torqued salt spray qualification test. The failure was ascribed to the excessive brittleness of the phenolic resin used and it was sought to improve the salt spray of the somewhat more flexible epoxy-aminoplast system by combining an epoxy with a phenolic resin.

The following series of formulations was then evaluated as shown in Table 3.

Table 3. Experimental Solvent-Borne Fastener Formulations

Component	Formulation (Weight Percent)				
	6	7	8	9	10
Phenolic resin "B"	22	55	15	30	20
Epoxy resin "C"	43	-	-		-
Epoxy resin "D"	-	10	50		15
Epoxy resin "E"	-	-	-	35	20
Viscosity modifier	1	1	1	1	1
Flow additive	2	2	2	2	2
Black pigment dispersion	10	10	10	10	10
Methoxypropanol	4	4	4	4	4
Methylisobutyl Ketone	10	10	10	10	10
Cellosolve acetate	-	-	-	8.0	8
Ethanol, 95%	8	8	8	-	-

Samples of fasteners coated in these formulations were torqued to twenty foot-pounds and then evaluated in salt spray. It was found that dilution with the appropriate solvent to a viscosity

of 30-35 seconds in a Zahn #2 gave an acceptable film build. The results that were obtained in this evaluation are shown in Table 4.

Table 4. Torqued Salt Spray Ratings

Formulation	Hours Salt Spray		
	120	240	360
6	9.5,9.5	9,9	9,9
7	10,10,9.5,9.5	9.5,10,9.5,9.5	-
8	(Formulation not stable)		
9	10,10,10	10,10,10	-
10	10,10,10,10	10,10,10,10	

As these results show, formulations nine and ten were especially good. The combination of epoxy resins and phenolic resin with suitable viscosity and flow modifiers appeared to give what would be acceptable results.

In order to further evaluate these leads, a series of fasteners were coated with formulations 7,9,and 10 and torqued to levels of twenty, thirty, and fifty foot-pounds before testing in salt spray. The results of these tests are shown in Table 5.

Table 5. Salt Spray Results - Varying Torque

Formulation	Torque, Ft.-Lbs.	Hours Salt Spray	
		120	240
7	20	9.5,9,9,9	9,8.5,8,8
7	30	9,8.5,9,9	8,7.5,8.5,8.5
7	50	9,9,9,9	9,8.5,8.5,8.5
9	20	10,10,10,10	10,10,10,10
9	30	9,10,10,10	9,10,10,10
9	50	10,10,10,10	10,10,10,10
10	20	10,10,10,10	10,10,10,10
10	30	10,10,10,10	10,10,10,10
10	50	10,10,10,10	9.5,9,9.5,9.5

These results indicated that formulation adjustments could give rise to accelerated test failures, depending on the torque applied. A fastener coating similar to formulation 9 has been approved for use for these applications where superior corrosion resistance is required.

Development of Water-Borne Fastener Coatings

Although the solvent-borne fastener coating that was described above was capable of and did meet the accelerated test requirements, it was thought that a water-borne fastener coating would find wider acceptance. In particular, job shops and others who treat automotive fasteners would be particularly concerned about the fire hazard associated with solvent-borne coatings.

In addition, a water-borne system would have added advantages due to the absence of noxious organic solvent odors and, as such, would be more desirable and safer to use. Lastly, the ever more stringent air pollution regulations would soon mitigate against use of low solids, solvent borne coatings unless expensive incineration equipment were installed. For these reasons, it was thought that a water-borne fastener coating that gave the same (or better) performance would be highly desirable.

Formulating such a water-borne fastener coating was a more difficult challenge than what was originally thought. For example, epoxy resins and phenolic resins, which were found to work well in combination, are not water soluble. Even when modified so as to introduce sites which can be solubilized in water by a neutralizing amine, most so-modified epoxy and phenolic resins exhibit only marginal long term stability.

A number of approaches were examined to achieve the technical requirements, and one promising approach which was found utilized a proprietary, water soluble epoxy resin technology. However, the initial tests with the water soluble epoxy resin when formulated with aminoplast or phenoplast crosslinkers were found to fail the torque test. It was further found that many attempts to modify the epoxy resin chemistry which made it water soluble resulted in gels or pastes and, of course, these formulations were useless as coatings.

Further attempts with the water-borne system showed the initial importance of controlling the molecular weight of the epoxy resin and the types and amounts of minor additives. With these leads in mind, a systematic evaluation of the critical components was begun. As the program progressed, it was learned that poor wetting and foam could be overcome by high shear mixing and filtering, that poor flow caused by some additives could be tolerated with a heavy zinc phosphate conversion coating, but not by a lighter one, and that extender pigments worsened test properties rather than improved them. In Table 6, torqued salt spray results following application of a number of water-borne fastener coating formulations are shown:

Table 6. Torqued Salt Spray Ratings

	Hours Salt Spray			
Formulation	120	168	240	408
11	9.6	-	-	8.9
12	10.0	-	-	9.4
13	-	9.9	9.9	9.9
14	-	10.0	10.0	10.0
15	-	10.0	10.0	10.0

Several of the water-borne formulations provide protection comparable to the results obtained using the best of the solvent-borne fastener coating formulations developed previously.

Commercial Practice

The heavy zinc phosphate conversion coating, chromic acid post-treatment, and emulsified oil are elements of a commercial processing sequence which are outlined in Table 7.

Table 7. Typical Heavy Zinc Phosphate Processing Sequence

1. Alkaline immersion clean, 8-10 oz/gal, 5-10 m, 180°F
2. Warm water rinse, 2 m
3. 15-35% muriatic acid pickle, 5-15 m
4. Cold water rinse, 2 m
5. Immersion zinc phosphate, 10-30 m, 210°F
6. Cold water rinse, 2 m
7. Chromic acid post-treatment, 1 m, 140°F, optional
8. Force dry/air dry
9. Emulsified oil, 20-30%, 1 m, 140°F
10. Dry

In practice, automatic tumbling barrel machines are used for maximum efficiency. If the organic fastener coatings are used, they must be applied in equipment separate from the automatic phosphating machine because of the obvious problems of continual film build up on the barrels and the possibility of drag-in of undesired inorganic contaminants into the organic coating and vice versa. Therefore, to utilize these coatings, the fasteners are prepared as outlined in the first eight steps above, coated with the fastener coating formulation adjusted to the proper application solids and viscosity, allowed to drain, centrifuged to remove the excess coating material, and then either allowed to flash dry for thirty minutes to one hour, or prebaked for ten minutes at 210°F, then baked for thirty minutes at 350°F. To eliminate holidays and defects caused by contact marks, the fasteners are coated again using the same sequence. After standing about twenty-four hours, the parts are dipped in the emulsified oil and allowed to dry. Despite several additional steps, the substantially improved corrosion resistance that is obtained with these and other such fastener coatings is an important and necessary improvement if the finisher is to help meet one of the automotive challenges of the eighties - the more corrosion resistant automobile body. Moreover, it is thought that many new applications and markets will develop that will be able to utilize the superior corrosion resistance these systems can deliver.

Conclusions

The types of pretreatment processes including both plating and conversion coating processes, which can be used to improve the corrosion resistance of automotive fasteners as measured by neutral salt spray accelerated testing have been described. It has been seen that the steadily advancing salt spray requirements have caused a new technology, organic fastener coatings, to be used following application of a conventional heavy zinc phosphate. Some of the evaluations that led to the development of a solvent-borne fastener coating which met the required specifications were explored, and, furthermore, it was seen that the same kind of performance could be obtained from water-borne systems. Finally, it was seen how these coatings are commercially applied, how they help the automotive fastener finisher meet the continuing challenges of the 1980's, and how new markets may develop that can utilize these superior performance finishes.

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N-5

ORGANIC FINISHING SESSION N

Low Solvent Organic Coatings and Strategies for the Eighties

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LOW SOLVENT ORGANIC COATINGS AND STRATEGIES FOR THE EIGHTIES

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ABSTRACT

This presentation covers what the user will face in the application of Water Bourne and Higher Solids Coatings compared to present Conventional Solvent Coatings. Strategies for compliance with EPA Guidelines for low solvent emissions using these technologies, and Transfer Efficiency under the Bubble Concept are discussed.

Introduction

As a result of heavy pressure by Government Regulations to make paint coatings environmentally acceptable, the manufacturers and users are in an intense period of change. The challenge to meet requirements of the Clean Air Act Amendments of 1977, are changing the game with new rules and strategies necessary to comply.

To meet these requirements, Water Bourne and Higher Solids are two coating candidates that in the 80's are expected to comprise over 50% of the coatings used. With this in mind, production line aspects of these two technologies are compared to conventional solvent coatings.

In using these coatings to meet emission regulations, the user has some options. It is not always necessary to make a complete transition from conventional coatings. It may be more practical to employ a combination with more efficient application. Some examples will illustrate this approach.

WATER BOURNE COATINGS VS. CONVENTIONAL SOLVENT COATINGS

In comparing these coatings we find the following advantages and disadvantages for Water Bourne Coatings:

Government Regulations	Meets all pending air laws.
Worker Safety	Less irritating vapors, however, odor is different.

Fire Insurance	Greatly reduced fire hazards
Supply at Booth	May keep more than 1 days supply so less handling cost.
Freight Rates	Possible savings - different DOT Classification, possible to have shipped with least amount of water and add balance on site prior to use.
Storage	Freezable, however, contains some solvent so freezing point is usually a little lower than 32°F.
Shelf Life	Stability not as good as C.S.C. It's important to rotate stock.
Equipment & Facilities	Some capital expenditures required, however usually compatible without major modifications.
Mixing and Transfer	Slow agitation and proper pumps are necessary so foam is not created from entrapped air. Stainless steel pump may be needed for some items.
Application Methods	May be supplied by Dip, Spray, and Flow coat. Electrostatic equipment, however, must be isolated. Reprogram thinking to use higher application viscosities.
Equipment Clean-Up	It's more difficult to change colors and clean lines.
Air Supply	Clean air, free of oil is more critical.
Ambient Weather Conditions	Best when relative humidity is between 40 & 60%. When too high, possible poor leveling. Air flow and temperatures are more important. Use of product may build up humidity and require control.

Metal Preparation	Requires superior cleaning. Less surface wetting properties and cratering can be a problem on poorly cleaned substrates.
Flash Off Period	May have to be extended so blistering due to entrapped water doesn't occur. More susceptible to dirt pick-up and contamination.
Bake Time & Temperature	Depending on flash off time it may be desirable to have a two stage oven. Bake times are similar to C.S.C. i.e. 20 min. @ 300°F. or 10 min. @ 350°F.
Line Speed	Line may have to be slowed down. Water of all solvents is harder to get out of film.
Cost Per Square Foot Coated	With Water Bourne, must compare applied cost, not the per gallon price of a coating. Water Bourne is approximately 20% more. However, with the increased cost of solvents and petrochemicals, the difference is closing.
Quality Performance	Water Bourne Coatings are available and offer performance of Conventional Solvent Coatings for most end uses.

Other Notes of Water Bourne Coatings

- Some limitations on use of corrosion resisting pigments.
- Possible color drift and streaking.
- Metallics are tough.
- Without proper cure, water sensitivity is affected.
- Check intercoat adhesion especially water bourne over solvent reducible coatings.

- Check recoatability and touch up for adhesion.

- Greater tendency to telescope substrate.

- Greater care must be exercised using additives to correct problems as they may affect water sensitivity, stability and salt spray resistance.

- Overall good control is necessary, along with an understanding there will be some continuing problems to live with. Water Bourne Coatings have different rules than conventional solvent coatings. For example, pH may require adjustment and there is tendency to blister if too heavy a coat is applied.

- Overall Water Bourne Coatings are good candidates for the Eighties and while not a "Plug-In Technology" will be used for a wide variety of applications.

HIGHER SOLIDS COATINGS VS. CONVENTIONAL SOLVENT COATINGS

Looking at Higher Solids compared to Conventional Solvent Coatings (C.S.C.) we find more similarities because Higher Solids are more like the traditional coatings we've been using for many years.

The following are advantages and disadvantages for High Solids Coatings:

Government Regulations	May meet pending air laws.
Worker Safety	Similar to C.S.C.
Fire Insurance	Similar to C.S.C.
Supply at Booth	Similar to C.S.C.
Freight Rate	Similar to C.S.C.
Storage	Similar to C.S.C.
Shelf Life	Similar to C.S.C.
Mixing and Transfer	Similar to C.S.C. although will use little or no solvent to reduce. Heavier mixing equipment and larger paint lines may be necessary due to higher viscosities and weight per gallon.

Equipment & Facilities	Can anticipate capital expenditures for application equipment.
Application Methods	Spraying is the main method today. Over spray builds up faster and is more expensive. Fewer passes required for same coverage. The fast build up of film thickness requires good control to maintain proper cost. Key is the transfer efficiency of the application equipment and/or operator technique.
Viscosity & Temperature	Important to maintain good control. Heaters may be necessary for viscosity control.
Equipment Clean Up	Similar to C.S.C.
Air Supply	Similar to C.S.C.
Ambient Weather Conditions	Similar to C.S.C.
Metal Preparation	Must be good. Less metal wetting properties due to less solvent in coating.
Flash Off Period	Similar to C.S.C. at same film thickness but greater potential for dirt pick-up.
Bake Times & Temperatures	Similar to C.S.C.
Line Speed	May be increased because film thickness is applied faster.
Cost	Cost per unit coated will be more. The difference may be in the area of 25%. Possible savings in the following areas due to less coating material required to coat same number of units: Freight In Storage and Inventory

	Material Handling Material Preparation Solvent Use Increased Capacity due to increased line speeds.
Quality & Performance	At least equal to Conventional Coatings.
Overall	We feel higher solids will be very important in the 80's especially as new resins are developed including materials that will air dry and coatings for dip and flow coat application.

STRATEGIES

The next area I want to cover involves a combination approach to comply with the EPA Low Solvent Emission Guidelines. To start, lets look at the Terms and Definitions involved.

Terms and Definitions

RACT DOCUMENTS (Reasonable Attainable Control Technology)

Guideline papers prepared by EPA and published in 1977. Each state was ordered to develop it's own State Implementation Plan (SIP) based on these Federal Guidelines. They mean the lowest emission limit that a particular source (Industry) is capable of meeting by the application of control technology that is reasonably available considering technological and economic feasibility. They basically restrict the pounds of solvent/gallon of coating at application point for various categories of industry.

VOC (Volatile Organic Compound):

For coatings this means all solvents and amines. It does not include water and there is no distinction between exempt and non-exempt solvents.

VARIOUS RACT - VOC LIMITS

Industry Category	Pounds/VOC Gallon
Coil Coating (2)	2.6#
Paper Coating (2)	2.9#
Auto & Light Truck (2) -	
Primer	1.9#
Topcoat	2.8#
Repair	4.8#

Metal Furniture	(4)	3.0#
Large Appliances	(5)	2.8#
Miscellaneous Metal	(6)	
	- Clears	4.3#
	- Interiors	3.0#
	- Outdoor/Harsh	3.5#

BUBBLE CONCEPT

An EPA policy that considers an industrial facility as if it were contained in an imaginary bubble that has a single stack emitting VOC. This allows a company to meet regulations by reducing the overall VOC emissions from individual sources within the plant. Therefore, trade offs can be made within a plant. If one coating product has less than the permitted VOC, another product could have above the allowed VOC but the two combined must average the allowable VOC per the particular RACT category.

TRANSFER EFFICIENCIES

This is the application efficiency of the production coating process.

Typical Efficiencies

Hand Held Air Atomizing Guns	40%
Hand Held Electrostatic Guns	60%
Automatic Electrostatic Guns	75%
Electrostatic Bells/Disc	85-90%
Dip/Flow Coat	90%

In meeting the EPA Guidelines, the user has some options. It is not always necessary to switch to all Water Bourne, Higher Solids and High Solids, rather it may be more practical and economical to employ combinations of coatings along with more efficient means of application.

The following examples show this combination approach and assume present Conventional Systems have 4.75 lbs. of VOC per gallon at application.

This example uses the Bubble Concept with Low Solvent Coatings with data is as follows:

Present Yearly Gallonage @ Application	100,000 gallons
VOC @ 4.75 lbs./gallon	475,000 lbs.
RACT #6 Harsh Environment Allowable VOC is 3.5#/gal.	350,000 lbs.

Breakdown of gallons used:

Primer	50,000 gallons
Topcoat	50,000 gallons

Now if the primer is changed to a Water Bourne @ 1.9# VOC/gallon;

Allowable VOC	350,000 lbs.
Primer VOC 1.9# x 50000 gal.	95,000 lbs.
Balance of VOC available for Topcoat	255,000 lbs.

Topcoat may use up to 5.1# VOC/gallon. With present Topcoat at 4.75 lbs. VOC this gives some room for clean-up solvent. Therefore, by changing the Primer to a Water Bourne the present Topcoat may continue to be used.

With the same format and if the allowable VOC is 3.0# per gallon, the allowable Topcoat VOC would be 4.1# per gallon. This would permit the Topcoat to be a medium solids item rather than Higher Solids and thus a better fit in present production facilities.

Another VOC reduction alternative uses the Bubble Concept, Transfer Efficiency and Low Solvent Coating. In this example all products are presently applied by hand held air guns. After a thorough study it is determined that one quarter of the products could be coated in a dip operation, one half would lend itself to a Water Bourne and the balance could be applied by hand held Electrostatic guns. Present yearly usage at application is 100,000 gals.

Dip Operation 25000 gallons $\times \frac{40\% \text{ Hand Gun T.E.}}{90\% \text{ Dip T.E.}} \times$ 11,111 gallons

11,111 gallons x 4.75 lbs. VOC/gal. = 52,777 lbs. VOC

Water Bourne
50,000 gallons x 1.9 lbs. VOC/gal. = 95,000 lbs. VOC

Electrostatic Hand Gun 25,000 gallons $\times \frac{40\% \text{ Hand Gun T.E.}}{60\% \text{ Electrostatic}} =$ 16,667 gallons

16,667 X 4.75 lbs. VOC/gallon = 79,168 lbs. VOC

Total VOC	=	226,945 lbs.
Total Gallons	=	77,778 gals.
VOC Per Gallon	=	2.92 lbs.
Total VOC Reduction	=	248,055 lbs.
Percent VOC Reduction	=	52.2%

While these examples are not meant to be typical situations they illustrate how Transfer Efficiency combined with Water Bourne and/or Higher Solids Coatings may be used to put a plant operation in compliance. Remember of course, any increases in Transfer Efficiency will have to be substantiated by test data and calculations.

CONCLUSION

Water Bourne and Higher Solids Coatings are not Plug-In Technologies. There will be problems and they will be different than those with Conventional Solids Coatings. In going to these new coatings it is important that a step by step program be followed before a full production transition is made. Get everyone involved early in the program. The teaching and training of people is critical.

Keep in mind there are alternates to achieve compliance with Low Solvent regulations. The best approach is one that is the most practical and economical for your operations and this may be a combination of Water Bourne, Higher Solids and Application Efficiency.