SUR/FIN "86"
Technical Bound
Volume. Conference
Price only.
$170.00

The Proceedings of the 73rd AESF Annual Technical Conference June, 1986 Philadelphia, PA

Published by the
American Electroplaters
And Surface Finishers Society, Inc.
12644 Research Parkway, Orlando, FL 32826

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A-1

Organic Finishing Session A

The Heat Cleaning Process

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THE HEAT CLEANING PROCESS

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It would be stretching one's imagination to use the buzz words "state of the art" "high tech" and "data base" to describe the process which I am going to discuss. However, Heat Cleaning does meet tomorrow's paint stripping requirements. Ecologically sound, controlled, low labor intensive, the heat cleaning process represents technological advances unique in the fact that born of the need to meet environmental regulations it presents the opportunity for improved quality, and productivity.

The heat cleaning process and modern heat cleaning ovens were originally introduced in the late 60's to solve a problem in the electrical motor repair industry where it is necessary to strip old insulation and wire from electric motor stators and armatures prior to remanufacturing. This stripping process was being done in bon fires out back or in chemical stripping tanks. The burning process was uncontrolled and generated a huge quantity of smoke. The rebuilder was faced with an air pollution problem or a chemical waste disposal problem. Heat cleaning ovens eliminated both of these problems.

In the mid 70's the heat cleaning ovens were applied to the automotive parts rebuilding application of stripping electrical insulation and wire from automotive alternators and starters. Initial installation of equipment to the high volume automotive component remanufacturer opened the door for various manufacturers to experiment with cleaning material handling of components such as hooks and racks along with reject parts.

Whatever the application the basic components of a heat cleaning oven include a primary processing chamber, an integral afterburner, temperature controls for burners and air supply, and a water mist injection system for controlling and flash temperatures that may occur when processing large loads of combustibles.

The primary chamber is typically cart loaded with a refractory firebox under heating the load. This provides fast heat transfer to bring the load rapidly to the devolilization temperatures of 300 - 350°F. The afterburner is kept off below this temperature to conserve fuel. At the controls adjustable low setpoint, the afterburner automatically switches on.

As temperature in the primary chamber rises 600 - 750°F, devolilization of the load increases. Afterburner temperatures rise from 1200 - 1400°F to oxide the fumes and smoke being discharged from the load.

Most paints and volatile coatings ignite in the 700 - 750°F range, causing rapid temperature rise to the control's adjustable high setpoint. This automatically shuts down the primary chamber burner and air supply. As oxygen is consumed, flame is extinguished and roasting conditions established.

Paints and other hydrocarbon-based materials are thermally degraded at typical temperatures of 600 to 750°F. As these products thermally degrade odor and smoke is released and gaseous products are passed into the afterburner chamber. Thermal oxidation or burning of this mixture requires introduction of secondary air and raising the temperature with a secondary burner, mixing the ingredients at temperature and holding them at temperature long enough to complete oxidation.

Hydrocarbons decompose into volatiles and carbon particles (smoke) in this low oxygen environment. The decomposition rate is primarily a function of temperature, providing oxygen remains excluded.

Gaseous products pass into the afterburner at 650 - 750°F. These are a low oxygen mixture of volatile vapors and smoke.

Oxidizing this mixture requires introducing secondary air, raising the temperature with a secondary burner, mixing the ingredients, and holding them at temperature long enough to complete oxidation.

Carbon monoxide, always present in controlled air stripping, has a reaction time of 0.7 seconds at 1400°F for 99% completion. Retention times of 0.9-1.0 seconds are required.

As air flow in the primary chamber is very low, velocities across the parts are low, and little ash is entrained and carried to the stack.

As devolitization starts at 350 - 450°F, the afterburner need not be on until this primary chamber temperature is reached.

The environmental aspects of the heat cleaning process center around the afterburner system.

The Federal government through the Environmental Protection Agency (EPA) has established a set of rules and regulations concerning the air quality standards for a piece of equipment that may cause pollution or equipment intended to control air pollution. The Federal government delegated to the States the authority to control these standards.

Most States reviewed the Federal standards and designed their own more stringent standards. Many States have delegated control to a lower level such as counties, regional districts, or cities. Within many of the States the local agencies have developed more stringent regulations than those of the State or the Federal government.

In virtually all air pollution control districts whether it be at a city level or a state level a permit system of control is in effect. The permit process typically consists of a Permit to Construct, which is basically an application to advise the air quality district that you are intending to purchase and install a piece of equipment that may cause air pollution or a piece of equipment intended to control air pollution, and a Permit to Operate. The Permit to Construct allows the agency to review the equipment and process and evalu-

ate if it can meet their standards. The Permit to Operate is issued after installation and the equipment is put into operation. The modern heat cleaning oven fits both of these catagories.

Heat cleaning ovens are not singled out for this permit process as it also applies to chemical cleaning systems and shot or bead blasting systems.

The permit system is designed to ensure that all facilities are properly controlled.

Although the actual air quality standards vary from local districts to State agencies to the EPA, modern properly designed heat cleaning equipment will comply with all of these regulations. The regulations do not just require that you eliminate odor or visible emmisions, but are stringent enough to require that a standard far greater than that visible to the naked eye be obtained. Manufacturers of heat processing equipment should make available to their customers, test reports and support data for submittal to their local agendy for issuance of a permit.

The heat cleaning oven with integral afterburner can eliminate the caustic chemicals many facilities are presently using. The elimination of the chemicals eliminates a pollution source.

Equally important as the elimination of a pollution source through the application of the heat cleaning process is the actual degree of cleanliness and labor savings that can be achieved in the conversion to a heat cleaning operation.

The heat cleaning process thermally degrades virtually all combustible materials from coating line hardware, such as hooks, fixtures, trees, racks and baskets. Many users reclaim reject coated parts, inclduing aluminum components without difficulty. There is virtually no end to the type of parts that are being cleaned in heat cleaning ovens. The controlled heat cleaning process does not warp or distort the parts being processed.

Cleaning hooks and clean fixtures minimize over spray and enhance the coating quality, thereby reducing rejects and conserving coating materials.

Metals that melt under 900°F cannot be stripped. These include zinc and its alloys. Aluminum, melting at 1200°F, can be heat stripped. Operating instructions include precautions and procedures. Heat stripping rarely affects the temper of heat treated ferrous parts, but can affect that of alloy aluminum.

Medium size ovens costing $8,000 - $10,000, can process a few hundred hooks, for as little as $3.00 worth of natural gas per cycle. Large ovens processing large tree assemblies have operating costs of $6.00 - $10.00.

Virtually all straight hydrocarbon based coatings can be heat cleaned. Chlorinated compounds (PVC) will generate hydrochloric acid and should not be processed. Fluorinated compounds (teflon) should not be heat stripped. Other

non-combustible ingredients should be investigated before processing. Check with your coating supplier regarding the heat cleaning of these or other questionable materials.

Heat cleaning ovens are not incinerators. They are designed for comparatively low combustible destruction rates and are thus afterburner limited.

Carefully evaluate the capacity of the various equipment manufacturers systems to process specific amounts (Lbs/Hr) of combustibles in a given cycle time.

Oversized afterburners are available for heavy combustible content applications. These include oversize burners and air ports and afterburner temperature controls.

There are wide differences in afterburner capacity between different oven brands. Very low capacity can lead to long cycles and low production rates. Long cycles will lead to higher fuel cost per cycle.

Heat cleaning is the modern, efficient environmentally sound approach to clean hooks for improved coating quality.

A-2

Organic Finishing Session A

A Systems Approach to Paint Spray Booth

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A SYSTEMS APPROACH TO PAINT SPRAY BOOTH

By
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A production paint spray booth should not be considered as only a collection of sheet metal, filters, lights, and an exhaust fan that is a necessary evil in the **BACK** of the plant. It should be a well engineered and fabricated **APPLICATION ENVIRONMENT**. The spray booth should be carefully designed with all at the implications of the finished product's requirements and the total economics of the process taken into account. It can be one of the major steps towards a profitable product rather than a necessary liability.

This paper will primarily deal with liquid spray booths. However, the concept of the booth as a system applies equally to powder booths as do many of the design points we will discuss.

What are the minimum requirements of a liquid spray booth:

- safe structural requirements
- located "legally" within the plant
- have the "legal" required air movement
- permit the application of the coating

What purposes and functions does a properly designed spray booth serve:

- An enclosure to contain paint overspray, and minimize the chances of it landing on the product.
- To meet the requirements of applicable laws or regulations.
- To make the working environment comfortable.
- To enhance the appearance and/or quality of your product.
- To aid in the profitability of your product.

The above two lists are not necessarily synonymous. For instance, "to enhance the appearance and/or quality of your product", is not synonymous with "permits the application of the coating". This is where this paper is aimed, that of considering the painting application a necessary evil (as has frequently been the case in the past) or looking at it **as a real profit maker** within your production system. One or the other has to be your guide when selecting a new paint booth. Hopefully, the second! This philosphy, of what is your criteria, should carry forward from the spray booth to the complete finishing line. It is best to consider the system

(the finishing line) as a whole, and as we will demonstrate later in this paper, such considerations can add to the total functionality of the line, but will also enhance the profitability of your products.

In todays competitive environment, we cannot have **"necessary evils"** in our production operations, if we want to win in the market place of our products.

It has been our experience that the single most wasteful effect of a poorly designed finsihing line and specifically, a spray booth, is the product rejects it creates.

It is safe to say that there are few of you who know accurately what your numerical reject rate is in the paint shop. Even if you are among the few who know what that number is, there are less who know what their real **"full"** costs are. That is, its financial impact on finished, out the door costs of your product. We have frequently seen finishing reject rates as high as fifteen percent (15%) and have even seen them as high as thirty percent (30%). The real "full" cost of this is only measured when you take careful accounting of:

- Lost production space (time).
- Inspection cost (sometimes three or four times on the same part).
- Manual correction - sanding, stripping, etc.
- Multiple handlings.
- Scraped parts.
- Repainting materials.

Remember, every one of these costs is directly taking profit away from your product. This is one reason we should be aiming to do it right the first time. Why, when considering a new spray booth, the best one, designed for **YOUR** product is the only thing that should be acceptable? Not the one with the lowest offered price without consideration for all aspects accounted for.

To complicate your problem of selection, there is a rather large list of the types of booths for you to select from. The two basic types and their major sub groups are:

1. Dry Filter Types
   a) filter pads
   b) filter rolls

2. Water wash (and oil) types
   a) back sections, water wash curtains
   b) bottom water wash

Then there is the various ways of introducing the air and its direction within the booth:

1. Open face type booths (both wet & dry)
   a) cross draft
   b) down draft

2. Enclosed type booths (both wet & dry)
   a) cross draft
   b) down draft

To attempt to control the environment within an open face spray booth is almost an impossibility. We are going to leave the discussion of open face spray booths by saying, in almost all cases, they meet the requirements of the law, and will, at best, give you an opportunity to put coating on your product.

We will concentrate the remainder of this paper on enclosed spray booths. This is the only way you have to accurately control the total environment in which you coat your product.

In looking at the design of a spray booth, one needs, first, to look at its construction and arrangement with respect to your finishing line. After having made the choice of what type of booth you need, now you must decide if it is one booth or more than one. Typically, if you are going to use a combination of manual and automatic spray applications, then you will, at least, consider two distinct booths, one for each operation.

Before we get into this area further, lets accept that each manufacturing process is different, and that there is a large variety of degrees of quality required for different finished products. Only you and your customer know what are your requirements. For the purposes of our discussion here, we are going to assume that you require a good looking, well protected finsih on your product. In the class of appliances, household or consummer goods, thus the need for something other than "barely acceptable" in the way of a spray booth.

We will not attempt to cover in detail within this paper the eliminator systems, that is, the separation of particulate (paint overspray) within the exhaust system of the spray booth. It will surfice to comment that the type of eliminator system you select will have significant impact on your meeting air quality regulations. Basically, you have to select from wet or dry types at this time.

The construction and fabrication of a spray booth may be likened, within the finishing line, to the foundation of a house. It is what you build on. It must be sound and capable of being consistant with the environment you are attempting to create within the booth. Long term durability, maintenance and cleanliness are key factors that must be incorporated into the design. Protection of the created environment must also be considered.

Of equal importance, is to insure you have the correct space within the booth to do the quality finishing you are aiming for. Some of the items to be considered here are:

- proper clearances of the part, part to part, and parts to booth walls
- appropriate space for manual operators and/or automatic spray equipment
- latitude for product changes with time, such as size or shape
- proper space between sprayers and/or automatic equipment
- proper means of observation, for supervision and inspection of work
- the ability to rotate parts, if needed, for coating of all surfaces.
- adequate consideration of the hanging arrangement and attitude of parts.

Remember, the spray booth will be with you for many years, do not make it too small.

The next item of concern within the booth itself is air movement. What is best for your product, and the way you are going to paint it? In most cases, we believe the best arrangement is to have **"down-draft"** type booths. Generally, these afford you the best transfer efficiency (lower coating costs, and lower V.O.C.) and excellent control of the overspray.

Here, design of the booth is extremely important. The legal requirements dictate the minimum air flow rates (volume of air per unit of time for a given booth area), and minimum physical requirements of the booth such as door locations, lighting, etc. More important for the quality of the finish, than the amount of air, is the control of the air within the booth. Too much air is extremely expensive as well as harmful to good quality finishes. Turbulent air will make the working environment poor, and will create rejects (lower profits) via dry spray deposits on the product. It will also add to your booth maintenance costs.

Proper uniform air flow is as important as proper lighting. Surprisingly, the two are even directly related. Lighting is a must, and the fixtures can be placed in such a way as to disturbe the air flow. Flush mounted, exterior serviced lights are preferred. They will then provide the proper light levels (the equivalent of an inspection area in manual booths).

We will come back to air distribution and uniformity a little later in this paper.

We now recognize we need air in the booth, let us consider where it is coming form.

First, a reminder for those familar with spray booths designs, and what may be a surprise for those not familier with them. The most expensive operating and maintenance costs of your spray booth is the conditioning of the air you move through it. By conditioning, we relate to all means of improving the quality of the incoming fresh air, filtering, heating, humidifying, etc. And, by move through it, we mean that, as for the most part, that is all the air does, move through.

If you are looking for bottom line profit expectations of your spray booth, this is where to start. It is also a significant part of your first time, capital cost of the booth.

Back to the source of the air that will be passd through a booth, and over and around your product while its being painted. You have some choices again:

- Ambient shop air
- Ambient outside air
- Heated outside air
- Heated and humidity controlled outside or shop air
- Recycled air from
  a) Shop air
  b) Other processes
  c) Spray booth exhaust

It should be clear why this air needs to be filtered, but let us make a few points in this regard at this time. A 10u size particle of particulate, in the west painted surface, is easily visible to the naked eye as a contaminent only after cure of most decorative paints.

The most common cause of painted parts rejects is dirt in the surface. Due to the shrinkage of the coating betweeen application of finish and its cure, small contaminates

cannot be seen until you have cured the coating. Thus, filtering of the booth air is essential, and its design consideations are critical factor in design of the booth. A 10u particle is not visible to the naked eye while it is being carried in the air.

Most plants, other than those in the far south of our country, will chose to use outside air for the spray booth's air supply. This is because of the quantity of air needed, and the contaminents that may be in the plant air.

As an example: A manual spray booth of twenty (20) feet long and ten (10) feet wide requires twenty to twenty-five thousand (20 to 25,000) cubic feet/min. of air, (20' x 10' x 125'/min). The requirement (NFPA-33) is for "not less than one hundred (100) feet/min. minimum air velocity", and in most cases, the design criteria will be one hundred and twenty-five (125) feet/min. To go to an automatic application - no operators or sprayers in the booth - this comes down to fifteen thousand (15,000) cubic feet/min. of air. Where the regulations require only "not less than seventy-five (75) feet/min." air flow. This is not a large spray booth.

Now back to filtering of the booth air. Assuming it is coming from outdoors, we prefer three stages of filtering: **coarse** (screen) for large particulates that maybe in the environment; **primary** to remove the majority of large contaminents; and **final** just prior to entering the spray booth. A fair question would be, why three filters?

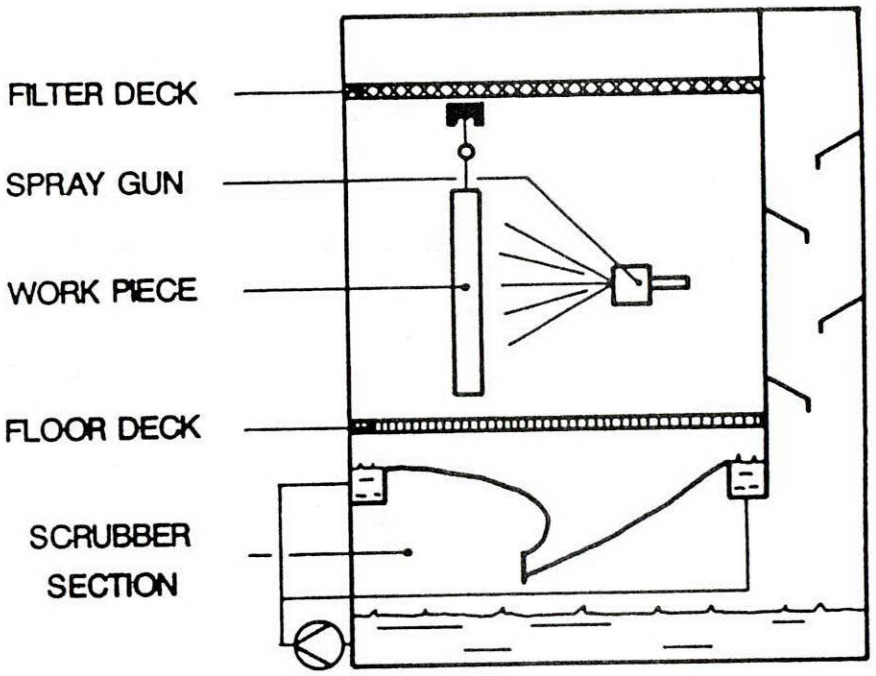
There are two reasons for this. First, to insured quality of the air, and secondary, the cost of filter replacements. Remember, we are filtering down to 10u in particulate size, and moving a great deal of air. The finer the filter the more costly it is for a given quality.

The replacement costs associated with filters to gradually clean the air, three steps, is less than the increased cost of frequent replacement of one fine filer. Then, with stages that are properly monitored as to the actual condition, (via differential pressure gauges) we can have insurance that we know when to service the filters and insure against dirt entering the booth via the air stream.

All of the above comments regarding air filtration are common for either down-draft or cross-draft enclosed booths. We will come back to uniform air flow in the booth later.

Recognizing that the final filter is an intregal part of the spray booth, that is, it is either in the ceiling in the

case of the down-draft or in the wall in the case of a cross-draft, it will have a major influence on the direction the air travels inside of the spray booth. We prefer what is called a full ceiling down-draft booth as depicted in this sketch.



SPRAY BOOTH WITH SCRUBBER

This arrangement allows for the start of uniform airflow throughout the full area of the booth. The air is uniformly and gently washed over the parts being coated form top to bottom, the same way the parts are normally coated, and then exits the booth into the exhaust system. As the air exits the booth, it carries with it the oversprayed paint, and minimizes contamination of the wet surfaces with dry overspray.

Still other factors to be considered for possible inclusion in conditioning of the air, temperature, and humidity. This is more common now than in the past, particularly when automatic electrostatic application equipment is being used. In the application of ceramic frit and powder coatings, this is even more important as it is in the application of water-

borne coatings particularly in humid climates. For our purposes here, we will state that if this type of conditioning is required, then it is usually put in between the first and second stage filters, and is an intregal part of what will be called the Air-Make-Up Unit.

We now see the need for the air in the booth. The need for filtering it, and in some cases, controlling its temperature and humidity. We also recognize it is costly to filter and to move. In most cases, it is then **exhausted** right out of the building. Look at those **BTU's** and **Dollars** going up the stack.

There are some ways to conserve on those BTU's:

- Insure that the minimum proper quantity of air is being used
- Use warm air from other processes in the plant.
- Use air staging for automatic booths.
- Use air to air heat exhangers from other energy sources.

Only by a proper analysis of the booth's requirements and the products needs can you insure that you are using the proper quanity of air within the booth. This is an extremely important part of the design effort.

The use of warm air from other processes within the plant, and specifically, from within the finishing system is practical. It should be the first consideration.

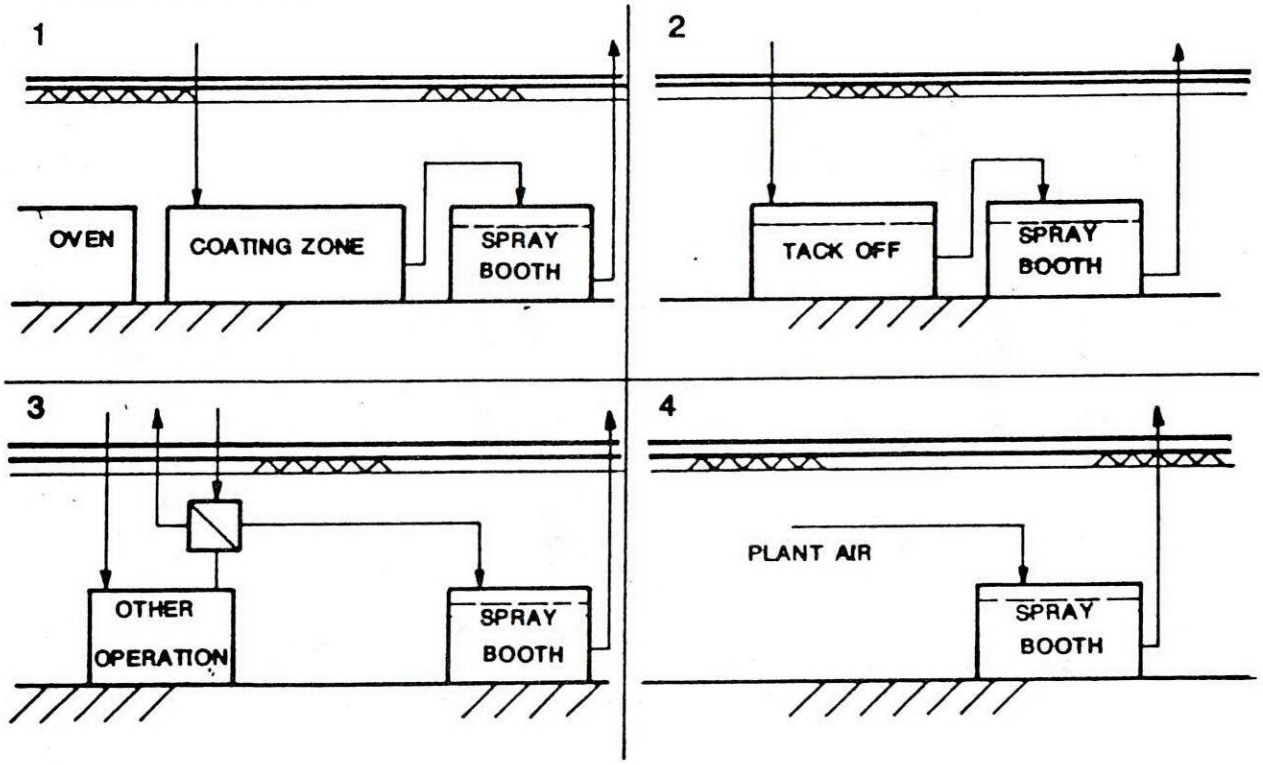
For spray booths, we have to consider two different conditions. First, a manual booth, and second, an automatic booth. In the case of the manual booth, we need to consider the **comfort** and **safety** of the workers as well as the safety from property loss, whereas, in the automatic booth, we need only be concerned with property loss.

First, lets look at some of the oppportunities to use pre-heated processed air in manual spray booths. Some of the possibilities are:

- Air from a cooling section prior to the spray operation.
- Air from a preparation or tack-off area.
- Air from another operation in the plant requiring exchange circulation of air.
- Air from the general plant environment. NOTE: Care must be taken to insure that there are not airborne contaminents that will not be filtered out by the booth filter system, and be harmful to personnel or

the paint process, such as silicone and some other oil vapors.

All of the above are heated air uses that will frequently only require filtration prior to putting the air into the spray booth. Typical examples of how this is accomplished for complete air supply or as partial air supply are shown in these sketches.



From these sources, the only contaminents of concern within the air is particulate. Again, we must caution that one must analyize the source of air to insure there is no airborne materials that would get pass the filters, and be harmful to either personnel or the coated products.

Continuing with our discussion of manual booths, there are additional possible economics that should be considered. Some are the use of other heat sources within the plant to aid, if not completely heat, the booth air via heat exchangers. Possibilities such as:

- Oven exhaust
- Oven incinerator exhaust
- Washer exhaust
- The booth's air exhaust
- Excess plant steam
- Other process exhausts.

Here we can consider heat sources that **ARE** contaminated with materials we **DO NOT** want in the spray booth environment. This is because it is an indirect means of transfering heat energy to the booth's air supply. For instance, air to air heat exchangers can be 70+% efficient in transfering energy from one air stream to another. You have already paid for that **heat**, it has done the job it was intended for, and up until now, most likely you have been exhausting it. Lets try to use it again or at least, a large part of it.

Heat exchanger and/or filters are relatively low cost as opposed to primary energy for heating. Yes, these approaches do add to the initial capital cost, and will have some additional impact on line maintenance. Only with a proper analysis and design study will you know what their payback is. But **PAYBACK** there is in almost all cases.

Now let us look at the case of automatic booths. We do not have the concerns of personnel safety to control our design. This increases our option from that of manual booths. Our concern now is primarily the Lower Explosive Level (LEL) of the environment within the spray booth. Added to all the possibilities shown for manual spray booths are now:

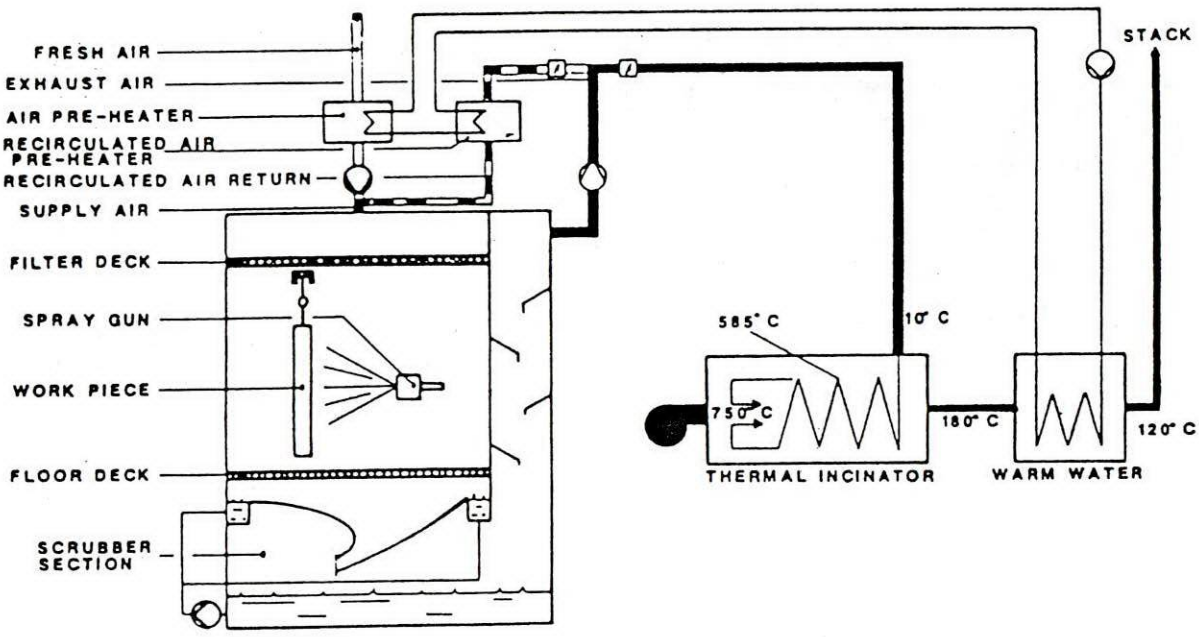
- Exhaust from flash-off zones.
- Exhaust from manual booths.
- Exhaust from ovens.

Again, we note that we can consider 100% exchange or partial exchange. We will install LEL monitors, and insure that we do not get into any problems with possible fires or explosions.

These are real opportunities to save money within the process, and maintain the highest possible degree of control of the spray environment.

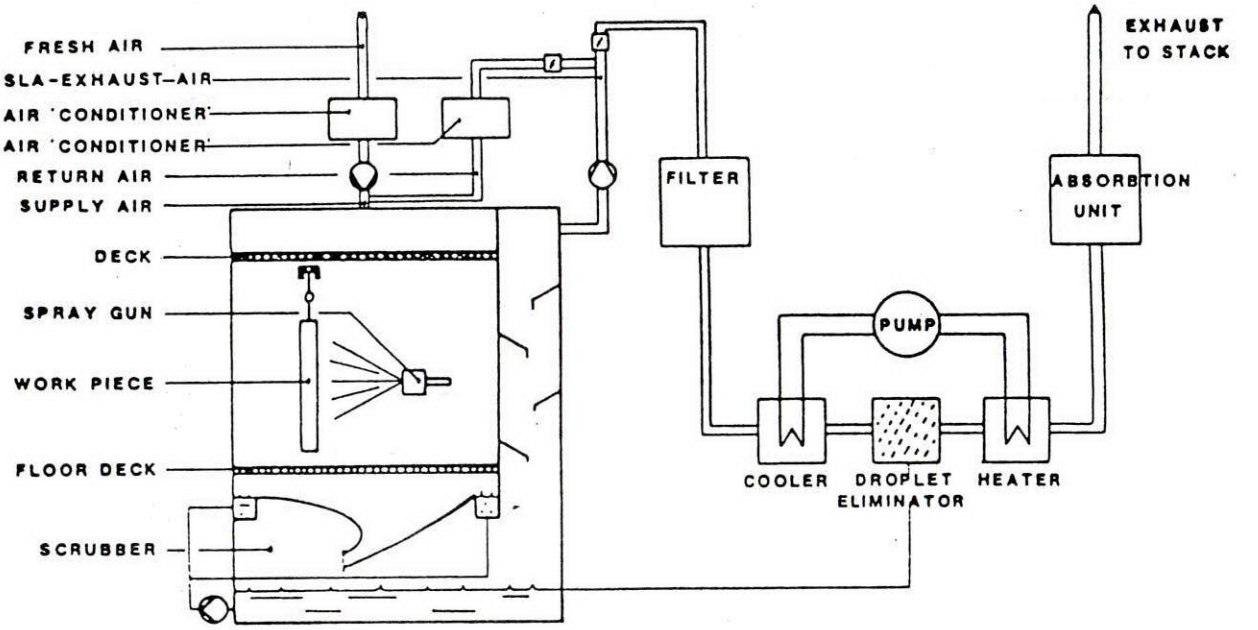
At this time, the particulate emissions standards and the VOC (volatile organic compounds) emission standards are relatively loose, and subject to local or state regulations. Yes, I said loose! My rational for using this term is that we believe, with time, most manufacturers are going to see significant tightening of the existing rules. Some specific locations, within our country, have already either tightened them or are in the process of doing so. Within a paint line, there is room to improve upon our present accepted standards in both areas. Yes, this will add additional cost to the installation of the paint line. However, with proper planning, some, if not all, of that cost can be recouped. We show in the following examples some approaches to this when a full system is properly designed.

In this first example, we show where a booth's exhaust is taken to an incinerator, and the output of the incinerator is coupled to an air to water heat exchanger that provides heat for the booth's input air. This will significantly reduce both particulate and VOC emissions.



SPRAY BOOTH WITH SCRUBBER
AIR RECIRCULATION AND AIR PURIFICATION
THROUGH THERMAL INCINERATION

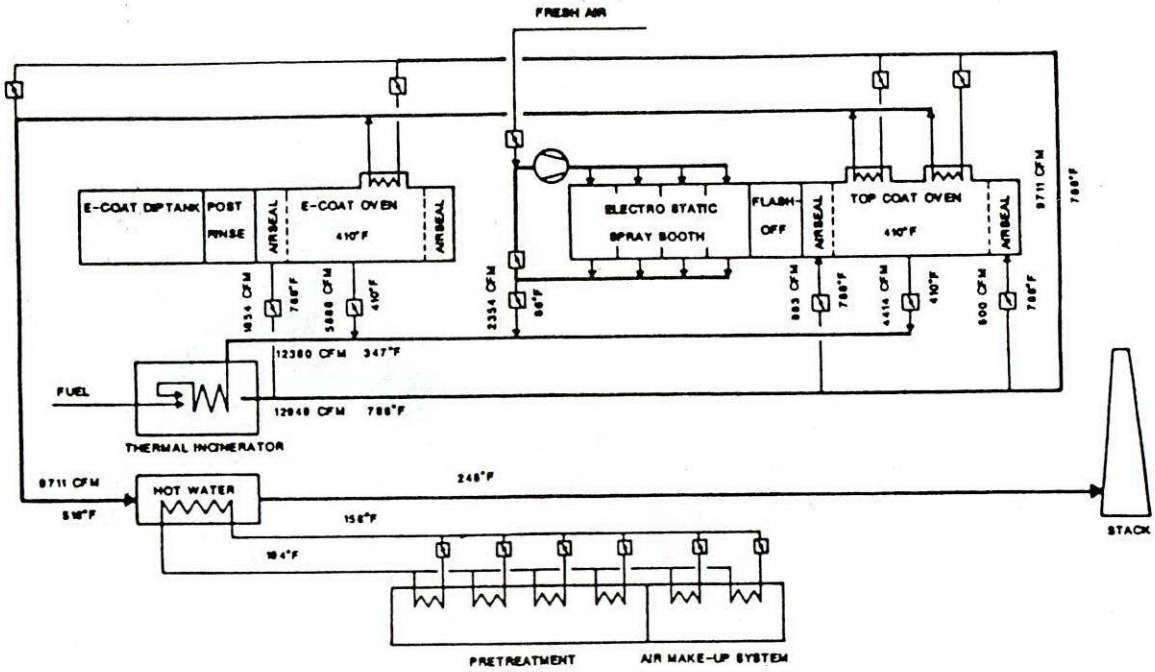
In this next example, we show the use of a water eliminator prior to an absorbtion type VOC scrubber combining fine filtration and partial recirculation of the booth's air.



SPRAY BOOTH WITH SCRUBBER
AIR RECIRCULATION AND PURIFICATION THROUGH ABSORBTION

EISENMANN

In this last example, we show a complete finishing line schematic utilizing a high degree of energy recovery, and circulation along with particulate and VOC elimination. An interesting point to note here is that with a systems heat discharge of some 12,400 CFM at ~350 degree F, we reduce this to ~250 degree F at the stack or a t of some 100 degree F. This indicates the amount of energy reused by the system. There are other economics within this type of systems approach. One exhaust stack for the full finishing line. Better control of the system on a year round basis via the ability to redirect heat or energy where it is needed to accommodate climate changes. With this type of system, you can operate your finishing line in any geographical location with any type of surrounding land use, and meet any forseeable emissions regulations. One of our best Public Relations Tools, as manufacturers, can be our demonstration of being concerned citizens and good neighbors. This is one way to do that.



PAINTSYSTEM WITH INCINERATION AND ENERGY RECOVERY

If you require a paint spray booth in your operation, why not have the best possible one? **YOU** can use it to your economic advantage, improve your **profitability**, and **minimize** your operating costs.

A-3

Organic Finishing Session A

Detackifying Chemicals for Paint Spray Booths

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DETACKIFYING CHEMICALS FOR PAINT SPRAY BOOTHS

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Abstract

The proper choice of chemicals to detackify paint overspray in spray booths is becoming increasingly important to control the volatile emissions and the handling of the waste paint. The new high solids paints and clearcoats are a particular challenge for detackification. The analytical capabilities and services provided to the customer are mandatory for control of the pits.

Introduction

In spray painting autobodies, appliances, and other consumer products, more than one-half of the paint may miss its mark and end up as overspray. In one modern practice this overspray is captured by a recirculating water curtain in the spray booth. The paint is captured in the water which cascades down the walls, or floors, of the booth and falls underneath into large retaining pits where the paint overspray either floats or sinks and is removed for disposal. The clarified water is recycled back to the spray curtain in the booth.

For this operation the recycled water must be chemically treated to detackify the paint, to render it free of stickiness and tackiness so it will readily separate itself from the water and not adhere to the curtain walls, pipes and pumps. It must remain in a loose granular form so it can be mechanically removed from the pits. If the detackifying chemicals do not work adequately, paint buildup will impede the water curtain, allowing the exhaust air from the booths to escape up the stack. These air emissions may contain live paint solids and excessive amounts of volatile organic compounds (VOC) that may exceed the requirements of the United States Clean Air Act. Furthermore, the accumulation of untreated raw paint in the bottom of the waste pits creates a serious problem when the system is periodically cleaned out, and has been known to actually shut down recirculating pumps. Much effort is required to remove the heavy buildup of tacky paint from the bottom of the pit.

The United States Environmental Protection Agency (EPA) has pressured the paint industry to rapidly advance their technology to meet the VOC air quality standards. This has led to the formulation of new water-based and high solids, solvent-based paints. Rapid changes in paints are also taking place to improve the appearance of the paint, such as the clearcoat lacquers, and to increase durability of the finish using urethane-based paints.

These new paints are more difficult to detackify and new chemical treatments had to be developed. Some of the chemical and application aspects of this changing technology are discussed in this presentation.

Chemicals For Detackification

Many chemicals and proprietary combinations have been tried for detackification. As early as 1960, U.S. Patent No. 2,585,407 mentions the then conventional practice of allowing the overspray to come in contact with water treated with caustic to pH above 8. This method became unacceptable as paints changed and in 1965, the use of cationic polymers in combination with ferric chloride was proposed to treat suspended matter comprising water and oil-based paints (See R. F. Day, Industrial Water Engineering, July, 1965). Subsequent to this, an extensive patent art disclosed the use of other soluble metal salts, anionic and cationic high molecular weight polymer flocculants, absorbent clays, and other materials.

Today, the chemicals used for detackification may, among other items, contain one or more of the following:

1. Alkalies such as hydroxides, silicates, phosphates, polyphosphates, borates, and carbonates of potassium and sodium. Also organic amines.

2. Soluble metals such as iron, aluminum or zinc as hydroxides, chlorides, sulfates and other forms.

3. High molecular weight polyelectrolyte polymers: anionic, cationic, or non-ionic.

4. Absorbents such as talc, chalk, starch, bentonite, clay, collodial silica, calcium silicate, magnesium silicate, aluminum silicate, and montmorillonites.

5. Minor ingredients such as defoamers and biocides.

The above materials are often combined into proprietary chemical specialties that are supplied by a number of vendors. Each vendor has his own way of meeting the objective of maximum effectiveness at minimum cost.

The following are some of the factors that have to be considered in designing a product:

1. There is no universal detackifier formulation that works on all paints in all spray booths.

2. The detackifiers have to be formulated, not only for specific paints, but may also have to be modified for specific paint booths. Different formulations may be required for detackifying water borne paints than for solvent paints, clearcoat lacquers, or urethane paints. The formulations may have to be modified

to float the detackified paint, sink the paint, or disperse the paint, depending on the method used for removal of the paint solids from the spray booths or the waste pits.

3. The detackifiers cannot cause any secondary problems in the pits such as excessive corrosion, biological growth, or foaming. This can be controlled to some extent by addition of defoamers, inhibitors, or biocides, but it is best to avoid these problems by proper formulation.

4. The chemical detackifiers cannot cause any environmental problems, serious safety problems, or undesirable reactions that would effect disposal of the waste paint, or the waste water such as:

   (a) The chemicals used cannot be highly toxic, or be known carcinogens.

   (b) The spray booth system should be near neutral pH or mildly alkaline to minimize danger to operators.

   (c) The detackifier should not contain soluble heavy metals which are limited by discharge regulations, such as zinc, unless proper precautions are taken for removal.

   (d) The detackifiers cannot react with water soluble components in the paint to form undesirable fluorescent color bodies, or other discoloration that cannot be removed from the waste water before discharge to the public waste water system, or to ground water.

   (e) The polyelectrolyte polymers and other chemicals used in detackification should be compatible with subsequent waste water treatment prior to discharge.

Application of Detackifiers

Even the best detackifier chemicals cannot be successful unless properly applied and properly maintained in the system. A good vendor should provide a complete service. Some vendors also provide additional waste water treatment services. The following are some important aspects to consider:

1. The vendor should work with paint suppliers so detackifiers are available that will work with new paints before introduction into the paint booths.

2. The vendor should cooperate in the design and testing of new spray booths.

3. Before using new detackifiers in existing spray booth systems, the vendor should survey the system and pickup samples of the paint for laboratory and pilot plant scale testing.

4. The paints to be detackified should be tried in a pilot scale paint booth with water curtain and waste pit--operated to simulate the commercial operation. Good vendors have such equipment available.

5. The vendor should provide a means of controlling the concentration of the detackifiers at the point of use. Simple titrations can be used for measuring alkalinity. More sophisticated methods are needed to measure polymer flocculant concentration. Some vendors have means of measuring polymer concentrations by titration.

6. Since detackification is a colloidal phenomena, it is very helpful to have a means of measuring the zeta potential of the suspended particles. Best coagulation occurs at or near zero charge. Some vendors have zeta meters available in their laboratories, as well as portable instruments that can be used to optimize the operation during start-up in the customer's plant.

7. The selection of proper feed points for detackifying chemicals to the spray booth is very important and depends on the type of chemicals used and booth operation. An experienced vendor can help with the installation.

8. Once the detackifier concentrations and points of application are optimized during start-up, it is absolutely essential to maintain these conditions. In larger installations metering pumps are utilized to maintain consistent chemical concentrations. These systems are normally monitored, or supervised, by the chemical supplier.

Summary

New chemical detackifiers have been developed and are being constantly improved to meet the rapid changes in paint and spray booth technology dictated by more stringent environmental requirements and paint changes being made to improve appearance and durability. Vendors are available who can provide a complete service ranging from the initial survey of the detackifier needs to maintenance of the detackifier operation and trouble-shooting the operation. To do this satisfactorily the vendors must not only have well trained field service persons, but also laboratory back-up with pilot scale paint spray booths and state-of-the-art analytical instrumentation, such as zeta meters for measuringng colloidal charge, as well as instrumentation for chemical analysis, such as infrared absorption, gas chromatography, energy dispersive spectroscopy, ion chromatography, and plasma emission spectrosocpy.

A-4

Organic Finishing Session A

Autodeposition of Organic Films - Some Unique Aspects

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AUTODEPOSITION OF ORGANIC FILMS - SOME UNIQUE ASPECTS

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Autodeposition is a method of applying an organic coating on clean metal surfaces without the use of an external current. In addition, there is no need for an iron or zinc phosphate pretreatment stage. A typical coating sequence consists of alkaline cleaning, water rinsing, coating in the autodeposition bath, water rinsing, and curing. This system has gained commercial acceptance due to its simplicity and ease of operation. An autodeposition process requires minimal floor space and is energy efficient. The chemicals employed in the coating bath contain no toxic heavy metals and low to no VOC levels while still imparting good corrosion protection to surfaces coated. These chemicals generate by themselves the potential required for a uniform coating with excellent throwing power to coat recessed areas. Bath solids are very low by volume (3-7%) and the system poses no fire hazard. The driving force for deposition comes from the chemical make up of the bath itself, greatly reducing energy requirements and giving freedom from the hazards and maintenance of a large external electrical power source. Aside from cleaning the soils produced in metal forming, no metal pretreatment is necessary.

A typical autodeposition bath consists of a complexing acid, an oxidant, and a latex. In the coating bath cleaned steel is etched mildly by an acid. This etching oxidizes iron in the steel causing the formation of positive sites. These positive sites attract anionically stabilized latex particles with subsequent destabilization and deposition. Because of this mechanism, the coating formation is diffusion controlled. After a monolayer of coating is deposited, the acid must diffuse through the coating to the surface to continue the deposition. Succeeding layers of coating provide a thicker barrier for diffusion resulting in increasingly slower deposition rates. Figure 1 shows graphically the rate of deposition.

This diffusion controlled coating mechanism imparts the unusual advantage of a self-leveling coating. This is extremely important in production applications where stamping and drawing can change the surface characteristics of the steel. The physical actions of stamping and drawing stretch and compress the metal unevenly across the surface. These stretches and compressions change the amount of iron in any given surface area of the steel. Since the deposition is driven by chemical attack on the iron, the deposition rate is determined by the amount of surface available for attack. Areas with relatively large amounts of reactive surface are extremely susceptible to attack and are termed "active" spots. It might be suspected that a coating would build unusually high in these areas, but this is not the case. Because of their activity, these areas do coat first, but the deposited monolayer of organic coating now provides a barrier for coating diffusion so the deposition rate slows quickly. At the same time the relatively inactive spots begin to undergo acid attack and latex deposition. The end result is an extremely uniform coating deposited on any given configuration.

Refering to Figure 1, it can be seen that at longer coating times the deposition rate slows and the leveling effect is maximized. This represents another advantage

because upon exiting the bath, parts carry (by surface tension) a layer of supernatant bath that is as yet not part of the film. If given time in air, however, this supernatant continues to react and become part of the film. Since most production lines are based on overhead monorails requiring 2-3 minutes transfer time between stages, this dwell time to react is automatically provided without any problem. This unique property also serves to maximize process efficiency since virtually all of the coating bath applied becomes part of the film, affording little to no rinse off.

Another demonstration of the uniformity of autodeposition coatings is shown by resistance to the "wedge" effect. The "wedge" effect is defined as the increase of film build from the top to bottom of a vertical work piece. This is a typical problem in immersion paint systems having low viscosities and solvents which evaporate slowly from the wet film. With an autodeposition process, the coating is chemically adherent to the substrate and any "wedge" effect is minimized. To demonstrate this, a steel test panel was immersed in a water-reducible alkyd enamel having a viscosity of 18 seconds with a Number 2 Zahn cup. The average film build was 1.14 mils. A second steel test panel was immersed in an autodeposition bath to develop the same film build. The average film build was 1.11 mils. It should be noted that commercially used autodeposited films need not be this high for good quality (generally 0.5-0.8 mil.), and the one mil plus film build was taken only to ensure a baseline in the experiment. The results are presented in Tables 1 and 2. On each panel 50 readings were taken with a standard induced-voltage-type film thickness measuring device (Elcometer 256). The readings were taken in sets of five vertically down the panel.

From this chart it can be seen that the "wedge" effect is extremely prominent with the alkyd enamel. In Table 1, increases are shown in each set of five readings taken vertically down the panel. The measurements over the entire panel surface ranged from 0.48-2.2 mils. In Table 2, which shows film build variations over the autodeposited panel, no pattern of increases can be seen; i.e., no "wedge" effect is evidenced. Although the mean film thickness on both panels is very close, the standard deviation for the dip enamel is 0.41 mil but only 0.10 mil for the autodeposited panel. The coefficient of variation is defined as the standard deviation divided by the mean value. This is a numerical representation of the scatter of results or, in this case, uniformity of film build. The lower the coefficient of variation, the more uniform the coating. The dip enamel panel shows a coefficient of variation of 35.8%. The autodeposited panel has a coefficient of 8.8%, roughly one quarter of that exhibited by the panel coated with the immersion enamel.

Though a conventional dip or immersion process has theoretically unlimited throwing power, unlike autodeposited coatings the films cannot be rinsed to remove the paint-bead from the bottom of the work piece because the wet film is very soft with no chemical adhesion. Autodeposition is similar to electro-coating except it does not use any external current. Both processes will be compared in their throwing powers.

Throwing power has been defined as the ability of an electro-coating paint system to deposit films inside a standard box. The box is made up of two test panels of either 4" x 12" or 4" x 18 "imensions. These panels are separated from each other by 3/8" strips of a non-conductive plastic spacer. Both sides of the box are covered with adhesive tape leaving the top and bottom areas open. When either of these boxes is immersed 11" or 17" in the coating bath, liquid enters only from the bottom. The box is then rinsed and baked, and a comparison of film thickness between the inner side and the outer side is made. Anodic electro-coating systems normally deposit up to 8"

maximum inside an enclosed chamber immersed 17 inches in the coating bath; cathodic paints normally coat up to 15" inside the chamber. In the case of autodeposition, a coating is formed to the full extent of the immersed section.

Another advantage of the autodeposition process is its ability to coat recesses. Because all potential for coating is contained in the bath itself, it has great throwing power. The generally applied rule is, "If the surface can be wet, it will be coated." This is a big advantage over coatings applied by means of external electrical sources. These coating systems, because of Faraday caging effects, are limited in their ability to "throw" or to coat recesses.

Figure 2 shows a steel tube of one-half inch interior diameter which has been coated by means of autodeposition and subsequently cut to enable examination of the interior. The tube was not totally submersed in the coating tank so that the bath could not enter and flow from both ends. All wetted surfaces of the tube have been coated, both exterior and interior, with the upper interior area having a somewhat lower film build. This condition arises from relatively low agitation of the bath in the interior. As with all diffusion controlled processes, agitation can serve to speed the reaction by increasing the transport rates of the acid and the latex. In a production condition, agitation can be increased by utilization of draft tubes, conveyor "humps" to create a vertical movement of the part in the coating bath, or even horizontal racking, parallel to conveyor travel, which maximizes the flow of bath through the tube. More simply, side-mounted agitators, with marine-type propellers, can generate a circular flow through the coating bath to increase diffusion rates.

In summary, this presentation stresses some practical aspects of autodeposition. Infinite throwing power over cleaned-only metal surfaces, plus the advantages of process simplicity, minimal equipment costs, and high quality levels, give autodeposition systems obvious advantages over other finishing operations.

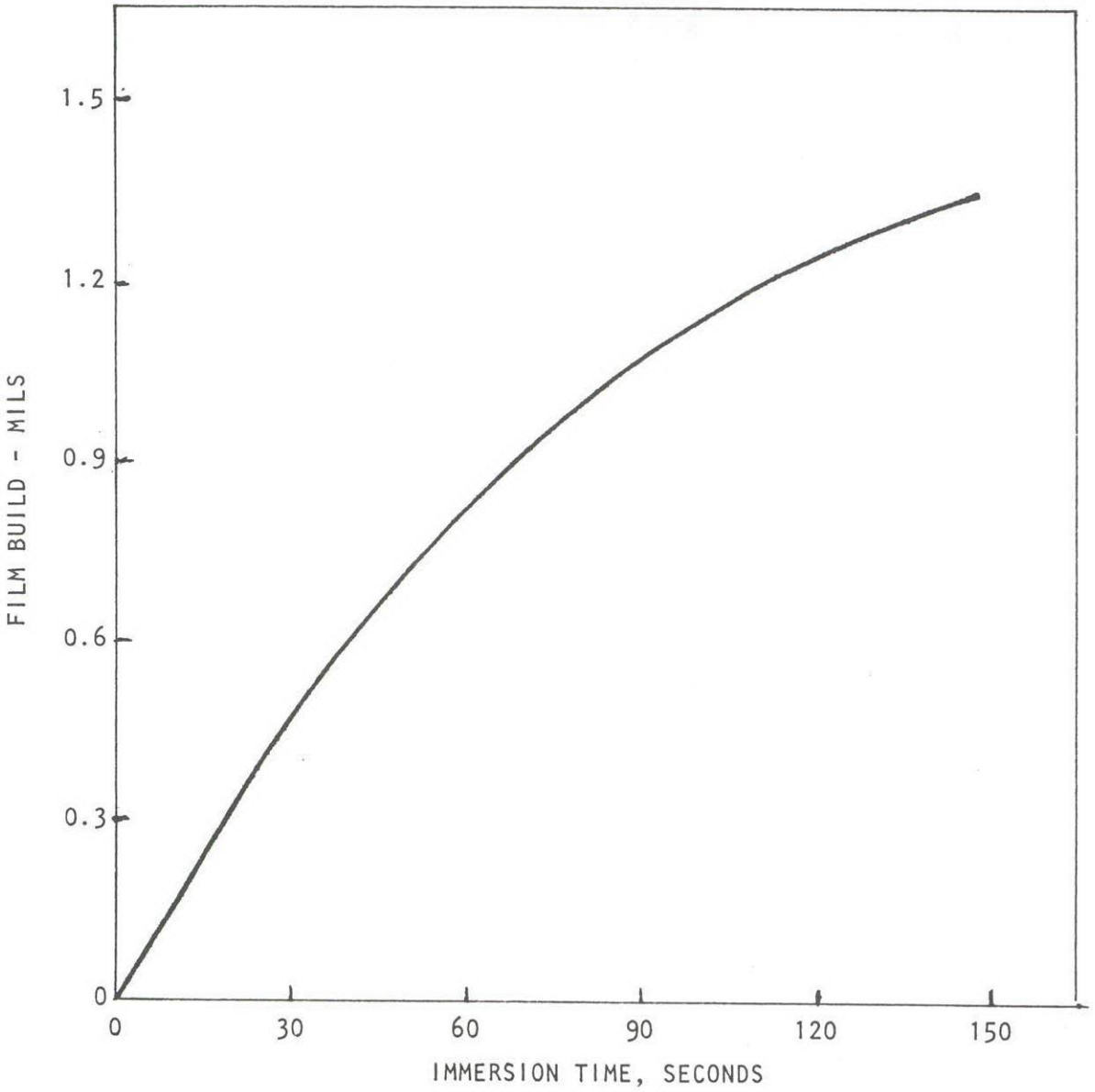

Figure 1 Film Build vs. Time of Immersion

TABLE 1

One panel dip coated with a water reducible alkyd enamel to approximate 1.1 mils film build.

1	0.45 mil	18	1.04 mil	35	1.65 mil	43	1.07 mil
2	0.85 mil	19	1.26 mil	36	0.83 mil	44	1.04 mil
3	1.09 mil	20	1.53 mil	37	0.82 mil	45	1.47 mil
·	1.36 mil	21	0.51 mil	38	1.05 mil	46	0.54 mil
5	2.02 mil	22	0.84 mil	39	1.19 mil	47	0.96 mil
6	0.57 mil	23	0.97 mil	40	1.66 mil	48	1.10 mil
7	0.85 mil	24	1.15 mil	41	0.65 mil	49	1.30 mil
8	1.14 mil	25	1.20 mil	42	0.87 mil	50	1.77 mil
9	1.44 mil	26	0.57 mil				
10	1.70 mil	27	0.88 mil				
11	1.49 mil	28	1.19 mil				
12	1.14 mil	29	1.62 mil				
13	1.49 mil	30	2.34 mil				
14	1.29 mil	31	0.60 mil				
1[illegible]	1.63 mil	32	1.01 mil				
16	0.51 mil	33	1.06 mil				
1[illegible]	0.96 mil	34	1.15 mil				

Number or Readings	50
Maximum Reading	2.34 mil
Minimum Reading	0.48 mil
Mean	1.14 mil
Standard Deviation	0.41 mil
Coefficient of Variation	35.8 %

TABLE 2

One panel coated with autodeposition to average approximately 1.1 mils film build.

1	1.12 mil	19	1.01 mil	37	1.07 mil	44	0.99 mil
2	1.06 mil	20	1.09 mil	38	1.03 mil	45	0.93 mil
3	1.09 mil	21	1.23 mil	39	0.96 mil	46	1.19 mil
4	0.96 mil	22	1.27 mil	40	0.96 mil	47	1.19 mil
5	1.01 mil	23	1.15 mil	41	1.21 mil	48	1.12 mil
6	1.30 mil	24	1.21 mil	42	1.19 mil	49	1.25 mil
7	1.09 mil	25	1.21 mil	43	1.15 mil	50	0.99 mil
8	1.11 mil	26	1.21 mil				
9	1.04 mil	27	1.17 mil				
10	0.99 mil	28	1.20 mil				
11	1.12 mil	29	1.13 mil				
12	1.24 mil	30	1.17 mil				
13	0.98 mil	31	1.23 mil	Number or Readings		50	
14	1.02 mil	32	1.15 mil	Maximum Reading		1.30	mil
15	1.02 mil	33	1.02 mil	Minimum Reading		0.93	mil
16	1.26 mil	34	1.06 mil	Mean		1.11	mil
17	1.13 mil	35	1.04 mil	Standard Deviation		0.10	mil
18	1.07 mil	36	1.15 mil	Coefficient of Variation		8.8	%



FIGURE 2a
Autodeposition Coating on Exterior of One-Half-Inch Tube

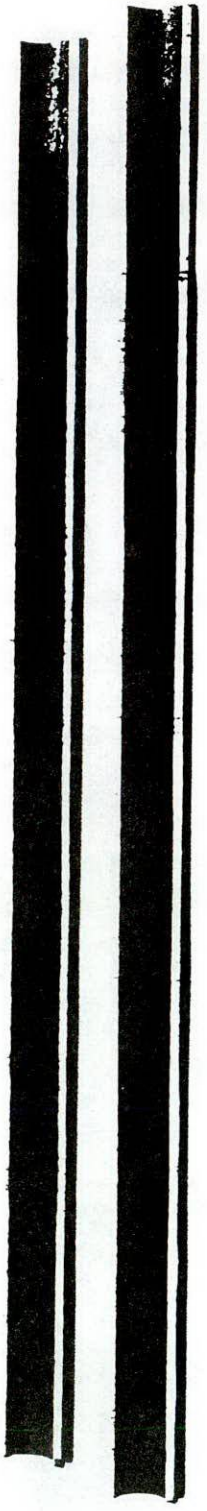

FIGURE 2b
Coverage of Interior Areas

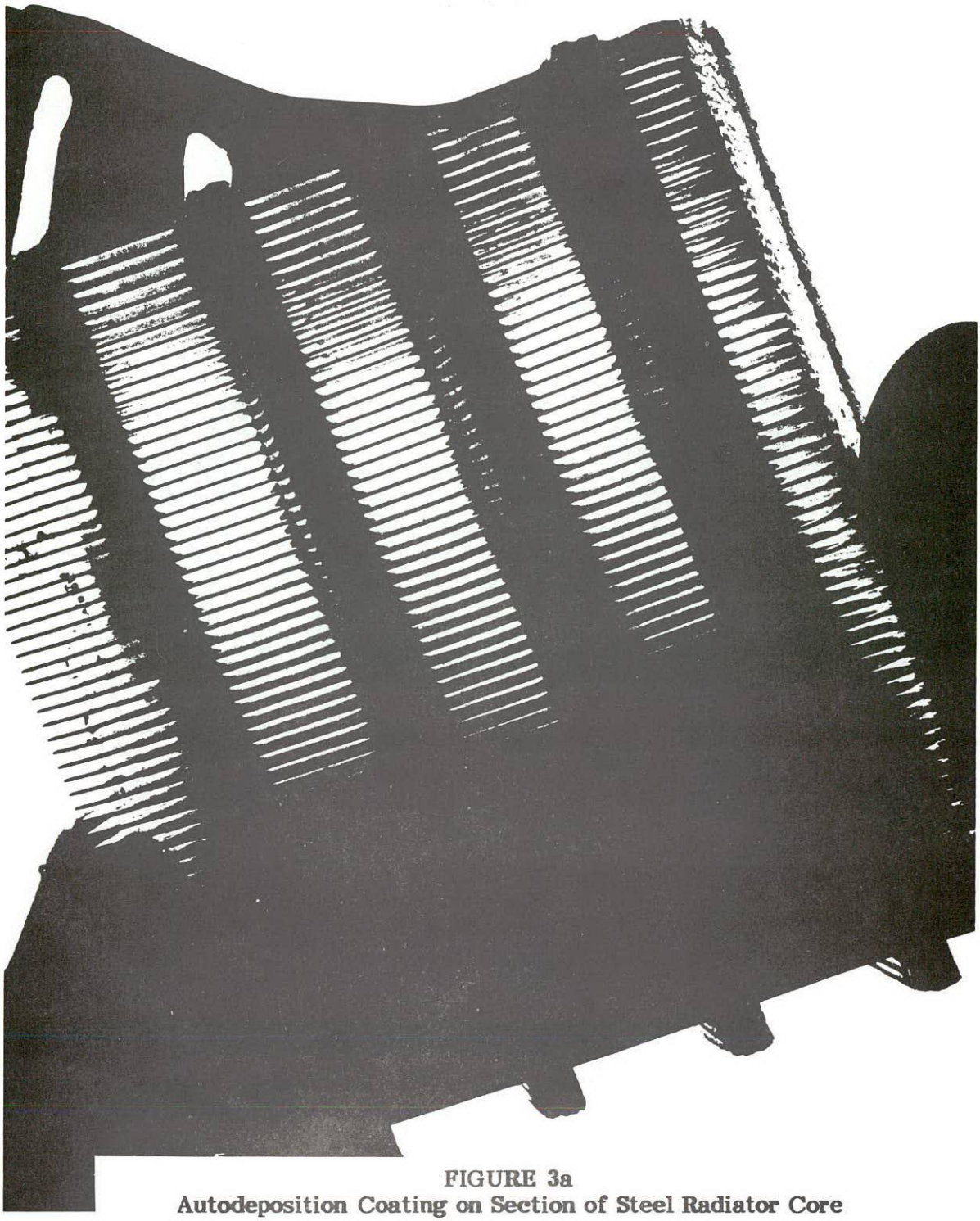

FIGURE 3a
Autodeposition Coating on Section of Steel Radiator Core

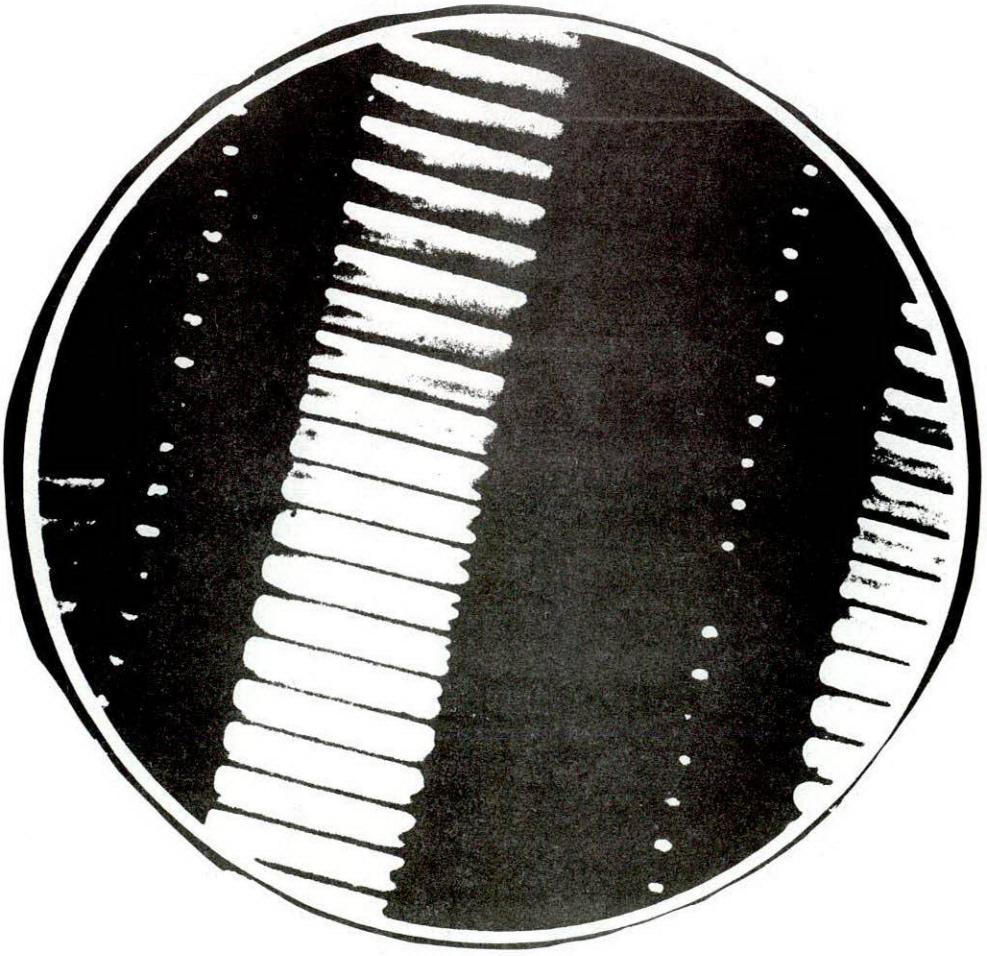

FIGURE 3b
Close-Up (Fin Spacing = 0.020")

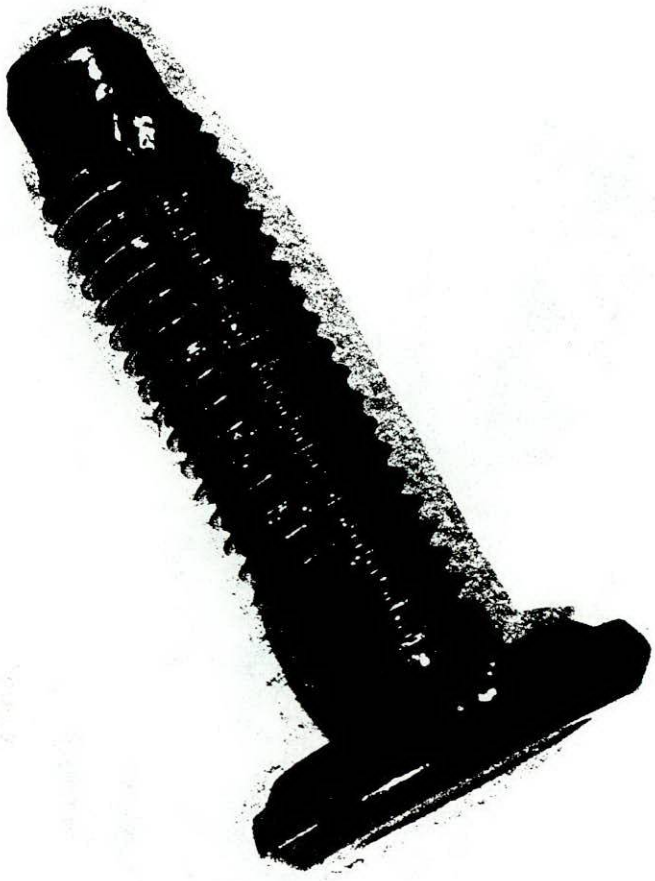

FIGURE 4a
1-1/2" Screw Coated by Immersion in Alkyd Enamel

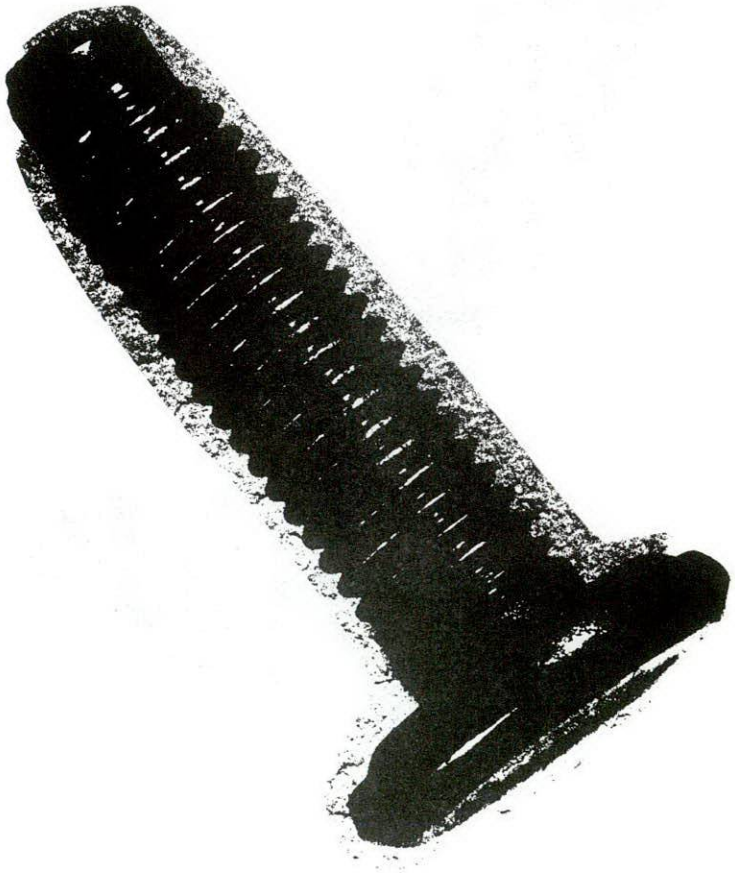

FIGURE 4b
1-1/2" Screw Coated by Autodeposition

B-1

Vacuum Coating Session B

Vacuum Metallisation with Closed Field Sputtering

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VACUUM METALLISATION WITH CLOSED FIELD SPUTTERING

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ABSTRACT

In recent years, sputtering became the favourite method for depositing highly adherent thin coatings on plastic, glass or metals for different applications. Advances in the technology of magnetron sputtering targets have permitted high deposition rate at lower acceleration voltage, lower substrate temperature and lower gas pressure. This led to a further improvement in the quality of the end product. Further advances resulted in the development of an industrial coating process called 'Closed Field Sputtering' which utilises a specially designed magnetic field to reduce the target temperature and at the same time increases the target life time and coating speed.

1. Introduction

Vacuum evaporation has been the conventional technique for depositing thin films on different materials including plastic and glass. Typical applications range from packaging, capacitor films, decorative and solar coatings. However, vacuum evaporation is limited in general to the deposition of pure metals. Of the many problems encountered in vacuum evaporation are the difficulties in evaporating metals with high melting points such as chromium and stainless steel because of the heat radiation from the source and the low brightness and cracking of such coatings. Further problems associated with the deposition of metallic alloys, compounds and dielectrics makes evaporation an unattractive technique in such applications. Recent demands for more complex film structures and materials for new applications led to the utilisation of magnetron sputtering as an alternative to evaporation in many applications[1,2,3,]. Advances in the technology of the high performance magnetron sputtering have permitted high deposition rate at lower acceleration voltage, lower substrate temperature and lower gas pressure than the conventional diode sputtering machines. Further developments has resulted in an industrial plating process called Closed Field Sputtering which utilises a specially designed magnetic field to reduce the target temperature by reducing electron bombardment and at the same time increases the target life and coating speed. Wide ranges of non-magnetic metals and alloys can be sputtered in this machine on a commercial basis. It is also possible to produce coating of some oxides, nitrides or carbides for different applications[4].

2. The Sputtering Process.

In a conventional diode sputtering, an electrical discharge is initiated between the cathode [target] and anode [substrate] in a vacuum chamber with an inert gas [usually argon] at a pressure of 1 - 100 m.torr.

Consequently, the cathode is bombarded with positive ions and neutrals leading to the ejection of atoms from the target surface. Secondary electrons emitted from the target during ionic bombardment produces further ionization and maintain the discharge. The ejected atoms will eventually deposited on the substrate and form a continuous film with properties similar to the target materials. The conventional sputtering however, suffer from basic limitations due to the relatively high gas pressure needed for the discharge and the excessive heat received by the substrate as well as the slow sputtering/deposition rate. High gas pressure can influence film adhesion, structure and physical and chemical properties. It can also lead to low deposition rate due to the scattering of the metal atoms after colliding with gas atoms. Heating of the substrate can result from two sources ; Radiation from target [about 2/3 of heat] and electron impact [about 1/3 ofheat]. Direct water cooling of the target [cathode] can eliminate radiation as a problem but heat produced by electron flow between the anode and cathode cannot be easily avoided and can damage plastic objects. While these problems can be partially eliminated by using RF discharge, great improvements can be achieved by introducing a magnetic field which is perpendicular to the electric field. This technique is known as magnetron sputtering.

3. The C.F.S. Process.

Closed Field Sputtering [CFS] involves the production of a magnetic field close to the surface of a cylindrical target [Fig.1]. The target [cathode] consists of the material to be sputtered and the magnetic field which is arranged so that the uniform field B is parallel to the cathode axis. The strength of the magnetic field is around 200 gauss so that it affects the plasma electrons but not the ions.

By biasing the cathode with a couple of hundred volts negative, secondary electrons will be emitted due to the bombardment of the cathode surface by Ar^+ positive ions. The electrons are deflected by the magnetic field surrounding the cathode into small diameter circular orbits and perform a magnetron motion at a point at which the magnetic field and electric field intersects. Any neutral argon molecules enter the space of rapidly moving electrons are immediately ionise and become positively charged. The argon ions will bombard the cathode surface causing the sputtering of metal ions. These atoms are mainly uncharged but their temperature corresponds to the melting point of the target material and in the case of chromium atoms, the velocity is approximately 6.68×10^5 cm/sec. at a temperature of 1990°C. and molecular weight 8.635×10^{-23} grams.

The rapidly revolving electrons produces a characteristic ring of bright ionized gas in the form of a toroid encircling the cathode at the centre of each magnet [Fig.2]. A faint glow discharge fills the remainder of the free space in the metal bell jar. The bright bands of ionization indicate the area on the cathode from which the metal atoms are being sputered. The dark area between the bright bands is at least four times the area of the bright bands. This means that the target [cathode] will erode in local spots by sputtering and consequently, will have a shorter life. To overcome this problem the magnet assembly inside the cathode tube is reci-

procated back and forth along its axis to drive the toroids of rotating electrons over the surface of the cathode to even the wear and prolong its life. Sputtered metal atoms are deposited on the substrate while electrons continue their magnetron motion around the cathode and are prevented from escaping towards the substrate. Therefore the substrate is maintained at low temperature during sputtering thus making low temperature, high speed sputtering possible. This is in contrast to coventional sputtering where electrons are continuously bombarding the substrate causing it to heat up to several hundred degrees and preventing the coating of plastic objects.

4. The C.F.S. Equipment.

Fig [3] illustrates one type of the CFS equipment. In contrast to typical batch metallisers, the system is a vertical configuration with a horizontal baseplate. Vessel sizes range from 1200 to 1900 mm. in diameter and 1500 to 2200 mm. in height. This permits a sputtered film of chromium, aluminium or other metals to be applied evenly on large plastic mouldings up to 1500 mm. or greater. The equipment is normally mounted with the diffusion pump in a pit so that the vessel baseplate sits just above ground level. Two carousels are used which can run sideways on a track.

5. Coating Process.

The full coating process consists of three main lines, the basecoat line, the CFS machine and the top coat line. The process usually runs in a clean room atmosphere because any dirt on a finished plate part is extremely apparent. Application of the high solids, UV - curable basecoat requires six stations, each of which requires minimum residence times[5,6]. These are :

1. Parts loading.
2. Degreasing [1 min].
3. Basecoat applicaiton [1 min.]
4. Infrared flash off [3 min.]
5. UV cure [1 min.].
6. Parts unloading.

To sputter the base coated parts in a bell entails racking them on a carousel that is then rolled into position. After pressing the start button the pumpdown sequence commences and the various types of vacuum pumps [i.e., rotary, booster and diffusion pump] are brought into operation automatically at the appropriate degrees of vacuum [Fig 4]. When a pressure of 1×10^{-4} torr is reached, argon gas is introduced into the chamber raising the pressure to 5×10^{-4} torr. At this pressure sputtering begins for a preset period of two minutes. Fig [5] shows the uniformity and the temperature rise of the coating in different positions in the chamber. The sputtering supply is switched off, the vessel is vented to atmosphere and the chamber is opened. The parts then removed from the carousel and re-loaded on the top coat line for infra red and UV treatment.

These treatments are necessary for decorative finishing and it is important to select lacquers which are compatible with the particular metal being sputtered[6].

6. Applications

The typical applications of the C.F.S. process ranges from decorative finishing to functional. Examples of the decorative finishing include items such as toys, cosmetic caps and picture frames. The decorative functional applications requires both decorative and performance characteristics. Typical examples are appliance end caps, automotive grills, knobs, buttons, door hardware, plumbing, overhead office lighting fixtures and spectacle frames coated with titanium nitriding. These applications allow areas such as corrosion resistance, impact resistance, reflectivity, durability, adhesion and even appearance quality. For functional applications typical examples might be EMI/RFI shielding[7] corrosion resistance metal parts, electrical connections and barrier coats. Fig [6] and [7] shows some of the typical applications of the CFS process.

7. Conclusions.

The main advantages of the closed field sputtering are summarised as follows :

1. High deposition rate can be achieved at short time and with minimum substrate temperature increase. Thus plastic parts can be coated safely.

2. Good throwing power and coating uniformity which gives very good coverage of complex parts.

3. Because of the high uniformity and reproducibility achieved by the CFS process it can be used to produce semi-transparent films and ultraviolet protective films amongst others.

4. Compound coatings of oxides, nitrides and carbides can be deposited by mixing reactive gases such as oxygen and nitrogen with argon gas during the sputtering process. Thus titanium nitride can be achieved with different colours ranging from yellow [thin coat] to dark blue [thick coat] by simply varying the coating time or reactive gas flow.

5. High melting point metals such as tungsten and molybdenum can be deposited onto plastic parts without any thermal damage to the substrate.

6. The CFS process is very easy to control and consistantly reproducible results can be obtained for coatings ranging from below 100 Å to well above 1000 Å in thickness.

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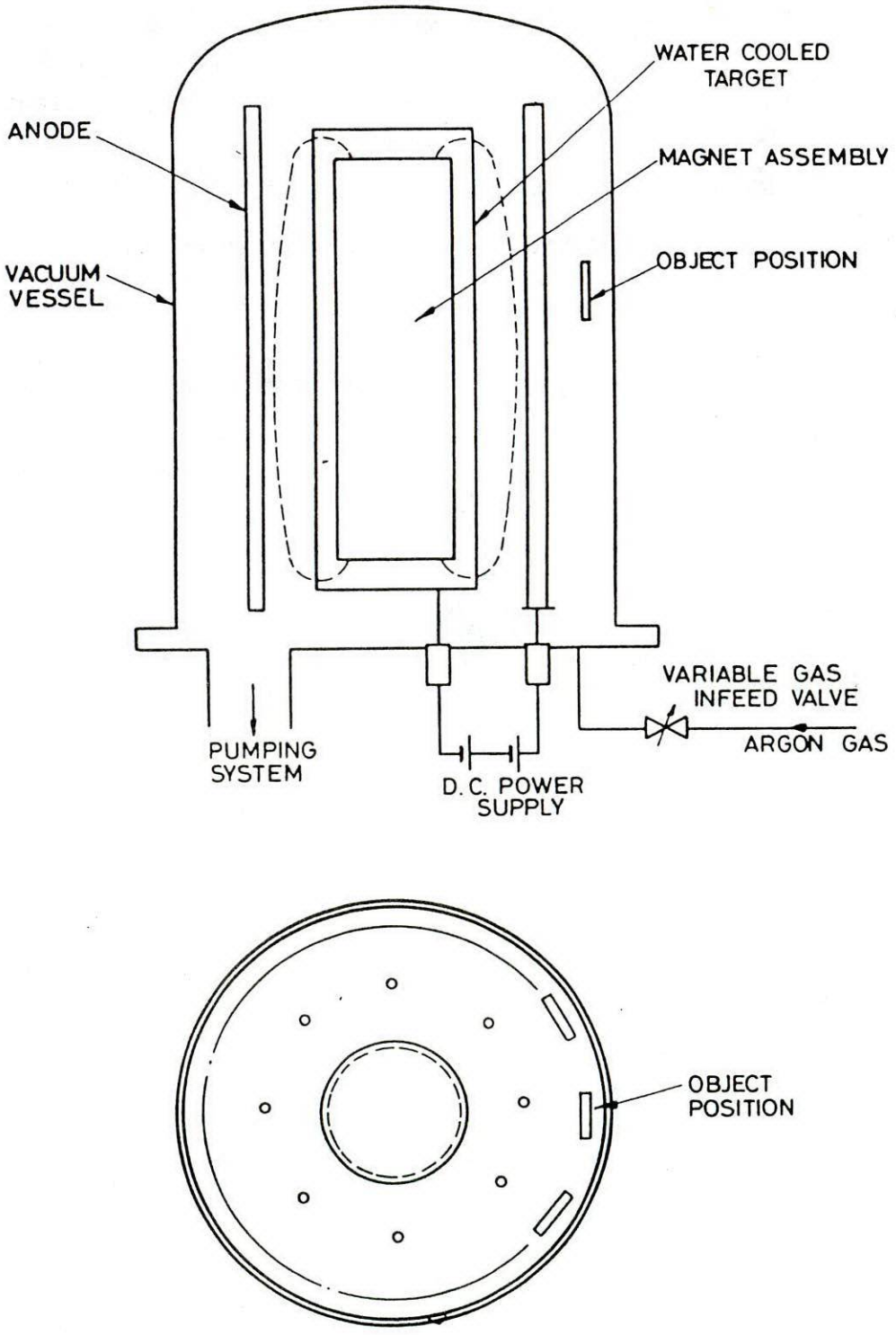

Fig 1 Constructional arrangement of C.F.S. equipment.

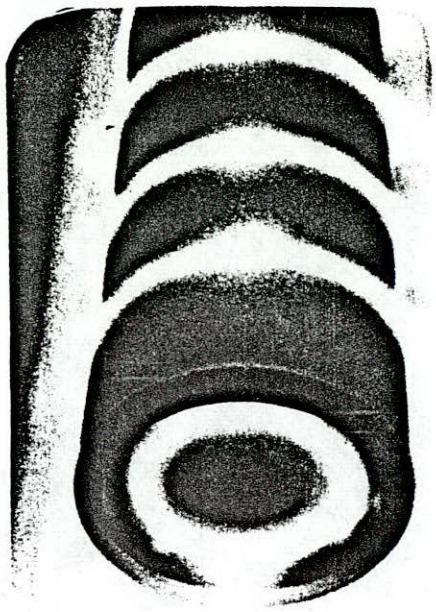

Fig 2 Plasma discharge around the cylindrical target [cathode]

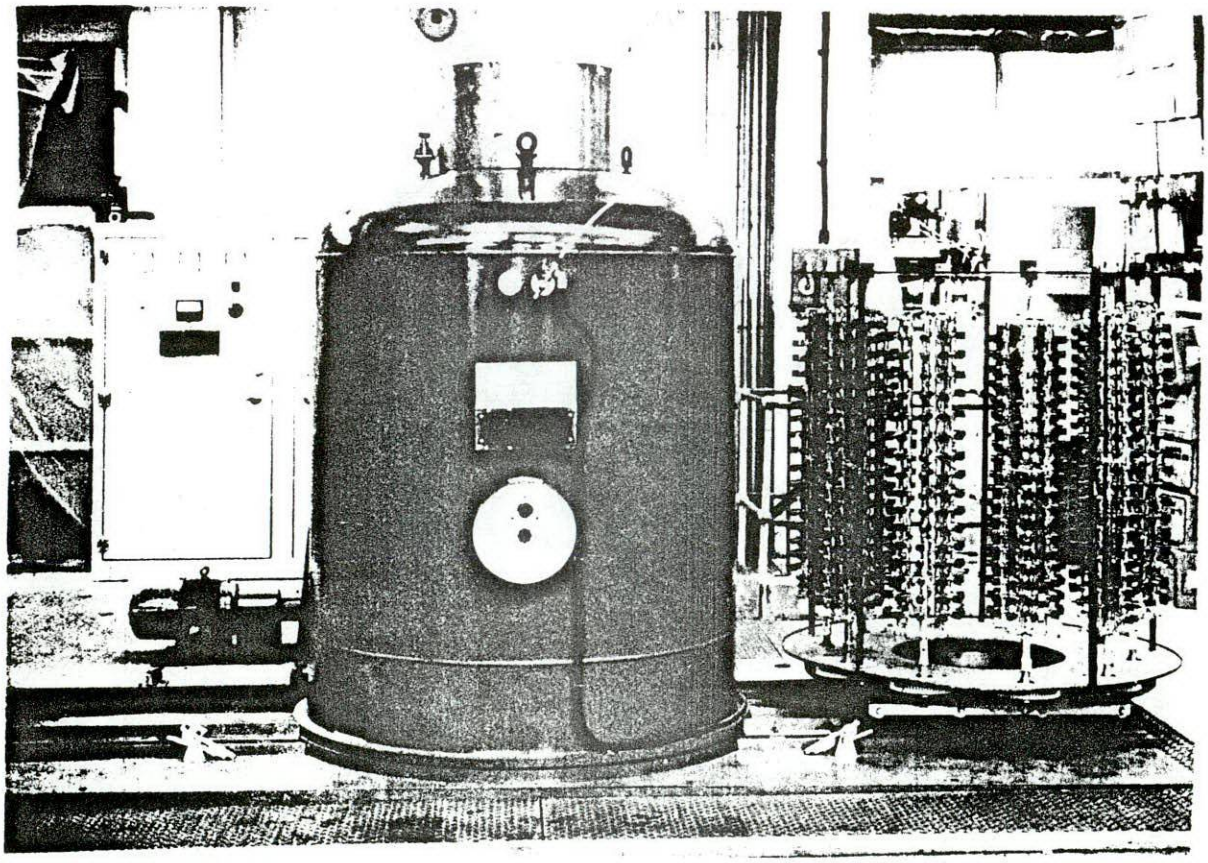

Fig 3 C.F.S. Equipment.

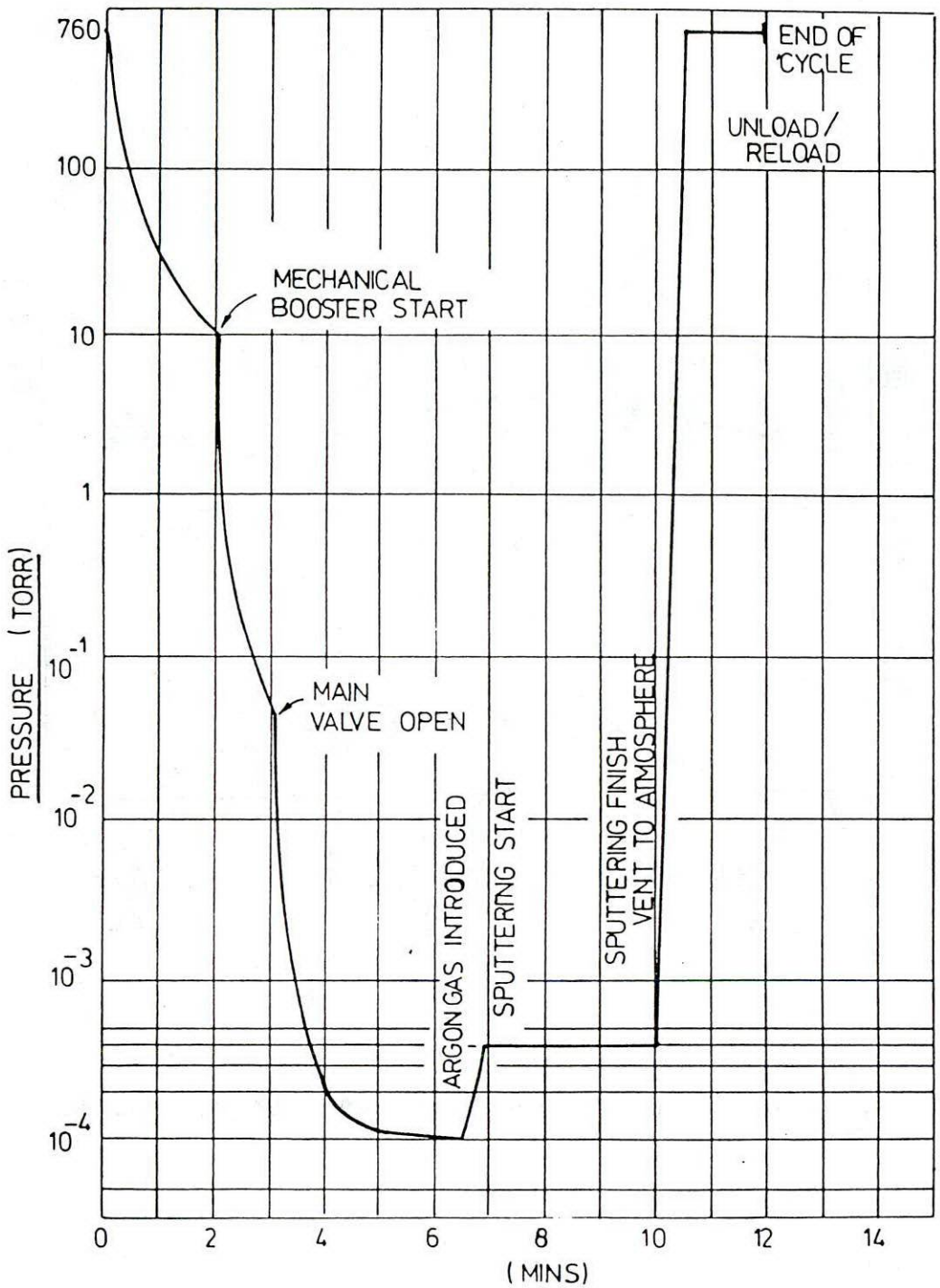

Fig 4 Typical cycle time of C.F.S. equipment loaded with objects.

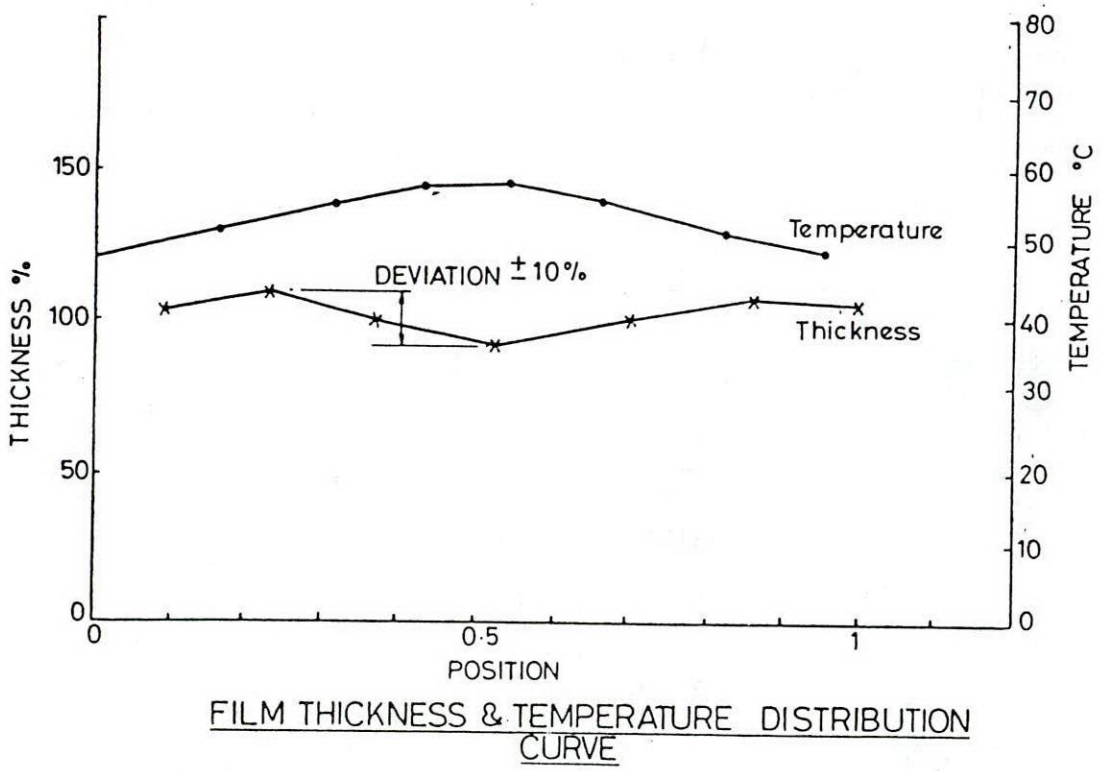

Fig 5 Coating thickness uniformity in different positions in the vacuum chamber.



Fig 6 Typical applications of the [C.F.S.] machines.

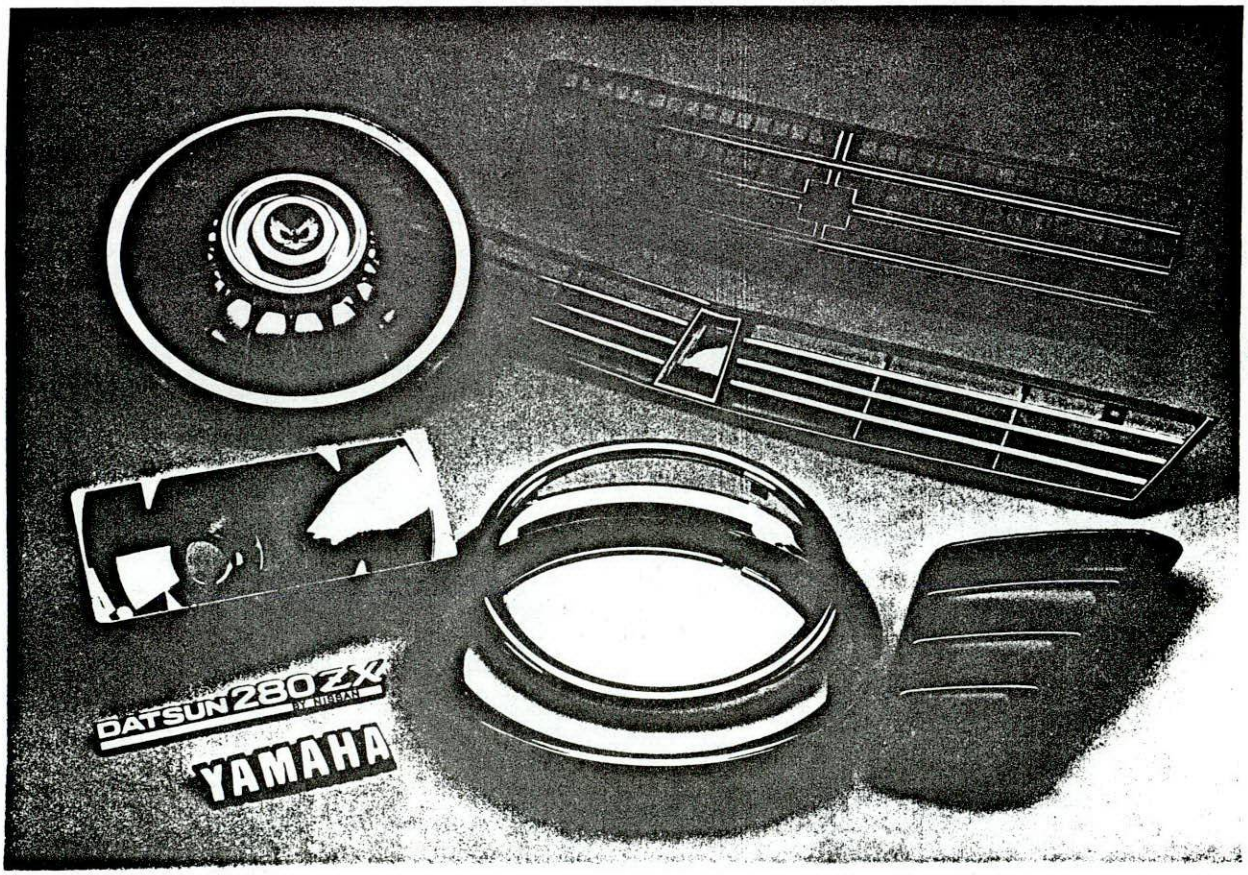

Fig 7 Applications of the [C.F.S.] in the car industry.

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Vacuum Coating Session B

Advances in Metallising Equipment

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ADVANCES IN METALLISING EQUIPMENT

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Aluminium foil which is energy intensive to produce and therefore expensive has been used extensively as the traditional barrier device for the packaging of cigarettes and food products.

Due to this expense many countries have turned to less energy intensive and inexpensive materials such as metallised substrates and in metallising it was Europe that had been in the forefront of the development of this technology.

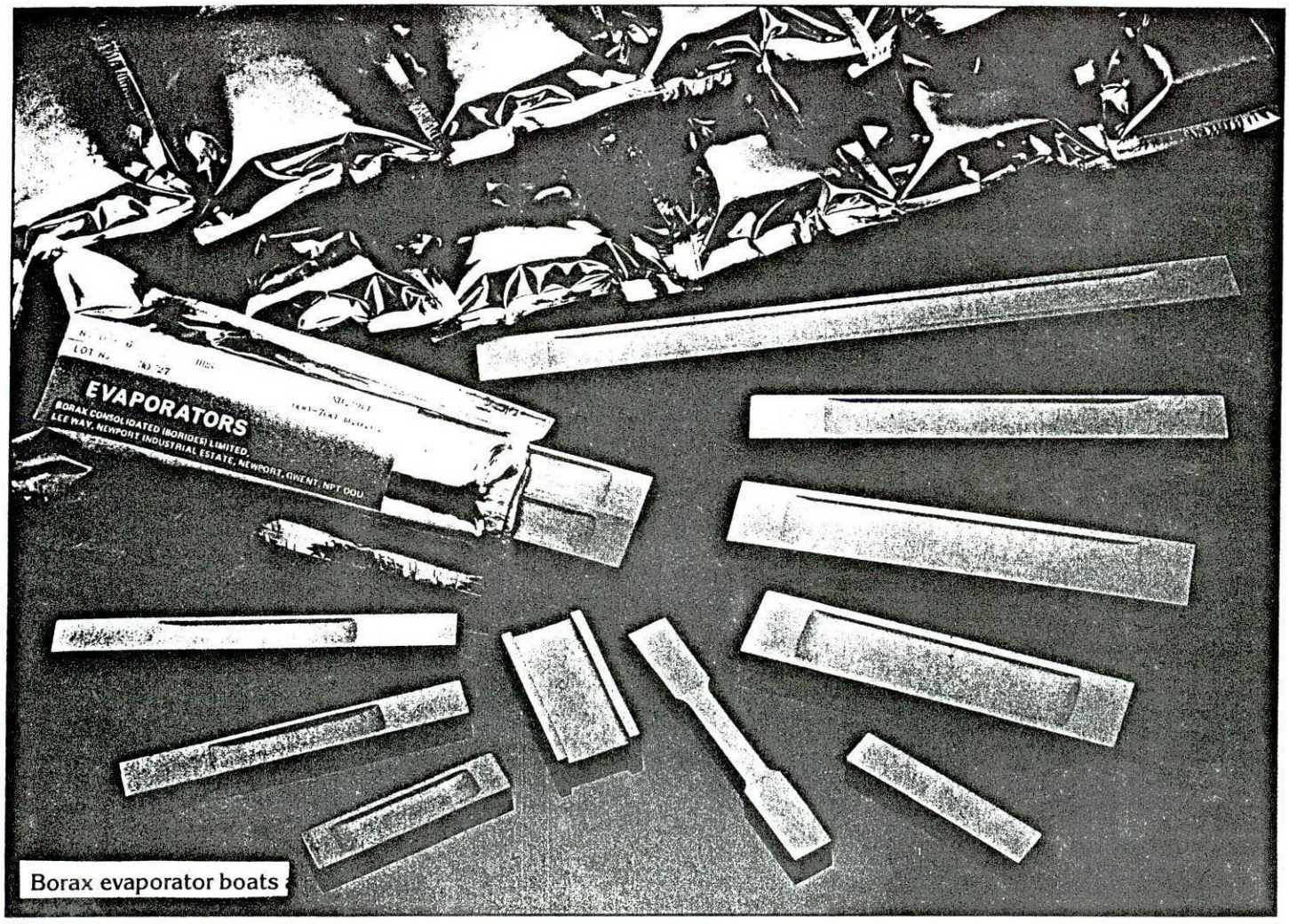
It was soon realised that the alternative to foil had additional desirable features quite apart from the economies and new markets soon developed to take advantage of them. All this demand led to a tremendous increase in the need for metallised products and a rapid growth in the industry. Unfortunately, the majority of metallising machines were either too old or too slow and their operation depended very much upon the expertise of the operators and hence were not able to meet the demand.

New, faster and wider machines had to be developed that could handle a much wider range of substrates and that would also consistently produce high quality products.

Conventionally, vacuum metallised substrates are produced by the deposition of a metal typically aluminium onto a non-treated or pre-treated substrate in specially designed and constructed equipment under conditions of high vacuum. Typical deposition thickness can range from 200 angstrom up to 1000 angstrom units.



Conventionally, the method of operation is the batch mode; a roll of substrate is loaded onto a winding mechanism which is then positioned inside a vacuum chamber, unwound and metallised at pressures of approximately 10^{-4} mbar.



Borax evaporator boats

Aluminium is evaporated at high temperatures from an intermetallic boat at around $1400^{0}C$ and the evaporant condenses onto the moving substrate as it passes over a chilled roller.

History shows that paper was actually the first material to be commercially metallised as can be appreciated when one considers the relative age of the thermo plastic films available today. In Germany, Busch were coating capacitor tissue with zinc as far back as the late twenties, again the low production efficiency limiting use to this single specialist application.

In the mid late 50's, metallised paper faded almost entirely in the face of competition from the newly developed plastic films and the continuing price disadvantage incurred as a consequence of production techniques and equipment.

Due to the increasing demands the specifications for the metallising equipment became more exact, with much thicker deposition rates. Pumpdown times had to be shorter as had to be the overall downtime of the machine. Reel diameters were increasing as paper mills began to supply material for metallising. Similarly, there was an increase in web width variation and capital cost of the equipment became a major factor.

The majority of paper which was being metallised had to be pre-dried to reduce moisture content levels, typically down to 1%. This however, was uneconomical as energy had to be used to dry the paper to these levels, before metallising, the paper then being remoisturised after metallising. Paper normally or naturally has a stable moisture level of 8 to 9% so the problem of drying is self evident. Hence the demand came to metallise papers having high moisture contents 4% typically and with the requirement for faster pumpdown times new thinking was required in the design of the equipment.

Twin zone metallisers appeared with the vacuum chamber having two distinct pressure zones separating the winding system from the evaporation system but still to all the passage of the substrate from one zone to the other. The pressure differential between these zones is now in the order of 2 decades difference, hence in high pressure low vacuum winding zone water vapour has a smaller volume than if the vapour existed in the evaporation zone.

However, even with this configuration the vacuum pumping groups had to be assisted in the pumping of this water vapour by the use of cryogenics.

This took the shape initially of a panel though which was passed liquid nitrogen to form a very cold - nitrogen boils at -196°C - surface on which to condense the water vapour. However, the use of LN_2 is a very costly and wasteful process as the LN_2 is merely discharged to atmosphere after passing through the metalliser. In the early days there was no real alternative as mechanical refrigeration units were either unreliable or could not reach temperatures low enough to condense the water vapour. Today, however, this technology has advanced considerably and on the new range of metallisers, cryogenics using compressor systems are an integral part of the pumping systems. Modern units can cool down to -130°C which is sufficient for the purpose when one considers that water vapour condenses at around -100°C at 10^{-4}mbar.

Now with this combination of twin zone, cryogenics and large vacuum pumps, higher moisture content papers could be metallised giving greater economics to the metallising companies.

In today's market, however, requirements are becoming even more diversified and in the paper market the requirements have increased from the standard range of paper thicknesses typically 30 gsm to 150 gsm and there is now a requirement for a metallised board up to 400 gsm. This now becomes a completely different ball game.

At this present time in Europe, major metallising companies are approaching this problem by two different metallising techniques.

Direct Metallising

This method is the most commonly used method of metallising paper at present. A roll of substrate has to be loaded into the vacuum chamber and metallised directly.

Direct Metallising (Cont'd)

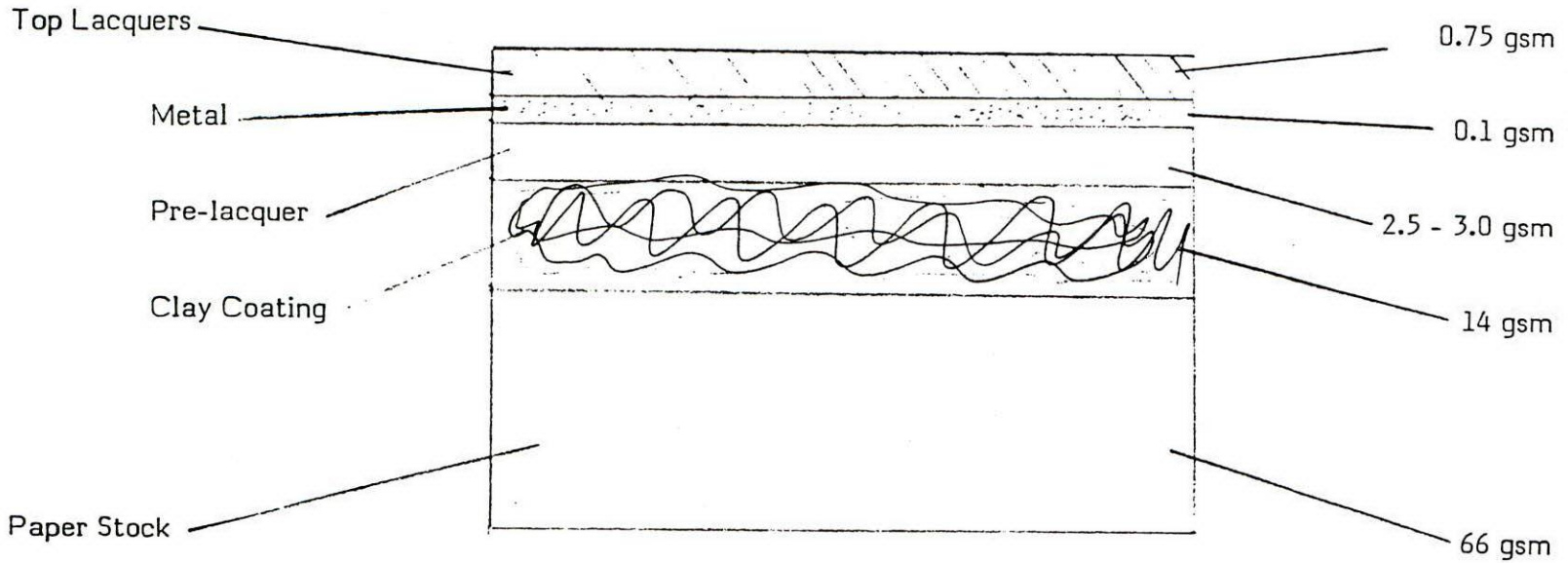
With exception all direct metallised papers employed in the decorative and functional packaging field are coated prior to metallising with a carefully selected pre-lacquer designed to improve and seal the paper surface to permit consistant levels of metal brilliance, adhesion and deposition within the metallising chamber and on the finished product. The level of brilliance quality of appearance of metallised finish can be altered merely by selection of lacquer or by level of coating weight.

When direct metallising board this pre-lacquer stage is very important as any scuffs or marks left by the lacquering machine will show through the metallising and if for example, this was to be used for the U.K. cigarette box - the hard pack, it would be instantly rejected.

The advantages and disadvantages of this system are now listed:

Advantages	Disadvantages
Minimum number of steps to achieve acceptable results	High capital cost
	Board quality has to be very good
In U.K. is the best cost effective system	New techniques/technologies to be learnt
Gloss can be varied by use of different primes	Gloss level still low relative to transfer metallising
All surface are machine applied	Board moisture control essential Rehumidification essential
Good value added to Metalliser companies	Lacquering has to be expertly applied to reduce event of scrap
Technology in line with that existing for other paper applications	Cost high relative to transfer metallising

TYPICAL CONSTRUCTION OF DIRECT METALLISED PAPER



Direct Metallising (Cont'd)

However, a supplier of metallising equipment had to put all its design expertise into evolving a generation of vacuum metallisers capable of handling high grammage boards, with high running speeds and high moisture contents.

From this design evaluation, a range of 3 zone vacuum metallisers was created capable of handling large reels up to 1.8 metre diameter (72") and up to 2 metres + wide (80") with water contents as high as 6%.

And today we have designs of equipment which will perform to these parameters.

A design is currently being evaluated which will be able to directly metallise board up to its natural water content of around 8/9%. This means that there will be considerable additional benefits to the metallising company due to the fact that pre-drying and re-humidification would not be necessary.

One can appreciate that from sheer size of these machines, due to the size of reels required to be metallised, that these machines are very expensive.

Transfer Metallising

As an alternative to the aforementioned system, the 'transfer' metallising process is rapidly gaining popularity over the direct system.

Here a reel of plastic film usually polypropylene film is metallised in the vacumm metalliser. The film is then removed from the vacuum metalliser and taken to a laminating/delaminating station. The film is unwound in contact with the board sustrate, the metal is transferred and the film rewound for re-metallising.

As an example, the Aluglas metalliser and repeat metallising of the base film is being achieved up to 30 times.

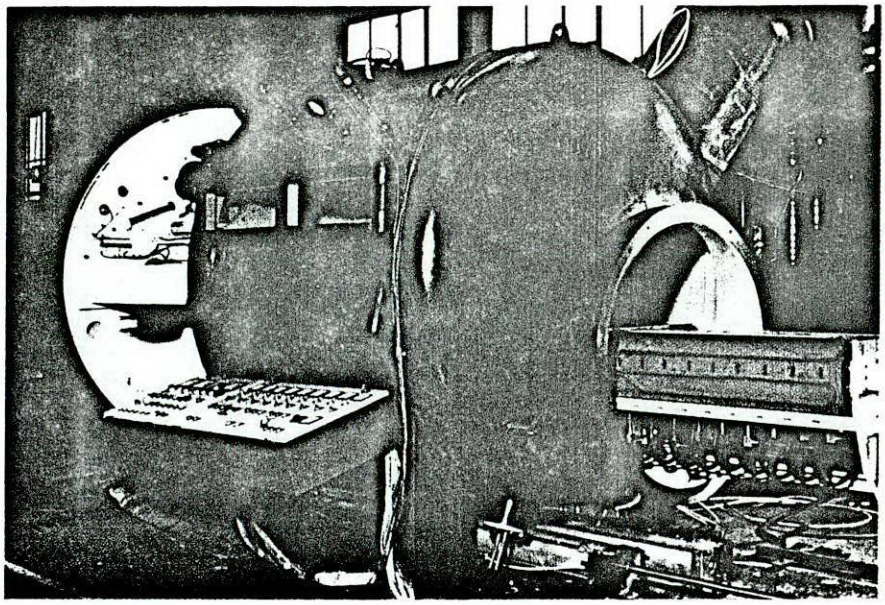
Transfer Metallising (Cont'd)

With this system there is no problem with lacquering drying or re-humidification and board with the natural water content can be easily used.

Advantages	Disadvantages
Much lower quality paper/board can be used	Board formation can show through metal if poor board used
Machinery is available for any market change	Matt finish not yet fully achieved although working on this
Very high gloss	200Å deposit not a good barrier
Mositure content not important	
Economically better	
Easily printed	

Overall the transfer system has many advantages over direct metallising and the interest to this technique is gradually increasing.

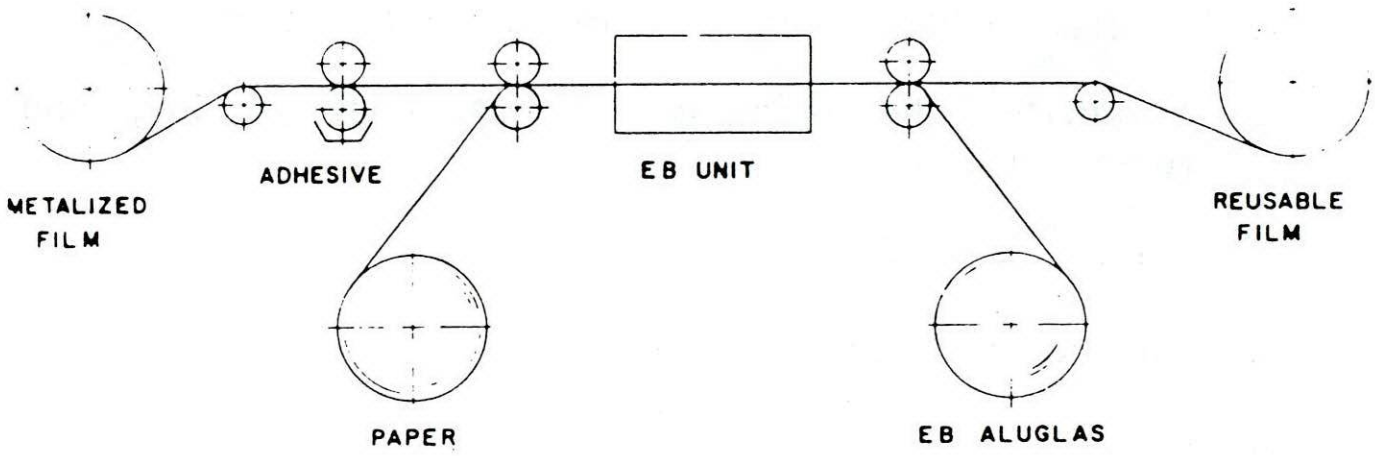
Years ago when this process started and during its related infancy there were many problems in commercialising the system, but now the process is economically sound, totally viable and installations are being supplied to all parts of the world with many more prospective takers.



The first step in the Aluglas Process is vacuum metallization of a transfer film with a thin aluminum layer.

One can see then from these two processes each aimed at the same end product that the demands on the metalliser manufacturers were becoming more exacting requiring higher technology.

Higher running speeds, larger reel diameters, widely varying substrates and increasing web width and overruling all these factors, higher reliability and increased machine control.



LAMINATION - CURING- DELAMINATION

Advantages of EB-Aluglas over Direct Metalized Paper

1. Has much better specular reflectance,
2. Offers a wide choice of stock, including board,
3. Eliminates the problems of outgassing, drying, and remoisturizing,
4. Makes more efficient use of vacuum metalizer,
5. Can be applied selectively,
6. Costs less.

Advantages of EB-Aluglas over Foil-Paper Laminates

1. Uses less aluminum,
2. Retains paper handling characteristics,
3. Has superior reflectance,
4. Is easier to die cut,
5. Curls less from humidity changes,
6. Can be applied selectively,
7. Costs less.

Micro-processors and programmable logic control systems began to be utilized in metallizer systems in order to reduce hard wiring in control panels, etc., to reduce maintenance costs, fault finding etc. Other advantages arose from this, being that additional control and operating features could be included in the system at no additional cost to the equipment price. Machine faults could be located in a matter of minutes hence reducing downtime drastically.

Again for the transfer system and for the winding of other film it became necessary to improve the drive and mechanism system. A unique four motor winding system has been developed to enable the metalliser to process these materials, with superb results. Gone are the days when films could not be metallised without wrinkling the film over the process drum and having the resulting unmetallised streaks on the surface. This is still a problem with conventional three drive systems.

With this metalliser you can actually put wrinkles in and out of the film depending upon your customers' requirements

During 1979 and 1980 the aim to air metallisation was being very seriously considered for many applications ranging for label stock paper up to thick board substrates for record sleeves, cigarette packs etc.

One air to air metalliser was built for a large U.S. cigarette producer. When considering the feasibility of design, high throughput low downtime the concept looked good. Where the project fell down was on the economics and the inability of the machine to adapt to a wide range of materials.

The machine was built as part of a development programme and ran successfully, however it was soon realised that the overall efficiency would never exceed 70% and the power consumed was enough to light a small town due to the very large pumping group required to pump the system due to the air inleakage.

Also two standard metallisers could outproduce the air to air machine by approximately 50% in terms of flexibility and output.

Early in 1984 standard vacuum metallisers were completely redesigned and now approximately 70 models to cover all areas of operation, economics and applications are available.

Machines are loaded and unloaded from the side this negates the necessity of having to climb on top of the metalliser with its resulting problem of operator safety etc.

For double side metallising it is no longer necessary to have a two source machine and with our new design total deposits of 2 optical density are achievable at 10 ms^{-1} either double sided or single sided in the same machine.

Current machines are capable of pumping down to operating vacuum levels, loaded with a reel of film for example, in 5 minutes with the machine in a clean condition this time extending to 10 minutes with the machine dirty.

More economical use and better design of pumping systems allows smaller pumps to be selected for a given size machine, and still result in faster pumpdown time.

Many processes have been taken out of the hands of the machine operator, automatic warm-up of the evaporation sources is now a standard feature as some of the large metallisers we have supplied had up to 36 evaporation boats still keeping individual power control over each boat.

To increase uniformity of deposit across the web control of each individual wire feed unit is also a necessity this being carried out via the microprocessor. With this facility and currect setting of the boats to uniformities of $\pm$5% can be easily obtained.

Coupled with the demand for greater tolerance on the deposit was the ability to read the uniformity during the machine operation.

For measuring light transmission through metallised plastic films an Optical Monitor System which can also measure optical density directly while metallising is used.

The standard measuring device for measuring the deposit on paper has tended to be the resistance monitor which gives an average deposit reading across the web. However, due to the nature of the paper surface this instrument does not give a true reading.

A non-contact resistivity monitor was developed which measures, at discrete points across the web, the actual deposit thickness, also this device has a much more extended measuring range than the optical monitor and so far most application replaces the optical monitor. However, for solar film metallising the optical monitor is still the best device.

These devices can be connected to a line printer or VDU units for data logging etc.

The applications for metallising are expansive and new applications are being evaluated daily (see attached list). Metallising began in the early days as a specialist operation but now a more diverse range of metallising people are purchasing equipment. These being the existing toll metallising companies, people with their own film line, packaging companies to vertically integrate metallising into their products etc.

When one considers that metallising has a value added of around $1500 per hour one can appreciate why this is happening.

One final application that we should just touch on is that of metallised film for capacitors.

Throughout the world there are many machines (metallisers) sold each year to metallise thin films for capacitors, thin films being from 1.5 micron polyester film to 25 micron polyester.

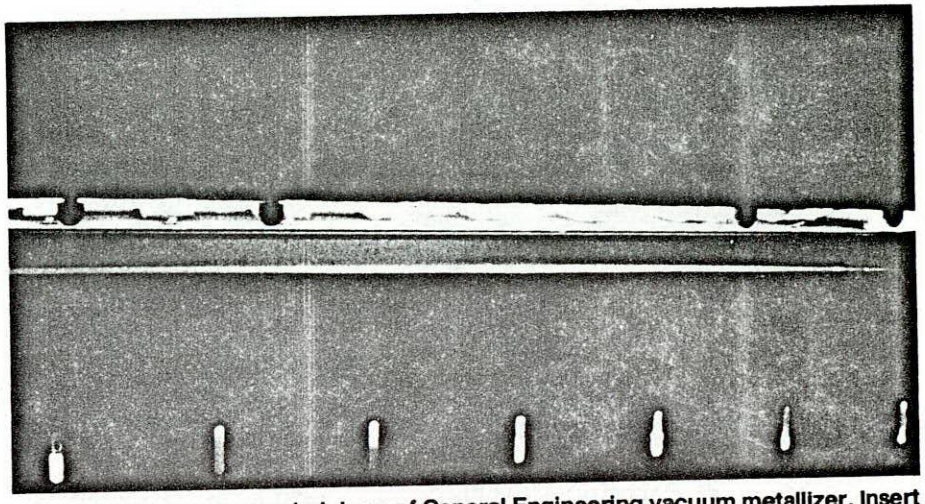
A new range of metallisers specifically to metallise these thin films is now available.

Polyester	1.5 micron to 25 micron
Polypropylene	4 micron to 25 micron
Polycarbonate	2 micron to 15 micron

Superb winding with excellent deposition techniques for future metallisers will mean that the product off these machines will surpass any existing products. The margin generation equipment employed on these machines will be both conventional moving bands and a new advanced oil masking techniques.

These few notes are intended to give some idea of where metallising has come from, where it is going is very unpredictable.

Surveys on the use of plastic film in metallising predict a rapid and continuing increase over the next few years.



Film lays flat on water-cooled drum of General Engineering vacuum metallizer. Insert shows full view slots of resistance source depositing aluminum onto ICI Americas polyester film. Mirror image of uniform boat condition below is clearly shown on surface of metallized film above.

3.3.86

VACUUM METALLISING AND LAMINATE APPLICATIONS

Cont'd

Optic Diffraction Tapes	:	Embossed Films for Special Effect
Peanut Packs	:	Laminates
Potato Chips	:	Decorative + U.V. Barrier
Perfumery	:	Cords Untarnishable Vacuum Trays, Luxury Labels and Packaging
Quilt Filling	:	Insulating Air Filled Material
Recording Tapes	:	End Trailer Pieces
Roof Insulation	:	Sheeting
Records	:	P.V.C. Records
Ribbon	:	Gift Tie Ribbons
Stocking Packs	:	Decorative - Soft
Solar Film	:	U.V. Screening and Reflection
Sequins	:	Metallised Acetate Material
Self-Adhesive Tapes	:	Metallic Colour and Silver Tapes
Sweet Wrappers	:	Stripe Metallised - Decorative
Spiral Covers	:	Decorative Covers
Shoe Lining	:	Insulating - Polythene Metal Barriers
Tear Tapes	:	Package Convenience and Bank Notes
Textiles	:	Fashion and Decorative Materials
Transer Foil	:	Embossing or Stamping Foils
Under Sheets	:	For Baby Cots
U.V. Protection Materials	:	Food Packaging Materials
Vacuum Forming Materials	;	All shapes for decorative products and Fool Packs
Wind Bags	:	Low Cost U.V. Barrier Materials
Wall Boards	:	Reflective and Protective Baking
Wallpaper	:	Decorative and Washable
X-Ray Plate Packs	:	Protection
Yarns Metallic	:	Weaving and Knitting
Zeta Bonding Tapes		

This list itemises a few of the applications for metallised Films and Laminates.

VACUUM METALLISING AND LAMINATE APPLICATIONS

Agricultural	:	Mulching Blankets, Microlimate Netting
Adding Machine Rolls	:	Special Electrosensitive Reels
Adhesive Tabs and Labels	:	Identification
Balloons	:	Gas filled and Meteorological
Beer Bottles	:	Labels
Boxes	:	Box Lines and Decorative Covers
Biscuit Pack	:	Decorative and UV Resistant
Bows	:	Stick on Bows - Stationary
Carbon Paper	:	Decorative use for quality image
Cigarettes	:	Soft Pack and Bundling Tissue
Cigars	:	Moisture Protection. Cello Overwrap
Cake Boards	:	Wedding Cake Layers
Capacitor Tapes	:	Tear Tapes
Cold Seal Packaging	:	Cake and Biscuit Packs
Christmas Products	:	Garlands, Trees, Icicles
Coffee Packs	:	Laminates, Protection +
Dental Tapes		
Dairy Products	:	Container Lidding Ice Cream Pack
Electrical Cables	:	Marker Tapes, Shielding Tapes
Easter Eggs	:	Eggs Decorating Chocolate Decorative Liners and Trays
Fishing	:	Fly Fishing Flies - Metallic Yarn
Foil Free Edge Tapes	:	H.V. Cables
Food Laminates	:	Various
Freezer Bags	:	Inhibits Temperature Rise
Giftwrap	:	Giftwrap, Printed Rolls and Sheets
Glitter Powder	:	Glitter, Non Glass
Home Insulation	:	Roof Reflective Lining
Hyperthermia Blankets etc.	:	Protection in case of accidents
Insulation	:	Reflective Panels
Ice-Cream Wrappers	:	Glassine and Film Overwraps
Jam Lids	:	Lidding for Sauce, Butter, Milk and Jam Packs
Kites	:	Decorative Metallic Kites
Labels	:	Labels of all kinds. Metallic look
Laminates	:	Various Kinds
Leader Tapes	:	Recording Tapes
Meat Packs	:	Reflector Backs for Meat Vacuum Pack Special Mirror Material. Non shatter
Numerical Control Tapes	:	Machine Tools

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Vacuum Coating Session B

IVD Coating Technology for Corrosion Protection

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Kennedy Space Coating.

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IVD COATING TECHNOLOGY FOR CORROSION PROTECTION

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ABSTRACT

Ion Vapour Deposition of Aluminium has become a recognised process of depositing highly adherent coating on different materials for corrosion protection. This technology which was invented in the sixties is now used commercially on a production scale to aluminise aircraft and other components for corrosion protection to replace cadmium electroplating. The continuous need to different applications has led to the growth of new and more reliable equipment designs. Coating operations have been shown to be clean, simple, non-labour intensive and facility and space requirements are minimal.

1. Introduction

In many applications, surface coatings are used to achieve better physical and chemical properties to improve the surface of bulk materials. Applications include optical coatings for lenses and mirrors, metallic coatings for electrical contacts, refractory coatings to increase hardness and decrease wear and protective coatings for corrosion and oxidation resistance. The general requirements for such coatings are excellent adhesion to the substrate, having dense and pores free structure, good uniformity and smooth finish. To achieve such requirements different processes and techniques have been employed including the use of ionic bombardment. In fact, the concept of improving surface coating by ionic bombardment go back as early as 1938 when Berghaus[1] described a vacuum coating technique in which vapour was deposited on a substrate in a glow discharge. The coating was claimed to have a perfect structure and adhering strength even for thicker layers. In 1963 Mattox[2] introduced a similar technique in which he used a glow discharge to ionize the atoms of gas and coating material and accelerated them through a suitable potential towards the substrate which was the cathode of the discharge. The process was named 'Ion Plating' and it was claimed that it produced films with excellent adhesion, even in the cases where the film and substrate material were mutually incompatible[3]. This work has stimulated great interests and since then vast numbers of papers have been published.

During the last 22 years the activity and interest in ion plating or Ion Vapour Deposition, IVD, as it is called today, has developed on two levels; The fundamental or laboratory levelland the industrial or technological level. On the fundamental level, there was a noticeable trend towards a better understanding of the physics of the process which generally leads to a better control of the coating properties and to establish the optimum plating conditions[4,5,6]. On the industrial level, IVD has proliferated into many areas in which other coating techniques have not been successful. For instance, IVD technology is now well established in the aerospace and aircraft industry for the application of tribological coatings to reduce friction and wear and protective coatings to resist corrosion and oxidation. The technique is currently used on aproduction scale to aluminize aircraft components for corrosion protection. it is also suitable for rack coating of large components and barrel coating for a large number of small steel fasteners[7,8,9]

This paper reviews some of the current applications of IVD aluminium coatings and in particular for the corrosion protection to replace cadmium. It also reviews the available equipment in the market which has been designed and operated for this purpose.

2. The IVD Process.

The typical IVD cycle consists of surface preparation, coating and supplemental processing. These are described in detail in the following sections.

2.1 Surface Preparation Prior to Coating.

In order to achieve good and reproducible adherent coating with good structure, the parts to be coated must be thoroughly cleaned prior to loading into the vacuum chamber. Cleaning is often described as a process of removing objectionable matter from the surfaces of manufactured products such as drawing and stamping lubricants, cutting fluids, heat treatment scale and oxides and finger prints[10]. Furthermore, it is well known that no one cleaner or cleaning method is best for all applications because of the many variables including the material of the workpiece, the contaminants and the requirements. Therefore, successful surface perparation for subsequent coating operation often requires the use of more than one type of cleaner and operation. Surface preparation prior to coating with the IVD process starts with vapour degreasing to remove oil and grease. Dry blasting with aluminium oxide grit or chemical cleaning is used to remove metal oxides or other scale. A grit size of 200 mesh is recommended to produce the surface texture required for optimum coating adhesion. Pickling with dilute acid products may be used in the case of titanium or titanium alloy to remove oxides and stains. Pickling operations should be followed with a water rinse to prevent attack on the metal and should be well dried prior to plating. Cleaned parts should proceed to IVD aluminium coat within 30 minutes of cleaning. For aluminium, titanium alloys and ferrous alloys which will be coated within 48 hours of cleaning, the parts should be wrapped well in a suitable material.

2.2 Coating Process.

Ion vapour deposition is an ion-aided coating process in which condensation of metal vapour takes place under the continuous action of a small number of

energetic ions and a much larger number of energetic neutrals[11]. The process is basically a diode system consisting of two electrodes. [Fig 1]. The specimen to be coated is the cathode of a high voltage D.C. circuit and the evaporant material and all earthed parts form the anode. An inert gas atmosphere [usually argon] at low pressure is contained in a vacuum chamber connected to an efficient vacuum system, continuously pumping the chamber. After loading the cleaned parts, the vacuum chamber is pumped down to a pressure of [0.013 Pa.]. The pumping time of the IVD machine [commercially known as Ivadizer] is between 25 - 40 minutes depending on moisture conditions inside the chamber. After reaching the required pressure, the chamber is then backfilled with argon gas to a pressure of [1.3 Pa.] and a high negative potential is applied to the parts to be coated. As a result, argon discharge is triggered and the parts are sputter cleaned due to ionic bombardment. The cleaning cycle takes between 10 - 20 minutes depending on the nature of the workload and its degree of cleanliness. Once the parts are assumed to be cleaned [as indicated from the drop in the discharge current], high purity aluminium wire is fed continuously into resistance heated crucibles that melt and evaporate the wire [Fig 2]. Part of the metal vapour will be ionized as it passes through the glow discharge and consequently accelerate with high energy [100 - 1000 eV] towards the work-piece to form highly adherent aluminium coating. Approximately, ten minutes of evaporation are required to deposit [8 μm] thick aluminium, coating on steel fasteners in the barrel coater and 20 minutes are required to deposit [25 μm] aluminium in the rack coater. For thicker deposition, the coating process must be interrupted to allow cooling using a flow of nitrogen gas when temperature sensitive parts such as aluminium alloy structures are coated with aluminium.

After unloading, the parts are then glass bead peened to densify the coating structure and to give smoother finish as well as to check the coating adhesion on each part. The peening is carried out manually for large parts or automatically in a barrel for small parts and fasteners. All peened residue must be removed with dry nitrogen gas or oil-free filtered air. Fig [3] shows a comparison between peened and unpeened IVD aluminium coating article.

In normal production, three classes of coating thicknesses and two types of coatings are used. Table [1] shows the different classes and types of coatings frequently used with its corrosion protection. Type 1 is the IVD

aluminium while Type II is the IVD aluminium with a chromated top coat. The supplemental chromate treatment is applied for additional corrosion protection and for adhesion of subsequent painting applications.

3. IVD Equipment.

In 1974 McDonnell Aircraft Company [McAir] developed an IVD process called Ivadizer to apply aluminium coating for corrosion protection.

IVD aluminium coating is now recognised by a number of government, industrial and commercial specifications in the United States. In recent years General Engineering Radcliffe Limited took out a U.K. licence from [McAir] to manufacture the equipment in Europe.

IVD equipment consists of a rack or barrel coater in addition to the surface preparation line, chromate treatment line and a system for stripping aluminium coating. The coating units are available as racked parts coaters, barrel coaters or combinations that can be converted for either racked parts or barrel coating. Fig [4,5] shows pictures of the two basic systems. The rack coater has 5 ft. wide and 10 ft. long parts holding rack from which parts are suspended over the evaporation boats. Large parts may require rotation of 180° and recoating to obtain optimum uniformity on both sides. Coating thickness can range from (8 - 50 μm] with a uniformity of $\pm$ 15%. The average total cycle time for a 25 μm thick coating is approximately 75 minutes. The barrel coater features two 14" diameter x 4 ft. long stainless steel mesh barrels. Table [2] lists details of process time, work throughput and labour requirements for various coating cycles on the Ivadizer.

4. Applications of IVD Aluminium Coatings.

For corrosion protection there are two general methods by which coating can protect a substrate[12].

1] The coating is electrochemically more active than the substrate in the environment.

2] The coating is less active [more noble].

In the first method, the coating is sacrificial and it usually gives substantial protection even when porous. In the second method, the coating must be non-porous and robust, otherwise the corrosive medium will find its way through pores and attack the substrate. For either methods IVD has been found to be useful in offering good protection against corrosion. However, since IVD process does not introduce hydrogen, hydrogen embrittlement is not a consideration and therefore the process can be used on steels at any strength levels. IVD also eliminates solid metal embrittlement of titanium and does not reduce the fatigue properties of aluminium alloys. The other characteristics of the IVD process with aluminium coating is being a non toxic and non polluting process which makes it the best alternative to replace cadmium electroplating for corrosion protection. The following are examples of some of the current applications of IVD process with aluminium coating for corrosion protection.

a] The Corrosion Protection of IVD Aluminium Coatings on Steel and Titanium.

IVD coating offers good corrosion protection of steel after exposing to both 5% neutral salt fog and SO_2 - salt spray environments. Fig [6] shows a comparison between the corrosion protection of cadmium and IVD aluminium after 168 hours in SO_2 - salt fog test. It is evident that cadmium plated fasteners were much severely corroded than the IVD aluminium. Fig [7] shows a comparison between IVD aluminium coated titanium fasteners and bare titanium fasteners after 24 days testing in SO_2 - salt spray. The test showed the appearance of blistering around the peripheries of the bare titanium fasteners which was more severe then around the IVD aluminium coated fasteners.

b] The Corrosion Protection of IVD Aluminium Coatings on Copper Alloy

The corrosion protection of IVD aluminium coated copper alloy springs was compared to similar springs electro-plated with zinc-gold chromated and used as a reference[13]. The springs have been tested in a salt spray chamber [ASTM B-117] and condense chamber [DIN 50017], Table [3] summarises the results of the corrosion test, while Fig [3] shows the two types of coating after one week in a salt spray test followed by 3 weeks in condensing chamber test and after 5 weeks continuous testing in the condensing chamber. It is clear that IVD aluminium coatings shows a good corrosion protection to copper alloy springs.

c] The Corrosion Protection of Aluminium Alloy Fuel and Pneumatic Line Fittings.

IVD aluminium coating provides the electrical bond across the fitting which dissipates static electrical charges generated by fuel or airflow, and also protects the fitting against corrosion [Fig 9]

d] Aluminium Alloy Electrical Connectors.

IVD aluminium has a distinct advantage over cadmium on aluminium alloy connectors. Cadmium does not adhere well on aluminium alloy and a copper or nickle strikes are used as a binding layer. IVD aluminium sticks well to aluminium alloy and provides the needed electrical conductivity along with corrosion protection to increase salt spray requirements to 1000 hours(Fig [10]) It can also replace nickle plating for high temperature applications.

e] High Temperature Applications.

IVD aluminium coating has a useful service temperature of 925°F. This feature and its excellent corrosion resistance has led to applications on the aft engine hangers on the DC-10 and Boeing 767 aircraft. United Airlines reported that before the use of IVD aluminium it was necessary to remove and refurbish DC-10 aft engine mounts every 1500 to 3000 flight hours. They now report some engine mounts coated with IVD aluminium (Fig [11])have 9000 flight hours and show no deleterious effects.

f] Depleted Uranium Substrates.

Aluminium coating of uranium reactor parts was one of the first applications of ion plating[14]. Investigation of this process was based on the knowledge that aluminium provides a low neutron cross section, has high thermal conductivity and has electro-negativity close to that of uranium so that galvanic corrosion is minimized. The reactor elements were first cleaned by sputtering after which the aluminium was ion plated. It was further shown that subsequent heating of this deposit layer resulted in $UA1_3$ providing a thermodynamic stable barrier to any reactor corrosion.

U.S. Army tests have also shown that IVD aluminium offers the best protection against corrosion and stress corrosion cracking on depleted uranium

penetrator cores. IVD aluminium will be used pending successful field tests[15].

5] Summary and Conclusions.

The excellent properties of the IVD aluminium coatings in terms of adhesion, structure and uniformity are now well established and the applications of the IVD process have been increasing steadily. However, since each application requires its own set of processing variables and design, that led to the growth of new equipment designs and to new applications. The IVD equipment has been in production use providing such a coating for nearly a decade. Coating operations have been shown to be clean, simple, non-labour intensive and facility and space requirements are minimal. The main advantages of the IVD process with aluminium coatings are :

1] Excellent adhesion to the substrate.

2] No hydrogen or solid metal embrittlement, allowing for steels of any tensile strength to be treated.

3] Suitable for use with high strength aluminium alloys which can be corrosion protected without loss of fatigue life [a disadvantage of anodising].

4] Effective at temperatures up to 496°C compared to 232°C for cadmium.

5] IVD can replace diffused nickel/cadmium giving better corrosion protection at all strength levels. Diffused Ni - Cad is limited to steels having strength levels below 200,000 lb/sq.inch due to hydrogen embrittlement.

6] IVD can be used in contact with fuel. Cadmium is prohibited.

7] IVD can be applied thinner than Alclad coating on aluminium alloys resulting in weight savings and is not limited to rolled forms.

8] IVD aluminium coated springs have good corrosion resistance and show an excellent fatigue life of 100 times more than any other process.

9] IVD aluminium coated DC.10 aft engine mounts have shown 9000 flight hours with no deleterious effects in comparison to 3000 flight hours before the use of IVD aluminium.

10] Neither the Al. coating nor the IVD process present ecology problems.

Coating in standard Ivadizer is not restricted to aluminium only and different coating materials such as copper, lead and tin can be deposited individually to form a single or multi-layered coating or jointly to form an alloy coating. However, the use of the IVD process is limited by the initial expense of the equipment and its c apacity which is similar to other vacuum coatings such as TiN or metallising process, but recent developments have increased product throughput significantly.

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Figure Captions

Fig 1. Schematic diagram of a basic ion plating set-up.

Fig 2. Wire feeder for continuous evaporation of metal at high evaporation rates.

Fig 3. Comparison between peened and unpeened IVD aluminium coating.

Fig 4. Standard Rack Ivadizer.

Fig 5. Standard Barrel Ivadizer.

Fig 6. Comparison between corrosion protection of Cadmium and IVD aluminium on steel after 168 hours in SO_2 salt spray test.

Fig 7. IVD aluminium on titanium and base titanium after 24 days in SO_2 salt spray test.

Fig 8. IVD aluminium and Zn gold chromated coatings on springs after one week in salt spray followed by three weeks on condensation chamber and for five weeks in condensation chamber only.

Fig 9. IVD aluminium on fuel and pneumatic line fittings.

Fig 10. IVD aluminium on electrical connectors.

Fig 11. IVD aluminium on DC.10 Aft. engine hanger.

Table 1. Difference classes of IVD aluminiun coating.

Table 2. Typical Equipment throughput and labour requirements.

Table 3. Corrosion testings of IVD Al and gold chromated zinc coated springs.

TABLE 1

Class	Thickness	Test Period: hrs	
		Type I	Type II
1	25 micron (min)	504	672
2	12.5 micron (min)	336	504
3	7.5 micron (min)	168	336

Class 1 Coatings are used in severe corrosion environments.

Class 2 Coatings are used in less severe interior corrosion environments.

Class 3 Coatings are used when fine tolerances are necessary on such parts as fine threaded parts.

TABLE 2.

Typical Equipment Throughput and Labour Requirements

Type IVD Coater	Coater Capacity	Cycle [Hour]	Throughput	Labour Requirement Man-Hour*
Standard Pack	50 Ft² [4.65 m²] Work Area.	1.25	40 Ft.²/hr** [3.75m²/hr]	2.0
Standard Barrel	60 lb [27.2Kg.] Steel Fasteners	0.67	90 lb/hr	2.0
Derivative Barrel	300 lb [136 Kg] Steel Fasteners	1.00	300 lb/hr [136 Kg/hr]	2.5
Derivative Barrel	1200 details aluminium alloy 1 1/4" [3.175 cm] diam. x 1 1/2" [3.81 cm] long.	0.77	1550 parts/hr	2.5

McDonnell Aircraft Co.
and Society of Automotive Engin··rs

* Includes part precleaning, processing and post treatment.

** The maximum flat plate area that can be coated per cycle is 50 Ft.² [4.65 m²] The total surface area of parts that can be coated depends on part configuration and the number of parts conveniently racked in a 50 ft.² [4.65 m²] area.

TABLE 3

Subjects: Al-coated springs (Ivadizing). Class 2 (13μ). MiL-C-83,488

ZnCro-coated springs, 5μ Zn. Chromated

Salt spray chamber (Redrust/Whiterust) ASTM B117	Salt Spray Test (hours) (SST)	4 h	28 h	48 h	72 h	120 h	168 h	+ 3 weeks CHT
	Al	10/10	9/10	9/10	9/9	9/9	9/8-9	8/5 (*)
	Zn	10/10	10/9	10/8	10/7	10/7	10/6	4/4

Condensing chamber (Redrust/Whiterust) DIN 50 017	Condensing Humidity Test (CHT) (hours)	4 h	28 h	48 h	120 h	168 h	792 h	-
	Al	10/10	10/10	10/10	9/9	9/9	9/7	-
	Zn	10/10	10/10	10/10	10/10	10/9	9/8 (*)	-

* Pitting/Pores

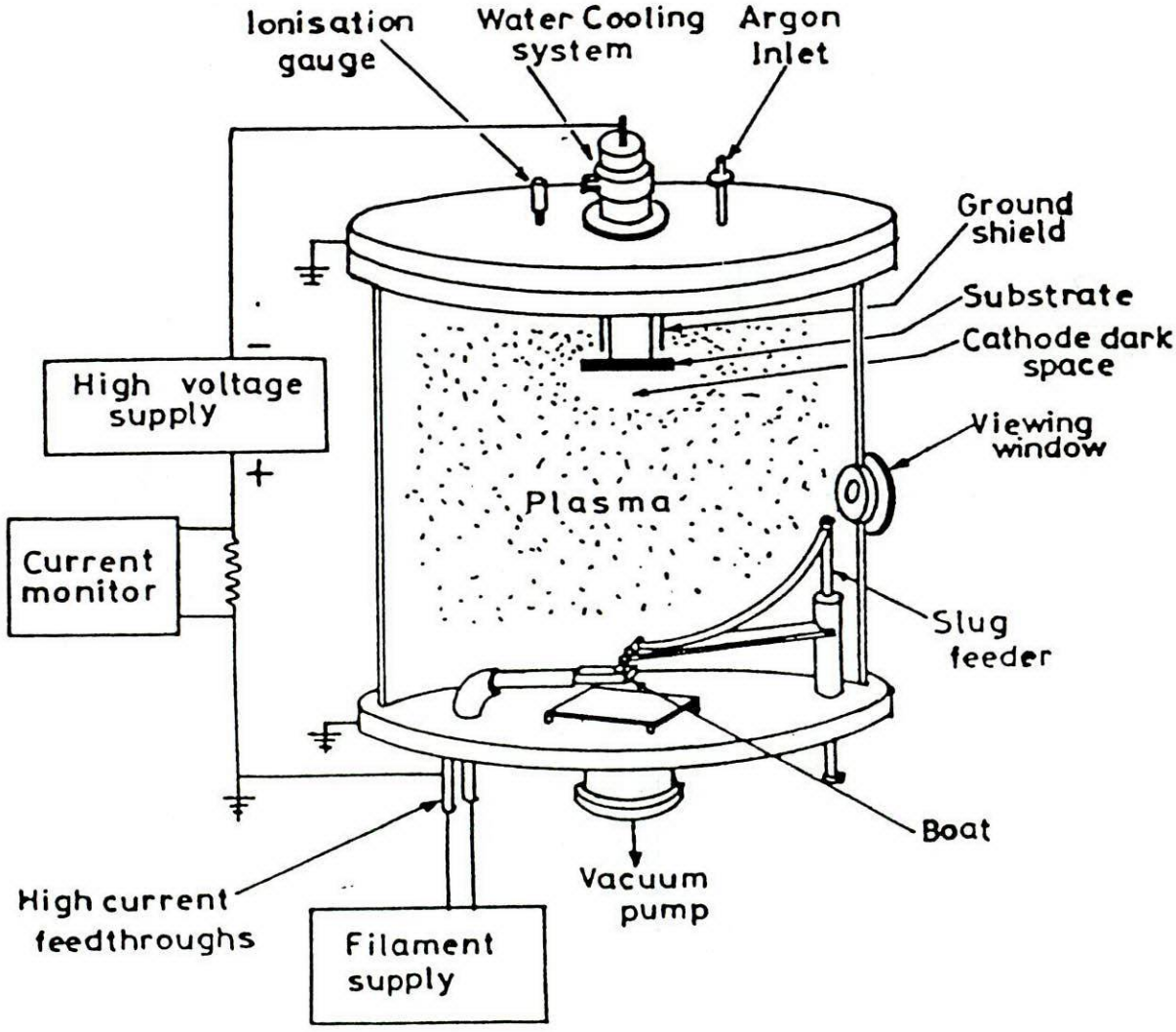


Fig 1. Schematic diagram of a basic ion plating set-up.

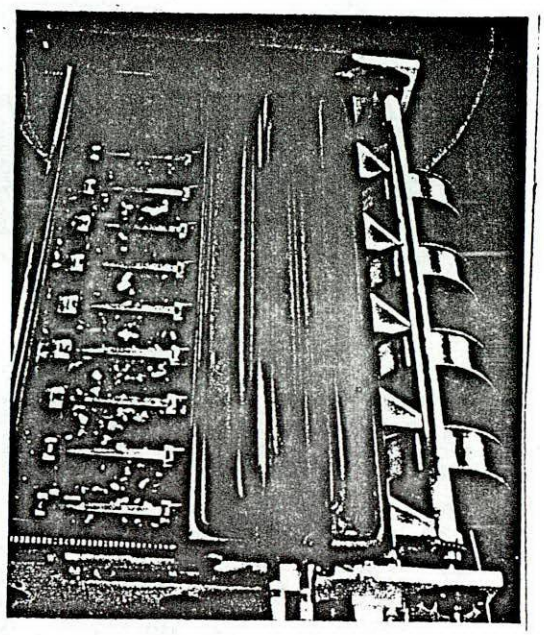
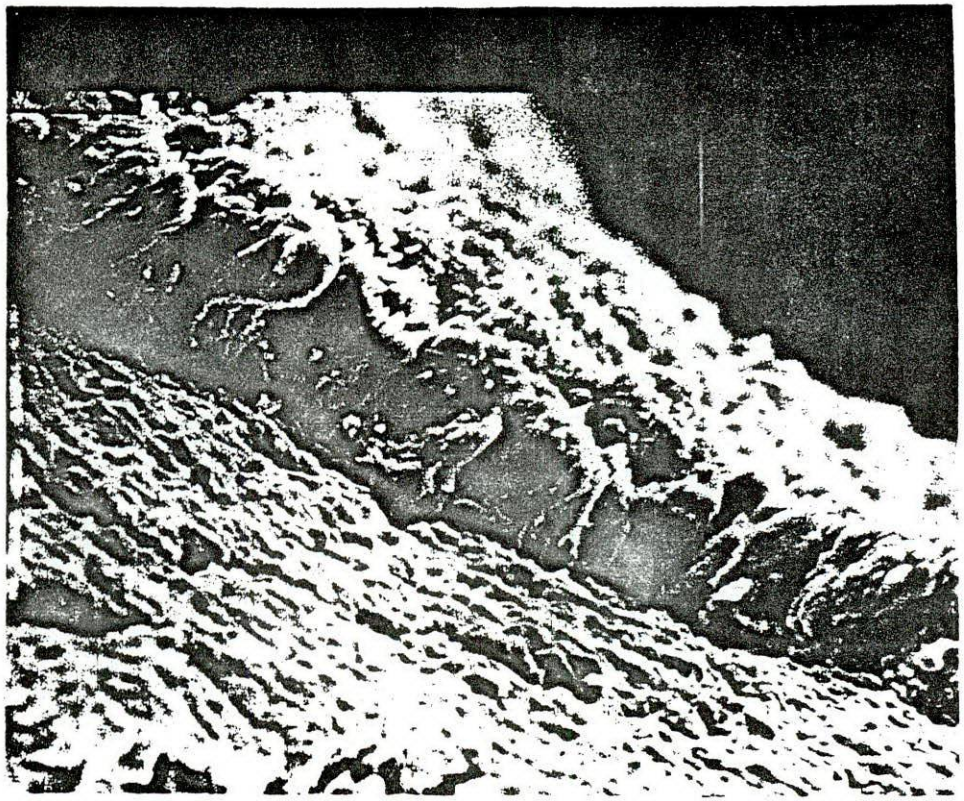


Fig 2. Wire feeder for continuous evaporation of metal at high evaporation rates.





Peened & Chromat

Not Peened

Fig 3. Comparison between peened and unpeened IVD aluminium coating.

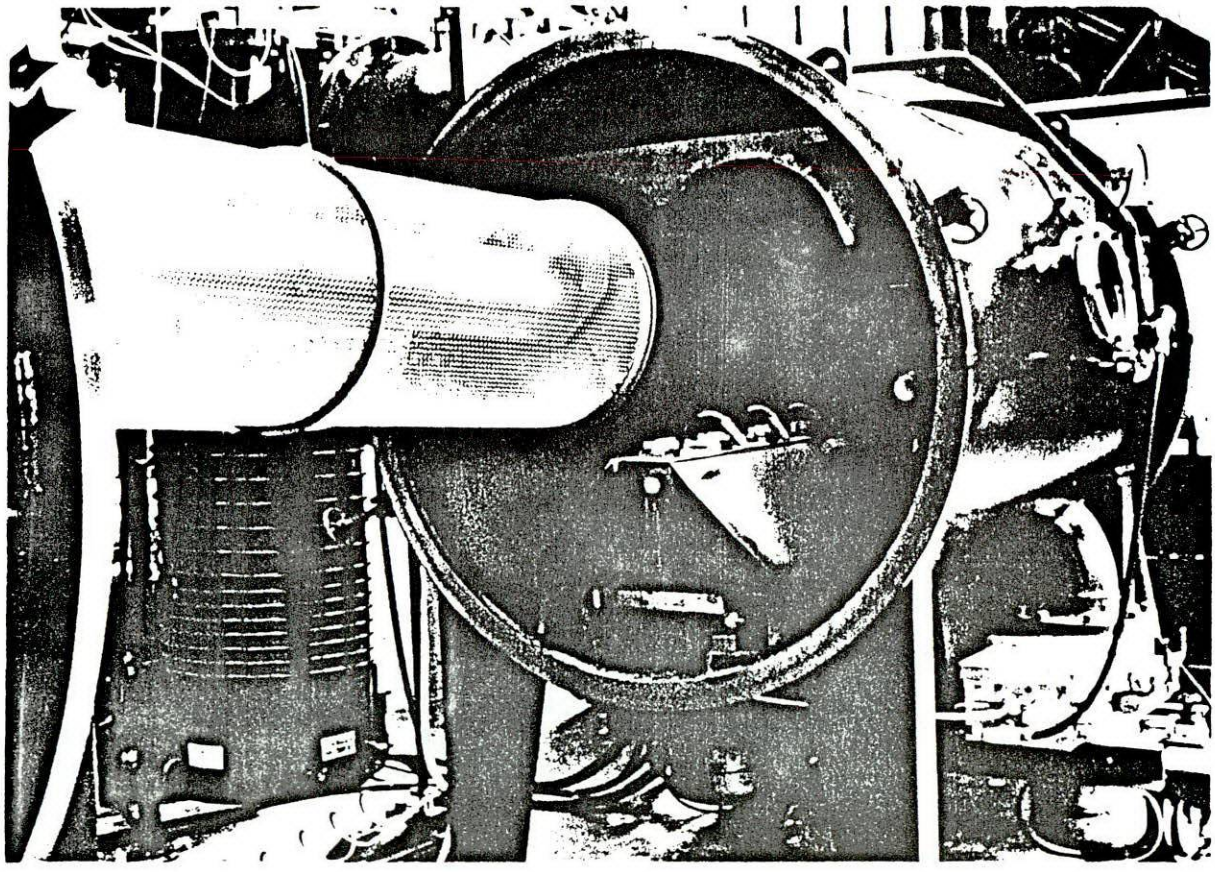


Fig 4. Standard Barrel Ivadizer.

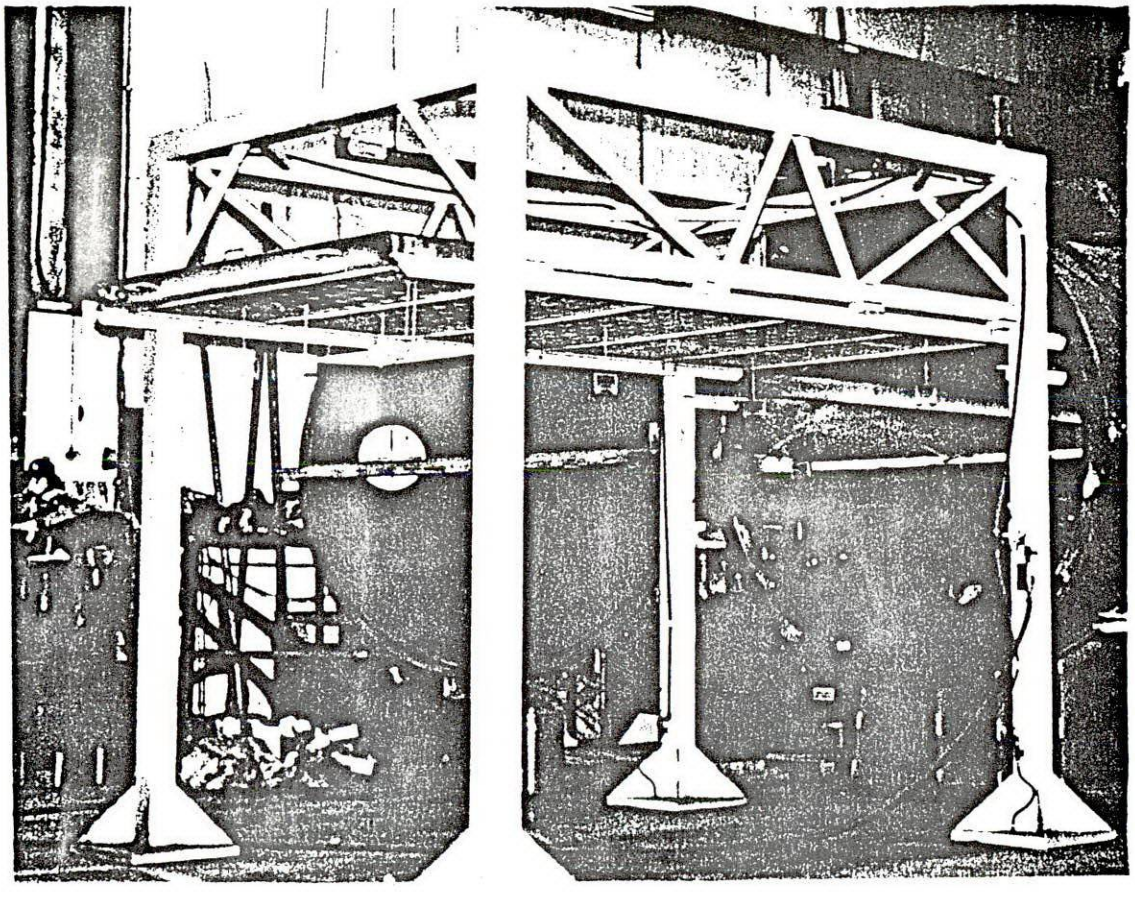


Fig 5. Standard Rack Ivadizer.

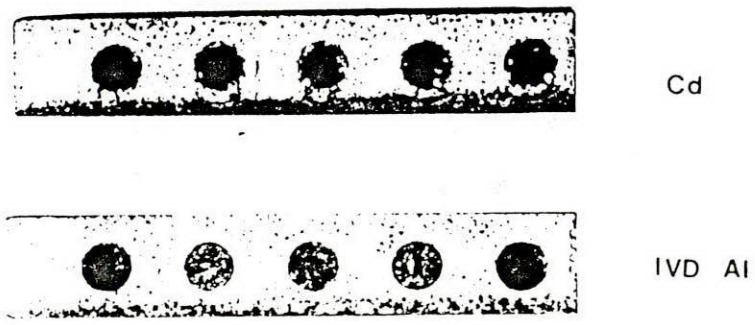


Fig 6. Comparison between corrosion protection of Cadmium and IVD aluminium on steel after 168 hours in SO_2 salt spray test.

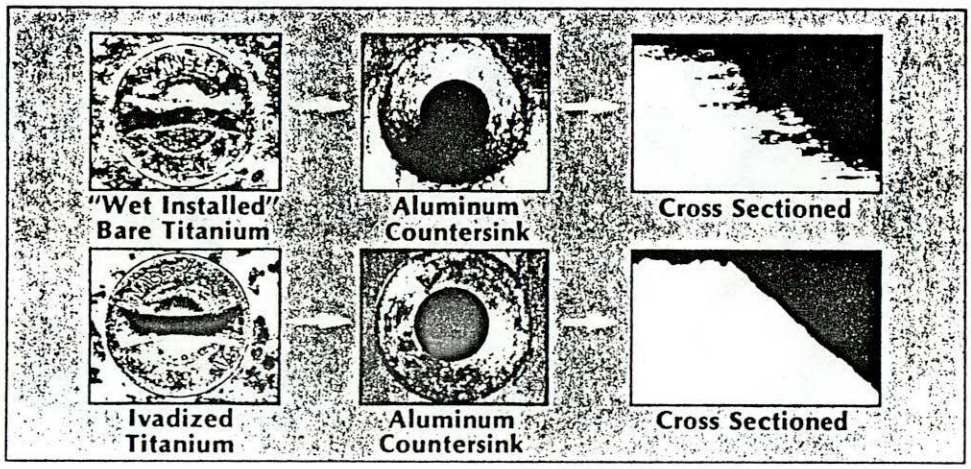


Fig 7. IVD aluminium on titanium and base titanium after 24 days in SO_2 salt spray test.

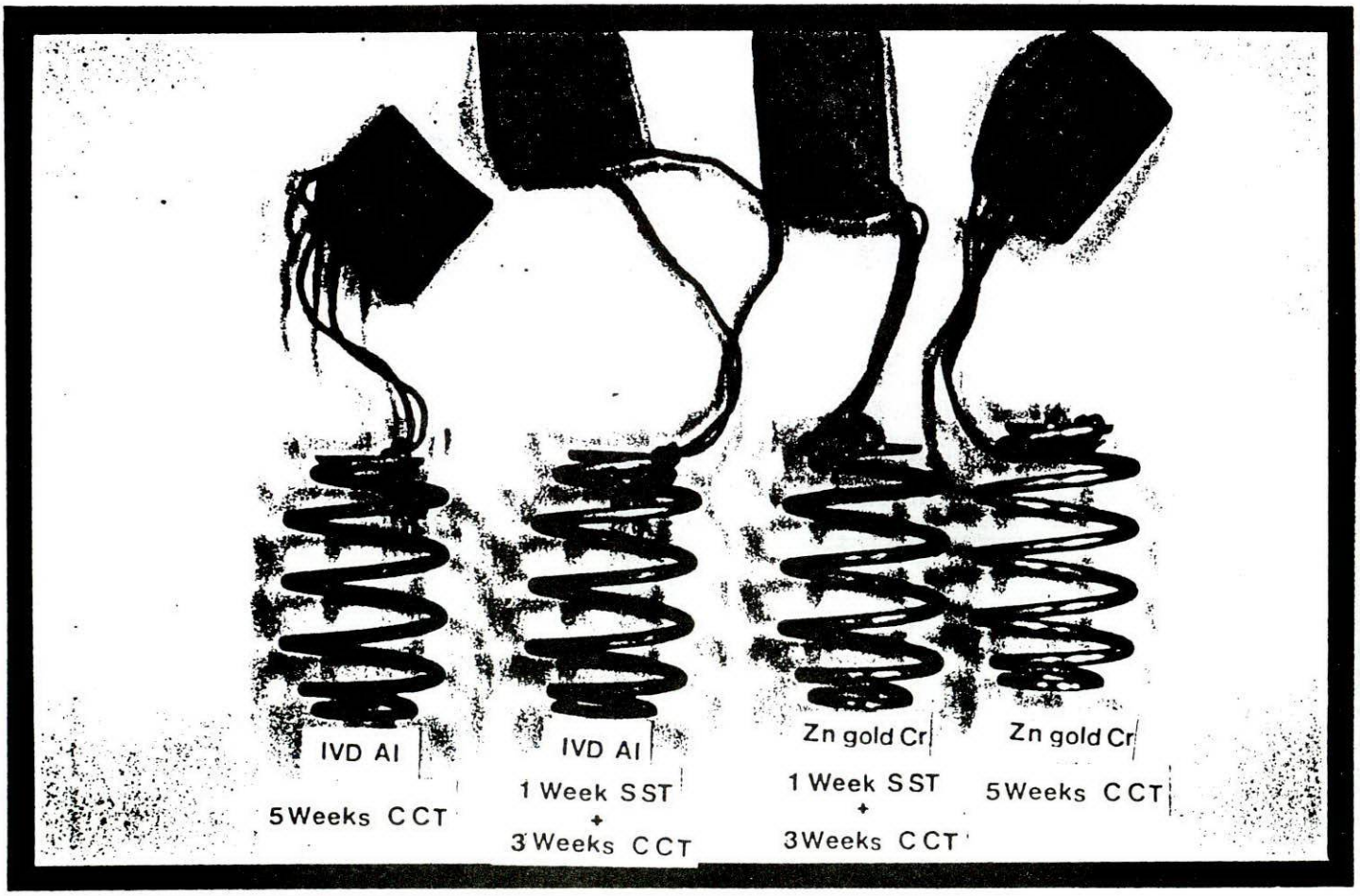


Fig 8. IVD aluminium and Zn gold chromated coatings on springs after one week in salt spray followed by three weeks on condensation chamber and for five weeks in condensation chamber only.



Fig 9. IVD aluminium on fuel and pneumatic line fittings.

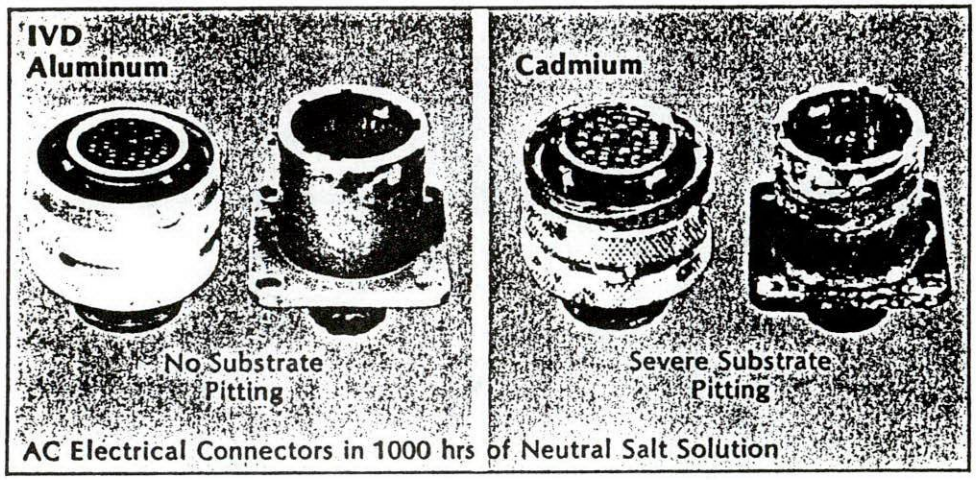


Fig 10. IVD aluminium on electrical connectors.

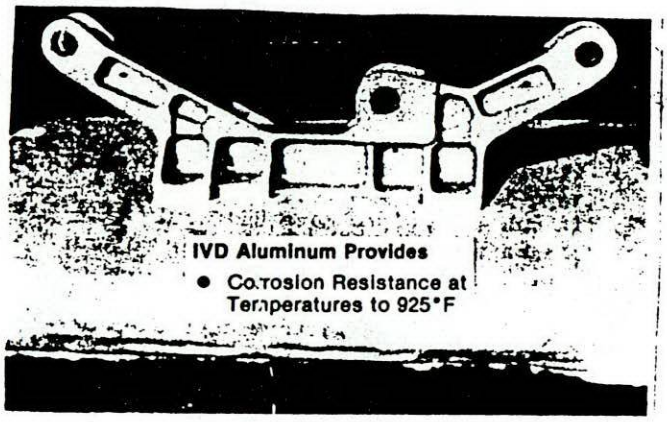


Fig 11. IVD aluminium on DC.10 Aft. engine hanger.

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Vacuum Coating Session B

Arc Vapor Ion Deposition

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ARC VAPOR ION DEPOSITION

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I. Introduction

Arc Vapor Ion Deposition (AVID) is a vacuum coating process whose use has been increasing rapidly since 1980. It is the most recent addition to a class of coating processes, known as physical vapor deposition (PVD), that are used in many commercial applications ranging from the fabrication of miniature semiconductor chips to coating large sheets of architectural glass. The term "physical" is applied because physical means, such as evaporation or "sputtering", are used to release the deposition vapor from a solid source. In the AVID process, arc evaporation sources produce metal vapor, having a very high ion fraction, that is deposited on substrates that are generally biased at a negative voltage. As a result of the metal vapor's high ion fraction, coating build-up characteristics of the AVID process are analogous to electroplating.

AVID films are being used in wide variety of industrial applications to decrease wear due to friction, metal-to-metal welding, abrasion and corrosion. Although the majority of applications have involved TiN coatings for the reduction of wear, the AVID process is versatile and well-suited for depositing metals, alloys, and chemical compounds onto a wide variety of substrate materials.

The purpose of this paper is to summarize the nature of the AVID process and present representative applications results. Key elements of the process include:

1. Vacuum arc sources produce metal vapor that is both highly ionized and very energetic.
2. The composition of films deposited in vacuum by condensation of this vapor is similar to the source material.
3. Compounds, such as metal nitrides and carbides, can be reactively deposited by introducing gases containing the desired constitutents.
4. As in electroplating, the substrate shape and the applied voltage influence the resulting film thickness distribution.
5. The energy of condensing metal ions can be controlled using a negative substrate bias voltage.
6. The high flux of energetic metal ions bombarding the growing film allows deposition of dense well-adhered films, including refractory materials, at temperatures as low as 175°C.

The paper consists of a description of AVID equipment and process steps, comments about process characteristics and a review of several applications.

II. Equipment

Figure 1 is a schematic illustration of a generic AVID system. Arc evaporation sources are mounted in ports on vacuum chamber walls. Because the arc evaporation involves only very localized melting, these sources may

be placed in any of the walls; bottom, side, or top. Because the evaporation occurs from the negative electrode, or cathode, of the electric circuit that maintains the arc, the terms "arc source", "evaporator" and "cathode" are used interchangeably. Substrates are mounted on an electrically insulated rotatable support. The negative outputs of the arc and substrate supplies are connected to the arc source and substrate support respectively; their positive outputs are grounded to the chamber. For deposition of compounds, such as TiN, reactive gas is fed into the chamber through a mass flow controller; the inlet position is not critical because a gas surplus is generally present. Substrate temperature is measured using an IR pyrometer that is swivel-mounted for aiming. The process may be viewed directly through a mechanically-shuttered UV-filtered port.

Arc sources are ignited either by momentarily shorting the metal cathode to ground with a pneumatically actuated trigger, or by applying a high voltage pulse to an electrode that is in close proximity to the cathode. Arcs are typically sustained at voltages in the 15 to 50 volt range, depending on cathode material. The most significant arc activity occurs in microscopic regions, called cathode spots, where a metal vapor pressure in excess of one atmosphere is produced by extreme localized heating. The survival of these arc spots is tied directly to the release of the metal vapor; the electrical discharge occurs in the metal vapor that is itself released by the discharge. The cathode spots move randomly over the cathode face at speeds on the order of meters per second. More systematic spot motion is obtained when magnetic fields are applied. Properties of vacuum arcs will be discussed further in the section on process characteristics.

When arcing ceases spontaneously, the lack of activity is sensed electrically and sources are automatically retriggered. This situation usually occurs only when operating at very low current where all of the current is carried by only one arc spot.

III. Process Steps

AVID process steps include precleaning outside the deposition chamber, conditioning and heating within the deposition chamber, and coating.

Effective precleaning is essential for removing contaminants and naturally occurring surface oxides that could reduce the bond strength between coating and substrate. A basic precleaning sequence used to remove common oils and inorganic salts consists of vapor degreasing in trichlorotrifluoroethane, ultrasonic cleaning in an aqueous detergent solution, rinsing with water, followed by water displacement and spot-free drying. Virtually all tenacious surface contaminants can be removed by adding a low pressure vapor honing step to the beginning of this sequence. The use of vapor honing has some limitations when highly polished surfaces are involved, but it is nonetheless a versatile precleaning method. It is beyond the scope of this paper to cover the special cleaning methods that might be required to clean particular materials and parts.

Precleaned parts are set into clean fixtures. Fixtures hold the parts so as to adequately expose surface during the conditioning and coating steps, while at the same time masking surfaces that should not be coated. The loaded process chamber is pumped to the low 10^{-5} Torr range before proceeding to the conditioning step.

During the conditioning step, substrate surfaces are sputtered cleaned

and mixed by the bombardment of metal ions from the arc sources. As substrate temperature increases due to this bombardment, inward diffusion of implanted atoms of the bombarding species becomes significant. The cleaning, mixing and diffusion effects of this bombardment lead to excellent coating adhesion.

Conditioning is typically done with bias voltages in excess of -1000V. The implantation and mixing effects occur in the first several atomic layers. There is net material removal when sufficiently high substrate voltages are used; the threshold for net removal is about -1100V for titanium ions bombarding type M2 high speed steel as shown in Figure 2. The average energy of incident titanium ions at this voltage is about 1980eV, based on an average ionization state of +1.8e [1]. Even when there is net material removal, the impinging metal ions form a surface that is highly enriched by shallow implantation and diffusion. This enhances adhesion.

Conditioning proceeds until substrates have reached a minimum coating

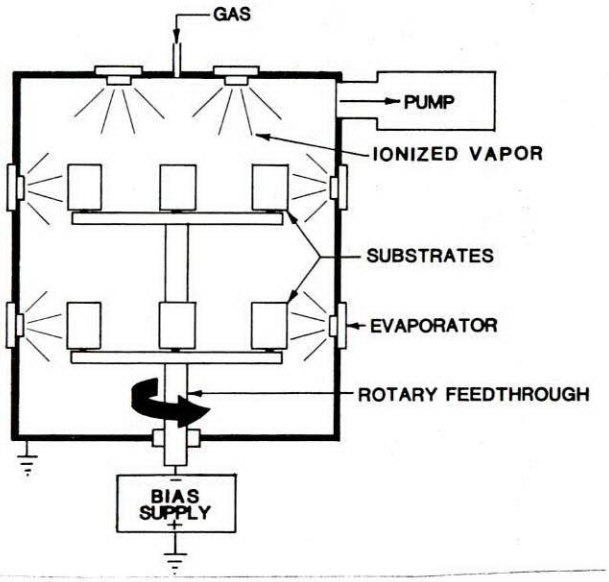

Figure 1. Schematic diagram of an AVID system.

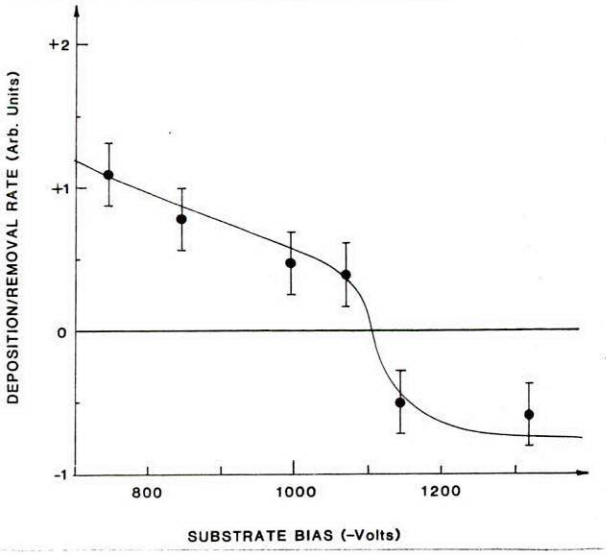

Figure 2. Relative deposition or removal rate verses voltage on a type M2 high speed steel substrate for Ti ions produced by an arc evaporation source.

temperature. It is halted at temperatures in the range 175 to 350°C, depending upon the substrate material and its surface condition.

Coating is done using a substrate bias in the 0 to 400 volt range. For reactive deposition, a gas containing the desired constituents is introduced. For example, N_2 is used to produce TiN, ZrN or HfN films and CH_4 or C_2H_2 are used to produce TiC, ZrC or HfC films.

Substrate temperature is maintained by absorption of the energy carried by arriving metal ions. To control substrate temperature within desired limits, one adjusts the input power using total evaporator current, substrate voltage and gas pressure as variables. This sets limits on the deposition rate which is also a function of total evaporator current, substrate voltage and gas pressure, as well as the location, size and shape of substrates. For TiN, deposition rates of 0.05 to .3 μm per minute, which correspond to substrate current densities of 1.25 to 7.5 mA/cm^2, are typical. The erosion rate for Ti cathodes during TiN deposition is approximately 10 μg/C.

Coating proceeds until the desired film thickness is obtained. Average coating thickness is proportional to the material erosion from all cathodes and inversely proportional to the area coated. Thicknesses in the range 1 to 5 μm are typical for wear and corrosion resistant TiN films.

Substrate rotation is used to maximize the number of parts that can be coated uniformly in one batch. The fixture assembly that holds parts is mounted to an electrically-insulated rotary-motion vacuum feedthrough that is driven by a motor located outside the vacuum chamber. Such a rotary motion feedthroughs is most commonly located in the top or bottom wall of the chamber. Planetary rotation of parts with respect to the rotating fixture assembly is another frequently used method of improving the uniformity of coating coverage.

IV. Process Characteristics

A. Vacuum Arc Characteristics

The most distinctive AVID process characteristics are the direct result of vacuum arc characteristics. In particular, a large fraction of the metal vapor is ionized and the charged particles within the vapor carry an energy that is much greater than one would expect [1, 2, 3]. In fact, positive ions must overcome the attractive force of the cathode to escape. Reasons for the anomalously high ionization fraction and ion energy will become clear in the following discussion of cathode arc spots. The effects of this highly ionized and energetic vapor on film growth are discussed at the end of this section.

The previously described cathode spots are microscopic regions where most of the electrical input energy is dissipated to produce extreme physical conditions. Direct measurement of physical properties within these spots is very difficult due to their small size and dynamic nature. However, a qualitative picture of the inner workings of cathode spots has been provided by various physical models that are the result of experimental measurements and theoretical calculations. Table 1 lists order of magnitude values for selected physical quantities within a cathode spot.

A schematic magnification of a cathode arc spot, as described by a model discussed by Daalder [4], is shown in Figure 3a. Electrons, metal atoms and metal droplets spew from superheated emission sites heading toward a cloud of

positive ions. Emission from a given site lasts only on the order of 10^{-7} seconds before jumping to other nearby sites under the same ion cloud [4]. The survival of individual cathode spots depends upon old emission sites being replaced by new ones before the ion cloud dissipates. Craters on the order of 1 to 20 μm in diameter are formed as cathode material is transported from the emission sites. The ion cloud is formed by collisions between electrons and metal atoms after the electrons have gained sufficient energy by acceleration from the anode. The cloud forms at a distance on the order of tens of microns from the cathode, where ionizing collisions are most probable. Once formed, the cloud serves as a virtual anode. As new ions are created by collisions within the cloud, ions at the periphery of the cloud are repelled both toward and away from the cathode by space charge of the cloud [2, 4].

The emissions from cathode spots, illustrated in Figure 3a, include electrons, ions, metallic droplets and neutral atoms. Electrons which emerge from the ion cloud, and flow to anode surfaces, carry between 107 and 110% of the arc current. This is offset by the coincident flow of positive ions that carrys between 7 and 10 percent of the arc current for a wide range of metals [6]. The amount of ionized vapor released from the cathode is proportional to the charge transport in coulombs [4]. It is likely that almost 100% of the metal vapor is ionized within the cathode spot region [6]. The ions are ejected in a direction that is more or less perpendicular to the cathode face [4]. The majority of metal droplets, which are produced as a result of the extreme temperature and forces existing within emission craters, leave the cathode at angles between 10 and 30 degrees above the cathode plane [4]. Droplet emission is generally greater for metals having a lower boiling point

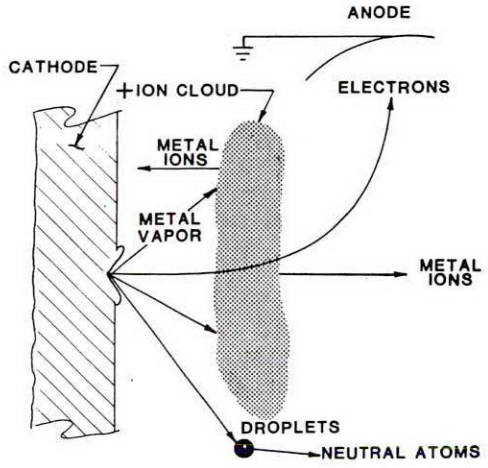

Figure 3a. Schematic representation of the cathode spot region of a vacuum arc [4].

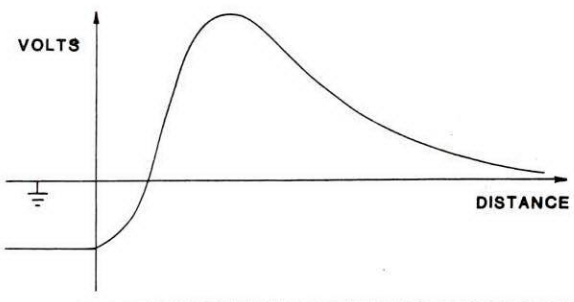

Figure 3b. Illustration of a positive hump in electric potential resulting from the positive ion cloud [2].

and for increased average cathode temperature [6]. Droplet emission decreases with increased cathode spot velocity [4] and with increased cathode surface contamination [6, 8]. The ratio of metal ions to metal vapor is on the order of 10% for low boiling point metals and 90 to 100% for refractory metals [9]. This suggests that a likely source of neutral atoms is evaporation from molten droplets in flight [9].

Table 2 summarizes ionization state and average ion energy data obtained by Lunev, et. al. for five arc-evaporated metals [1]. These data show that a typical ion has been stripped of one or two electrons and carries an energy on the order of 100 eV. The following two examples illustrate the unusually high magnitude of these values: First, even in very efficient gas discharge processes, only 1 to 10% of the atoms are ionized to a state of +1e [10]. Second, in sputter deposition processes, which produce the highest energy vapor of all the traditional PVD processes, vapor atoms have an average energy that is only on the order of 10 eV [11].

Table 1. Physical conditions within a cathode spot.

Current Density	10^6-10^8 A/cm^2	[4]
Power Density	10^7-10^9 W/cm^2	[4]
Electric Field	10^4-10^5 V/cm	[2]
Temperature	4-10x10^3 °K	[4]
Pressure	1-100 Atmospheres	[5]

Table 2. Average ionization state and energy for ions emitted by vacuum arcs from various metals [1].

	Arc Current	Arc Volts	$\bar{z}$	$\bar{E}$
Fe	100A	19	+1.5e	106 eV
Cr	100	19.5	2.0	79
Ti	100	20	1.8	76
Cu	100	22	1.7	82
Mo	170	28	2.9	152

The source of high energy ions emanating from cathode arc spots was first explained by Plyutto, et. al., who proposed that the density of positive ions within the ion cloud region is sufficiently high to produce a positive "hump" in the electric potential distribution as shown in Figure 3b [2]. Such a potential hump provides a mechanism that allows positive ions to escape the attraction of the negative cathode region and to acquire a high energy in the process. A potential hump on the order of 50 volts above anode potential is required to produce ions having an energy in the range listed in Table 2. A hump of this magnitude is sufficient to produce ion currents of approximately equal value directed both toward and away from the cathode.

The AVID process is ideally suited for depositing alloys since material is flash evaporated without general melting of the arc source. Thus, alloys can be converted to vapor form without changing their composition. The major difficulty in faithfully producing a film of given alloy composition occurs at the substrate during condensation. Elements having a higher vapor pressure tend to have lower sticking coefficients. Consequently, alloy films tend to be somewhat deficient in the highest vapor pressure elements, independent of how the coating vapor is produced. Compensation for this effect can be made by increasing the concentration of high vapor pressure elements in the source material.

B. Ion Collection

A general characteristic of the AVID process is that the collection of metal ions is affected by substrate shape and the proximity of substrates to one another. The electric field surrounding substrates controls the quantity of ions transported to various surfaces. As previously stated, compound films are deposited in the presence of reactive gases. As a general rule, one would expect metal ions to be neutralized in charge exchange collisions between ions and gas molecules. Collisions between Ti ions and N_2 molecules are an exception; because of the high binding energy of electrons to N_2, charge exchange between Ti ions and N_2 molecules is very unlikely. This has been observed experimentally by comparing TiN deposition rates obtained with and without a biased screen placed in front of a planar substrate. The results indicate that more than 90% of the Ti from an arc source reaches substrates as ions, even after passing through 150 mean free paths of N_2 gas. Thus, electric fields also strongly influence the collection of Ti ions during TiN depostion.

Figure 4 shows the collection of Ti ion current as a function of increasing substrate voltage for three cylindrical substrates of different diameter. The sharp increase in current between 0 and 100 volts is due to greater ion collection that occurs as the negative bias separates more

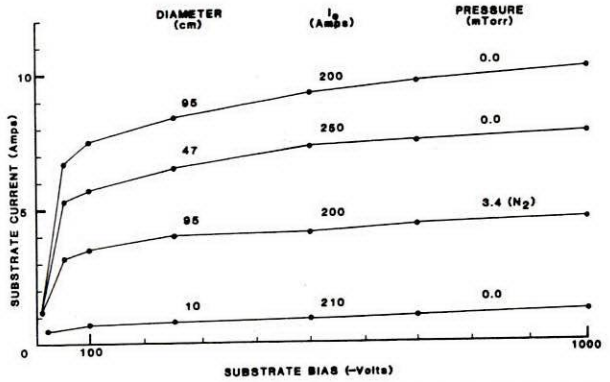

Figure 4. Substrate current, collected by cylindrical substrates, versus voltage for Ti ions produced by an arc evaporation source. Substrate diameter, total evaporator current (I_e), and pressure are noted over each curve.

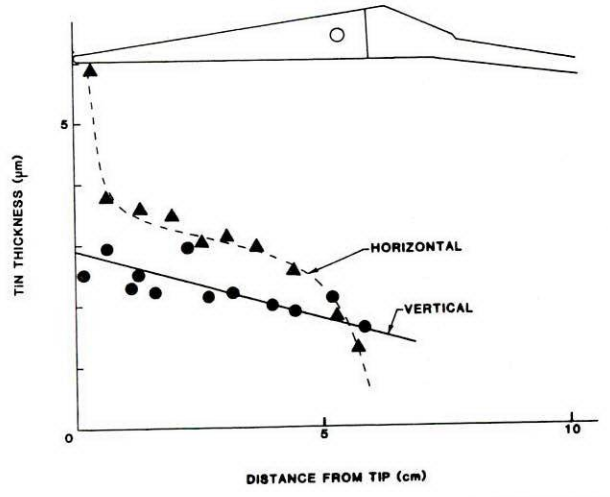

Figure 5. TiN thickness versus distance from the tip of a scissors blade coated with a substrate bias of -200V at 20 mTorr.

positive ions from the evaporated plasma stream. Larger substrates collect a greater proportion of the available ions. Ions not collected by negatively biased substrates recombine with electrons in flight or condense on chamber surfaces. The 30% increase in substrate current between -100 and -1000 volts is largely due to secondary electron emission from substrate surfaces. The decreased substrate current for the curve measured in the presence of 3.4 mTorr N_2 is largely due to a reduction in ion emission from the cathode, although scattering from gas molecules does cause a gradual decline in ion current as a function of increasing gas pressure.

Enhanced ion collection by strong electric fields is illustrated in Figure 5 which shows the coating thickness distribution of TiN deposited on a scissors blade for two orientations with respect to the cathode. The tip of the "horizontal" scissors blade was pointed toward the cathode and the "vertical" scissors blade was parallel to the cathode plane. There is a sharp maximum in thickness at the tip for the horizontal orientation because the tip was closest to the cathode and is the location of highest field strength. The linear drop in thickness with distance from the tip in both cases is due primarily to the linear increase in surface area.

Although deposition rates always tend to be greater at corners, sharp edges and on isolated surfaces that have little competition for ions, coating thickness uniformity can be improved by reducing the bias voltage and by placing substrates in arrays that balance the competition for ions. In cases where close tolerances are required on irregularly shaped parts, additional fixturing surfaces can be used to improve film thickness uniformity. On the other hand, in many cases it is more important to achieve a highly adherent coating on particular surfaces or edges than to achieve uniformly thick coatings over the entire part. To this end, it is always good practice to face parts toward the cathodes such that the most critical surfaces are directly exposed to the coating vapor.

Scattering of metal atoms and ions by gas molecules also affects the distribution of coating vapor. For neutral atoms, gas scattering always improves the distribution of vapor that would otherwise travel in a line-of-sight path from the source. The effect of gas scattering on metal ions is not as straight forward. While ion scattering from molecules can improve the distribution of vapor, especially on the backside of substrates, it can also serve to reduce ion speeds, making their collection at points of highest electric field strength more likely. In some cases, this concentrating mechanism can be desireable. For example, in coating arrays of drills pointed toward arc sources, gas scattering can increase the amount of TiN deposited at the cutting tips at the expense of reducing the deposition nearer the shanks where the film is primarily of cosmetic benefit.

C. Film Growth

The energy deposited by incident ions or atoms in the surface region of growing films is a very influential factor in producing films that are dense, strong and adherent. It is important that atoms condensing on the surface of growing films have sufficient mobility to move about until they are trapped at sites of highest binding energy. It is also important to promote atomic rearrangement in the surface region in order to break up branched structures and to fill vacancies between crystallites.

In the qualitative structure zone model (SZM) proposed by Movchan and

B. Ion Collection

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Figure 5. TiN thickness versus distance from the tip of a scissors blade coated with a substrate bias of -200V at 20 mTorr.

The energy of condensing metal ions in the AVID process is controlled by varying substrate bias voltage and gas pressure. The growth of metal films at pressures less than 10^{-3} Torr usually occurs under the strong influence of metal ion bombardment, expecially for the refractory metals whose vapor is nearly 100% ionized. For certain metal/gas combinations, such as Ti and N_2, where the metal ions retain their charge in collisions with gas molecules, the growth of compound films is also dominated by the bombardment of energetic metal ions. At low pressure, where gas scattering is insignificant, the energy of ions emitted from an arc source is in the middle of the optimum range for film growth modification (see Table 2). When gas scattering is significant, substrate bias voltage can be adjusted to achieve the desired level of bombardment energy for optimum film growth. A further advantage of the AVID process is that the energy of a large fraction of the metal ions can be adjusted to have the optimum bombardment energy; this produces less structural damage than when the average energy per deposited atom is carried by only a small percentage of very energetic ions, as is the case with many of the ion-assisted PVD processes.

AVID TiN films can be deposited over a wide range of substrate temperature, bias voltage and pressure. This is a result of the large energy and ion fraction carried by the metal vapor. Figure 6 shows a TiN film that was deposited at 200°C, with no bias, at a N_2 pressure of 10 mTorr. The fine-columnar-grained Zone T structure is a result of the Ti ions losing much of their energy in passing through the equivalent of 40 mean free paths of nitrogen. Figure 7 shows a TiN film that was deposited at the same temperature and voltage, but with only 1.5 mTorr N_2. The Ti ions, which passed through the equivalent of 8 mean free paths of N_2, retained enough of their initial energy to produce a film with Zone 2 structure. The temperature parameter, T/T_m, is about 0.15 for these films, whereas in the SZM the Zone 1/Zone 2 boundary occurs at about 0.5 in the absence of ion bombardment [13, 14].

The properties of TiN films deposited with the AVID process are relatively insensitive to deposition temperature between 175 and 500 °C, to substrate voltage between -50 and -400 volts, and to N_2 pressure between 1 and 50 mTorr. Figure 8 shows a dense well-adhered Zone 2 film that is typical of TiN deposited within these parameter ranges.

Approximately stoichiometric TiN films are produced over an extraordinary wide range of deposition rates and pressures that is equivalent to a variation in the Ti to N_2 arrival ratio of 50 to 10,000. This is thought to be a result of weakly bound excess nitrogen being ejected from the growing film by energetic Ti ion bombardment. It appears to be very important that the Ti be selectively ionized in comparison to the N_2, as it is in the cathode spot region, in order to achieve stoichiometric TiN films so easily. AVID TiN films that are produced in the presence of nitrogen that is activated by a gas discharge do exhibit brownish or reddish hues that are characteristic of overnitriding [16, 17]. This is consistent with the results obtained when using ion assisted PVD processes in which ions are created unselectively by a gas discharge; in these cases, the N_2 is activated and the Ti to N_2 arrival ratio must be carefully controlled to achieve stoichiometric TiN films [10, 16, 17].

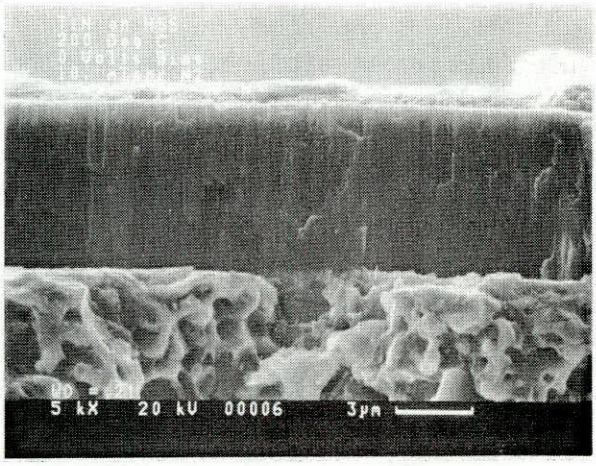

Figure 6. Fracture section of an AVID TiN film deposited at 200°C, with no substrate bias, using 10 mTorr N_2.

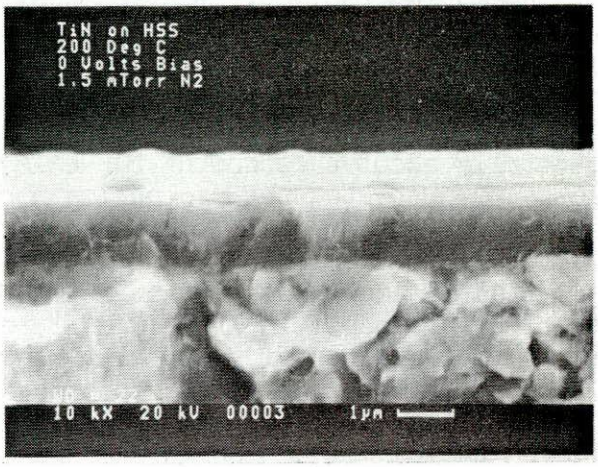

Figure 7. Fracture section of an AVID TiN film deposited at 200°C, with no substrate bias, using 1.5 mTorr N_2.

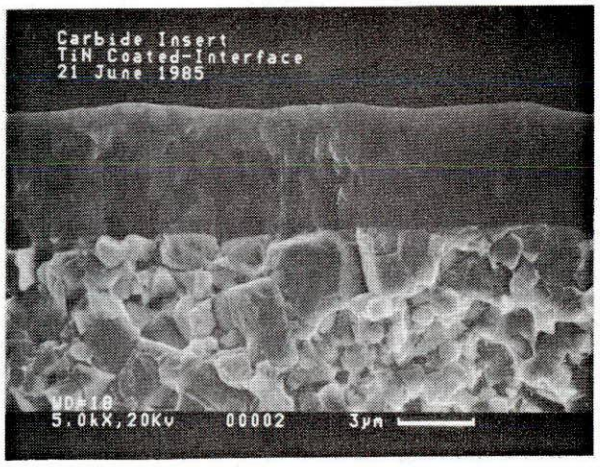

Figure 8. Fracture section of an AVID TiN film deposited at 400°C, with 225 volts substrate bias, using 25mTorr N_2.

V. Applications

Although the AVID process can be used to deposit many different materials, most applications developed over the past several years involve the use of TiN. The following examples provide an indication of the importance and potential of AVID TiN coatings for improving the life and performance in a wide variety of applications. For any application, the success of TiN or another coating depends not only on the coating adhesion and film properties, but also on the ability of the substrate to support the coating.

TiN is best known as a coating that improves the wear and performance of metal cutting and forming tools. It has gained wide acceptance in these applications during the last five years. Life increases of three to ten times are typical for drills, endmills, gear cutting hobs and shaper cutters, broaches, punches, forming dies, and many other tools. Even after resharpening, the wear resistance of most coated tools is still two to six times greater than for uncoated tools. A productivity increase of twenty to thirty percent and improved part quality are also frequently observed.

Recoating tools after resharpening was recently demonstrated to be economically attractive for gear cutting. In one plant hobs and shaper cutters, that were recoated with TiN after each resharpening, wore only about one half as much as coated tools that were not recoated after resharpening. The wear of tools that were coated only once, prior to first use, was generally about a factor of three less than for uncoated tools. In-plant tests demonstrated that recoating hobs and shaper cutters can decrease the cost of producing gears substantially. Tools have been successfully recoated up to twenty times.

Plastic and rubber injection molding is another broad field where TiN coatings are achieving very useful results, including greatly reduced mold wear and increased productively. Injection molds are frequently made from A, O and P series steels that begin to soften between 200 and 260°C, which dictates use of a low temperature coating process. The optimum thickness for TiN on typical injection mold parts is about 2 μm.

Field results indicate that TiN-coated injection molds exhibit useful-life increases in the neighborhood of 3 times due to reduced frictional, abrasive and corrosive wear, while showing a dramatic improvement in release characteristics, a reduction in mold maintenance and cleanup requirements, and improved part quality. These results are summarized as follows:

Frictional wear between moving parts is greatly reduced. Best results are obtained when the mating surfaces of sliding pairs are coated.

Abrasive wear caused by materials such as mineral or glass fillers is also reduced. This is an important factor in maintaining close tolerances of fill gates to assure uniform filling of multiple-cavity molds.

Corrosive wear caused by acids and hot gases generated in molding processes is also greatly reduced. TiN coated molds show increased resistance to HCl and other corrosive by products; significant improvements over Cr and Ni platings have been observed. TiN coatings virtually eliminate corrosion pits caused during injection by diesel explosions of compressively-heated volatile gases.

Release compounds are often required to achieve a clean separation of parts from their mold. TiN coatings have improved the release properties of

parts molded with acetals, polyamides, styrenes, polyesters, flame retardant ABS, PMMA and silicone rubber, allowing successful molding while using little or no release compound.

Another very important benefit of good release is faster maintenance and cleanup. Injection mold sets require periodic disassembly and cleaning of residue buildup. The time required for complete overhaul and cleaning of TiN-coated mold sets is often reduced by a factor of two or more. In one dramatic example, involving a flame retardant ABS plastic, the cleanup frequency of a TiN-coated mold was reduced by more than 15 times and the residue was removed with much less difficulty.

In addition to helping to produce consistently good quality parts by maintaining original mold dimensions and by inhibititing the buildup of material on internal surfaces, in some applications TiN coatings have also improved part quality by promoting a more even flow of molten material into mold cavities. The dimensional tolerance of molds coated with 2 to 3 μm of TiN are most often close enough to use without further adjustment. This represents an improvement over traditional electroplated Cr or Ni coatings where thicknesses of 10 to 25 μm are typical, resulting in buildup at corners and edges which requires regrinding to restore the original dimensional tolerances.

Finally, inspection of molds for wear and corrosion damage is facilitated by the visual color contrast between golden TiN and the mold metal. With little effort, molds can be removed from service when the substrate metal just begins to show, before serious damage occurs. This allows recoating of undamaged molds without the use of costly refurbishing methods, such as welding-in filler metal and regrinding.

Results similar to those observed with TiN-coated injection molds have been observed in spin molding, transfer molding and plastic extrusion applications.

Other applications of TiN coatings that show promise include aluminum die-cast molds, food processing equipment, electrical connector contacts, and turbine components. While the number of applications for TiN coatings is growing rapidly, there are many other useful coating materials that will also gain prominance in the coming years including nitrides and carbides of Zr and Hf, erosion and corrosion resistant superalloys, and many others.

VI. Conclusion

There is almost no limit to the number of uses that surface enhancement coatings will have in coming years. Unique advantages associated with the inherently high ion fraction and energy of metal vapor emitted from arc evaporation sources assures the AVID process a significant role in the development and application of these coatings.

Acknowledgements

The author thanks James H. Dontje and Michael W. Schultz for use of their experimental data, Olive A. Johansen and Arthur E. Anderson for reviewing the manuscript, and numerous other Multi-Arc staff members for their help in preparing this article.

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Vacuum Coating Session B

The Finishing Touch, Vacuum Metallizing or Electroplating

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THE FINISHING TOUCH, VACUUM METALLIZING OR ELECTROPLATING

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Abstract

Decorative coatings have been applied to various products for centuries. These coatings enhance the value and utility of the finished article. A bright shiny metallic appearance is perhaps one of the most appealing and yet elusive finishes available. From our comercial-job-shop perspective, vacuum metallizing and electroplating are compared as methods of applying a bright shiny metallic coating. Although both are well known methods, electroplating continues to surpass vacuum metallizing as the coating method of choice in the marketplace.

Presentation

From the name of our firm, Providence Metallizing Company, you could imagine that vacuum metallizing was our first approach to surface finishing. Frankly speaking, if we had ventured toward electroplating first, I am sure that we would never have gone into vacuum metallizing as an economical method of surface finishing.

We at Providence Metallizing Company have been performing vacuum coating for almost 40 years and we have been doing contract electroplating for about 12 years. Basically there are very few similarities between these two methods of surface finishing. Because those attending this conference are for the most part electroplaters, we will spend very little time describing the electroplating method. Working in the electroplating field exclusively, however, makes one take this method too much for granted. If we could give you one insight, for example, take the Hull cell. For less than $500.00 and some very small quantities of chemicals and various metal anodes one can plate sample coupons of a whole host of metals. To do that same metallic finish in vacuum deposition, $100,000.00 wouldn't be enough to start up and the know-how needed would be staggering.

There have been many terms that describe what is commonly known as vacuum metallizing. To name some of these: vacuum deposition, vacuum coating, vapor deposition, vacuum flash evaporation, vacuum plating. All of these names generally are referring to decorative flash evaporation of aluminum metal in a vacuum of approximately 10^{-4} torr.

Then there are other coatings done in a vacuum such as roll coating or web coating. In this process metal is usually deposited in a vacuum of approximately 10^{-4} torr but is done on a continuous roll of plastic paper or cloth. In this process the metal is continuously vaporized from heated sources and deposited onto a web of material that is running by the vapor and being unrolled and rolled up after deposition.

Still another vacuum process is referred to as optical coating. This process is usually more sophisticated as far as the vacuum deposition is concerned. The degree of vacuum for this process can be anywhere from 10^{-4} to 10^{-8} torr. The products are usually glass substrates of one sort or another. In this process, metals, oxides, nitrides and many other materials are vaporized. They also use a variety of heat sources such as tungsten, molybdenum, tantalum, carbon, intermetallics such as boron nitride, and electron beam guns. These coatings are usually multiple layers of metal, oxides or nitrides, etc., usually measured by light meters in angstroms. Sometimes more than 30 different layers are deposited on the glass substrates to accomplish a particular optical coating. I will not go on discussing this process because it becomes very involved and surpasses the scope of this paper.

Another vacuum process is sputtering. In this process a chamber is evacuated, usually to approximately 10^{-4} to 10^{-6} torr, then backfilled with an inert gas such as argon. It is usually backfilled to approximately 10^{-3} torr. This process uses a cathode that has a DC or RF current applied to it. Once the current is applied, the gas is ionized and a plasma is formed, which then plays on the cathode, called the target. It is usually made of metal. The gaseous ions bombard the target and liberate metal particles from the target, which are then deposited onto the substrates in the chamber. The metal or alloy does not melt and vaporize as in the other vacuum deposition methods. In this process, almost any metal or alloy can be deposited.

Still another vacuum deposition method is called ion plating or ion deposition. In this method, vacuum deposition comes close to electroplating. The metal is vaporized in a partial vacuum with an inert gas such as argon. The metal vapor is ionized in the gaseous atmosphere and is negatively charged. The negatively charged metal ions are attracted to the positively charged substrates. This process could be called gaseous electroplating. Again it is not our objective to go into this process in depth.

The process called vacuum metallizing, vacuum coating or vacuum plating for the most part describes a process that is done on decorative parts such as trophies, lamp parts, low priced jewelry, plastic toys, and picture frames. The products can be made of plastic, glass, metal, wood, paper, cloth, stone, sea shells, etc. Practically anything that can take a paint, lacquer, varnish or coating can be vacuum coated. The part does not have to be a conductor of electricity.

The article is usually base coated or undercoated with an organic material that is dipped, sprayed, flow-coated or otherwise coated. Thereafter, it is usually baked in an oven to harden the base coat. The base coat gives a smooth finish to the substrate. In the case of metal it fills up the scratches or porosity; in the case of plastic it gives a sheen and luster to the base plastic that it does not have as it comes out of the mold. Some parts may look smooth, but not smooth enough to give a polished look to the substrate. Of course, as in any finishing system, the articles are usually cleaned so that they can accept the organic finish and so that they will be clean and have good adhesion. The parts can be cleaned either on or off the racks but they must be racked before the organic base finish can be applied. After the base coat has been applied and baked, the racked parts are ready for vacuum metallizing.

The racks are usually placed on a jig holder, which is rolled into the vacuum chamber. The jig that holds the racks solidly is capable of rotating the racks within the chamber. On most decorative vacuum chamber jigs there are two electrical buss bars that go down the center of the chamber. They are placed along the length of the vacuum chamber so that the vaporized metal will coat all the parts in the chamber as they are rotated around the buss bars. Attached to these buss bars are usually tungsten filaments that are capable of being heated to more than 3,000 F. There are many of these filaments across the two buss bars, sometimes 15 or more. Before the racks are put on the jig, small pieces of aluminum metal wire are usually attached to the tungsten filaments. Aluminum is used in conjunction with tungsten filaments because aluminum wets tungsten very well and also because it is extremely reflective and inexpensive.

After the jig is prepared, it is rolled into the vacuum chamber, which is then sealed and pumped down to remove the air. There are 4 types of pumps used to pump down the vacuum chamber. First a conventional mechanical vacuum pump is engaged, which brings the vacuum down to about 200 microns. Then a roots vacuum blower is engaged, which brings the vacuum down to about 5 to 10 microns. At this point these are closed

off from the chamber and an oil diffusion pump is engaged, which brings the vacuum down to below 1 micron to the 10^{-4} torr range. Cold traps or cryo panels are sometimes used to increase the pumping speed of the diffusion pump stage. These pumps are capable of going down to much better vacuums but then it is a matter of economy because the longer you pump the better vacuum you get, but the longer the cycle takes the less product you can fire in one given day.

The desired degree of vacuum for evaporation of the aluminum is usually about 10^{-4} torr. This type of vacuum is used so that when the metal vaporizes it does not run into too many oxygen molecules. Obviously, if there is too much oxygen left in the vacuum chamber it will oxidize the aluminum and there will be a dark aluminum deposit on the parts. The aluminum is heated by the tungsten filament, which gets its power from a transformer and a Variac that brings up the power slowly so that the aluminum melts and then vaporizes. This all takes place at about 1,600 F. The metal vapor leaves the hot tungsten filament, flies off in all directions, and deposits on the articles being rotated around the buss bars. The thickness of the aluminum deposit is usually about 1 to 3 millionths of an inch. The objective is to have a bright aluminum deposit that is thick enough to cover the base material entirely. This is called flash evaporation and it is the way almost all decorative vacuum deposition is done. The evaporation portion of this cycle is usually only about 20 seconds. From the time the parts are first rolled into the chamber until they are finished takes about 1/2 to 3/4 of an hour depending on how many pieces are placed in the chamber and the degree of outgassing that goes on in the chamber.

Outgassing is one common problem that increases the cycle times and slows down the pumping speed of the system. Vapors are generated from the articles themselves, the base coating or dirt in the chamber. Dirt is organic or inorganic material that is capable of vaporizing at a vacuum of 10^{-4} torr. It comes from the walls of the chamber, the jig, the racks or the oils in either the mechanical pump or diffusion pump.

After the parts have a deposit of aluminum, the valves are shut down and air is returned to the chamber. The door is opened, the racks are taken off the jig, and another cycle is started.

At this point the racks and parts all have a thin film of aluminum, which has relatively poor adhesion and very poor abrasion resistance. Therefore, the parts need a clear organic protective overcoating. The clear top coating is put on in the same manner as the base coat but the top coating must be very clear so as not to discolor the very bright

aluminum film. This top coating is also baked the same way as the undercoat so that it will be hard and have good abrasion resistance. To make the finish gold or some other color, the top coat can be tinted with dyes.

We have, provided a glimpse into the decorative vacuum coating process. The electroplating process is well known to this audience. In fact, anyone who has taken a 7th grade science course learns about electrolysis and generally about electroplating, anode, cathode, electrolyte and all.

Why should anyone want to do decorative vacuum coating rather than electroplating? In a brief statement anything that can be electroplated should be done that way. Vacuum coating is a substitute or spot finish. If it is a gold color, you cannot call it gold. If it is a silver color, you usually make up a name for it because aluminum does not have much glamour going for it. Vacuum coatings have relatively poor abrasion resistance and poor adhesion in comparison to electroplated finishes. This is a batch process that does not lend itself to an in-line system. In vacuum coating everything must be racked rigidly; decorative barrel vacuum coating produces disastrous results.

In racking parts for electroplating, a piece of copper wire can work wonders. Wire cannot be used in vacuum coating because the base and top coating would glue the wire to the racked part. Vacuum coating a few new samples is a big chore, whereas in electroplating it is as simple as wrapping a copper wire around the part.

Except for racking and unracking time, in electroplating, an average start to finish cycle is about 20-30 minutes, so the same rack can be reused as many as 15 times in an 8-hour day. In production job shop vacuum coating it can take as long as 16 hours for one rack to make a complete cycle. This means that it takes about 30 times as many racks to do the same number of pieces. It also means that it is almost impossible to run a one-shift vacuum coating factory and make money. To the best of our knowledge there are no profitable vacuum coaters who run one shift, but there are thousands of electroplaters who do quite well with just one shift. Our vacuum coating runs three shifts and our payroll to sales percentage is very high despite the three-shift operation. On the other hand, our electroplating department runs only one shift and our payroll to sales percentage is consistently lower. Here we are comparing one shift to three shifts, not just taking a per shift percentage. This gives you some idea of how hard it is to run a successful vacuum coating factory.

At this point, one might ask why are we in the decorative vacuum coating business? Because we didn't know any better, our company started vacuum coating with three shifts about 35 years ago. About 15 years ago we decided to add electroplating. It took us some years to learn this phase of the business, it has become profitable on one shift and it is now the fastest growing part of our business. In the next five years, we expect that we will be doing much more electroplating than vacuum coating. There may come a time when we might abandon decorative vacuum coating altogether.

If we had put all our efforts right from the beginning into electroplating instead of vacuum coating, we might be the largest and most profitable electroplating factory in the world. That might sound like tall words but we feel the pain everyday.

When you electroplate gold your customers give you credit for gold plating. When you vacuum coat gold, you are just a cheap imitation. In the United States there are probably more than 5,000 contract electroplaters but hardly more than 25 contract vacuum coaters. There is nowhere near the demand for vacuum coating and there is more competition for those few jobs in vacuum coating than there is among the 5,000 electroplaters. There are at least 500 electroplating jobs to each vacuum coating job.

One job in which vacuum coating does have an edge over electroplating is plastic or glass reflectors that need an aluminum coating without a base coat. Generally the customer does this kind of job himself because it is usually a large volume job and it is easy to do because there is no lacquer involved. The customer can call a vacuum equipment supplier, tell him what he wants and for X dollars he gets a turnkey installation. We know because it has happened to us.

Pollution control is a fact of life in electroplating. More varied controls are needed in the vacuum plating shop. The vacuum coater still must clean the basic parts - one source of pollution. Solutions used to strip some parts and to strip aluminum from the jigs are two more. Then there are lacquer sludges, clogged filters, dirty lacquer thinners, and so on. Spraying laquers is a major portion of a vacuum coater's operation. Most electroplaters don't have to worry too much about this, except those who use lacquers to protect brass or copper as an overcoat. This is sometimes taken care of in a tank with a water lac. In vacuum coating, paint or lacquer is filtered out in air dry or water wash spray booths,

but these booths do not capture the solvent fumes. Controlling these can put a vacuum coater out of business. We prefer to tackle the waste water problems in electroplating because they are more manageable.

We could go on and on about this subject of electroplating versus decorative vacuum coating. You are probably wondering why anyone would want to be in the contract vacuum coating business? The best answer to this is the question why should anyone want to be a coal miner? Most coal miners are usually stuck with that job for some reason or another; the same goes for us in vacuum coating.

In general, we find that vacuum coating does have a small place in surface finishing. Electroplating is by far the better method from the standpoint of profit margin, engineering, and pollution control. It is for these reasons that we are seeking to expand our electroplating facilities and curtail our vacuum coating.

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Vacuum Coating Session B

Estimating the Production Cost of a Deposition

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Estimating the Production Cost of a Deposition

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Abstract

A production cost analysis has been developed for thin film coated products combining the physical models of a deposition process with a financial analysis. Cost data supplied by the prospective PVD user and supplemented with data obtained from experience are entered to generate the estimated production cost per module of coated product. Computer codes are available both for batch coater and for in-line coater production. Examples of the analysis are presented.

Cost Analysis for a Coating

The following figures 1 through 7 show the output of the program for a hypothetical example of a two-layer coating on 24-inch-wide substrates in an in-line coater, using unreactive sputtering for film 1 (1000Å tantalum) and reactive sputtering for film 2 (1500Å zinc oxide). On each line, a preceding black bar (or two bars) indicates that the datum was entered as an input to the program; unmarked lines are results calculated by the program from the given data. The final summary of production costs is listed in figure 7; in this example, the price of the substrate has not been included in the analysis.

BOC Temescal — Berkeley, CA

Example of Production Cost Analysis

Production Conditions

▮ Substrate Width	24.0 in.
▮ Percent Area Covered	90%
▮ Line Speed	24.0 in./min

Figure 1. The production conditions defined in the specification are summarized. The line speed is derived from the desired throughput by preliminary calculation. Note that the line speed is the true line speed during production; the effect of 15% unscheduled downtime has already been included.

Film Specifications

Film 1

- Tantalum
  - Target Thickness: 0.250 in.
  - Target Utilization: 25%
  - Target Price: $11,000.00
- Unreactive Sputtering
  - Film Thickness: 1,000.000 angstroms
  - No. of Sources: 1
  - Sputtering Source: HRC-1800
  - Source-Substrate Distance: 5.5 in.
  - Aperture Opening: 18.0 in.

The total thickness variation over the substrate width is expected to be 10%.

Collection Efficiency	35.7%
Power/Source Required	13.7 kW
Total Power Required	13.7 kW
Target Usage	
erosion rate	0.206 lbs/hr
target use rate	0.823 lbs/hr
Useful Target Life	97.5 hrs

Figure 2. Film 1 specifications are listed. The total power required, the uniformity, the collection efficiency and the useful target life (25% utilization of the target's initial mass before replacement) are calculated for the given sputtering source and the chosen geometry. Experience shows that 13.7 kW are readily handled by a source of the given size, so the program is told that only one source will be required.

Film Specifications

Film 2

- Zinc Oxide
  - Target Thickness: 1.000 in.
  - Target Utilization: 25%
  - Target Price: $ 2,000.00
- Reactive Sputtering
  - Film Thickness: 1,500.000 angstroms
  - No. of Sources: 2
  - Sputtering Source: HRC-1800
  - Source-Substrate Distance: 5.5 in.
  - Aperture Opening: 18.0 in.

The total thickness variation over the substrate width is expected to be10%.

Collection Efficiency	35.7%
Reactive Gas Usage	0.370 scfh of O_2
Power/Source Required	17.6 kW
Total Power Required	35.2 kW
Target Usage	
erosion rate	0.084 lbs/hr
target use rate	0.335 lbs/hr
Useful Target Life	823.6 hrs

Figure 3. Film 2 specifications are listed. The total power required is somewhat high for a zinc target of this size, and since zinc has a moderately low melting point, two moderate-powered sources are specified. The rate for the reactive sputtering of zinc oxide is known from empirical studies, and is entered from stored data tables in the course of the calculation.

Throughput

▮ Line Speed		24.0 in./min
▮ Unscheduled Downtime		15%
▮ Hours/Year/Shift		2,000 hrs
Average Throughput		
		184 sq ft/hr
	1 shift	367,200 sq ft/yr
	2 shifts	734,500 sq ft/yr
	3 shifts	1,102,000 sq ft/yr

Figure 4. The throughput is calculated for the given production conditions and estimated unscheduled downtime.

Material and Energy Usage

▮ Equipment Power (pumps etc) 300kW

Film	Film Material	Material Usage Per 1,000 sq ft	Material Usage Per Year Per Shift	Energy Usage Per 1,000 sq ft (kWhr)	Energy Usage Per Year Per Shift (kWhr)
1 NS	Ta	1.04 lbs	381 lbs	69	25,380
2 RS	ZnO	0.42 lbs	155 lbs	178	65,210
	O_2	1.87 scf	685 scf		
sputtering gas		13.35 scf	4,902 scf		
equipment power				1,634	600,000
Total Power		kWhr/1,000 sq ft		1,881 kWhr/year/shift	690,600

Figure 5. The material usage and energy usage (including a realistic allowance of 300 kW to power the coater equipment) are calculated and expressed per 1000 square feet of product and per year per shift.

Cost Analysis

Material Substrate and Energy Costs

▮ Energy Price	$ 0.100/kWhr
▮ Substrate Price	$ 0.000/sq ft
▮ Sputtering Gas Price	$ 0.670/scf
▮ O_2 Gas Price	$ 0.490/scf

Film	Film Material	Material & Sbstrt Cost Per 1,000 sq ft	Material & Sbstrt Cost Per Year Per Shift	Energy Cost Per 1,000 sq ft	Energy Cost Per Year Per Shift
1 NS	Ta	$ 568.48	$ 208,800	$ 6.91	$ 2,538
2 RS	ZnO	$ 24.47	$ 8,985	$ 17.76	$ 6,521
	O_2	$ 0.91	$ 335		
sputtering gas		$ 8.94	$ 3,284		
substrates		$ 0.00	$ 0		
equipment power				$ 163.39	$ 60,000
Total Cost		$ 602.80	$ 221,404	$ 188.06	$ 69,059

Labor and Equipment Costs

▮ No. of Operators	3.00
▮ Operator Price	$20.00/hr
▮ Hours/Year/Shift	2,000 hrs
▮ Unscheduled Downtime	15%
▮ Equipment Price	$ 3,000,000
▮ No. of Years Amortization	4 years

Labor Cost/1,000 sq ft		$ 326.77
Equipment Cost/1,000 sq ft	1 shift	$ 2,042.32
	2 shifts	$ 1,021.16
	3 shifts	$ 680.77

Figure 6. Various price inputs, including the target prices entered in figures 2 and 3, are used to estimate the material, energy, labor, and equipment cost components. In this example, the cost of the substrate is not included.

Cost Summary

Cost Per 1,000 sq ft

Material Cost/1,000 sq ft		$ 592.95
Susbstrate Cost/1,000 sq ft		$ 0.00
Sputtering Gas Cost/1,000 sq ft		$ 8.94
Reactive Gas Cost/1,000 sq ft		$ 0.91
Energy Cost/1,000 sq ft		$ 188.06
Labor Cost/1,000 sq ft		$ 326.77
Equipment Cost/1,000 sq ft		
1 shift	$ 2,042.32	
2 shifts	$ 1,021.16	
3 shifts	$ 680.77	
Total Cost/1,000 sq ft	1 shift	$ 3,159.96
	2 shifts	$ 2,138.80
	3 shifts	$ 1,798.41

Cost Per Year

No. of Shifts	Material Sbstrt & Gas Cost Per Year	Energy Cost Per Year	Labor Cost Per Year	Equipment Cost Per Year	Total Cost Per Year
1	$ 221,400	$ 69,060	$ 120,000	$ 750,000	$1,160,000
2	$ 442,700	$138,100	$ 240,000	$ 750,000	$1,571,000
3	$ 644,100	$207,200	$ 360,000	$ 750,000	$1,981,000

END OF ANALYSIS

Figure 7. The principal cost components are summarized. The estimated production costs (less substrates) range from $1.80 per square foot (3-shift operation) to $3.16 per square foot (1-shift operation), showing the importance of equipment costs in this example and the necessity of keeping equipment in full-time production. Direct labor contributes $0.33 per square foot to the production cost (for the assumed labor prices), and energy contributes $0.19 per square foot.

Environmental I
Session C

Pollution Control Using Sodium Borohydride

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POLLUTION CONTROL USING SODIUM BOROHYDRIDE

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ABSTRACT

A major goal at many printed wiring board facilities is the reduction of sludge volume coming from their wastewater treatment system(s). This paper discusses the use of sodium borohydride to reduce metal contaminants (ie. Cu, Ni, Pb, Co, etc.) in batch and continuous treatment systems. Chelated and non-chelated concentrates and rinses treated with sodium bisulfite and sodium borohydride solution (12% sodium borohydride in 40% sodium hydroxide) under controlled pH and ORP (oxidation-reduction potential) conditions give a dense, compact metallic sludge and an effluent typically less than 1 ppm of any target metals. Generally, a five to ten-fold reduction in sludge volume is realized as compared to conventional waste treatment. The sludge obtained is potentially recoverable which is a very inviting alternative to other increasingly expensive disposal methods. Sodium borohydride chemistry, sludge reclaimability and a brief review of several general case studies will be presented.

Introduction

The printed wiring board (PWB) industry has responded favorably to the use of sodium borohydride ($NaBH_4$) technology (1) to remove toxic metal contaminants (ie. Cu, Ni, Pb, Co, etc.) from industrial process waste streams. Early laboratory testing on various wastes showed dramatic sludge reduction in comparison to conventional (ferrous sulfate and/or lime) systems. With increasingly stringent government regulations concerning discharge of metals into the environment, minimizing the volume of sludge to be landfilled was a very favorable result.

Various PWB facilities were contacted to discuss their waste treatment needs and to promote sodium borohydride solution (2) as a viable method for removing dissolved metals from PWB manufacturing wastes. Many of these waste treatment systems were operating consistently below discharge requirements for metals subject to limitations using conventional treatment technology but were producing excessively large volumes of hazardous waste to be landfilled. In response to these needs sodium borohydride technology was developed, evaluated and then tested on actual plant solutions along with evaluating the sludge for reclaimability.

Sodium Borohydride Chemistry

Sodium borohydride solution is an effective reagent for the reduction of metal cations from aqueous industrial waste streams. (1,3) It has a reducing capacity of 8 electrons/mole or an equivalent weight of 4.75 g/molar electron and a standard electrochemical potential of -1.25 volts.

In the first step of the borohydride process a 10% solution of sodium bisulfite is prepared by adding sodium metabisulfite powder to a dilute caustic solution. The addition of caustic is necessary to prevent the bisulfite from lowering the pH and giving off SO_2 gas. This solution has an ORP of approximately -200 mV and is added to the incoming waste stream at a pH of 6-7.

The bisulfite reduces or neutralizes any oxidizing agents in the waste stream (ie. persulfate, permanganate, peroxide and/or oxygen) but does not reduce the metal cations present.

1) $HSO_3^- + S_2O_8^{2-} + 2\ OH^- \longrightarrow 3\ SO_4^{2-} + H_3O^+$

2) $3HSO_3^- + 2\ MnO_4^- \longrightarrow 3\ SO_4^{2-} + 2\ MnO_2 + H_3O^+$

3) $HSO_3^- + H_2O_2 \longrightarrow SO_4^{2-} + H_3O^+$

In the second step sodium borohydride solution (diluted 1 part borohydride solution to 10 parts water) is added. (4) Dilution allows for faster mixing, and therefore improves the reaction, especially with low level metal concentrations. Dilution of the borohydride solution also helps to prevent over-dosing, which can result in the formation of small hydrogen gas bubbles that can disturb flocculation and settling.

Sodium borohydride reacts with any residual bisulfite from step one to form sodium dithionite.

4) $8\ NaHSO_3 + NaBH_4 \longrightarrow 4\ Na_2S_2O_4 + NaBO_2 + 6\ H_2O$

The dithionite provides further neutralization of oxidizing agents left in the stream and partially reduces metal cations.

5) $S_2O_4^{2-} + S_2O_8^{2-} + H_2O + OH^- \longrightarrow 2\ SO_3^{2-} + 2\ SO_4^{2-} + 3\ H^+$

6) $Na_2S_2O_4 + 2\ M^{2+} + 2\ H_2O \longrightarrow 2\ M^+ + 2\ NaHSO_3 + 2\ H^+$

The oxidation of dithionite regenerates bisulfite, which in turn maintains a mildly reducing environment that stabilizes the precipitated metal.

While the mechanism of sodium borohydride reduction in the presence of chelating agents is not fully understood, we believe that in a copper containing solution the Cu^{2+} is reduced through a Cu^+ species to give Cu°. As the Cu^{2+} is reduced to Cu^+ the chelate to metal bond is weakened and/or broken, thus promoting rapid reduction to the metallic state.

7) $NaBH_4 + 8\ Cu^+ + 2\ H_2O \longrightarrow 8\ Cu° + NaBO_2 + 8\ H^+$

The results are a dense, compact metallic sludge and an effluent typically less than 1 ppm Cu. The sludge from the borohydride reduction is then easily dewatered.

For nickel bearing waste solutions the mechanism of reduction involves the intermediate formation of an unstable nickel borohydride, which decomposes to the reduced nickel species. This species can be either a nickel boride or nickel metal, depending upon the reaction conditions:

8) $Ni^{2+} + 2\ BH_4^- + 4.5\ H_2O \longrightarrow 0.5\ Ni_2B + 1.5\ H_3BO_3 + 6.25\ H_2$

9) $4\ Ni^{2+} + BH_4^- + 2\ H_2O \longrightarrow 4\ Ni° + BO_2^- + 8\ H^+$ (pH < 7)

10) $4\ Ni^{2+} + BH_4^- + 8\ OH \longrightarrow 4\ Ni° + BO_2^- + 6\ H_2O$ (pH > 7)

The likely product is the nickel boride, formed according to equation 8. (4) Again, the results are a dense, compact sludge and an effluent typically less than 1 ppm Ni.

A binary flocculation system is recommended for rinse systems to improve solid/liquid separation. A cationic polymer, generally a polyquaternary ammonium, is added in step two and an anionic polymer, usually a hydrolyzed polyacrylamide, is added to a flash mix tank just prior to the clarifier. When treating concentrated wastes, an anionic polymer alone is most often added to aid separation. It is critical to get proper dosage levels and mixing when using flocculating aids. Over-dosing as well as under-dosing polymers can result in dispersion of particles instead of agglomeration.

Case Studies

At the printed wiring board manufacturing sites chosen for full scale trials (continuous treatment and/or batch systems), the waste treatment facilities were operating at a very high sludge loading. In some cases concentrated liquids had to be drummed for off-site disposal or treatment.

The following general requirements have been established to evaluate trial results:

1. Sludge Volume Reduction
2. Effluent Compliance
3. Low Capital Cost
4. Competitive Economics

The primary concerns of these PWB manufacturers were to reduce sludge volume while continuing to meet metal limits.

When implementing sodium borohydride solution in a waste treatment system several key process considerations should be noted:

1. Retention Time - a 15-30 minute relative reaction time is necessary to assure complete chemical reduction. This is more critical in dynamic flow-through systems than in batch processes.

2. Pre-reduction Chemistry - sodium bisulfite ($NaHSO_3$) is necessary to lower borohydride requirements and to stabilize the resulting metallic precipitates, as discussed in the Chemistry section.

3. pH Control - good control is necessary for efficient chemical reduction as well as consistent compliance. Generally, lower pH gives a quick reaction time and higher pH requires a long reaction time.

4. Flocculation - sodium borohydride adds very few solids to the waste treatment process which may hinder flocculation. When treating a continuous flow through rinse system a binary flocculation system is used. For batch treatment processes, which are generally much higher in concentration (ie. higher solids level), a single anionic flocculating aid is extremely effective.

5. Final Filtration - generally, only a continuous system would require a final filter due to the unpredictability of the waste effluent composition. In a batch process the solids are settled out and are usually sent directly to a filter press.

A. Batch Treatment Process

Generally, a batch treatment process is done all in one cone bottomed reaction vessel appropriately sized for the individual facility's needs. When converting to sodium borohydride very few modifications are necessary, the major one being addition of ORP control to the tank.

The process should have in place:

1. a variable speed mixer to ensure thorough mixing and adequate flocculation

2. pH and ORP control

3. Chemical feeds for:

    a. acid and base (should already be in place)

    b. sodium bisulfite solution (sodium metabisulfite can also be added directly as a powder)

    c. sodium borohydride solution (to replace $FeSO_4$ or other reducing agent)

    d. flocculating aids (anionic and possibly cationic)

    e. lime slurry (may be used to aid in solid/liquid separation and pH control)

The sodium borohydride process for copper or mixed metals waste concentrates requires initial pH adjustment to 5.5-7 with caustic or sulfuric acid then bisulfite addition with mixing for 5-15 minutes. At this point the pH is readjusted if less than 5.5. Next the sodium borohydride solution (diluted 1 part borohydride solution to 10 parts water) is gradually added. The pH of the solution will increase, the ORP value will decrease and the solution will react to give a dark brown-black precipitate. Once the ORP reading is less than -600mV the borohydride addition should be stopped. The final pH should be slightly less than 9. If not, adjust with a minimum quantity of acid. Now the solution should mix for several minutes to ensure a stable ORP reading and initial particle formation. If the ORP reading is not stable, further addition of borohydride solution and pH adjustment will be necessary. The addition of an anionic polymer at this point aids in the settling of solids. Once the solids have settled, they can be drawn off the bottom of the tank and sent directly to the filter press or to a sludge holding tank.

In the case of waste solutions containing high levels of nickel the basic treatment is essentially the same but the final pH should be from 8 to 10. The addition of a lime slurry for pH adjustment can help in the solid/liquid separation. Also, a cationic flocculating aid prior to anionic polymer addition can aid in separation of these generally difficult to separate solids. (3e)

B. Continuous Treatment Process

Many of the conventional continuous waste treatment processes for chelated rinses incorporate the use of ferrous sulfate ($FeSO_4$). In one such case (1f) the process consisted of two reaction stages, a flocculation step, clarification and final filtration. In the first stage reaction tank, the pH was controlled at 2-3 and a 0.7% $FeSO_4$ solution was added generally with a 14 to 1 iron to copper ratio. The waste solutions then overflowed into the second tank. Here the pH was raised to 8.5-9.0 with 25% caustic solution resulting in a ferric hydroxide-cupric hydroxide precipitate. Anionic polymer was added in a flash-mix stage immediately before the clarifier to improve flocculation.

Residence times for the different reaction steps were 20-40 minutes in the first and second tank and 5-10 minutes in the flash-mix stage. The clarifier was sized for 1-1.5 hours of retention and dual, parallel, cross-linked sand filters removed any floc carryover from both the chelated and a second non-chelated system. Sludge from the clarifiers was sent to a holding tank for further dewatering.

The conversion of this $FeSO_4$ system to a sodium borohydride system was simple and straightforward (Figure 1). The only process control function necessary to add was ORP control. To implement the sodium borohydride system, the pH control point in the first tank was changed from 2-3 to 5.5-6.5. A 10% solution of sodium bisulfite ($NaHSO_3$) was substituted for the $FeSO_4$ solution, which was subsequently optimized to be a 30 to 1 weight ratio of bisulfite to borohydride. When the $NaHSO_3$ dosage is too low a sludge stability problem occurs and when the dose is too high a very fine pin floc occurs which is difficult to coagulate.

The second reaction tank modifications included: conversion of the pH controller to ORP control which is set at -500mV (determined via total system optimization); replacement of 25% caustic feed with a 1.2% sodium borohydride solution; and addition of cationic and anionic polymers. At this point the solution flows into the flash mix stage where additional anionic polymer is added. This two stage addition of anionic polymer provides extended retention and mixing time to give better flocculation.

Initially, very low incoming copper levels (less than 20 ppm) resulted in settling and clarification problems. Concentrated wastes were bled into the continuous treatment system at a constant, uniform rate to maintain minimum copper levels greater than 20 ppm. Instantaneous addition would upset the system resulting in incomplete reduction, over consumption of sodium borohydride and poor flocculation and settling. One solution that was encountered in this system was a high pH photoresist stripper that made treatment and flocculation very difficult. However, when bled into the system at 0.25 gpm rate (0.5 - 1.0% of total flow) this solution was treated with little disturbance to the system chemistry or flocculation.

A cost comparison of the borohydride versus $FeSO_4$ systems over a sixty day work period showed an overall cost decrease of 12% per day or approximately $10,000.00 per year when using sodium borohydride. Chemical cost was greater but the sludge generation from chelated wastes decreased by 82% therefore reducing the overall cost.

Sludge Reclaimability

Typical sodium borohydride reduced copper sludge sample analyses are:

1. 38 - 65% copper
2. 6 - 12% sulfate
3. 3 - 10% silicon
4. <0.2% boron
5. <2.5% tin
6. <1.0% lead
7. 1 - 7% carbon
8. 1 - 5% hydrogen
9. <1.0% nitrogen
10. 30 - 50% solids

Through our contacts at various smelting operations, we were able to determine that the borohydride reduced sludge contains no inherent technical limitations to smelting feasibility.

Several smelters contacted are interested in this type of sludge as opposed to a $FeSO_4$ type (generally, containing less than 5% Cu and no more than 35% solids) due to the higher level of copper. Interest would be increased further if these sludges were to contain even trace quantities of precious metals, which sometimes they do.

SUMMARY

With essentially no capital costs sodium borohydride can be implemented into a batch or continuous waste treatment system and provide reduced sludge volumes along with meeting effluent metal levels typically less than 1 ppm. By reducing the chelated sludge volume 82% the sludge disposal costs were decreased by the same amount for the continuous treatment system. Also, this decrease in volume allowed the filter press to be run three times per week with cycle times cut in half instead of being operated continuously.

The copper smelting/reclamation aspect of sodium borohydride technology is becoming an economic plus. Sodium borohydride users see the lower disposal and shipping costs associated with reduced sludge volumes while copper refiners recognize the opportunity to obtain sludge containing greater than 30% copper. The higher metallic content of borohydride sludge eliminates the concentration step necessary during conventional processing. If the above technology and refining processes can be implemented the liability associated with hazardous waste disposal can be minimized, if not eliminated.

Figure 1: Sodium Borohydride Continuous System

(VenMet™ System)

VenMet™ SYSTEM

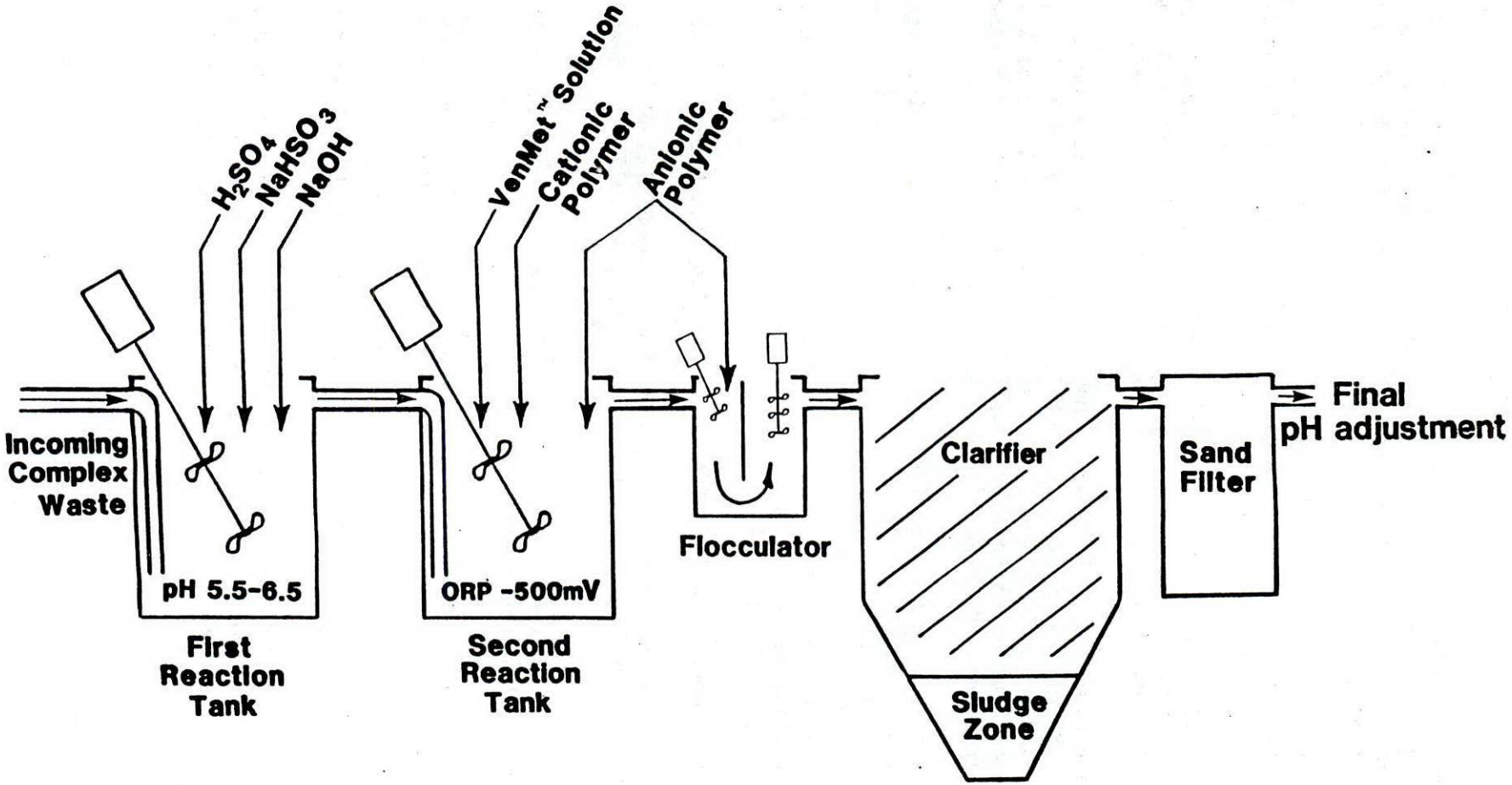

FIGURE 1

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2. A stable aqueous solution of $NaBH_4$ containing 12% $NaBH_4$ and 40% NaOH.

3. (a) "Metal Removal and Recovery with Sodium Borohydride", T. F. Jula, presented at the Institute of Printed Circuits, 1977 Fall Meeting, Chicago (1977).

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- Metal Removal and Recovery with Sodium Borohydride
- Metal Recovery with Sodium Borohydride
- Inorganic Reductions with Sodium Borohydride - Principles and Practices (and references therein)
- Heavy metal Recovery with sodium borohydride
- Sodium Borohydride
- The VenMet™ System

C-2

Environmental I
Session C

Buoyant Media Filtration of Metal Finishing Wastes

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BUOYANT MEDIA FILTRATION OF METAL FINISHING WASTES

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1.0 INTRODUCTION

In the past, the use of downflow filters to remove solids from wastewaters was common practice. (The past, present and future filtration methods are shown in Figure 1.) The downflow was usually influenced by gravity or pressure motivation. To clean this type of filter, a periodic backwashing was required. The backwash was preceded by either air scour or a surface wash. The backwash cycle was long in duration and required extensive auxilliary equipment.

Recently, the concept of up-flow filtration has been considered. This concept uses a buoyant type media which has proven to be very efficient in removing solids from metal finishing wastes. It does not require long backwash cycles and expensive auxilliary equipment. It has also been proven that the buoyant media filter has the abiity to accommodate very high influent suspended solids concentration and could be used to replace conventional clarifiers and filters that are now used in series flow.

Usually the buoyant media filter is used as a polishing filter for the improvement of conventional clarifier effluent. It will continue in its high efficiency of solids removal even when severe upsets occur in the clarification phase upstream.

Another advantage of the buoyant media filter as shown in Figure 2. is the very low head loss across the media bed. This pressure drop has been measured as two to six inches of water across the buoyant media bed of six inches depth.

Backwashing is simplified due to its short duration and the elimination of an outside reservoir and pump. Surface

wash and air scour have also been eliminated. The reduction of capital cost is substantial.

The purpose of this presentation is to bring to the attention of those scientists and engineers, who are engaged in wastewater treatment in the metal finishing field, this new technology. Met-Pro Corporation, Systems Division of Harleysville, Pennsylvania has manufactured and sold this type of filter since 1981. We have been able to obtain some operational data from our customers who use the device while operating it as a substitute for a clarifier and also as a polishing filter for a Met-Pro Slant Tube Clarifier.

2.0 FILTER DESCRIPTION

When we refer to buoyant media filtration, we refer to liquid that is passed upward through a bed of granular buoyant media. This media has a specific gravity less than the aqueous stream being filtered. The filter is shown in Figure 3. Those parts of the filter shown are:

A) Inlet Stand Pipe

B) Inlet Stand Pipe Level Control

C) Inlet Distributor

D) Sludge Collection Zone

E) Sludge and Backwash Removal Valve

F) Media Bed

G) Effluent Reservoir

H) Effluent Overflow Weir

I) Backwash Control Monitor

3.0 FILTER OPERATION

At this time all of our filters have been designed to be used as polishing filters. The effluent of the upstream clarifier flows by gravity into the inlet stand pipe. Initially, a head loss across a clean media bed could be as low as 1/2 to 3/4 inches of water. Distribution of the influent of the buoyant media filter under the media bed is important and is accomplished by the inlet distributor. Any settleable solids will gather in the sludge hopper at the bottom below the inlet distributor. Any precipitate not readily settleable will be swept up against the bottom of the buoyant media bed and filtered out. The media bed is comprised of several layers of hollow spheres of various diameters. The rise velocity through the hollow spheres is important. The spheres will layer out according to their diameter after each backwash cycle.

An effluent reservoir above the bed will act as storage for the backwash water. Backwashing is accomplished by increasing a downward flow velocity through the bed so that the media is disturbed. The trapped solids under the media are shaken loose by this disturbance.

The control of the filtration and backwashing is completely automatic. Operator attention is not needed nor desired.

4.0 MEDIA DESCRIPTION - FIGURE 4

At the present time, only three sources of buoyant media exist. The design of the equipment is based on the various characteristics of the media. Each source of media has a product of which not all the characteristics are the same. These characteristics are: Density, Diameter of Sphere, Abrasion Quality, Materials of Construction, and Resistance to Chemical Attack.

The media behavior during the filtration cycles is such that very litle of the solids penetrate into the bed. There is stratification of the bed in respect to sphere size. The largest spheres are more buoyant than the

smaller and their rise rate in a liquid media is greater. Thus they will reach the retaining screen first. The smallest have a rise rate much slower and will stratify on the bottom of the bed.

A backwash cycle will disturb and expand the bed. The smallest diameter spheres could be lost if expansion were not held to the limits of the filter cell. The charging of media to a filter cell requires special techniques. Special charging ports and equipment have been designed into the system.

The cost of the media is high but its life is considered to be as long as, if not longer than sand.

The typical application of the filter in a plating process is as shown on Figure 5. When several different waste streams are generated a separate treatment of each may be made. These streams are then combined and prepared for clarification and/or filtration. The solids recovery and disposal are incidental to the clarifier and filter operation.

Results on commercial operation of the filter are hard to come by. Very rarely does a plater wish to divulge his business. Very early in the development of the filter, a series of tests were run by EPA, AES and 3M Corporation. Samples were taken and analyzed and some of the results are as shown on Figure 6. These were taken and reported by Dr. John S. Hunter of 3M. It can be seen that the efficiency of the filter is excellent in the area of removal for chrome, zinc and iron. The removal of tin and copper would be improved if the pH value of the wastewater were not adjusted to favor precipitation of the other metals.

Optimum use of the filter is for polishing of clarifier effluents. If the device is used as a replacement for a clarifier, the user must maintain strict control of the process. There can be no concentrated dumps. There should be equalization of upstream flows and prior to that, there should always be individual treatment of chrome, cyanide and other possible problem waste streams.

If there is need for energy conservation, the buoyant media filter is the most suitable filtration device. Operator attention is minimum. High efficiency remains

even though the process must start and stop frequently.

Precautions should be taken to avoid very large solids loadings for long periods in the use of the filter. The device can accommodate large solids loadings due to a clarifier upset for short periods. Of course, this situation results in reduced filtration periods and a possible dilution of the backwash/sludge effluent concentration. The entrainment of oils and greases in the wastewater will have an adverse effect on the media. Experience has shown that the media will stick together when the influent contains oils and greases, and cleaning must be done manually.

A programmed sludge removal in supplement to that occurring during the backwash cycle will extend the operating length of the filtration period considerably. Some filtration periods have been know to last 120 hours in length.

Manual operation of the filter must be avoided. The influent stream is never stopped even during backwashing.

The basic design of the filter depends on several factors. The geometry is very important. A width to length ratio must be considered. Backwashing depends on the reservior of clean filtrate available. The fluid velocities are held to specific values. These velocities are: Inrush, Distribution and Rise Rate. The backwash velocities are also very important and these will depend on the bed expansion, media flow resistance and media stratification behavior as shown on Figure 7.

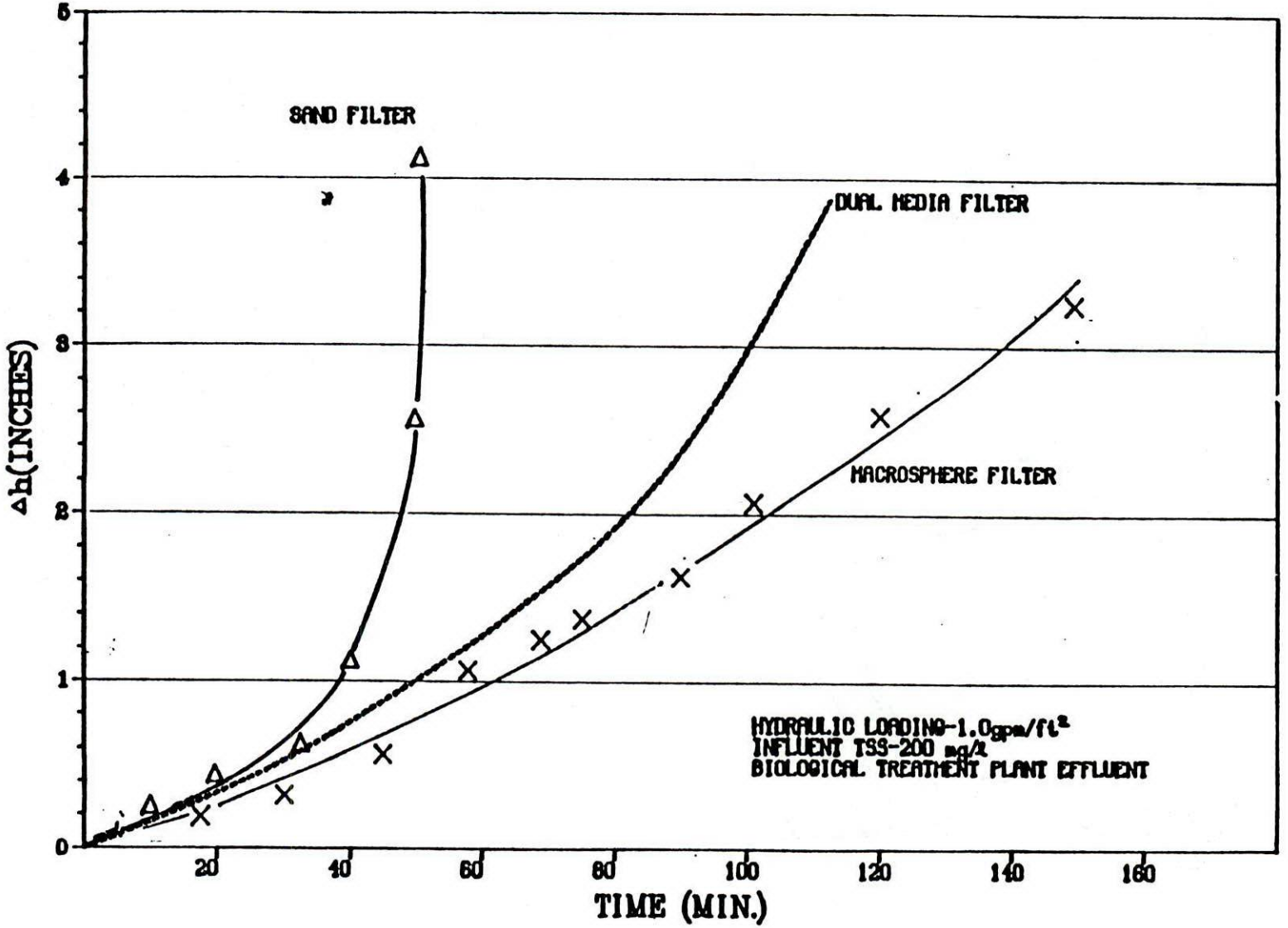
FIGURE 1

FILTRATION SYSTEMS - METAL FINISHING WASTEWATERS

PAST:	CARTRIDGE CHAMBER GRAVITY SAND PRESSURE SAND FILTER PRESS
PRESENT:	CARTRIDGE CHAMBER GRAVITY SAND PRESSURE SAND FILTER PRESS MOVABLE SAND BED BUOYANT MEDIA
FUTURE:	CARTRIDGE CHAMBER BUOYANT MEDIA ULTRA FILTRATION

FIGURE 2

COMPARISON OF CONVENTIONAL AND MACROSPHERE FILTER HEADLOSS VERSUS TIME CURVES



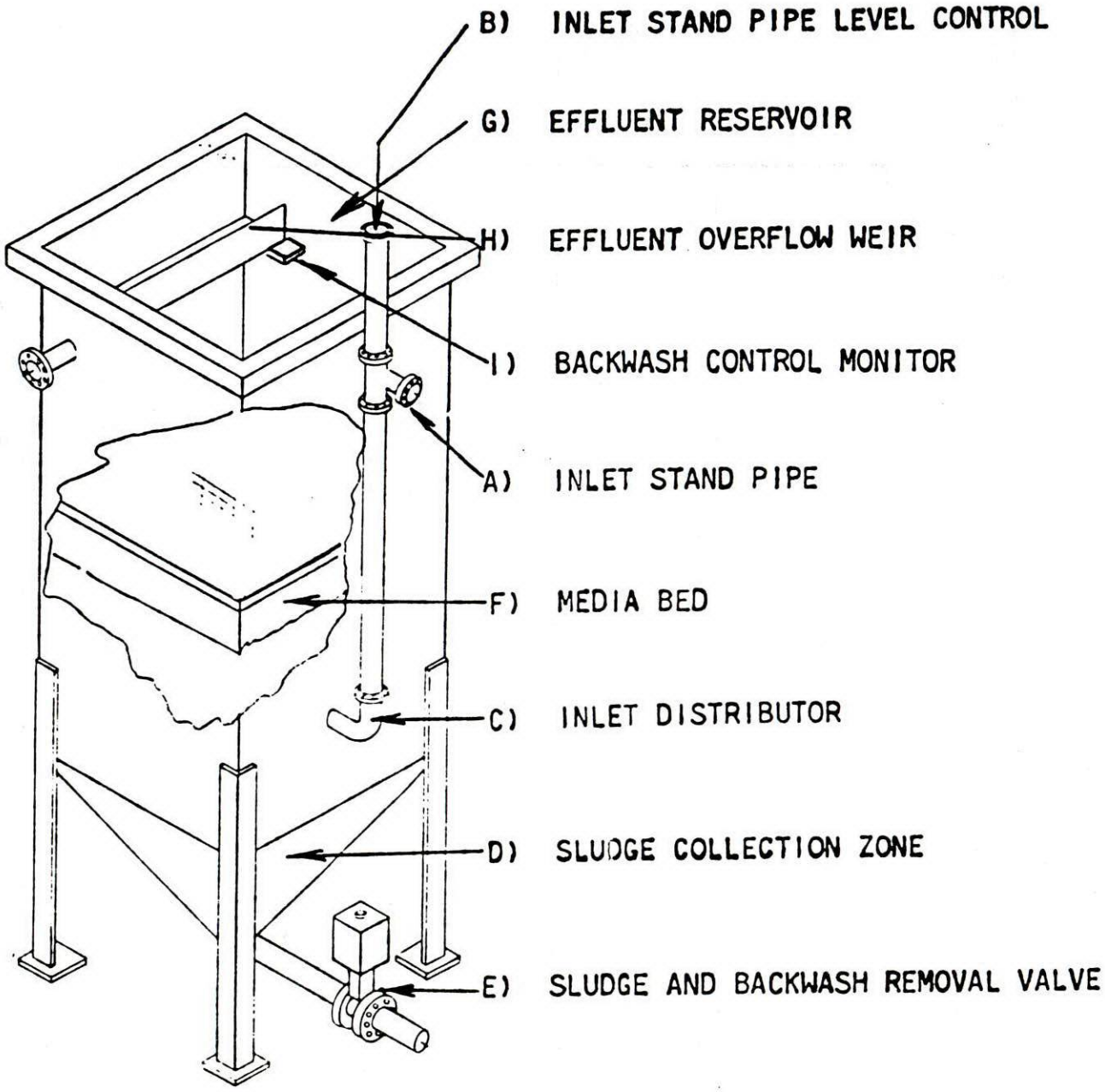


FIGURE 3

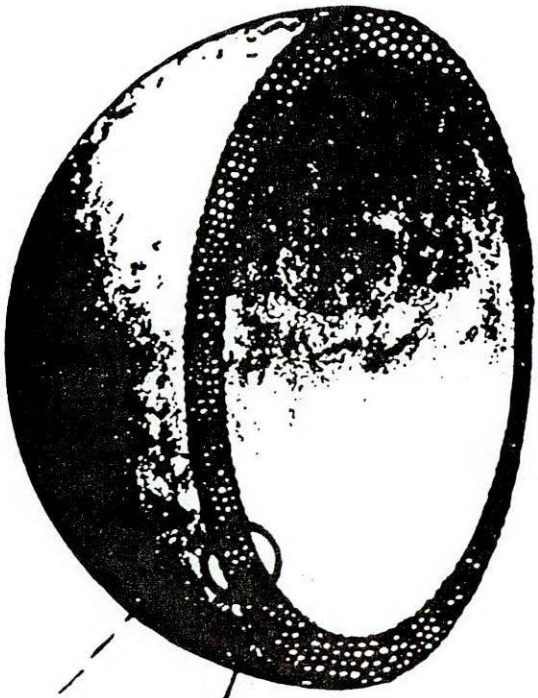
BUOYANT MEDIA FILTER

INLET FLOW GPM	DIMENSIONS			WEIGHTS POUNDS		TOTAL BACKWASH VOLUME GALLONS
	LENGTH L	WIDTH W	HEIGHT H	SHIPPING	OPERATING	
12	2'-9"	2'-9"	8'-6"	700	3800	113
24	5'-6"	2'-9"	8'-6"	1300	7500	226
36	8'-3"	2'-9"	8'-6"	1900	11200	339
48	5'-6"	5'-6"	8'-6"	2500	14900	452
72	8'-3"	5'-6"	8'-6"	3300	23200	679

ILLUSTRATION OF

MACROSPHERE CONSTRUCTION

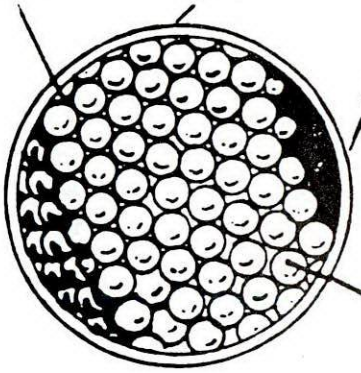
FIGURE 4



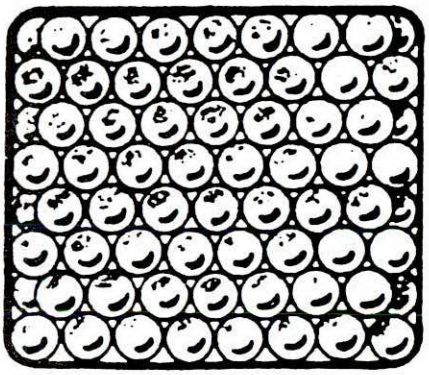
INDIVIDUAL
HOLLOW
MACROSPHERE

(MAGNIFIED
CROSS SECTION)

RESIN



HOLLOW
GLASS BUBBLES



FURTHER MAGNIFICATION
OF MACROSPHERE WALL
SHOWING GLASS BUBBLE
CONSTRUCTION

9/78

3M Brand Hollow Macrospheres

MACROSPHERE
PACKING QUALITY
A FUNCTION
OF INSULATION

TYPICAL PROCESS FLOW

OF METAL FINISHING WASTEWATER TREATMENT SYSTEM UTILIZING

BUOYANT MEDIA FILTER MODULES

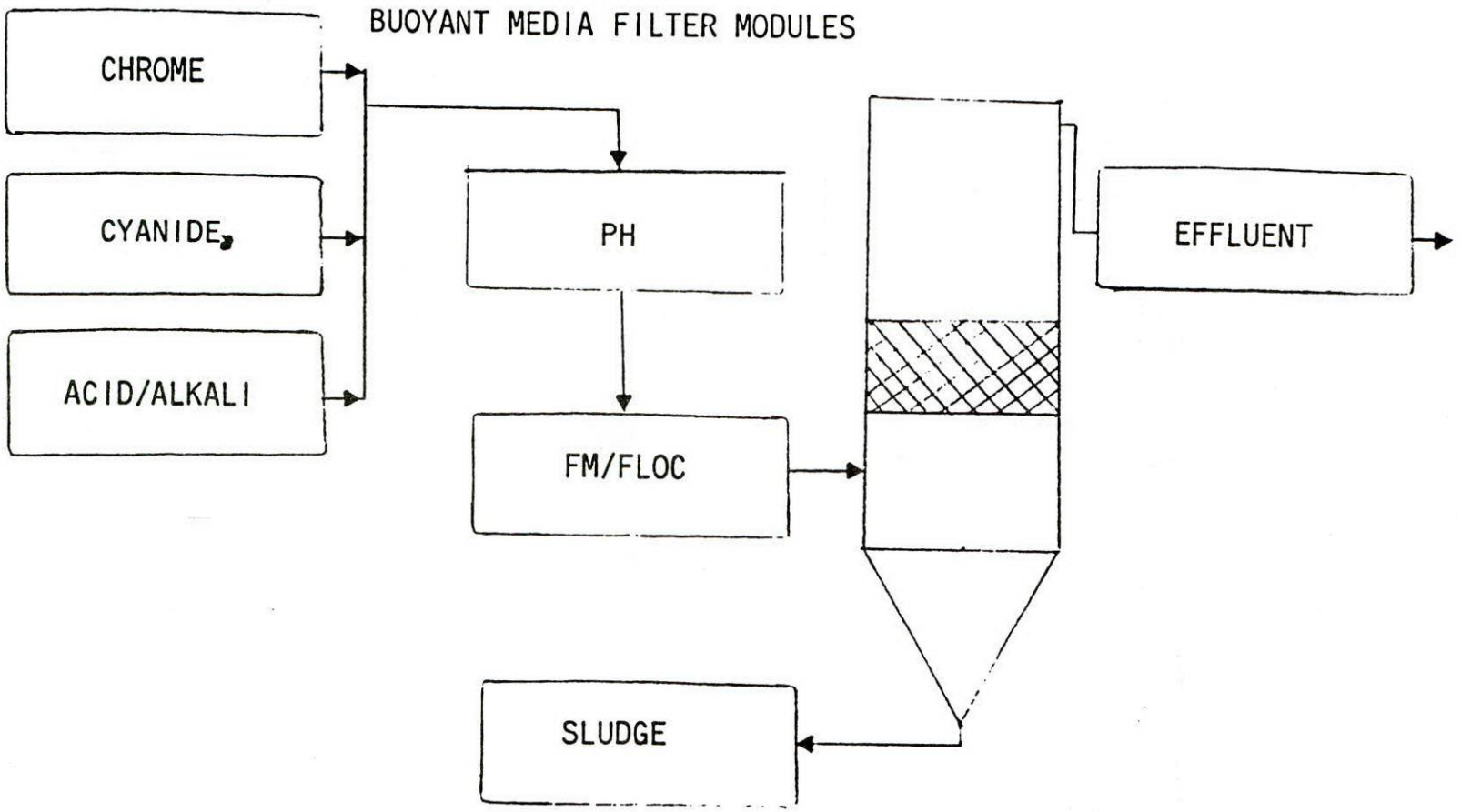


FIGURE 5

C-3

Environmental I
Session C

Selective Recovery of Metal Values From Electroplating Sludges by the Phosphate Process

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SELECTIVE RECOVERY OF METAL VALUES FROM ELECTROPLATING SLUDGES BY THE PHOSPHATE PROCESS

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INTRODUCTION

Most metal finishing hydroxide sludge materials are disposed of in hazardous waste sites. The Environmental Protection Agency has supported several projects directed toward treatment of these sludges for metal value recovery (1,2,3). A recent and potentially cost effective treatment sequence has been developed by L. G. Twidwell, D. R. Dahnke, and R. Robins (4) at the Montana College of Mineral Science and Technology (Montana Tech), i.e., the Phosphate Process.

The results from a continuing study at Montana Tech to selectively separate trivalent cations from mixed metal aqueous solutions are reported in this presentation. The current major emphasis of the research is directed toward the selective separation of trivalent cations; such as iron, chromium, and aluminum from divalent cations, zinc, cadmium, and nickel.

Advantage of the Phosphate Process

Previous studies have illustrated potential flowsheets to accomplish the separation of metal values from releached hydroxide sludge materials (1,2). These flowsheets required recovery unit operations such as aqueous oxidation of chromium, solvent extraction, and ion exchange. An alternative and potentially more cost effective separation is by precipitation of phosphate compounds.

Important features of the phosphate process include:

- Selectivity in acid solution for removal of trivalent cations from divalent and monovalent cations. Therefore, Fe(III) (or Al(III) or Cr(III)) can be precipitated selectively from Zn(II), Ni(II), Cd(II), Na(I), etc., bearing solutions. Also trivalent cations can be, in some cases, selectively separated from other trivalent cations.

- Solid/Liquid Separation is excellent because the precipitated phase consists of agglomerated spherites. The filterability feature is very important, i.e., the phosphate products filter easily and can be compacted to a high solids content.

- Conversion of the phosphate precipitate to a hydroxide product (and subsequently to a commercial product) regenerates the phosphorus reagent for reuse; thereby improving the process economics.

Selectivity of the Phosphate Process

Stability diagrams provide useful data for designing metal separation flowsheets. Several illustrative examples are presented in Figures 1-3 for trivalent cations and in Figures 4-7 for divalent cations (5). Superimposition of these diagrams allows the user to predict the possibility of potential selective separations of metals fom an aqueous solution; e.g., iron from nickel (see notes on Figure 8); iron from zinc (see notes on Figure 9). From such diagrams it is apparent that iron(III) should be selectively precipitated from nickel or zinc in acid solutions.

In general, trivalent cation phosphates can be stripped selectively from solutions containing divalent or monovalent cations under acid conditions. Similar general statements can be made concerning the precipitation of trivalent hydroxides from divalent hydroxides. However, hydroxide solids are difficult to separate from solution. Phosphate precipitates are readily filterable.

Flowsheet Applications

The thermodynamic basis for the Phosphate Process has been presented in Figures 1-9. The basic experimental benchscale test work confirming the applicability of phosphate precipitation to mixed metal solutions has been reported elsewhere (3,4,5). The objective of this presentation is to illustrate the application of the process to active metal finishing hydroxide sludge materials. Three examples will be presented.

Cu-Fe-Cr-Zn-Cd-Ni

The phosphate precipitation process has been applied to leach solutions produced from mixed metal electroplating sludge materials (5). The test work reported here is for the selective removal of copper, iron and chromium from zinc, cadmium and nickel bearing solutions (6). The experimental flowsheet is presented in Figure 10.

Electroplating hydroxide sludges respond well to sulfuric acid leaching. Typical results (2) are presented in Table 1. The particular starting leach solutions reported here contained: 3.60 gpl Cu, 0.85 gpl Fe, 5.62 gpl Cr, 3.37 gpl Zn, 3.60 gpl Cd, 6.85 gpl Ni. The leach residue was removed from solution and the solution was subjected to iron cementation. Iron cementation provided two important results, i.e., copper was removed from solution and iron(III) present in the solution was reduced to iron(II). The solution copper concentration was lowered to 32 mg/liter.

The cemented copper product was removed from solution, phosphoric acid was added (two times the stoichiometric requirement for precipitating chromium(III) as chromium phosphate) and the pH of the solution was raised in increments; Figure 11. Note that chromium phosphate can be effectively precipitated to less than twenty mg/liter at a pH less than three without appreciable contamination of Zn, Cd, Ni or Fe.

The precipitated chromium phosphate was separated from solution; air was blown into the solution to oxidize the iron(II) to iron(III). Iron phosphate precipitated as shown in Figure 11. The precipitation at each pH was rapid; i.e., it was completed within 20-40 minutes. The previously precipitated chromium phosphate and the iron phosphate were physically made up of distinct spherites and agglomerates of spherites. The filterability of both solids was excellent; e.g., the filterability resistance (7) was in the range $4-8 \times 10^{9}$ cm/g (compare this with ferric hydroxide which has a resistance of above 2×10^{11}).

Another important feature of the process is that the phosphate reagent can be regenerated by treatment of the precipitated phosphates at an elevated pH to convert the phosphates to hydroxides. The pH at which such conversions should occur can be seen in Figures 1-7. In practice, however, it appears that higher pH levels are required. Rate studies are presently being conducted. Example results are presented in Figure 12 for the conversion of ferric phosphates to ferric hydroxide.

Further treatment of the final filtrate solution for zinc, cadmium and nickel recovery have been discussed elsewhere (2) and is beyond the scope of this presentation.

Fe-Cr-Al-Zn-Ca

The phosphate process has been applied to leach solutions produced from mixed metal electroplating hydroxide sludges containing 3.1% Fe, 9.7% Cr, 2.5% Al, 14.5% Zn, 13.2% Ca, 5.0% PO_4. The experimental flowsheet is presented in Figure 13.

The leach solution (sulfuric acid leach) contained 0.7 gpl Fe, 3.0 gpl Cr, 1.2 gpl Al, 5.3 gpl Zn, 0.7 gpl Ca. The leach produced excellent metal value recovery and good calcium rejection to the solid residue. The leach residue was separated fom solution; the solution pH was raised to 2.5 at 80°C. (The phosphate contact was high enough that additional phosphate was not required). A mixed metal phosphate precipitated from solution lowering the Fe to 48 mg/liter, Cr to 73 mg/liter and Al to 16 mg/liter. No loss of zinc occurred. The zinc bearing solution can be recycled to the leach stage to build the zinc content to the level desired for recycling to the process line.

An alternative treatment flowsheet was also investigated; reduction of iron(III) to iron(II); precipitation of chromium and aluminum at 78.5°C (chromium solubility is a strong function of temperature), 121 mg/liter Cr, 30.0 mg/liter Al at pH 2.9; 84 mg/liter Cr, 12 mg/liter Al at pH = 3.1. Only minor loss of zinc occurred, e.g., at pH = 2.9, 1.2% of the zinc was removed

and at pH 3.1, 4.3% was removed. After removal of the precipitated chromium and aluminum, the ferrous iron can be oxidized and precipitated as ferric phosphate selectively from the zinc.

Fe-Cr-NI

A study has been performed on hydroxide sludges produced from an electrochemical machining (ECM) operation. The uniqueness of this material is that the chromium is present in a mixed valence state, chromium(III) and chromium(VI). The experimental flowsheet studied is presented in Figure 14. The starting sludge contained: 9.0% Fe, 6.7% Cr, 25.9% Ni.

A sulfuric acid leach (pH = 1.0, 19°C) resulted in a solution containing 3.5 gpl Fe, 2.7 gpl Cr, 9.7 gpl Ni. The solution was first treated for iron removal by phosphate precipitation at a pH of 2.3. The iron content was lowered to 60 mg/liter without appreciable loss of chromium or nickel. The solids contained 26.5% Fe, 46.2% PO_4, 0.6% Ni, and 0.2% Cr. The solution (filtrate from the iron phosphate solid/liquid separation) temperature was raised to 50°C and the pH to 3.5 to precipitate chromium(III) phosphate. The solution chromium content was lowered to 2.3 gpl (Cr(VI)). The solids contained 17.5% Cr, 41.8% PO_4, 0.16% NI and 2.1% Fe.

The solution from the chromium phosphate solid/liquid separation was treated for nickel recovery by phosphate precipitation at 19°C, pH = 6.5. The nickel phosphate solid contained 32.3% Ni, 39.4% PO_4, 1.4% Cr. The filtrate solution from the nickel phosphate solid contained 2.0 gpl Cr(VI). This solution was treated with lead sulfate to precipitate lead chromate. The lead chromate was subsequently treated to regenerate the $PbSO_4$ reagent and chromic acid. The final chromium content in the final effluent was 14 mg/liter. A large portion of this water could be recycled into the process as make-up water.

SUMMARY

Mixed metal hydroxide sludges can be treated for metal value recovery by a relatively simple series of leach-precipitation steps. The process can be made selective for separation of trivalent cations from divalent and monovalent cations. Under some siuations separation selectivity can be achieved for separating trivalent cations, especially iron from chromium, by controlling the solution temperature. A major advantage of the phosphate approach over hydroxide and sulfide precipitation flowsheets is the ease of solid/-liquid separation and the ability to dewater the solids to a high solid content (60-65% solids). Bench scale test work has produced very encouraging results. The presently reported work is being extended to include a pilot study. The results of the pilot study and detailed economic evaluations will be presented in the near future.

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ACKNOWLEDGEMENTS

The authors of this paper would like to acknowledge the financial support of the Montana College of Mineral Science and Technology Organized Research Division.

TABLE 1. EXAMPLES OF METAL VALUE RECOVERY BY SULFURIC ACID DISSOLUTION

Sample No.	Condition	Metal Extracted (%)						
		Fe	Cu	Zn	Ni	Cr	Cd	Al
533	100 g, pH=0.5	96.4	94.7	96.9	95.9	99.4	93.0	89.9
534	100 g, pH=1.0	91.3	89.9	91.8	92.9	94.7	93.0	85.7
535	100 g, pH=1.5	92.0	93.7	95.9	95.9	96.5	93.0	87.1
942	650 g, pH=1.5	95.4	94.9	90.5	97.8	96.7	100.0	95.7
532	1,000 g, pH=1.5	95.8	94.3	94.2	85.0	96.7	97.0	96.0
2116	15,900 g, pH=1.9	62.3	75.9	83.8	82.4	84.6	90.0	90.3
2621	22,700 g, pH=1.5	65.0	92.0	96.9	92.1	92.3	100.0	98.6
2492	50,600 g, pH=1.5	92.0	93.7	95.1	95.9	96.5	93.0	96.9

Note: . All sludge samples were undried.
. H_2SO_4 added equivalent to 100% of solid weight
. One-half hour, 40-50°C
. Sludge/solution = 0.8

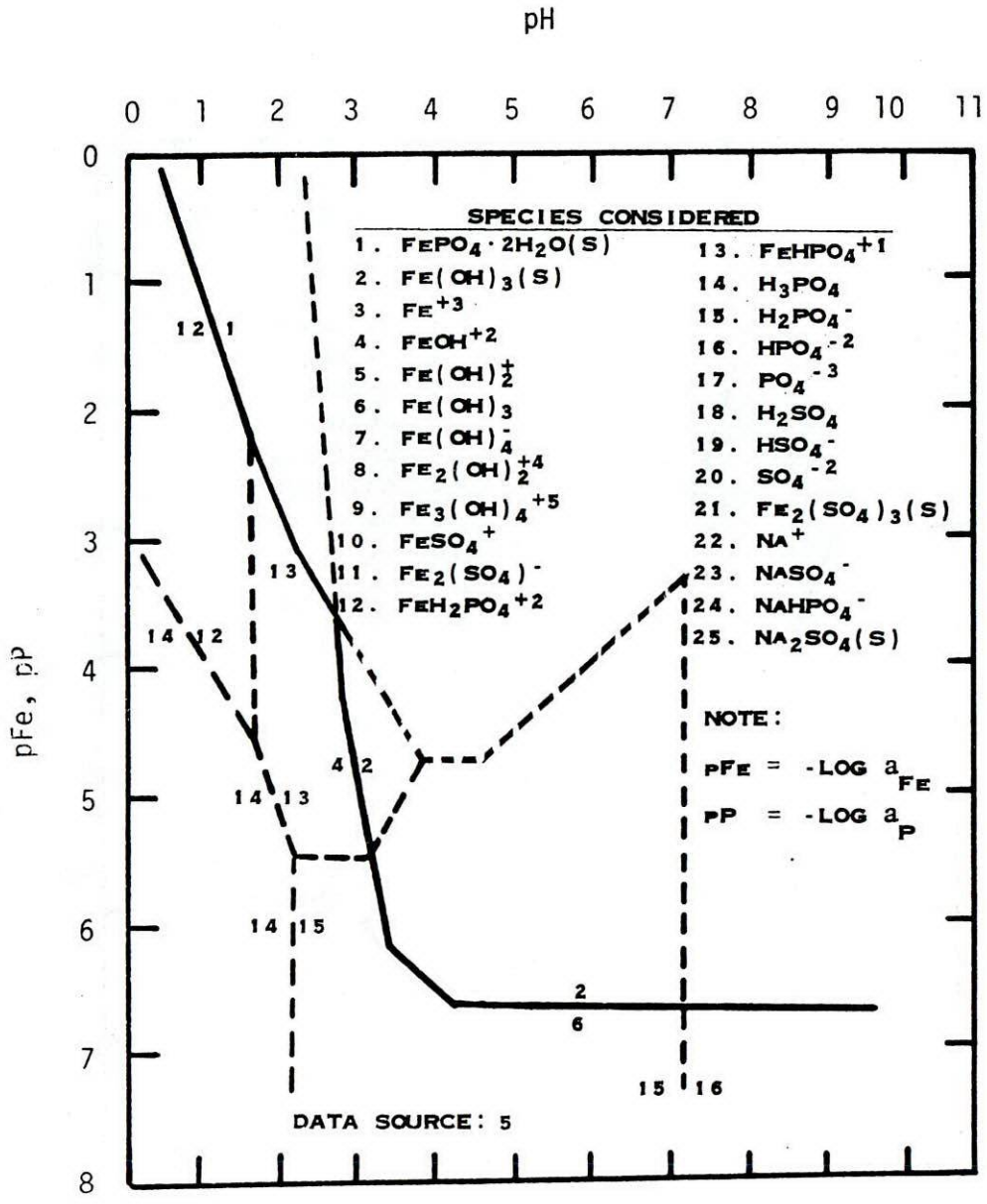

FIGURE 1. FERRIC PHOSPHATE STABILITY DIAGRAM FOR THE FERRIC-PHOSPHATE-SULFATE-WATER SYSTEM (5).

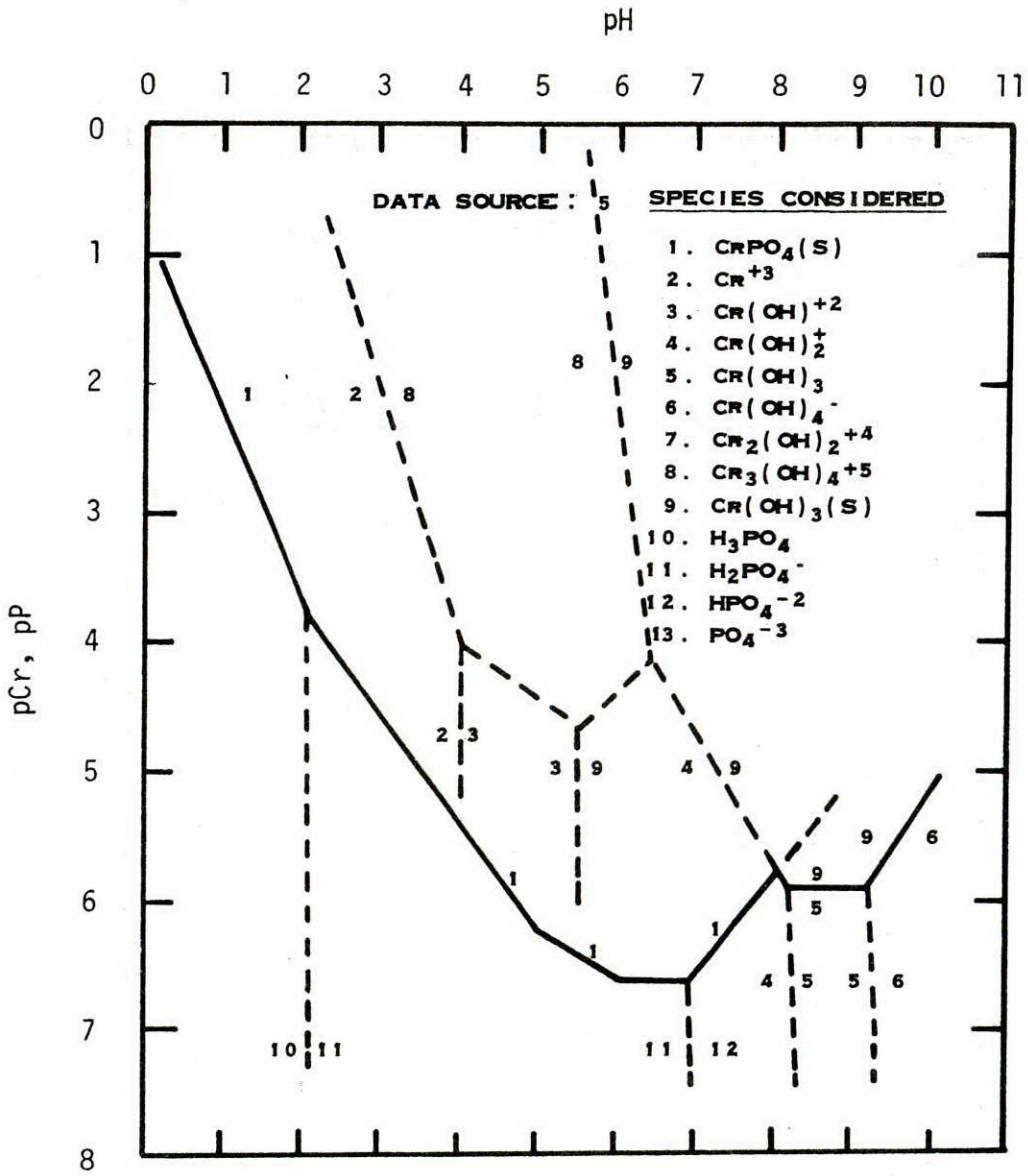

FIGURE 2. CHROMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CHROMIUM-PHOSPHATE-WATER SYSTEM(5).

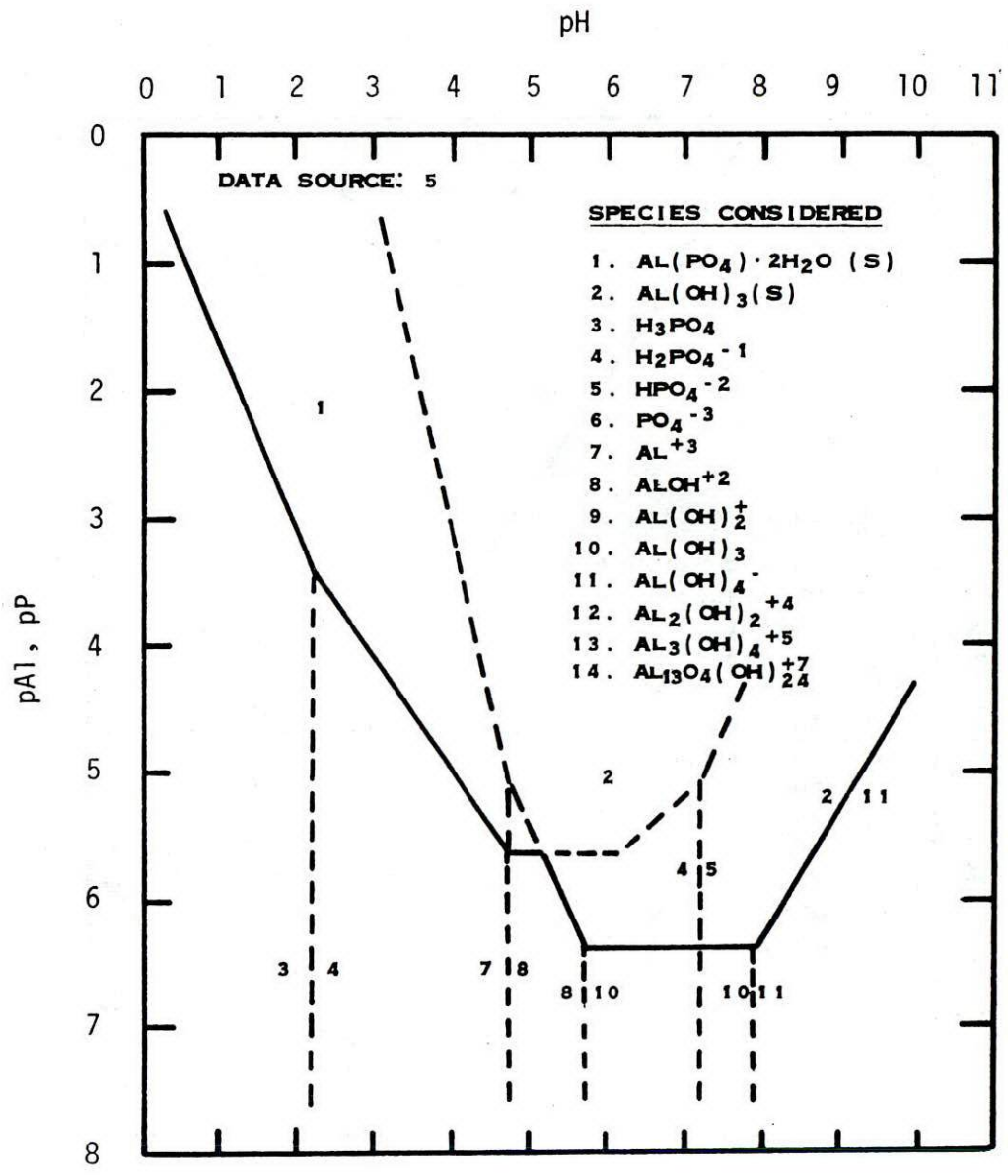

FIGURE 3. ALUMIMUM PHOSPHATE STABILITY DIAGRAM FOR THE ALUMIMUM-PHOSPHATE-WATER SYSTEM (5).

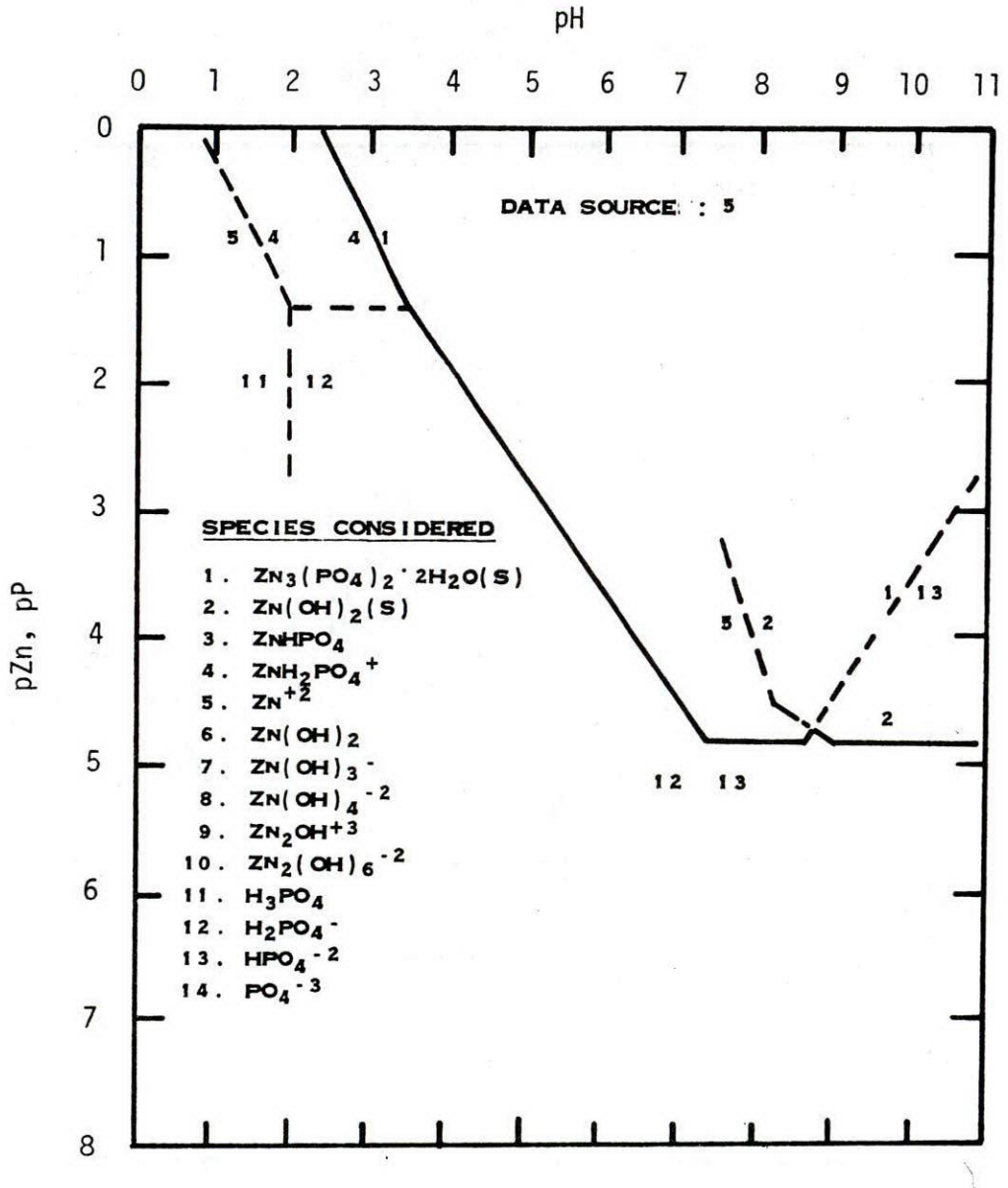

FIGURE 4. ZINC PHOSPHATE STABILITY DIAGRAM FOR THE ZINC-PHOSPHATE-WATER SYSTEM (5).

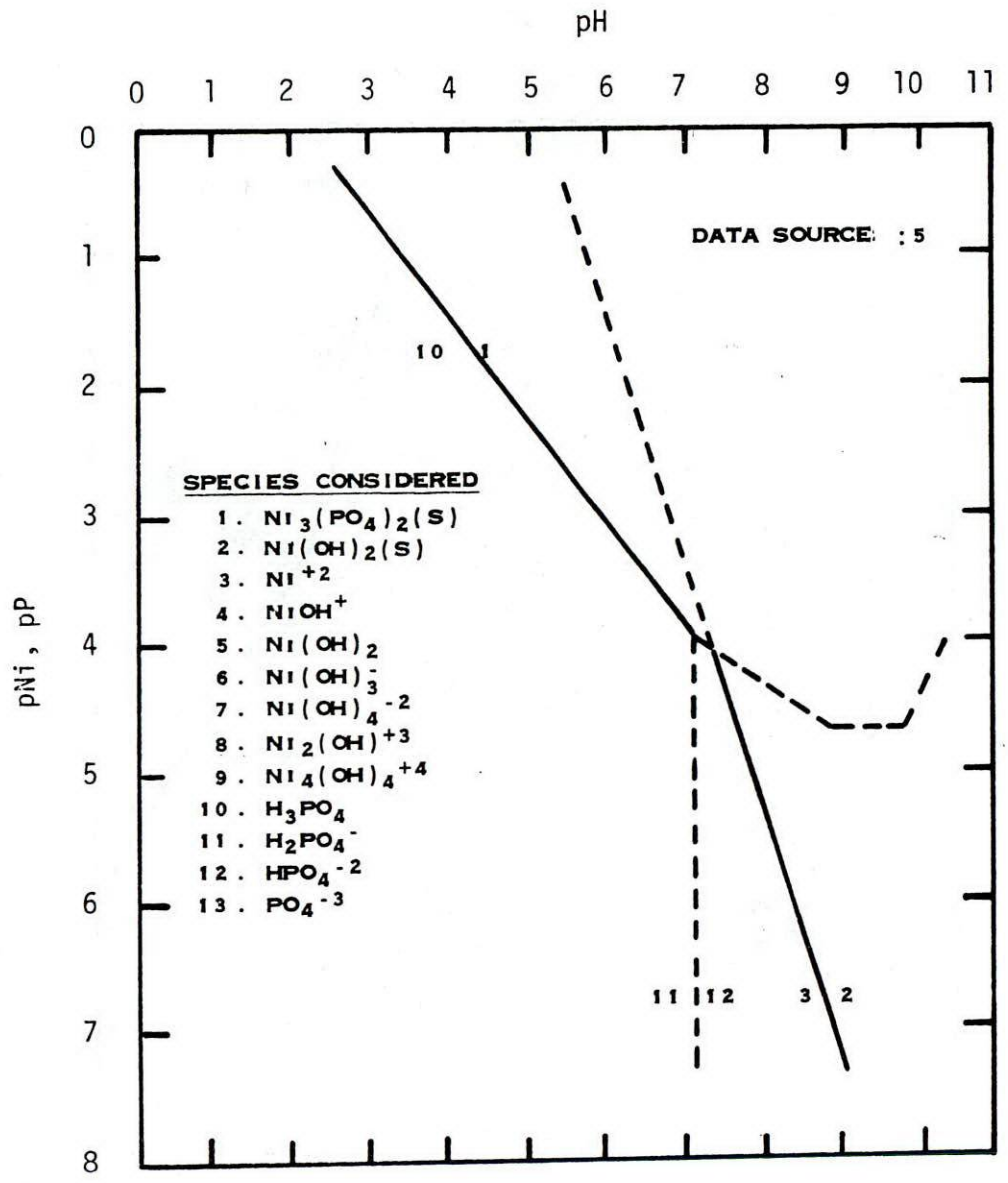

FIGURE 5. NICKEL PHOSPHATE STABILITY DIAGRAM FOR THE NICKEL-PHOSPHATE-WATER SYSTEM (5).

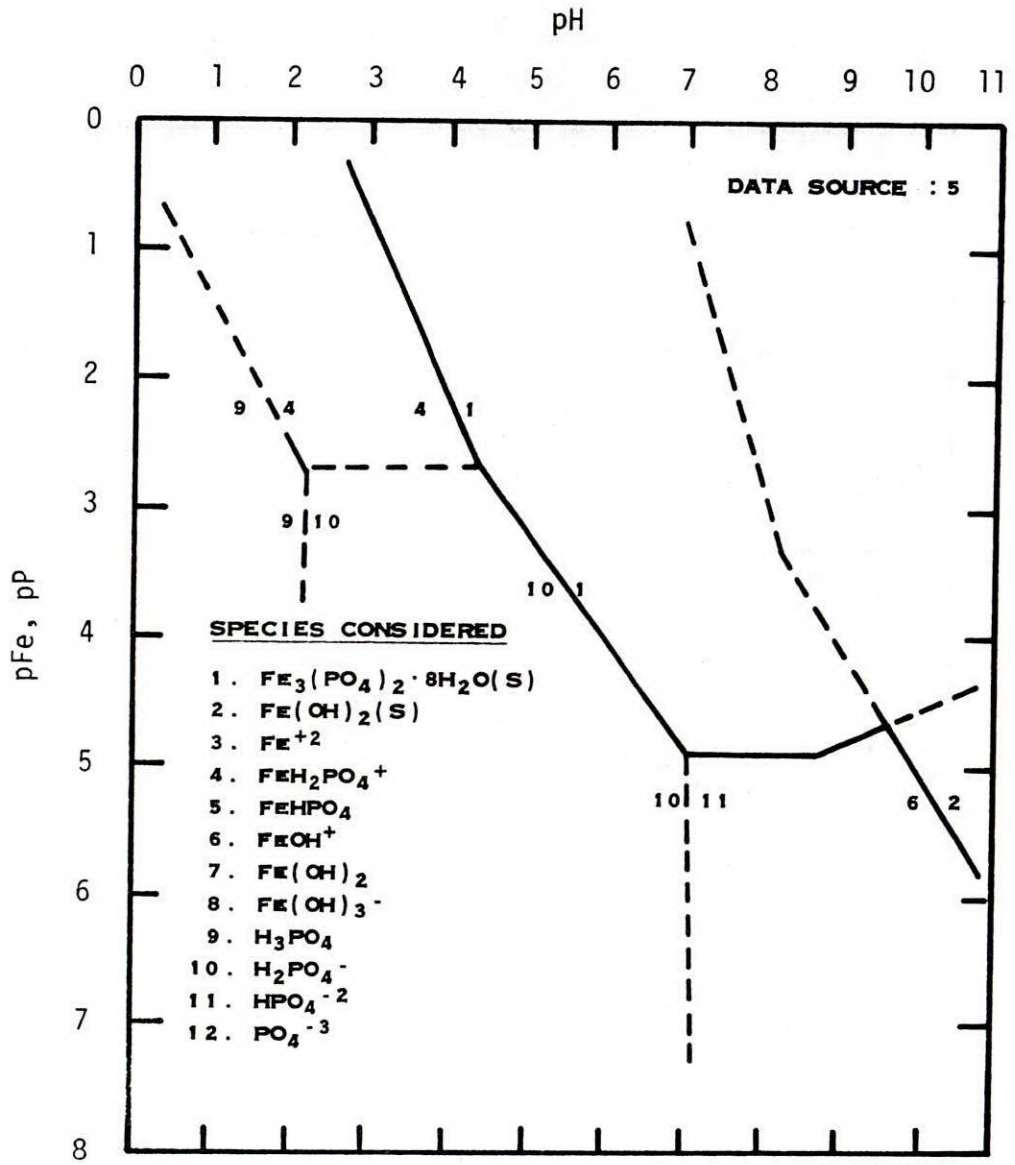

FIGURE 6. FERROUS PHOSPHATE STABILITY DIAGRAM FOR THE FERROUS-PHOSPHATE-WATER SYSTEM (5).

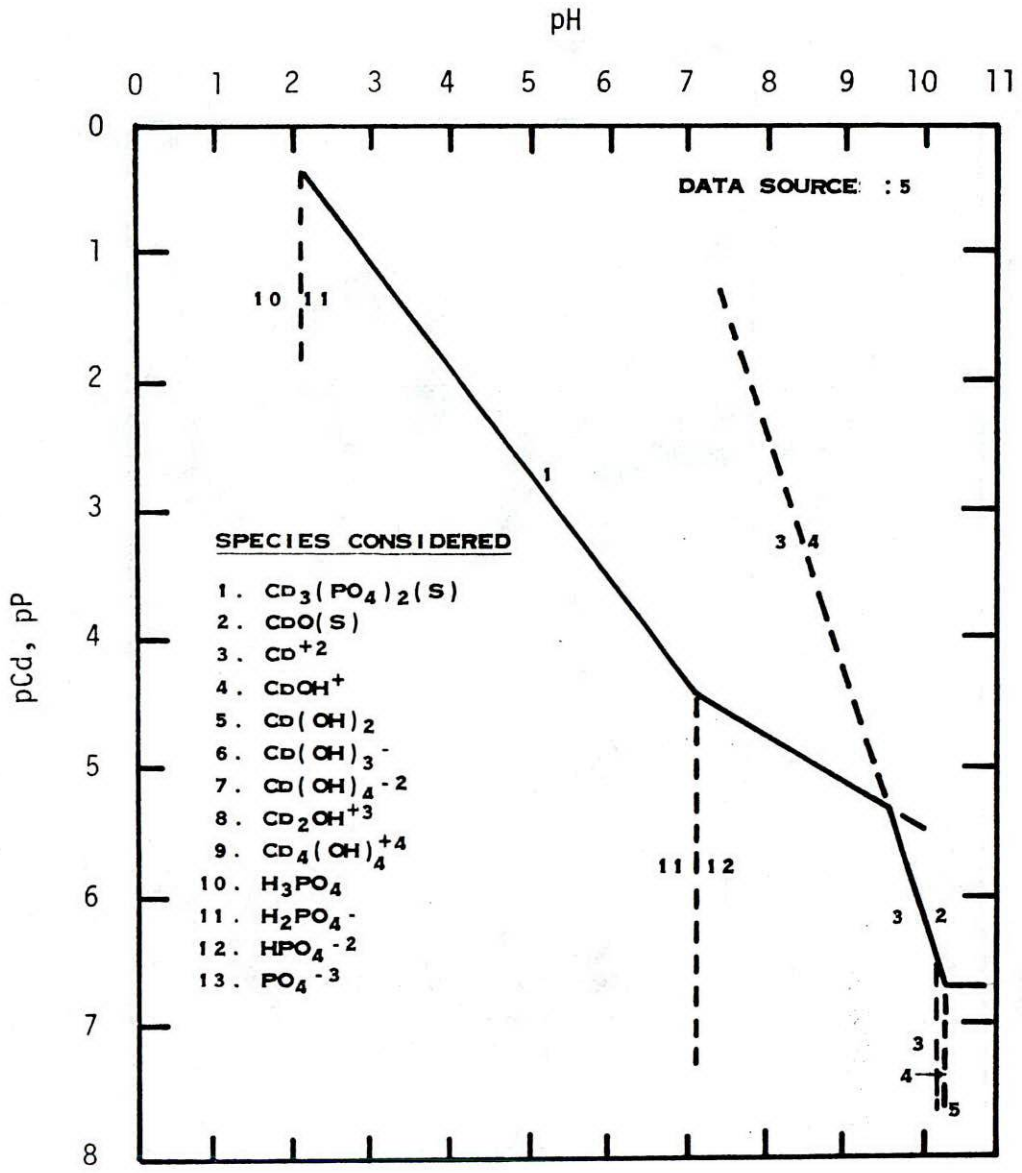

FIGURE 7. CADMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CADMIUM-PHOSPHATE-WATER SYSTEM (5).

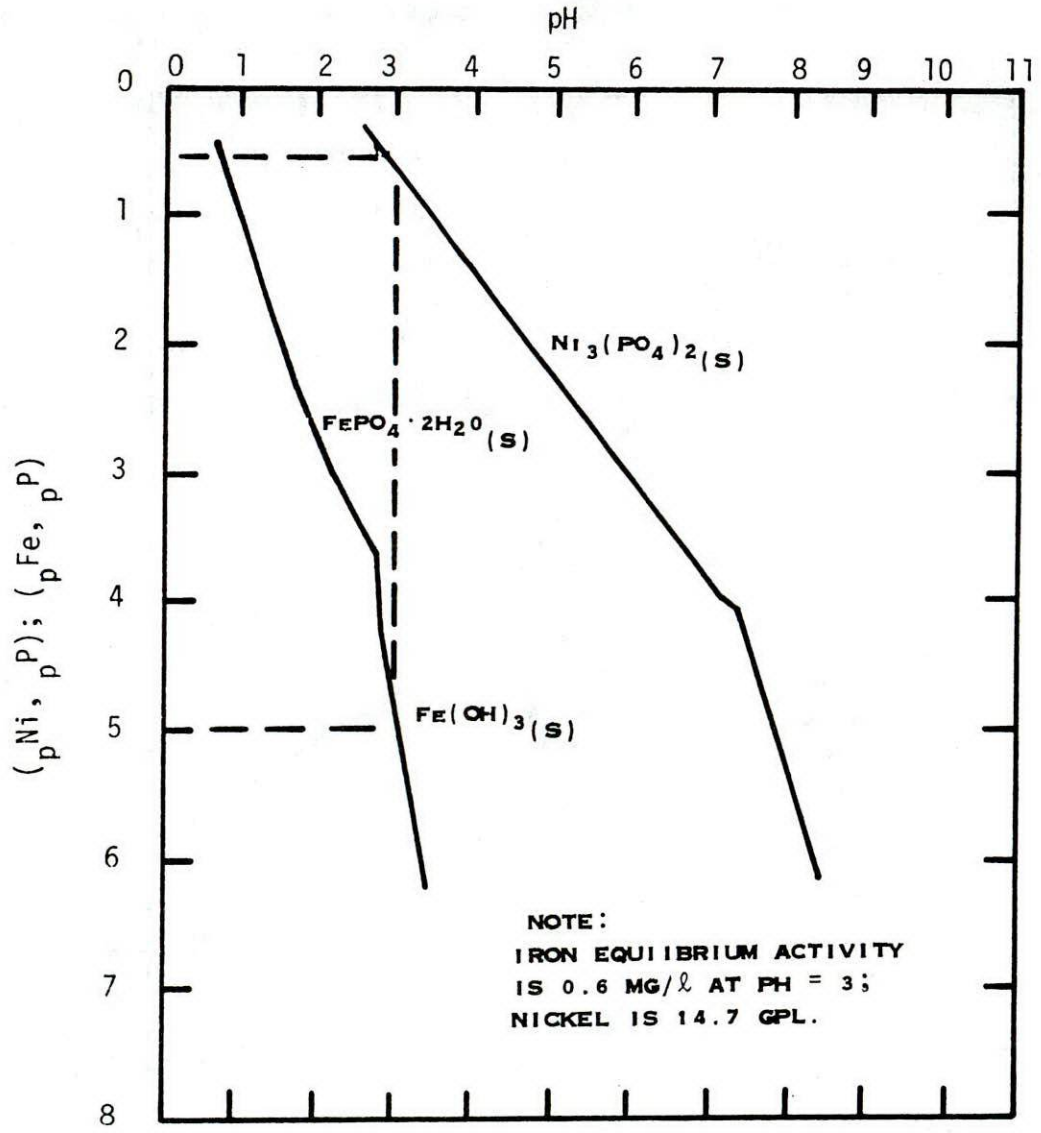

FIGURE 8. IRON REMOVAL FROM NICKEL BY PHOSPHATE PRECIPITATION.

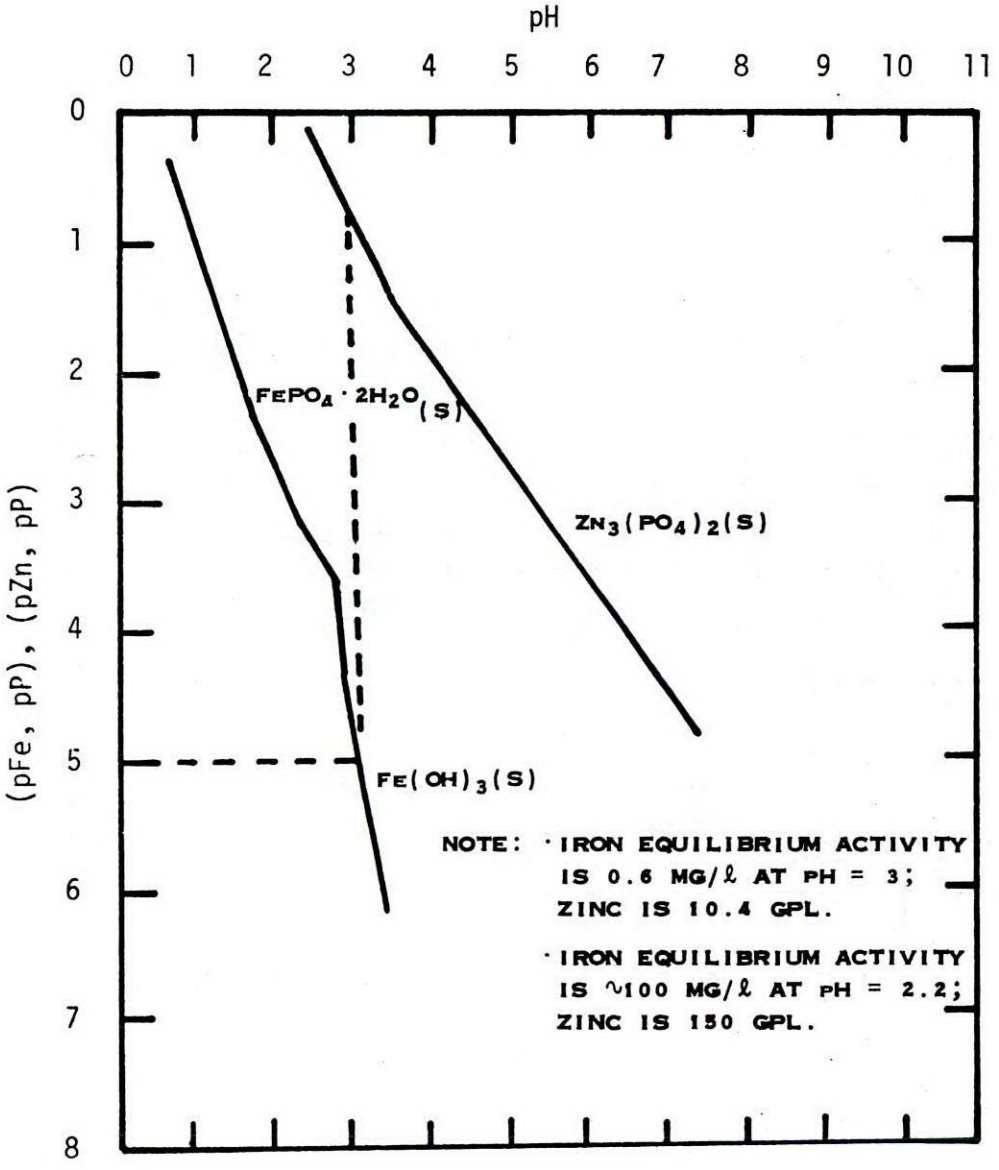

FIGURE 9. IRON REMOVAL FROM ZINC BY PHOSPHATE PRECIPITATION(5).

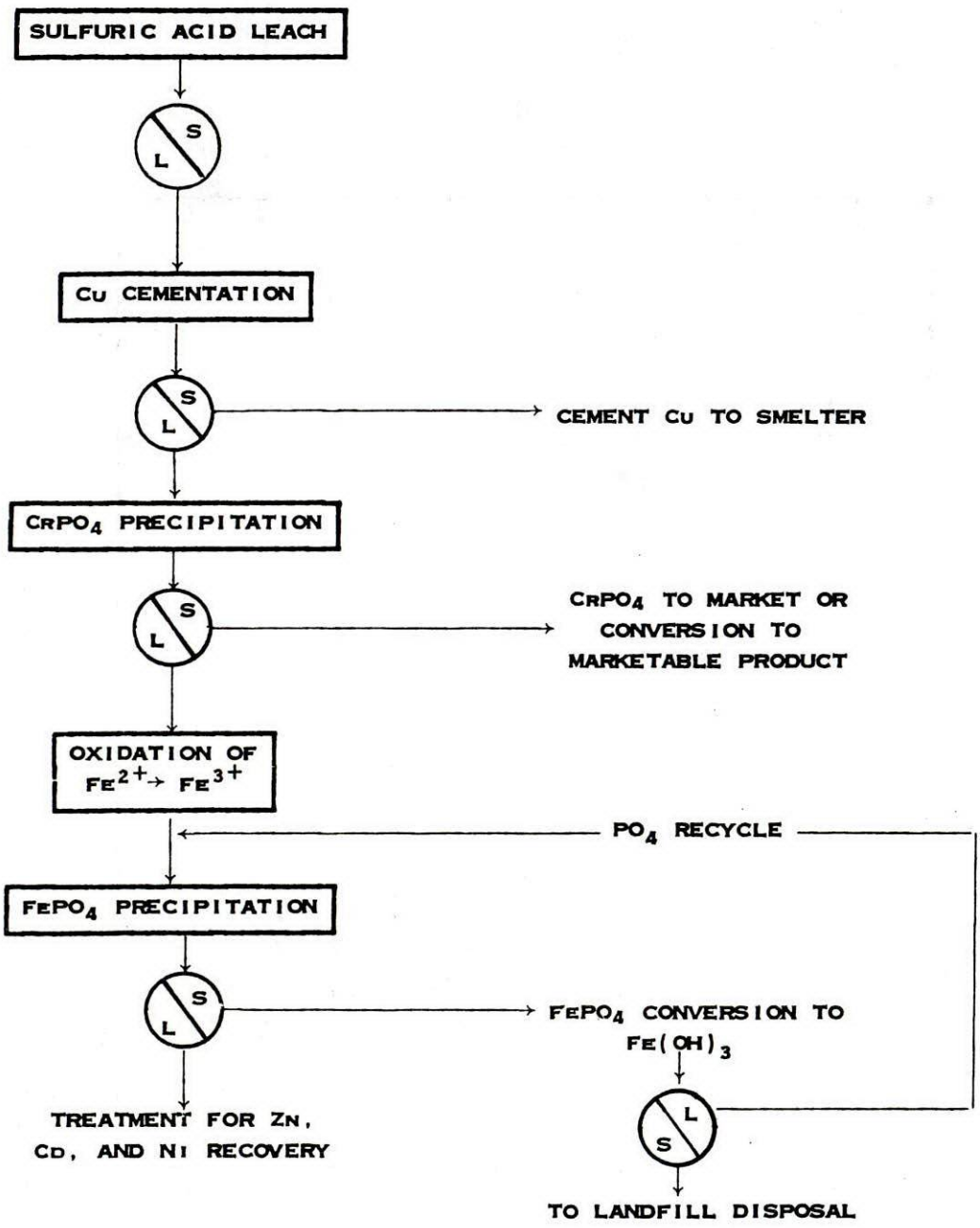

FIGURE 10. FLOWSHEET FOR THE RECOVERY OF CHROMIUM AND REMOVAL OF IRON FROM ELECTROPLATING SLUDGE LEACH SOLUTIONS

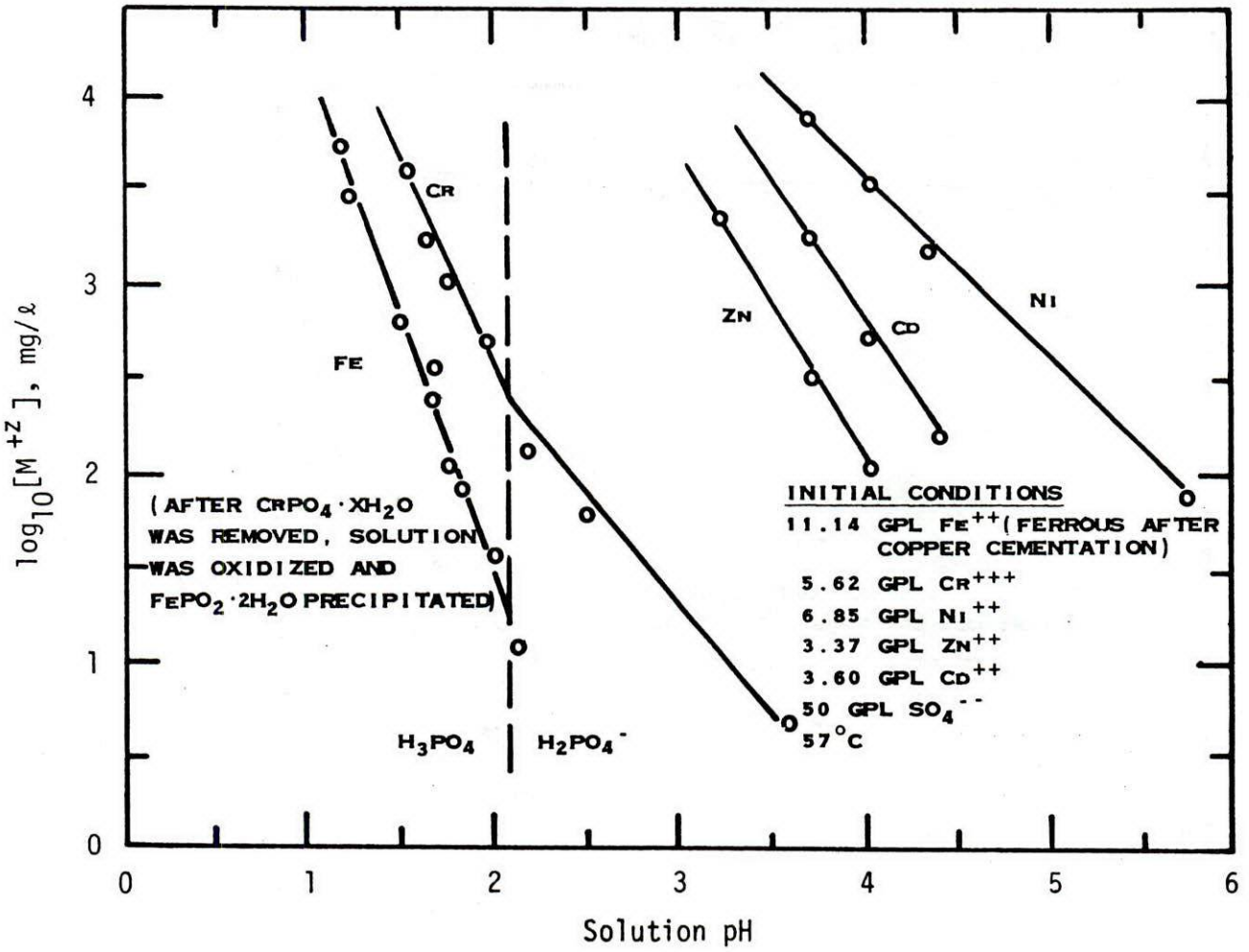

FIGURE 11. . SELECTIVE REMOVAL OF CHROMIUM AND IRON FROM DIVALENT CATIONS IN ELECTROPLATING SLUDGE LEACH SOLUTIONS (5).

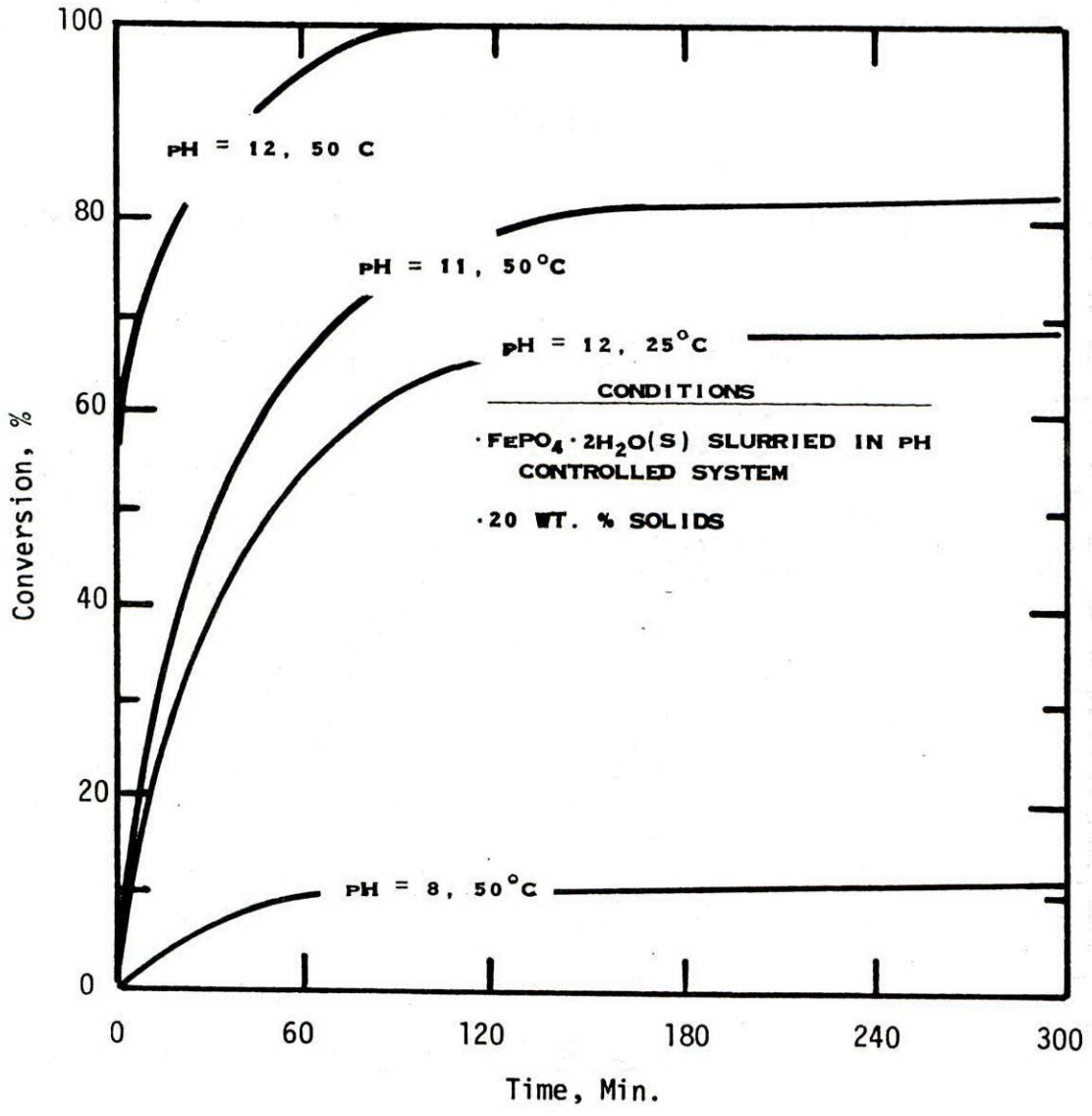

FIGURE 12. THE RATE OF CONVERSION OF FERRIC PHOSPHATE TO FERRIC HYDROXIDE AS A FUNCTION OF PH AND TEMPERATURE (5).

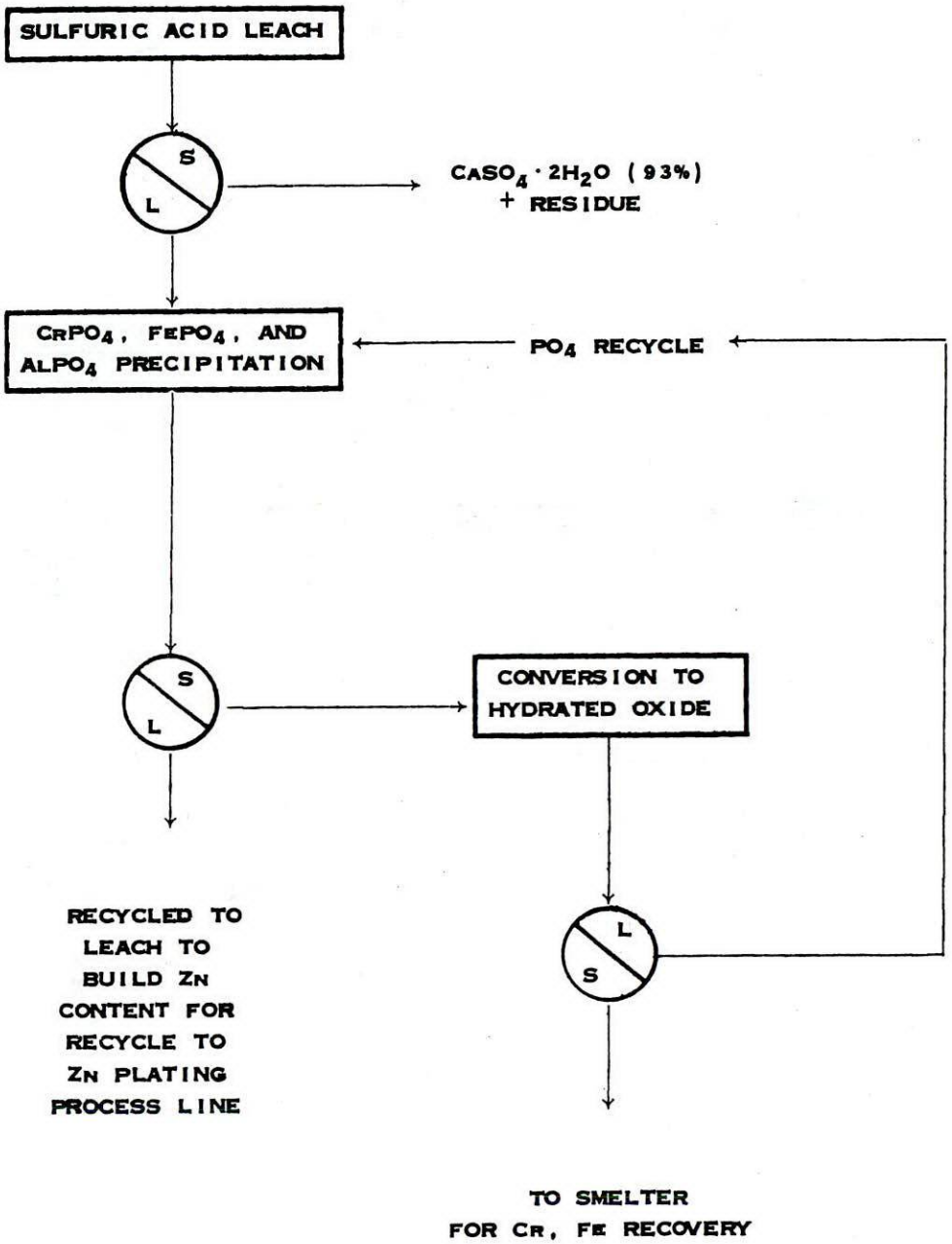

FIGURE 13. CO-REMOVAL OF IRON, CHROMIUM, AND ALUMINUM FROM ZINC BEARING LEACH SOLUTIONS

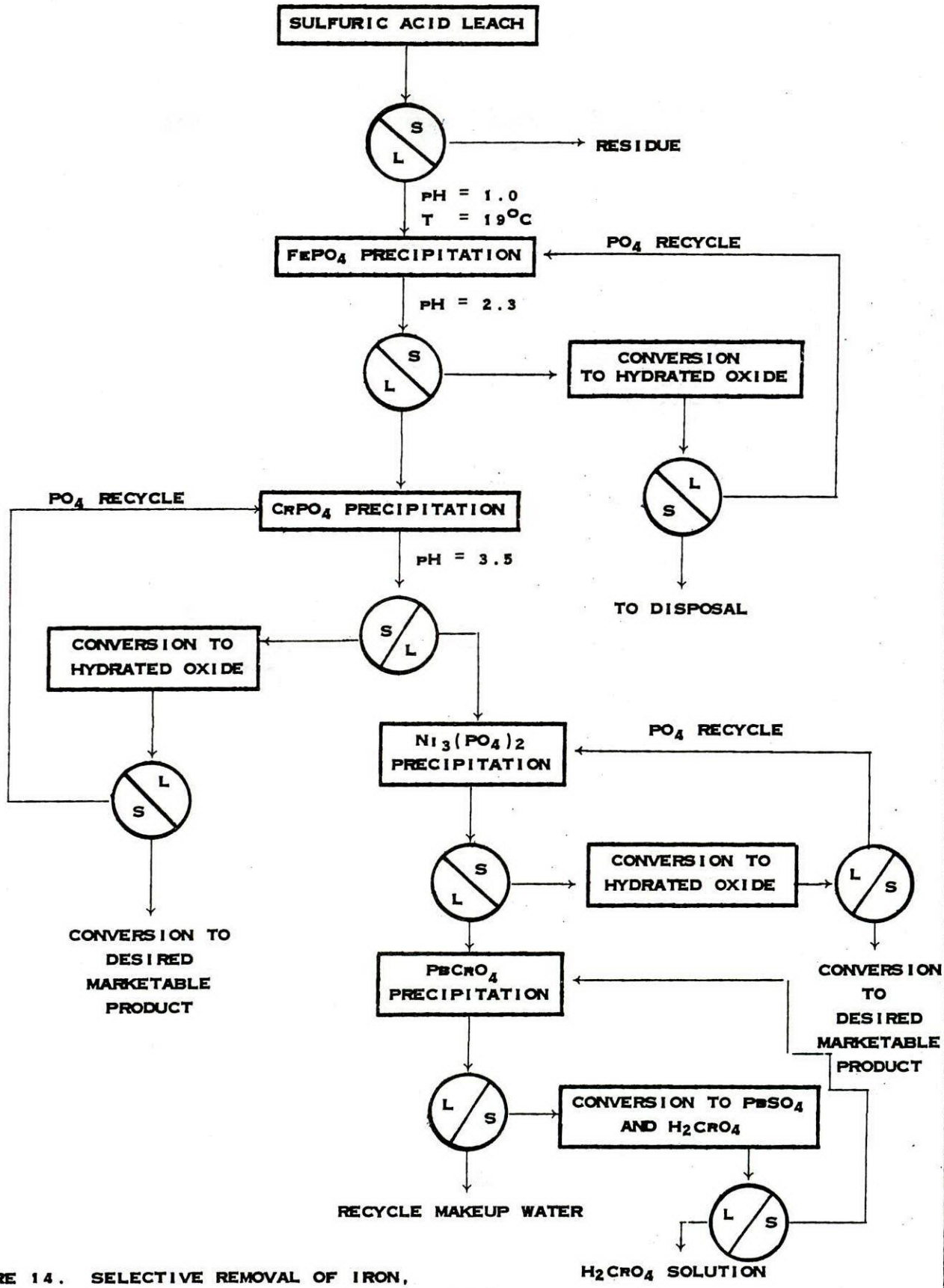

FIGURE 14. SELECTIVE REMOVAL OF IRON, CHROMIUM (III), AND CHROMIUM (IV) FROM NICKEL BEARING LEACH SOLUTIONS

C-4

Environmental I Session C

Health Assessment Aspects for Chromium

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HEALTH ASSESSMENT ASPECTS FOR CHROMIUM

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EPA has announced that it intends to add chromium or hexavalent chromium to its list of hazardous air pollutants. This means that the agency believes there exists the potential for serious illness from public exposure to emissions of chromium or hexavalent chromium into the ambient air. The author will describe the process that EPA goes through in mkaing this kind of determination, using chromium as a case study.

PAPER NOT RECEIVED IN TIME FOR PUBLICATION.

C-5

Environmental I
Session C

Preliminary Assessment of Chromium Emissions from Chromium Electroplating Facilities

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PRELIMINARY ASSESSMENT OF CHROMIUM EMISSIONS FROM CHROMIUM ELECTROPLATING FACILITIES

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Abstract

The United States Environmental Protection Agency (EPA) intends to add either chromium or hexavalent chromium to the list of hazardous air pollutants under Section 112 of the Clean Air Act. A preliminary assessment performed by EPA has identified several categories of stationary sources as emitters of significant quantities of chromium to the atmosphere and for which the proposal of national emission standards seem warranted. Included among these source categories is the electroplating of chromium from conventional chromic acid baths.

This paper presents the findings of EPA's preliminary assessment as it pertains to chromium electroplating. There are an estimated 9,700 chromium electroplating operations in the U.S. Collectively, based on the levels of control estimated to be currently in place, these operations emit about 62 tons of hexavalent chromium per year. These emissions result in an estimated annual incidence of 32 statistical lives lost per year and a maximum lifetime risk to the most exposed that may exceed 1×10^{-4}. Additional control is available at what appears to be reasonable cost. The implementation of these additional controls would result in risk reductions across the source category ranging from about 75 to 90 percent.

A. Definition of Source Category

The chromium electroplating source category comprises two distinct types of plating operations: "hard" and "decorative." In hard plating, a relatively thick layer of chromium is deposited directly to the base material (usually steel) to provide wear resistance, low coefficient of friction, hardness, and corrosion resistance or to build up surfaces that have been eroded by use. Hard plating is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, plastic molds, engine components, and marine hardware. In decorative plating, the base material (e.g., brass, steel, aluminum, plastic) is generally plated with a layer of nickel followed by a relatively thin layer of chromium to provide a bright, tarnish-resistant surface. Decorative plating is used for items such as automotive trim, metal furniture, bicycles, hand tools, and plumbing fixtures. Although other types of operations performed at electroplating plants involve chromium in some form, this source category includes only those processes that use chromic acid in an electrolytic cell to deposit chromium metal on a product.

1. Plants in Operation and Processes.

There are an estimated 9,700 chromium electroplating operations in the country.[1] In general, these operations are located at or near the industries they service, which are usually located in more populated areas. Plating operations range in size from small, consisting of one small tank operated only a few hours per week, to large, consisting of multiple large tanks operated as many as three shifts per day. Many plating operations are "captive" and are performed as one operation within a larger manufacturing facility; while others are "job shops" that provide custom plating services for many different clients. Captive platers and job shops may perform either hard or decorative plating or both.

The actual chromium plating process is similar for hard and decorative plating although pretreatment processes and operating parameters differ somewhat. The plating process involves placing the item to be plated in a tank containing chromic acid solution and a small amount of sulfuric acid as a catalyst. A generator or rectifier supplies direct current which results in the flow of electrons from the anode (positive electrode) to the workpiece which acts as the cathode (negative electrode). Positive chromium ions in the plating solution migrate to the cathode (workpiece) where they are reduced to chromium metal and are deposited on the workpiece. (In the case of plating a plastic, the pretreatment process includes steps to render the surface conductive prior to plating.)[2] Typical operating parameters for both hard and decorative plating are shown in Table 1.

The chromium plating process is very inefficient. Only 10 to 20 percent of the power applied is used to deposit chromium onto the workpiece. The remainder is consumed by the generation of a considerable quantity of hydrogen gas at the surface of the cathodes.

TABLE 1. RANGES OF OPERATING PARAMETERS FOR HARD AND DECORATIVE CHROMIUM PLATING OPERATIONS[4]

	Hard plating	Decorative plating
Plating thickness, μm (mil)	1.3 to 762 (0.05 to 30)	0.03 to 2.5 (0.001 to 0.1)
Plating time, min	20 to 6,000	0.5 to 5
Chromic acid concentration, g/ℓ (oz/gal)	225 to 375 (30 to 50)	225 to 375 (30 to 50)
Temperature of solution, °C (°F)	49 to 66 (120 to 150)	38 to 46 (100 to 115)
Voltage, volts	(Depends on the distance between the anodes and the items being plated.)	
Current, amperes	(Depends on the amount of surface area being plated.)	
Current density, amperes/m^2 (amperes/ft^2)	1,600 to 6,500 (150 to 600)	540 to 2,200 (50 to 200)

Plating efficiency can be improved in some situations by adding fluoride to the plating solution. However, fluoride cannot be used in all types of plating solutions and may cause "etching" or "burning" of exposed steel surfaces if used in hard plating solutions.[3]

2. Projections of Industry Growth.

Chromium electroplating is not a distinct industry; it is a process performed within and for a wide variety of industries. Thus, the growth of chromium electroplating operations is determined by trends in the industry sectors that require these services. Although new electroplating operations may be built to accommodate growth in specific industries or to replace obsolete or relocated equipment, no net increase in the use of chromium electroplating is expected. The following considerations form the bases for this conclusion: (1) chromic acid consumption by metal platers has remained relatively constant over the past 10 years and (2) the demand for decorative plating in the automobile industry (one of the largest consumers of chromic acid for metal plating) has decreased because of the use of substitute materials for bumpers and trim.

B. Emissions and Controls

Hexavalent chromium is emitted during the chromium electroplating process in the form of a visible yellow mist. The mist is composed of entrained chromic acid droplets that form when the hydrogen and oxygen gases are released from the surface of the plating solution. The hydrogen gas is generated at the cathode while oxygen is liberated at the anode.

Factors affecting the amount of mist generated from plating tanks include the amount of current applied, the amount of surface area plated, the amount of chromium deposited, the duration of plating, and the surface area of the tank. Uncontrolled emission factors that can be applied to chromic acid consumption have been developed by EPA for both hard and decorative plating and are presented in Table 2. The factors are based on results of EPA source tests at one hard plating facility and one decorative plating facility.

The plating operations tested are representative of a large job shop performing hard chromium plating of industrial rolls and a large captive shop performing decorative chromium plating of automobile bumpers. Although these two operations do not characterize the chromium electroplating source category in every respect, they are representative of other plating operations in terms of the processes and types of emission controls. The emission capture systems at both plants were effective in withdrawing mist from the plating area. The decorative plating tank contained a fume suppressant to inhibit misting, which is believed to be common practice for about 90 percent of decorative plating operations. Emissions from both plating operations were controlled by multiple packed-bed scrubbers.[5,6]

TABLE 2. UNCONTROLLED EMISSION FACTORS USED TO ESTIMATE EMISSIONS FROM CHROMIUM ELECTROPLATING OPERATIONS[7]

Type of operation	Emission factor, kg Cr^{+6} / kg CrO_3 used	Basis
Hard	0.0094	EPA source test at Carolina Plating--Roll Division plant in Greenville, South Carolina.
Decorative	0.00024[a]	EPA source test at C. S. Ohm Manufacturing Company plant in Sterling Heights, Michigan.

[a]Based on the assumption that the fume suppressant used during the test controlled 80 percent of the misting.

There are several methods used to reduce chromium emissions from chromium electroplating operations. One method used by many decorative platers involves adding chemical fume suppressants to the plating solution. Although there are different types, most fume suppressants generally contain a surfactant or wetting agent that reduces the surface tension of the plating solution. This results in the formation of much smaller hydrogen and oxygen gas bubbles that are released from the surface of the plating solution less violently, reducing substantially the amount of chromic acid mist formed. In addition, some fume suppressants also create a layer of foam on the surface of the plating solution, which aids in inhibiting misting. Although several manufacturers of fume suppressants were contacted, no actual performance data were obtained.

Another method of reducing chromium emissions involves the application of exhaust systems to the plating tanks and the treatment of the resultant exhaust gases by a control device. Two types of control devices are typically used: impingement-type mist eliminators and packed-bed wet scrubbers. The mist eliminators are equipped with baffles that continually change the direction of the gas flow. This promotes impingement on the baffles of droplets of mist entrained in the exhaust gas. The collected mist is discharged either into a holding tank or directly back into the plating tank. Control device vendors estimate removal efficiencies to be 80 to 85 percent for impingement mist eliminators.

In packed-bed scrubbers, the exhaust gases are saturated with water and then passed through one or more beds of packing material. The beds are several inches deep and are continuously wetted or sprayed. Typically, the scrubbers used contain one or two packed beds. Any mist or fume entrained in the exhaust gas impinge on the packing and is washed away by the scrubbing liquid. Control device vendors estimate removal efficiencies to be 95 to 99 percent for these devices.[9] Actual EPA source tests conducted across a double packed-bed scrubber controlling emissions at the Carolina Plating--Roll Division plant indicated that 95 percent removal efficiency was being achieved.[10]

C. Potential for Improved Control

There appears to be significant potential for improved control in this source category. Although no statistical data are available, it is estimated that emissions from about 50 percent of the hard platers and about 10 percent of the decorative platers currently are uncontrolled.[9,11] Information obtained from almost 60 plants supports this assumption, which is based on estimates from control device vendors and fume suppressant manufacturers.

Fume suppressants may be used to reduce hexavalent chromium emissions from decorative plating operations that are currently uncontrolled. The achievable control efficiency is conservatively assumed to be 80 percent. The bases for this assumption were observations at several plants, which demonstrated that generally fume

suppressants appear to be added according to the operator's discretion or judgement rather than a systematic schedule or plan.[12] Although fume suppressants also are available for use in hard chromium plating operations, hard platers have cited problems with electrical sparking and "pitted" surface finishes when these chemicals are used in the plating solutions.[13]

Add-on control devices may be used to reduce hexavalent chromium emissions from either hard or decorative plating operations. The capture efficiency of a well-designed and -operated ventilation system is estimated to approach 100 percent. Achievable control efficiencies are conservatively assumed to be 85 percent for impingement mist eliminators and 95 percent for packed-bed scrubbers.

Estimates of costs and emission reductions are presented in Table 3 for different types of emission controls applied to each of the four model plants used to estimate maximum lifetime risks (see Section D-2). The model plants are representative of different sizes (small and large) and types (hard and decorative). Although the emission reductions achievable by the controls may be subject to question, the actual values are probably no lower than those listed in Table 3.

D. Risk Assessment

Risk assessment is the process used by EPA to develop quantitative estimates of public health risks associated with individual or population exposure to a hazardous or toxic air pollutant. The resultant estimates are considered by EPA to be rough, but plausible approximations of the upper-bound risks. Two measures of risk are calculated. One is maximum individual risk and the other is aggregate risk. Maximum individual risk is an estimate of the probability of contracting cancer experienced by the person or persons exposed to the highest predicted annual average concentration of the pollutant. Aggregate risk is a measure of the overall health impact on the entire population exposed. It is expressed in terms of annual incidence or number of cancer cases per year.

The estimates are calculated by coupling a numerical constant that defines the exposure-risk relationship for a particular hazardous pollutant with estimates of public exposure to the pollutant. The numerical constant used by EPA in its analysis of carcinogens is called a unit risk factor. It represents an estimate of the increase in lifetime cancer risk over the background occurring to a hypothetical individual exposed continuously over a lifetime (about 70 years) to a concentration of 1 microgram per cubic meter ($\mu g/m^3$) of the pollutant in the air breathed by the individual. For compounds of hexavalent chromium, the unit risk factor is estimated to be 1.2×10^{-2} or 1.2 chances in 100. A discussion detailing the development of this estimate is presented in EPA's Health Assessment Document for Chromium.[15]

TABLE 3. EMISSION REDUCTIONS AND ANNUALIZED COST OF CONTROL FOR FOUR MODEL CHROMIUM ELECTROPLATING OPERATIONS[14]

Item	Model plant A	B	C	D
Type of plating operation	Small hard	Large hard	Small decorative	Large decorative
Uncontrolled emission factor, kg Cr^{+6}/kg CrO_3 used	0.0094	0.0094	0.00024	0.00024
CrO_3 consumption, kg/yr (lb/yr)	820 (1,800)	9,600 (21,200)	1,100 (2,400)	16,300 (35,900)
Uncontrolled emission rate, kg Cr^{+6}/yr (lb Cr^{+6}/yr)	7.7 (17)	90 (200)	0.26 (0.57)	3.9 (8.6)
Packed-bed wet scrubber[a]				
Achievable emission reduction, kg Cr^{+6}/yr (lb Cr^{+6}/yr)	7.3 (16)	86 (190)	0.25 (0.55)	3.7 (8.2)
Capital cost of control,[b] $	10,500	35,400	10,500	43,300
Annualized cost of control,[c] $/yr	4,520	15,300	4,380	19,400
Impingement mist eliminator				
Achievable emission reduction, kg Cr^{+6}/yr (lb Cr^{+6}/yr)	6.5 (14)	77 (170)	0.22 (0.49)	3.3 (7.3)
Capital cost of control,[b] $	2,690	8,500	2,690	9,400
Annualized cost of control,[c] $/yr	960	2,580	1,020	3,540
Chemical fume suppressant				
Achievable emission reduction, kg Cr^{+6}/yr (lb Cr^{+6}/yr)	N/A	N/A	0.21 (0.46)	3.1 (6.8)
Capital cost of control, $	N/A	N/A	0	0
Annualized cost of control, $/yr	N/A	N/A	1,830	26,600

N/A = not applicable.
[a]Packed-bed scrubber with two layers of packing to control emissions.
[b]Does not include cost of connecting existing ventilation system to control device.
[c]Does not include cost of wastewater treatment.

Estimates of public exposure are derived using dispersion models and census data contained in EPA's Human Exposure Model (HEM).[16] Dispersion models are used to predict concentrations of a pollutant in the ambient air at varying distances from an emission source. By combining predicted ambient concentrations with population data, both the number of people exposed and their level of exposure can be calculated. Details on the methodology used in developing the health risk assessment are described below.

1. Aggregate Risk

The aggregate risk or annual incidence estimated for chromium electroplating was derived somewhat differently than is usual for most source categories. Generally, the individual plants that comprise a source category are located and modeled as separate point sources. The aggregate risk for the source category is then calculated by summing the annual incidence for each individual plant. Because of the large number and widespread distribution of plants that comprise the chromium electroplating source category, the point source approach is considered impracticable. As a result, an alternative area approach was used.

The area approach is based on the simplifying assumptions that (1) chromium electroplating activities and thus emissions are distributed across the entire United States according to population density, and (2) each person in the U.S. is exposed to hexavalent chromium as a result of these activities. Nationwide emissions of hexavalent chromium from chromium electroplating operations is estimated to be 56 megagrams (62 tons) per year. The estimate is based on the emissions factors presented in Table 2 for hard and decorative plating, information obtained on chromic acid consumption, and assumptions regarding the level of control currently in place within the source category. Limited information on chromic acid consumption suggests that 75 percent of the chromic acid consumed by chromium electroplating is consumed by hard platers and 25 percent is consumed by decorative platers.[17] For hard platers, it is assumed that 50 percent use mist eliminators or scrubbers and are controlled to 90 percent and that the remainder are uncontrolled. In the case of decorative platers, it is assumed that 90 percent are controlled to 80 percent. The 80 percent control level is based on a conservative estimate of the effectiveness of fume suppressants in inhibiting misting. The total population exposed, based on the 1980 census, is 226,546,000 people.

In performing the actual aggregate risk calculations, nationwide emissions were apportioned by county on the basis of the number of people living in each county. An annual average county-wide concentration of hexavalent chromium was then estimated based on the assumption that emissions are evenly dispersed over the county area and using a dispersion model contained in HEM for modeling area sources. The resultant county-wide ambient concentration in $\mu g/m^3$ multiplied by the number of people in a county result in an estimate of exposure. The nationwide aggregate risk or annual incidence was calculated by summing the nationwide county exposure values and multiplying the aggregate

value by the unit risk factor divided by 70 years (a lifetime). The resultant estimate of annual incidence due to current annual emissions of hexavalent chromium emissions from chromium electroplating facilities is 32 statistical lives per year.[18]

2. Maximum Lifetime Risk.

The risk assessment inputs used for calculating maximum lifetime risk are presented in Table 4. Four model plants were used to represent the following general subcategories of chromium platers: small hard platers, large hard platers, small decorative platers, and large decorative platers. Chromic acid consumption and stack parameters for the four model plants were based on data provided by four actual plating plants. The model plants were sited at the location of a fifth plating plant in a commercial/residential area near Detroit, Michigan. This location is representative of the type of area in which many plating plants are located.

Although each of the four actual plants has air pollution control devices in place, all emissions from the model plants were assumed to be uncontrolled for the purpose of assessing maximum lifetime risk. Emission rates were calculated using the chromic acid consumption for each plant and the factors for uncontrolled emissions listed in Table 2.

The annual incidence and maximum lifetime risks attributed to uncontrolled hexavalent chromium emissions from these model plants are listed in Table 5. As shown on the table, the calculated maximum lifetime risks range from a low of 1.3×10^{-6} for the small decorative plater to a high of 8.2×10^{-5} for the large hard plater.

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TABLE 4. RISK ASSESSMENT INPUTS FOR CALCULATING MAXIMUM LIFETIME RISK DUE TO HEXAVALENT CHROMIUM EMISSIONS FROM THE CHROMIUM ELECTROPLATING SOURCE CATEGORY

Model plant[a]:	A	B	C	D
Type of plating operation:	Small hard	Large hard	Small decorative	Large decorative
Chromic acid usage, kg/yr:	816	9,607	1,089	16,330
Total tank surface area, m^2:	4.6	18.9	5.6	22.3
Type of source:	H (stack)	H (stack)	(H stack)	(H stack)
Uncontrolled emission rates, kg/yr:				
Total Cr	7.7[b]	90.3[b]	0.26[c]	3.9[c]
Hexavalent Cr	7.7[b]	90.3[b]	0.26[c]	3.9[c]
Discharge parameters:				
Stack height, m	7.3	23	7.9	25
Vertical area, m^2	50	250	50	250
Vent type	0 (vertical)	0 (vertical)	0 (vertical)	0 (vertical)
Stack diameter, m	0.61	1.3	0.61	1.6
Gas exit velocity, m/s	9.7	7.1	10.1	7.1
Gas temperature, °K	300	294	294	294

[a]For the purpose of determining maximum lifetime risk, each plant is to be located at the site of an existing plant in the Detroit area (UTM zone 17; 3, 35, 122 E; 47, 02, 244 N).

[b]Based on an uncontrolled emission factor of 0.0094 kg Cr^{+6}/kg CrO_3. (Ref.: EPA Source Test at Carolina Plating--Roll Division plant.)

[c]Based on an uncontrolled emission factor of 0.00024 kg Cr^{+6}/kg CrO_3, which assumes an 80 percent control efficiency for the fume suppressant used during the EPA source test. (Ref: EPA Source Test at C. S. Ohm Manufacturing Company plant.)

TABLE 5. RISKS ASSOCIATED WITH EXPOSURE TO UNCONTROLLED HEXAVALENT CHROMIUM EMISSIONS FROM MODEL CHROMIUM ELECTROPLATING OPERATIONS[18]

Model plant[a]	Annual incidence	Maximum lifetime risk
Small hard	0.003	4.1×10^{-5}
Large hard	0.026	8.2×10^{-5}
Small decorative[b]	0.0001	1.3×10^{-6}
Large decorative[c]	0.001	2.8×10^{-6}

[a]Model plants were sited at the location of an existing plating plant in Warren, Michigan, a representative commercial/residential area.
[b]Risks are scaled up by a factor of 0.26/0.05 (estimated uncontrolled emissions/estimated emissions when using a fume suppressant).
[c]Risks are scaled up by a factor of 3.9/0.51 (estimated uncontrolled emissions/estimated emissions when using a fume suppressant).

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D-1

Electroforming Session D

Some Unusual Design Problems Solved by Electroforming

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SOME UNUSUAL DESIGN PROBLEMS SOLVED BY ELECTROFORMING*

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Introduction

Electroforming has been used at our Laboratory to assist our design staff in obtaining 1) parts that could not be fabricated by any other manufacturing process, 2) parts that have configurations requiring elaborate machining, 3) parts with walls too thin to machine, 4) limited numbers of development parts, and 5) parts where fabrication time is short compared with that required by conventional fabrication procedures. Typically, we have used copper and nickel metal for the majority of our parts because their mechanical and physical properties, as well as the plating solutions and procedures, are well defined and established (Ref. 1). We have also combined photolithography with electroplating to produce some unusual electroformed parts (Ref. 2).

This paper discusses four different electroforming applications at our Laboratory, each having a unique solution to a fabrication problem:

- a thin-walled nickel barrier can
- a light-weight particle collector
- a free-form cable protector
- a hole pattern in a cylindrical filter

Nickel Barrier Can

A precision thin-walled (0.025-0.05 mm), leak-tight barrier can was needed to protect a component (see Figure 1). The design also called for a flange on the bottom where a plate was to be welded. Development parts were needed in a short time, but there was also an interest in electroforming when the part reached production.

To demonstrate the feasibility of electroforming the can, expendable aluminum mandrels were first used. Nickel was plated to the desired thickness, and the aluminum was dissolved in a caustic solution. Table I describes the plating solution and operating conditions for the fabrication of the various parts discussed in this paper. The time from the initial request until the engineer had his first part was less than 8 hours. While this procedure was fine for development hardware, it was unsuitable for production because of the tight tolerances desired for production parts and the cost of machining the aluminum mandrels. A one-piece permanent stainless steel mandrel was investigated, but because of the part's thin wall and shape, it proved almost impossible to remove the electroform.

*Work supported by the U.S. Dept of Energy under Contract No. DE-AC04-76DP00789.

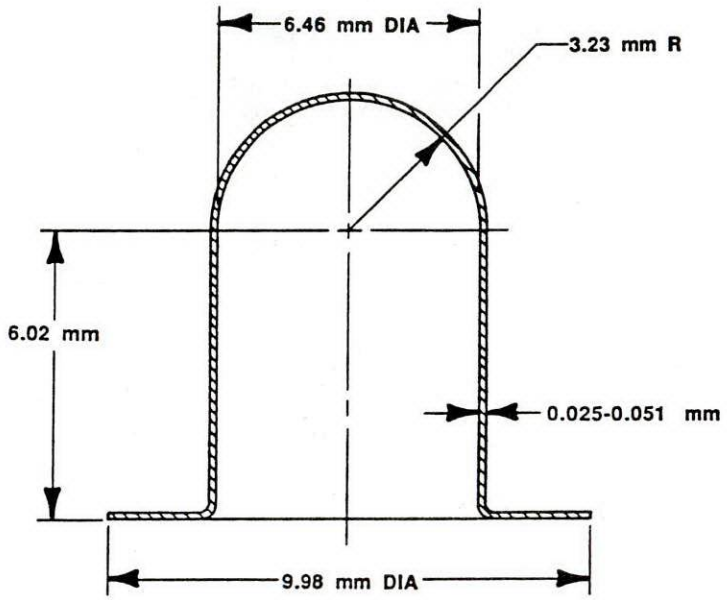

Figure 1. Design of Thin-Walled Barrier Can

Previous work at our Laboratory (Ref. 3) had demonstrated that a thin part (< 0.025 mm thick) could be electroformed and separated from its mandrel by overplating the electroform with a dissimilar metal for additional strength. After separating the electroform from the mandrel, the overplated metal is dissolved. To eliminate this time-consuming and costly procedure, a permanent type-two piece mandrel was designed that allowed the electroform to be separated from the mandrel without any distortion. Figure 2 depicts the mandrel and illustrates the technique.

Table I.
Composition and Operating Conditions for Nickel Sulfamate Solution

Nickel (as nickel sulfamate)	81 g/l
Nickel chloride	< 1.0 g/l
Boric acid	40 g/l
Surface tension	38 dyne-cm
pH	3.8 - 4.0
Anodes	Sulfur depolarized
Current density	215 A/m^2
Temperature	49°C

Figure 2a shows the two-piece mandrel, the plastic shield that limits the flange diameter, and the nickel electrodeposit. In machining the mandrel, it was determined that the final cut had to be taken with both parts joined. Otherwise, if the parts of the mandrel were machined separately and then assembled, a small step would be present that could prevent separation.

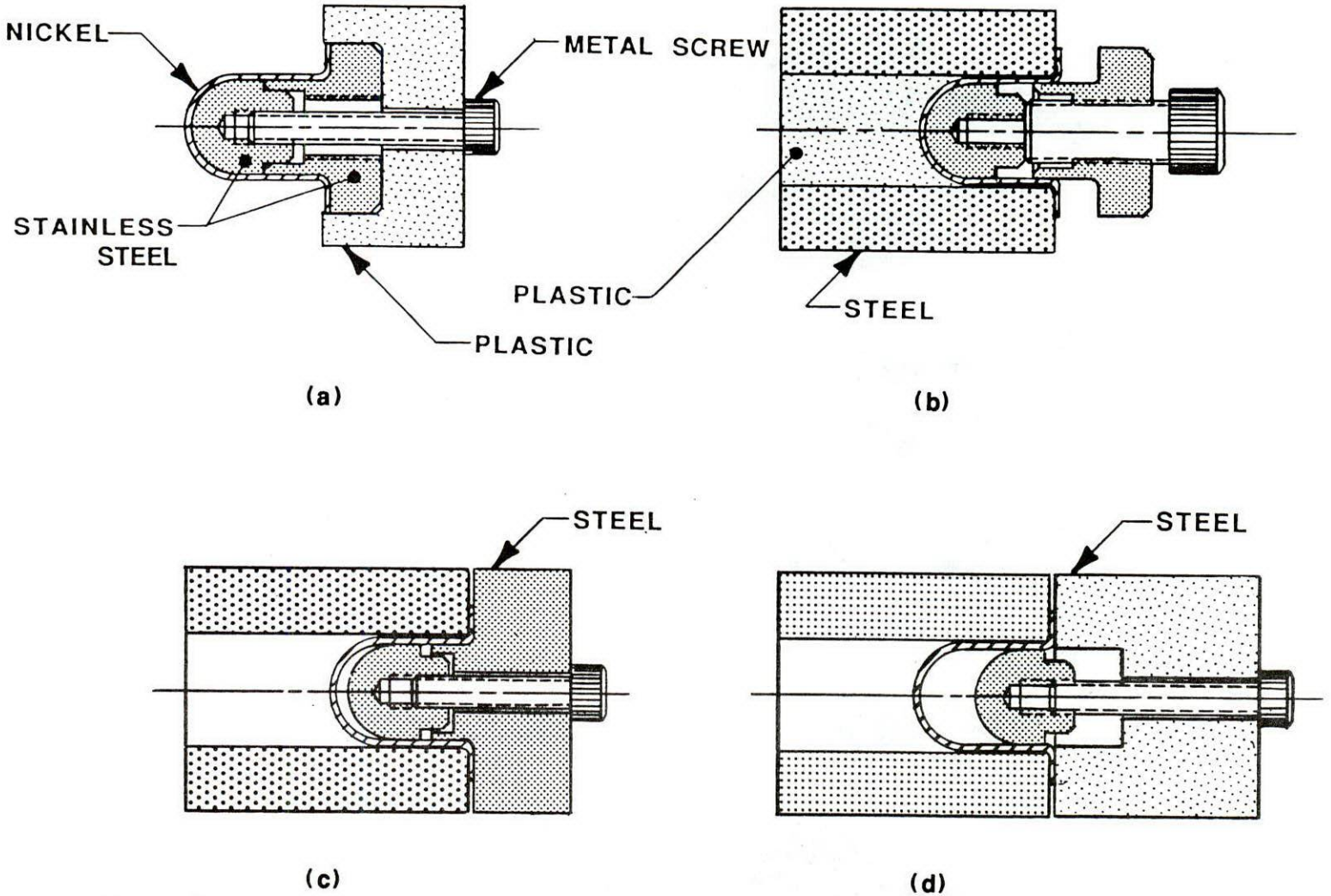

Figure 2. Fabrication Steps for Barrier Can. (a) Nickel electroform on two-piece mandrel; first, the metal screw and plastic shield are removed. (b) Electroform and mandrel in steel die; the back part of the mandrel is being removed. (c) Fixture for breaking the front part of the electroform loose from the mandrel. (d) Fixture for completely removing the mandrel from the electroform.

Figure 2b shows the electroform/mandrel in a steel die with the back portion of the mandrel being pulled out. Next, a steel part was attached to the front portion of the mandrel as shown in Figure 2c. The purpose of this step was to break the front portion of the mandrel loose from the electroform. (If the separation fixture shown in Figure 2d were used at this point, the side walls would buckle.) The front portion of the mandrel was then removed. Figure 3 shows a finished part and the mandrel.



Figure 3. Mandrel (left) and Finished Part (right)

Particle Collector

Three electroformed nickel parts were vital in the development of a real-time particle mass detector in an advanced combustion system that measures particulate material suspended in gaseous process streams and exhausts (Ref. 4). At the heart of the detector are particle collectors. Because the weight of particles is measured by taking the difference between the weights of the collector with and without particles, the accuracy and the sensitivity of the system depends on the weight of the collector: the lighter the collector, the more sensitive the measurement. Electroforming was chosen because of its capability for making strong light-weight parts.

Figure 4 shows three different particle collectors--a W-shaped cup, a cup-shaped filter holder, and a cup-shaped filter. The filter was the most difficult to electroform and is the one discussed here. Particles collect on the external surfaces of a matrix of 0.78-mm-diameter tubes; the spacing between them is set so that particles 50-100 micrometers in diameter will be trapped.

The fixturing and positioning of the small, thin-wall stainless steel tubes (2 mm o.d., 1.6 mm i.d.) are the most difficult steps in the electroforming process. Table II summarizes the procedure developed. The

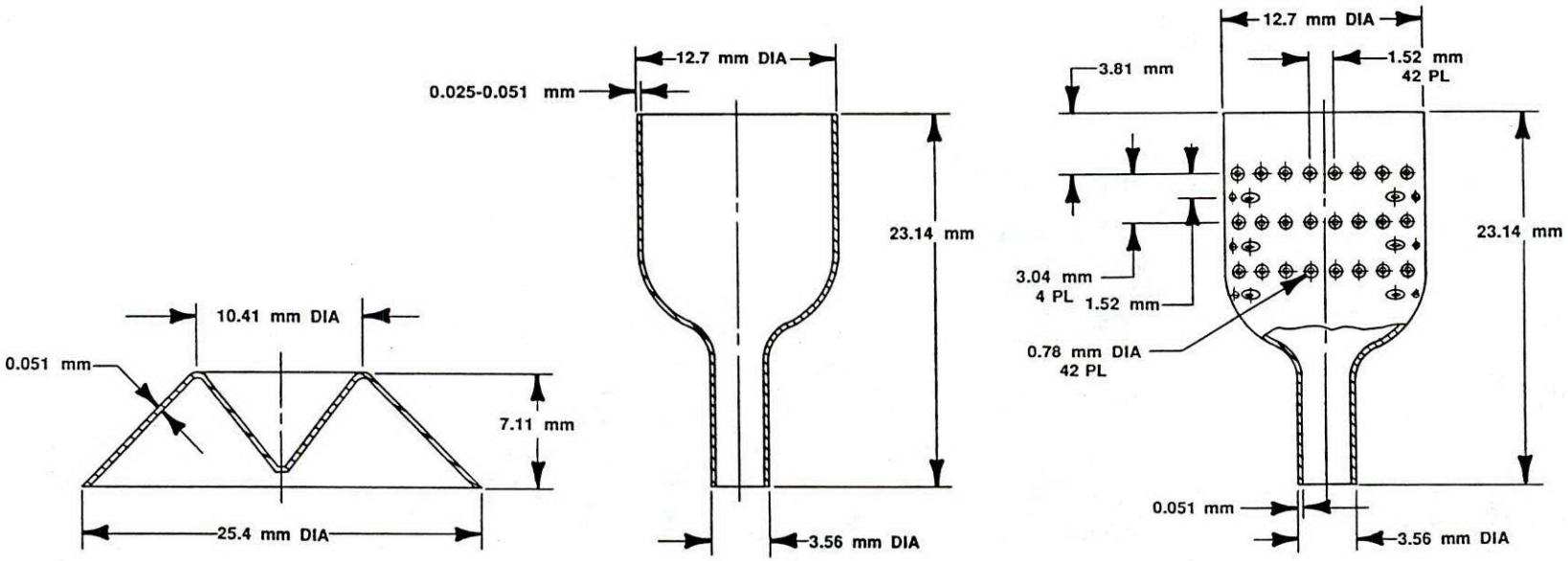

Figure 4. Design of Mass Detector Components. From left to right: W-shaped cup, filter holder, and filter.

Table II. Procedure for Fabricating Particle Collectors

1. Copper strike outside surface of aluminum mandrel
2. Insert tubes
3. Pour wax inside mandrel
4. Electrical-discharge machine tubes flush to mandrel surface
5. Apply Wood's nickel strike
6. Plate with nickel (see Table I)
7. Remove wax
8. Dissolve aluminum

copper strike prevents attack of the aluminum during the Wood's nickel strike. The wax holds the tubes firmly while the ends are electrical-discharge machined flush to the mandrel surface and also during plating. The Wood's nickel strike promotes adhesion of the nickel to the stainless steel tubing. After plating with nickel, the wax is melted and the aluminum mandrel is dissolved in a caustic solution. The fabrication steps and the finished part are shown pictorially in Figures 5 and 6.

Cable Protector

A cable passing between a curved surface and a bulkhead required protection from mechanical damage in the intervening region (Figure 7). Because of development test schedules, there was insufficient time to design and fabricate an aluminum mandrel for electroforming a cable protector. Since, however, the critical features for the protector are the flange where it bolts onto the curved surface and the location of the hole where the cable passes through the bulkhead, it was decided to mold (with clay) the part configuration onto the curved surface, with the bulkhead in position. The bulkhead was then removed and silicone material was cast around the clay model while it was in place. Later, the self-supporting silicone mold was used to cast wax mandrels (Figure 8). The wax was made conductive by painting with a silver paint. (Eventually a source was found for a silver conductive wax.) The mandrel was then masked except for the area to be plated (Figure 9). After plating with nickel to the desired thickness (0.37 - 0.5 mm) the maskant was stripped away and the wax melted. The procedure is described in Table III. The finished part (Figure 10) was delivered to the engineer within two days of the initial request.

Table III. Procedure for Fabricating Cable Protector

1. Mold configuration onto surface with clay
2. Cast silicone material around clay model
3. Pour wax into silicone mold
4. Make wax conductive (unless conductive wax is available)
5. Mask areas not to be plated
6. Plate in nickel solution (see Table I)
7. Dissolve wax

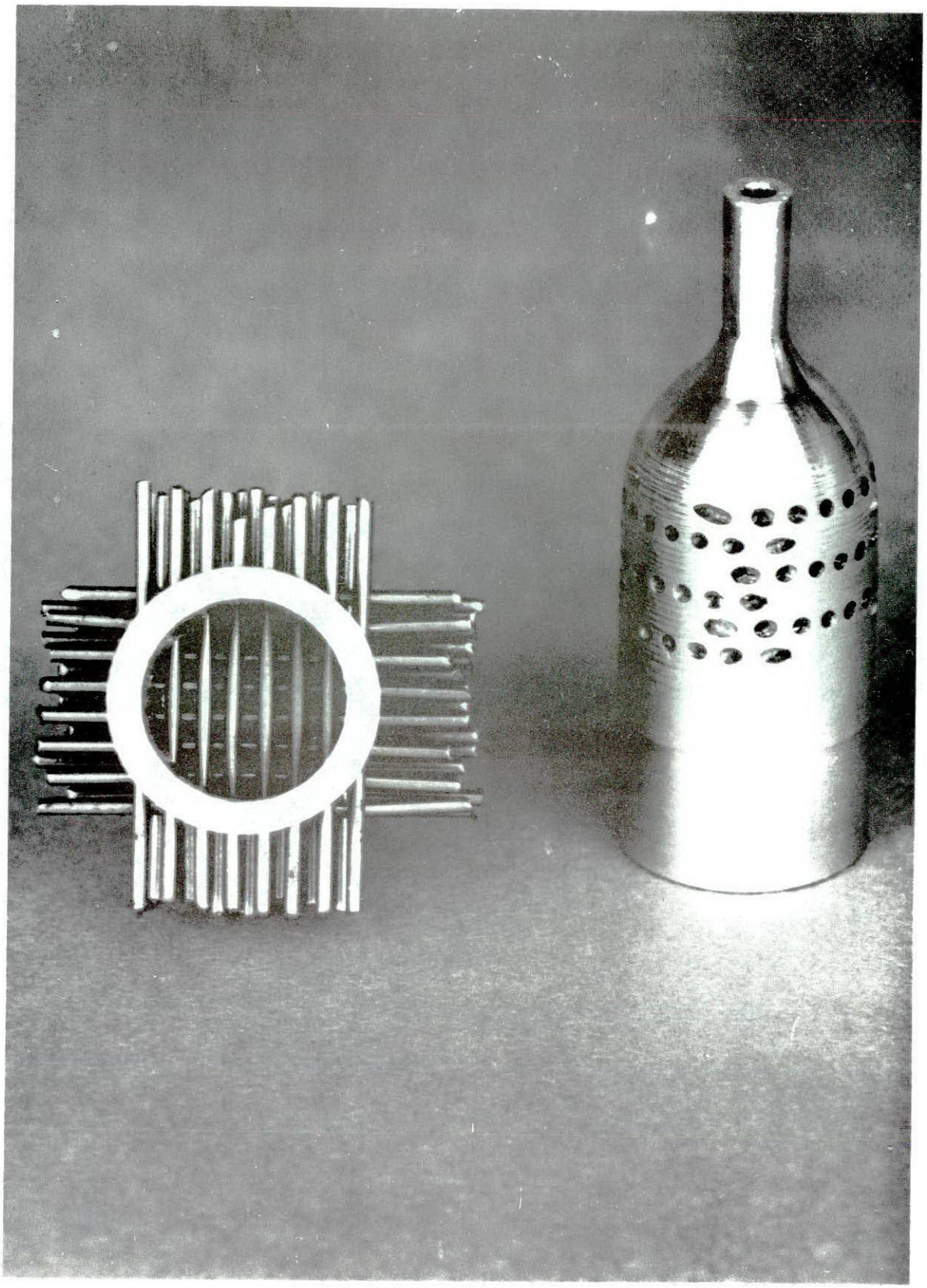

Figure 5. Fabrication of Filter. From left to right: Mandrel with tubes inserted and machined mandrel.



Figure 6. Finished Filter for Particle Mass Detector

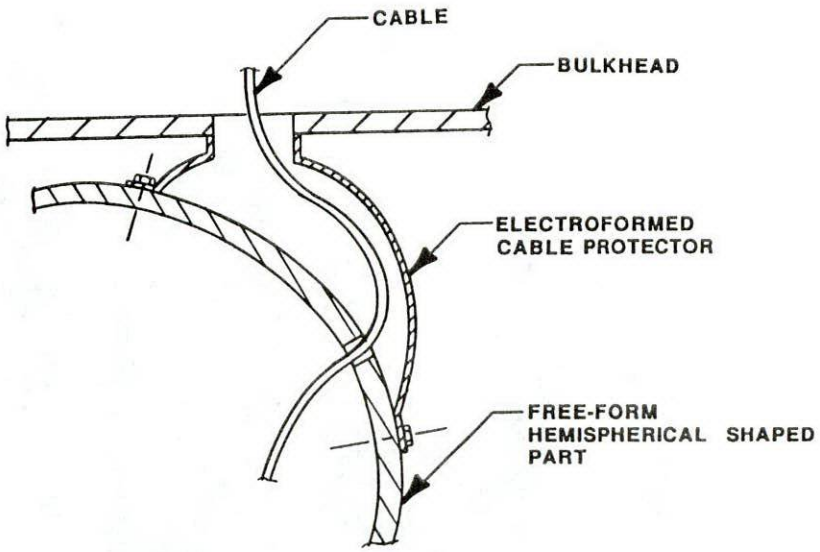

Figure 7. Configuration requiring a Cable Protector

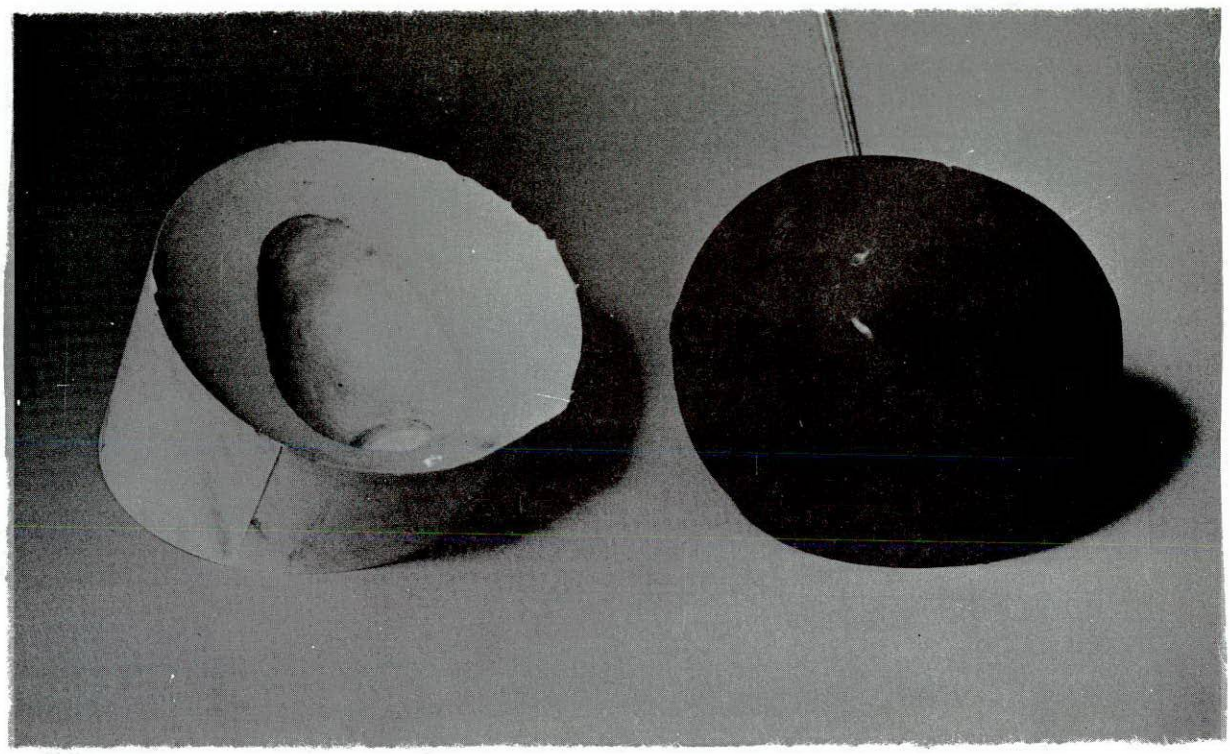

Figure 8. Silcone Mold and Wax Mandrel for Cable Protector

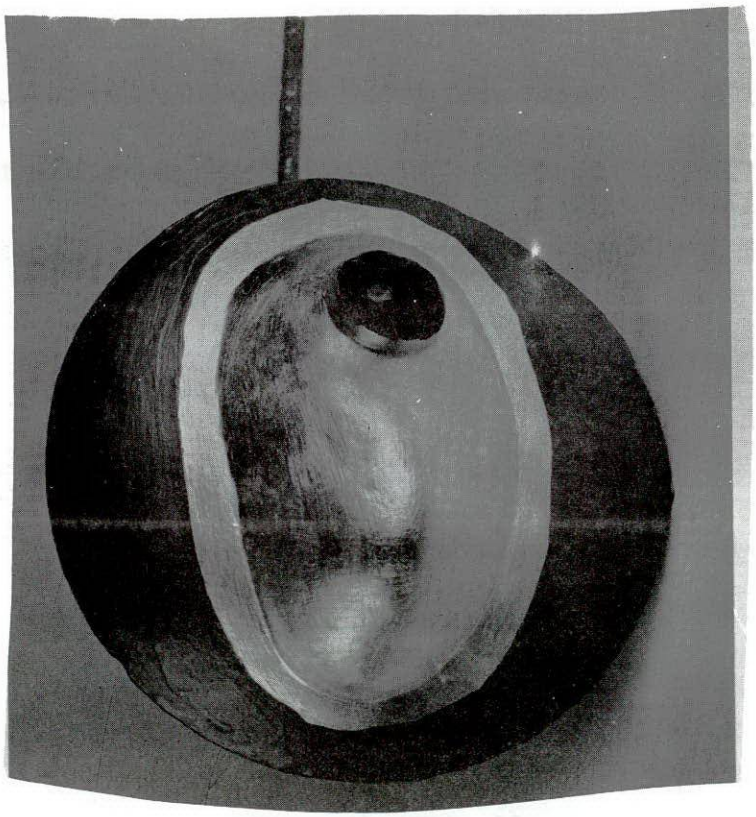

Figure 9. Masked Wax Mandrel Prior to Plating

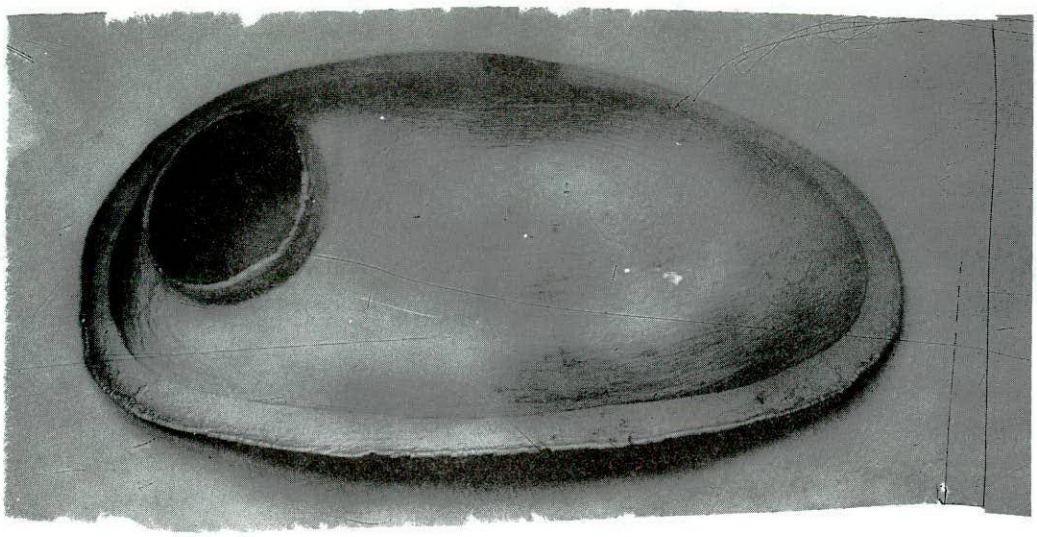

Figure 10. Electroformed Cable Protector

Filter Tube

A special filter was needed that was to be made from 6.25-mm-diameter, 0.25-mm wall thickness stainless steel tubing. It was to have holes 0.2 ± 0.025 mm in diameter, spaced every 0.5 mm, in rows spaced 0.3 mm apart. Early efforts in fabricating this part involved laser drilling of stainless steel tubing. Because of irregular hole patterns produced with this technique, as well as its cost, this approach was abandoned in favor of a photolithography/electroforming process based upon a proprietary, thick photoresist (0.025 - 2.0 mm thick) for creating straight side walls (see Ref. 5 for details).

At the time of the initial work, a thick photoresist was not available commercially and demonstration parts were made by the vendor. Later the photoresist became available to the public, and it has opened up new areas for electroforming and printed circuit applications.

The procedure for making the tubes has been previously described (Ref. 5) and is similar to conventional photoresist/plating technology. Figure 11 shows the quality of the hole patterns obtainable with the thick photoresist on nickel, which we were able to substitute for stainless steel in this application. The photoresist/electroforming technique allows consistent and economical parts to be fabricated.

Another area where we have taken advantage of the thick photoresist is in the fabrication of tensile bars for the measurement of electrodeposit properties. The results are superior to those obtained by chemical etching, since undercutting is eliminated, or by machining, since no cold working or notching is induced into the surface. Figure 12 shows some fabricated tensile bars.

Summary

We have given four examples of unusual parts that would be difficult if not impossible to fabricate by conventional machining techniques, but that are well suited to electroforming, which excels in producing strong, thin-walled parts and/or producing parts in a short time. In one of these examples, photoresist technology contributed to improved electroforming capabilities.

Acknowledgments

We would like to thank Ray Gott and Jim Rego for their assistance in fabricating the silicone mandrel, and Jack Bolen for clay modeling the cable protector.

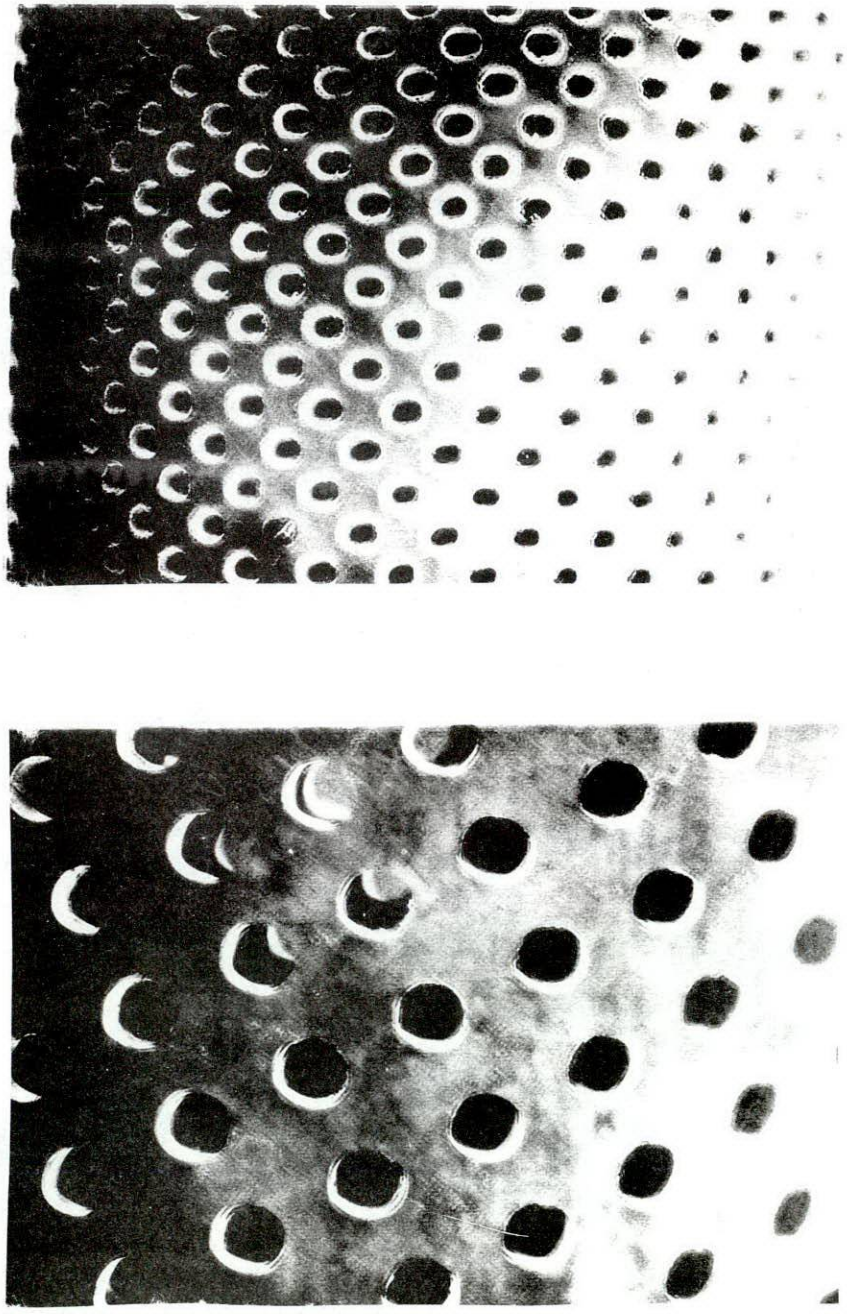

Figure 11. Hole Pattern Generated with Thick-Film Photoresist showing Straight Side Walls. Top, at 20X; bottom, at 40X.

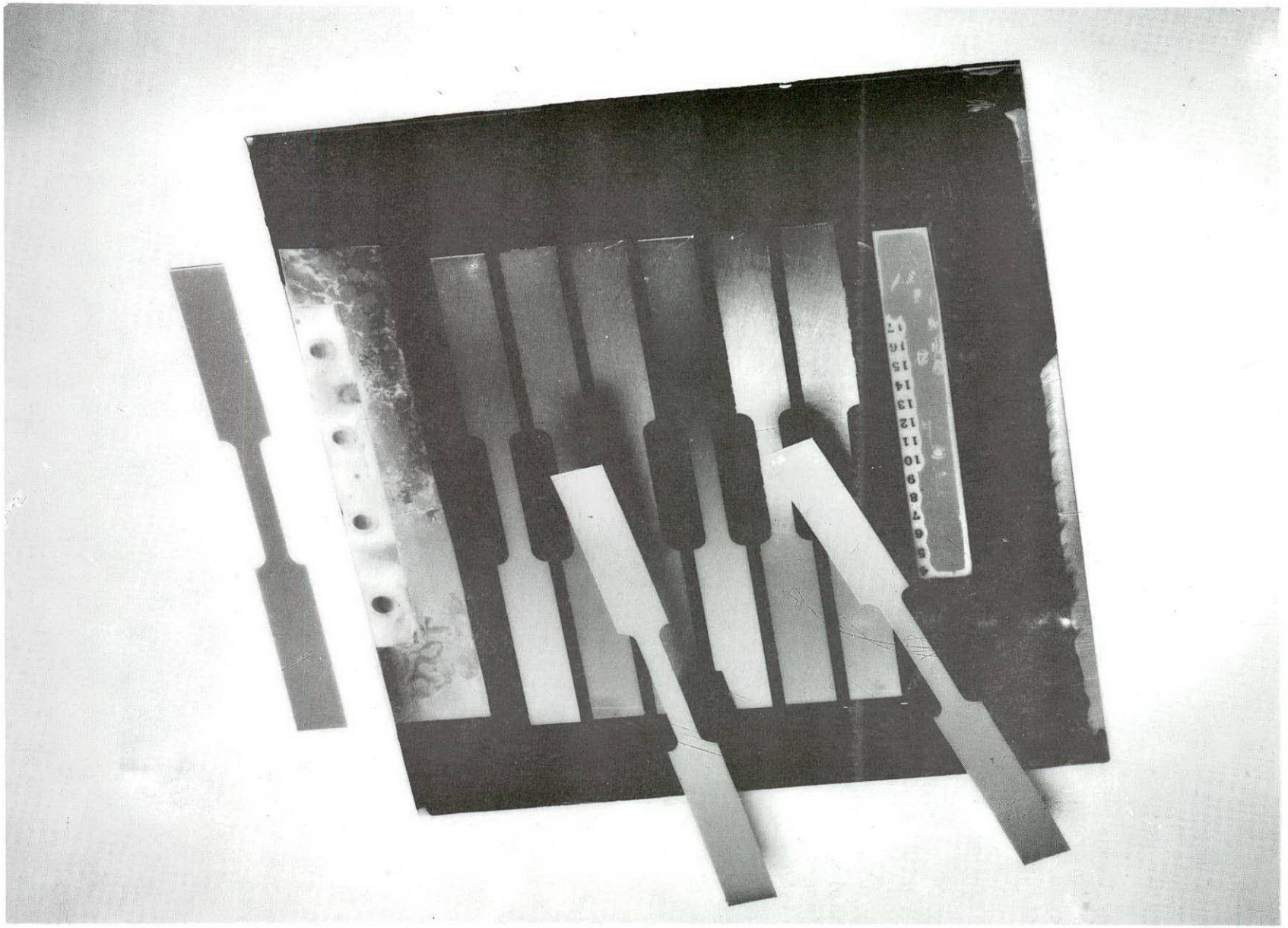

Figure 12. Tensile Bars Fabricated with Thick-Film Photoresist

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D-2

Electroforming Session D

Mandrel Making for Electroformed Holloware

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MANDREL MAKING FOR ELECTROFORMED HOLLOWARE

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Abstract: Electroformed Holloware Mandrels

While the electrodeposition activity for this research follows standard operating procedures with a copper acid electrolite, the mandrel making techniques provide the technical breakthrough that is original both for design and for the distinctive techniques that make the unique contributions of this paper. For the twenty-five examples in the exhibit there is a mixed media approach including: paper, cardboard, acrylics, plastics, marble modeling paste, waxes, organic materials, wood, found materials, stones and gems, and metal foils and light guage sheet metal. Embellishments are induced in advanced stages of electrodepositon by using resists and appliqued elements. The final products are one-of-a-kind art objects or limited editions of holloware pieces for domestic uses.

Introduction

Creativity in research is common both to the scientist and to the artist. We build on the past, move on from traditional solutions of a problem and seek new and different ways to advance the concepts of form and function.

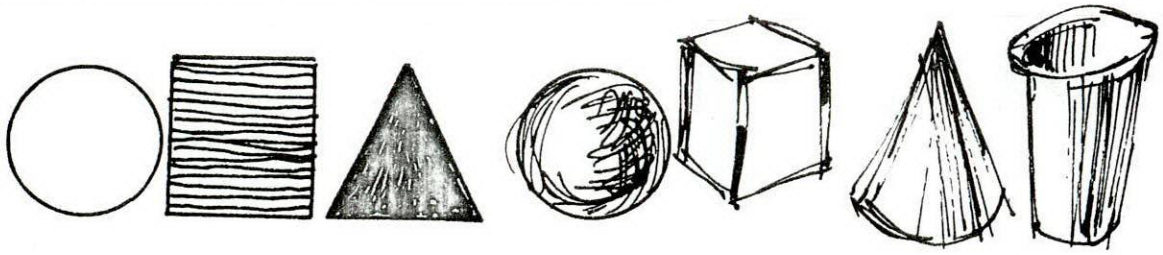
Traditionally holloware has been created by using the hammer and a multitude of stakes. In developing form, sheet metal has been used and by beating, stretching, trapping, forging and fabricating a product is created.



There are sign posts of progress to suggest adherence to visual concepts presented in renderings and working drawings. One-of-a-kind pieces result from individual pieces designed and carried through production. As man has become more mechanized, jigs have been made and chucks for spinning; stampings are accomplished with heavy equipment and standard forms are turned on metal lathes and items are electroformed over these mandrels.

In the artist studio there is still a place for the unique mandrel to be made with a one-of-a-kind product to be developed. If such a creation is chosen for mass production, it is a technical problem to adapt the form to mass production techniques. Here we have a concept that deals with the creative techniques appropriate to developing one-of-a-kind product -- a research possibly into a probable form -- one that can be enjoyed as a single work of art or which may be selected as a prototype for production if it is determined that the form has a universal appeal to justify production for a mass audience.

The challenges here are to go to the basic design forms of the circle, square and triangle or the 3-dimensional counterparts of the sphere, the cube, and the cone and the infinite variations that can be made from these combination when assemblages occur.



In search for "found objects" that can speed up the assemblage process the interest has been carried on to four different areas: (1) paper products that may be discarded by-products from the household i.e. toilet tissue core cylinder or packaging elements of boxes or circular cardboard cans; (2) plastic or synthetic elements i.e. juice cartons, yogurt cups, butter pad cups, plastic bottle containers; and (3) organic forms that nature has packaged i.e. orange skins, egg shells, banana skins, avocado pear skins, and dehydrated fruits and vegetables; and (4) is the use of thin skin metal products o.e. sheets of foil (copper or aluminum), old cans, tubes, pipes, etc. and similar objects.

With all of these there are many forms that can be used in combination to create new design forms. Basic material segments can be fashioned to create transition or to be hand fashioned to work. Products to be made under the holloware tab are any form of container for liquids or dry measure i.e. boxes, pans, dishes, bottles, vases, chalices, etc. and all of these and such structure can have unlimited number of configurations.

As these items are assembled the methods of joining are most important for good bonding is essential. It must be complete enough to hold together through the bath build up. Smooth transitions and the avoidance of voids seems essential so that a clean build up of metal may take place. When active design elements show low areas and great contrast in heights and undercuts, one must remember that these undercuts tend to build at a slower rate than direct line of sight elements facing the anodes. Sometimes special anodic units need to be placed in close proximity to build into the hidden areas.

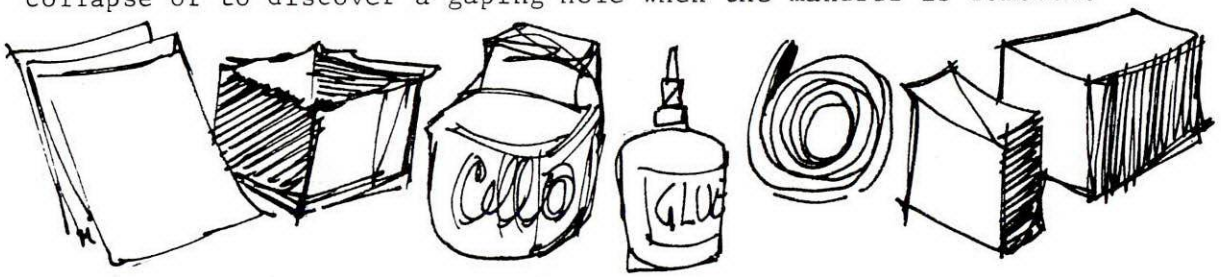
The surface coatings put on absorbent materials may be sprayed or brushed on when it comes to lacquers or shellacs with little effect to surface finishes. Often hot waxes and thick mastic coats will change the surfaces drastically thus allowing for another dimension to the final product that is formed.

When all parts to be formed are ready for the bath standard metallic sprays or paints can be used if a light binder is used or the solutions are cut with lacquer thinner or the appropriate solvent for the medium used. Sometimes a tacky lacquer will allow metallic dust to be blown onto the surface to produce the conductive surface that will excite the electroform build up.

Powdered graphite or graphite in solution can be used as an inexpensive conductive surface. A technique I find satisfactory when not too much detail is required can be done with a couple of drops of lacquer and lots of lacquer thinner mixed together with powdered graphite. The consistency control can be adjusted easily and small brushes help in a thin coverage.

Paper and Pulp

In design with paper, cardboard, cellulose, glue and tape the ideas can come rolling out and the forms can come rolling out and be developed quickly and easily. It is important to think metal as these designs are being created. Great care is needed to develop forms that can easily build to a metal form. If undercuts are part of the design, special attention is necessary to get a good throw into the recesses. Sometimes special wire or rod anodes need to be placed to give an adequate build up. There is no greater disappointment than to find an area collapse or to discover a gaping hole when the mandrel is removed.



Lightweight cardboard, heavy paper and even layered tissue can be used to develop the form. If a clay understructure is used, it should be removed before the item is put into the bath. Mandrels made of paper stock or found paper forms that are assembled into unique constructions become the bases for an electroformed holloware piece. At this point these are one-of-a-kind art form pieces. Once the build is heavy enough for the piece to stand by itself the mandrel is removed, the details of the form are checked and additional parts can be soldered in place or elements glued in place and made electric conductive by painting and put back into the bath for final electroforming.



In the creative process the part that is so exciting for the designer is the search and find, the adaption and the relationship of the parts, the bridge and transition the expression and communication. Part of the design is dictated by the forms that are used and the theme of the creative expression. Unity is brought about by the use of mastic glues, pulp, wax and the smaller elements employed to produce the meaningful message. Once the elements are in place the thought is given to make the mandrel electroconductive and to attach it to the wires so the structure will build to a desired thickness.

Examples of vases, candle holders, chalices, mugs, porridge bowls and decorative parts are some of the holloware forms to be made. After the basic form is built the addition of handles, feet, hinges, latches, etc. .. all will contribute to the finished expression. Chemical and physical finish take care of the surface quality and plating with bright nickel, gold, silver, tin, or whatever enhances the final effect. If food and liquids are to be put into the containers, special handling to keep items safe and to make sure that there is no leakage of liquids is essential.

In organizing the found systhetic element there are ways of assembling such as the use of rubber cement, acrylic glues, super glues, or hot glues. Adhesive or bonding tapes also can hold pieces together and the transitions in design can come by using cellulose fiber made into a clay like mixture and waxes can be used to smooth the transition from one part to another.

Applied design or dimensional space can be provided by using elements to create the dimension and wax forms, here again, can give a transitional flow by blending with hot tools. In all instances it is desirable to design form so that there is no undercut so that consistent thickness may be maintained.

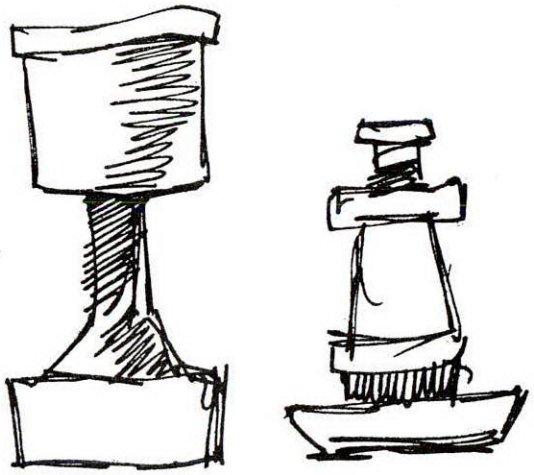
After the design has been completed and electroconductive coating is applied, an inexpensive procedure is to use graphite powder mixed with a lacquer solution that has been thinned down at least three to one with lacquer thinner. If the model material will not be destroyed by the lacquer, a complete coat can be painted or sprayed on to give a complete surface coverage.

Plastics and Synthetics

If you have ever found pleasant forms in plastic bottles and containers interesting contours in products for use with foods or interesting relationships of different container together, then you have an idea of what is the basis for this section on plastics and synthetic materials. Such things are elements from which models can be made by con-



structing, assembling found objects, altering and relating parts in an unexpected combination of forms in a new configuration. Such mandrels take advantage of prefabricated parts that are combined to make the mandrels for a unified form. Of special concern are the points of



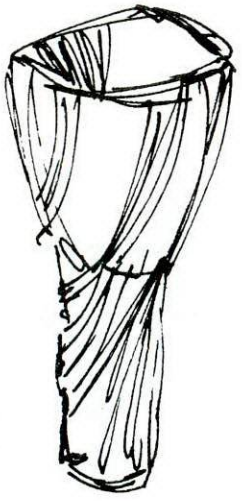
contact and the free flowing transition from form to form. All decorative elements such as the straws in the illustration need the transitional smoothness to insure a uniform build up and to avoid "blind spots" where little or no build up will take place.

In searching for ideas there are some basic considerations that help to organize the process. The circle, square, or triangle (observed as sphere, cube, cone or cylinder) and the combination forms are used with design principles of rhythm, balance and proportionate emphasis to develop a complete expression. Surface textures can be made with modeling paste or wax and the applique of designed pieces can enhance the aesthetics of the piece.

Now that the form is settled the electric conductive surface is established and attachment wires are put in place.

When the piece is put into the copper sulfate/sulfuric acid electrolite bath it should be set at a low amperage of 2 or 3 amps and monitored for the first several hours. The author will often leave items in the bath for 7 or 8 days for this first phase of electroforming.

After the basic build up the synthetic mandrel is eliminated with heat in an oven or by torch. The elements that are thermo plastic often can be heated until they start to melt and the parts can be removed with tweezers or tongs. Further heat may be necessary to burn out tape, pulp and elements that may be thermo-set. Once cleared out tests should be made for solid and sealed containers, especially if the final product will have to hold liquids. At this point should any pin holes or incomplete areas of build up be noted, patches should be made. Those of a delicate nature may have to be reestablished by using tape and wax. New electroconductive surfaces will be needed to recover the problem area. The repair can be done by solding metal elements. A careful blending of these parts is necessary.





Stone setting and findings or handles, spouts, bases, or feet may be put in place once the base unit is ready for phase 2 build up. After another extended period of build up (with inspections at least once an hour) leave until the structure is as heavy as you wish it to be.

After removal from the bath a careful evaluation should be made to determine its state of finish. If all is well, continue into chemical cleaning, wire brush and soap and water buffing and chemical or manual polishing. Going into bright nickel and then a gold, silver, rhodium, tin or chrome finish will give us a finished piece of holloware.

Organic: Vegetable or Animal

Organic materials can be used to advantage in the creation of hollow forms. Part of their charm is in the fact that natures formation of texture, line, and form can be used as focal elements and that the man-made additions create a more subtle transition from the original character to a new functional product in metal.



If natural elements are fresh and come right off the plant, they can be put into the bath after having been made electroconductive. If the elements have been dehydrated or dried, it will be necessary to make them inpervious to the liquid bath. After varnish, wax or surface changes have been made, they can be beautifully employed with other materials to preserve their character for the electroformed build up. It is practical and proper to eliminate the mandrel after electrodeposition to avoid a carryover of contaminated parts and to have a completely metallic creation.

Since often mandrels of this sort are developed by using wax or other materials when using dehydrated fruit and vegetables, they need to have a protective coating or surface impregnation to keep them from absorbing the electrolite solution.

Thin parowax can be used to protect a surface before the conductive coating is applied. Paint on hot wax and put into a warm kitchen oven to heat soak and eliminate excessive wax materials so that the natural testure can remain on the surface. A thin solution of lacquer may be used instead of wax if an extended period of time is allowed so that the organic material becomes saturated with the lacquer.

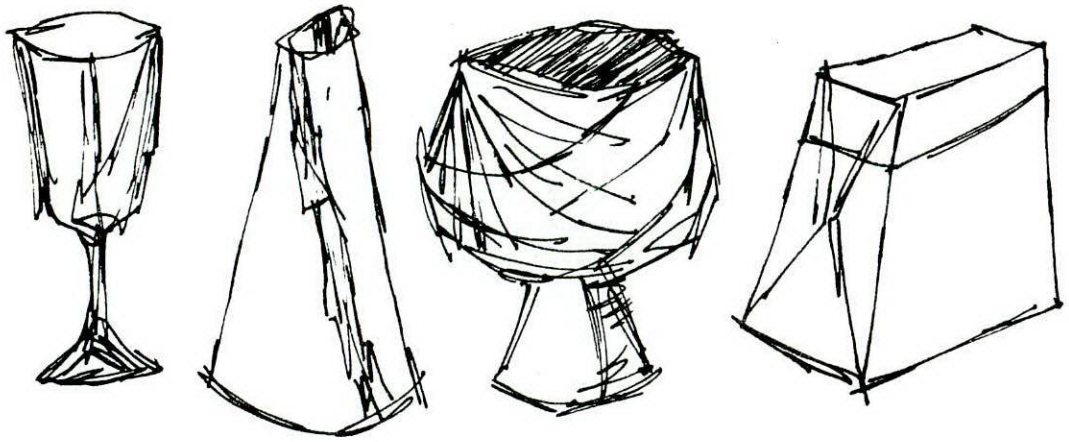
Even a pin hole or a bubble can be enough to turn the dried element into a sponge. If a good conductive surface has been put on the mandrel, the build up can be rapid enough to avoid distortions or broken contact of a surface that would be changed by absorption of the bath. If such a metal surface builds solidly, the piece can remain in the bath until a thick enough build up is completed.

In the mandrel making phase the size of the form will dictate proportions and the size of the final metal piece of the holloware form.

Metallic

While electroforming is primarily done over mandrels that are removed there is that area of activity where light metal foils and tooling copper, shim stock, brass and aluminum foil can be used as the basic model, and the build up is on top of this form.
These materials are easily formed by hand or by pressing into molds or over stakes. Once an adequate model is formed the inner structure (already electroconductive) is attached to the negative terminal and built over on both sides.

If the original form is not assembled, the parts may be soldered together after basic build up. Resist materials such as tape, asphaltum varnish, hard-fired enamels and resin materials may be used to develop pattern or texture treatments. Even after these resist materials are removed a new total skin can be built over everything to make it a solid structure.



If these resists are so placed that the build up is on a flat surface or in spots, the surface build up acts only as a new piece of metal and does not have a molecular bond to the base form. Any vibration will cause it to pop off the surface after the resists have been removed. In order to insure that it will exist as a permanent part either those elements so built will have to be soldered in place or if they stay, attached before being disturbed; it will be necessary to do an overbuild of a complete new skin to lock over edges, around corners or over the base form. This new skin will encase and build evenly over all parts -- background and texture or surface embellishment. A thin plate will leave a distinct and clear pattern but if the overbuild is allowed to remain for a longer period in the bath, the surface will smooth out and level the build up.

A thin metallic surface provides a base where non-metallic elements, such as gem stones or appliqued forms may be glued to the surface. Conductive paint can be painted on these items to make prongs, bezels or coverings over the pieces and the build up will lock the items into place as the forming continues.

Metal folding, crimping, box forming and shell shapped forms can be very direct hollow forms. Since the thickness doesn't allow much stretching, the overlapping or bending of parts will largely dictate a kind of form that can be made.

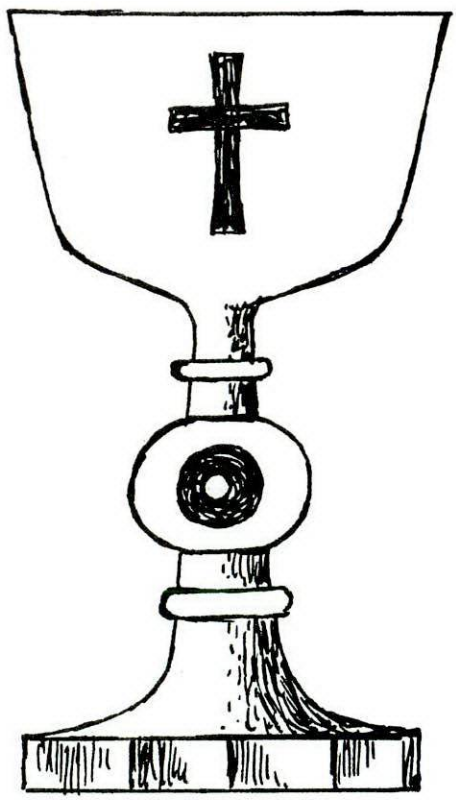


Conclusion

In creating mandrels for hollow forms the idea, the expression, the communication, the function and the materials start with design and the relationship of the elements used in concert with the principles of rhythm, balance and emphasis. All factors working in harmony are essential for the successful, completed product.

The potentials are here for an infinite variety of creations. The grand situation is that through the electroforming process that a greater variety of hollow forms in metal can be rapidly realized more than by most other one-of-a-kind creative forming methods. It has its own unique contributions to make to the art world that springs from the techniques used for the mandrel making and which come from the materials used in the processes.

As one works the ideas into mandrels there will be a set of personal preferences that the worker will build and a set of practical rules that he will invent to guide him through the creative process. It is a very rewarding area of creative activity.



D-3

Electroforming Session D

Precision Electroforming for Optical Disk Manufacturing

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PRECISION ELECTROFORMING FOR OPTICAL DISK MANUFACTURING

Carl M. Rodia, C.E.O.

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Abstract

Precision electroforming in replication of optical discs is discussed with overview of electroforming technology capabilities, limitations and tolerance criteria. Use of expendable and reusable mandrels is treated along with techniques for resist master preparation and processing.

A review of applications and common reasons for success and failure is offered. Problems such as tensile/compressive stress, roughness and flatness are discussed. Advice is given on approaches, classic and novel, for remedying and avoiding specific problems.

An abridged process description of optical memory disk mold electroforming is presented from resist master through metallization and electroforming. Emphasis is placed on methods of achieving accuracy and quality assurance.

I. Introduction

I have made many presentations on disk manufacturing over the past fifteen years. And I have found that the electroforming process is the most misunderstood and probably the most maligned of all the major steps in the mass production of disks.

Of the major process steps required for optical disk manufacturing, electroforming is looked at as the least controllable, the most difficult to automate and a very unpredictable thing indeed. It is also potentially the dirtiest process, involving open chemical vats, hot, fuming green and orange liquids and potentially sloppy work areas when compared to the pristine computer consoles and work stations associated with disk mastering and molding operations.

Yet no other optical disk manufacturing process offers the relative simplicity and low capital cost that electroforming does. Through all the changes in the disk industry from 78, 45 and LP records to compact discs, OCD and DRAW disks, the electroforming process remains remarkably reliable and intact, although new techniques and monitoring technology have gilded the lily.

It's somewhat ironical that disk electroforming processes, being wet and messy, don't seem to mix well with the clean room style of optical disk manufacturing, yet in actual practive, clean room requirements for electroforming of optical disks are usually lower than the other major processes, owing to the fact that rinsing and chemical cleaning operations can wash settled particles of dust off of sensitive surfaces. For example, acceptable background clean room levels for CD electroforming are Class 10,000 with local Class 100 laminar flow sources over the baths. I think I can safely predict that these requirements will be relaxed even further as we in manufacturing move along our rapidly sloping learning curve and as manufacturing engineers bring these processes up from their tender R&D roots into the realm of cost competitive manufacturing processes.

II. Theory

Electroforming is well-suited for optical disk mold manufacturing. In the process, an exact negative image of the CD, CD-ROM or DRAW pre-grooved resist master surface is produced in solid metal. The metal, negative image can be used in a molding machine to press numerous positives into suitable plastic. Electroforming is excellent for this process because it involves the deposition of metal, atom-by-atom, onto the microtopography of the ROM, CD or DRAW pre-grooved resist master's surface. Metallic crystals are grown rather rapidly by the process, atom-by-atom, as the metallic ions dissolved in the electrochemical bath surrounding the substrate are reduced, becoming metallic atoms of a lattice crystal, by the electrochemical process taking place in the plating cell.

In this model of a simple electrochemical cell we can see an electrode system comprising:

1) An electrolyte or metallic salt solution (Nickel Sulfamate) contained in a vessel made of a compatible material.

2) An electrode system in the vessel including a cathode (negatively charged plate) onto which metallic ions from the electrolyte (Ni^{++}) will be reduced to atomic members of a new metallic crystal.

3) A power unit for supplying direct current (D.C.) to the cell and an anode made of the metal whose salt is dissolved in the electrolyte. In our case the anode will be solid Nickel. Since the Nickel metal salt of the Sulfamic acid, Nickel Sulfamate, is the basis of the electrolyte, the anode serves as a source of metal ions for the replenishment of the electrolyte solution.

In this way, chemical stability is maintained in the cell, anode material is depleted and solid metal is deposited at the cathode, conforming exactly to the microsurface topography of the cathodic resist master immersed in the electrolyte.

This equilibrium is not 100% efficient. There are side reactions that occur in the cell. By-products, soluble materials other than solid Nickel, are produced at the cathode. These can enhance or hamper the chances for success, depending on their nature and concentration. But for now it is sufficient to note that some of the by-products are alkali so acid is consumed. Additionally, sludges are formed at the anode. Both must be checked if proper results are to be obtained.

Consumption of acidic radicals ions, resulting in a rise in bath pH, must be compensated for by acid additions. In conventional electroforming, sulfamic acid is added. This adjusts pH and replaces sulfamate radicals which are consumed in the anodic reaction and are essential for maintaining stability in the system. Sludges produced at the anode usually comprise undissolved intergranular materials such as Nickel Sulfide or carbon. The nature of the sludge depends on the type of anode material selected. Most commonly, Sulfur-depolarized nickel is used as an anode material. This anode material is electrolytic and contains a small amount of intergranular sulfur to enhance solubility of the anode.

III. Techniques

In order to accomplish the electroforming of a precision disk mold - a negative replica of a microsurface - we first need a master or mandrel of the CD-ROM, Digital Audio, or DRAW pre-grooved surface, which we would like to duplicate. This substrate or master must have certain special characteristics if electroforming is to succeed.

1) It must be mechanically stable. (Able to support itself in the electroforming cell.)

2) It must be dimensionally stable and accurate. (What we put in is what we get out.)

3) The master must be made of a material compatible with all subsequent process steps.

The surface of the substrate must be electrically conductive on its modulated side. This is obvious. Electrochemical processes depend on a D.C. and potential being present. The electrically conductive surface must, too, be compatible with the subsequent electrochemical process conditions. This usually means that the conductive material selected must be chemically indifferent to the mildly acidic nature of the electroforming baths into which it will be immersed. Hence the popularity of relatively passive Silver, Gold and Nickel in the metallizing step.

Thirdly, there must be a means of making a cathodic (-) electrical connection to the conductive surface of the substrate while it is in the electroforming bath. This connection must not shade, mask or otherwise interfere with the surface to be replicated, so it usually ends up in the center or on the edge or back of the resist master.

Fourth, there must be a special electroforming cell in which the mold can be successfully formed on the conductive surface of the resist master. This cell can be as simple as a rectangular vat containing the bath chemicals, temperature control equipment, anodes, etc. But in most cases it is an elaborate, highly specialized electroforming system designed especially for disks. These systems are engineered to optimize the quality of the electro-deposit and give special attention to the criteria important in optical disk manufacturing.

The more advanced precision optical disk electroforming system will have microprocessor-controlled power supplies. The operator can carefully control and monitor the rate of plating and the quality of the Direct Current delivered to the electrodes. The system will include an anode system which takes into account the importance of containing anodic sludges. It will include a rotary cathode holder capable of rotating the resist master in the tank at various speeds and parallel to the anode plane. And it will include bath maintenance systems such as an electrolytic purification system and a fine filtering system capable of removing all particles as small as 0.2 microns absolute from the bath.

A successfully electroformed optical disk mold should have an extremely smooth back surface with a microsurface topography with mean peak height of 6 microns or less. The surface should be free of nodules.

The system should also include some means of producing an extremely flat electroform within the specifications required for optical disks. This spec is plus or minus 3 microns.

There are various techniques for producing extremely flat plates. Most manufacturers prefer the use of electrode shields. In any case, this problem must be addressed by the designer of the electroforming equipment system or the processor.

Given the task of replicating a microsurface topography many hundreds, thousands, or hopefully, millions of times, electroforming has been conventionally called upon because inexpensive, highly precise negative plates or molds can be made by the process.

There are various criteria for success in this endeavor, all relating ultimately to the criteria established for what makes a good optical disk. Among these criteria are flatness, smoothness and dimensional precision.

IV. Processing

I'll now lead you through a step-by-step description of the optical disk electroforming process. I'll skip carefully over the conventional aspects of the process, in the interest of conserving time, and concentrate on those special aspects that are most interesting to the manufacturer of optical disks.

1. Resist masters

The resist master, prepared in a conventional manner, will typically be an optically flat glass disc 8-12 inches in diameter, coated on one side with photo-resist material. The coated disk is exposed to a pulsed or guided source of laser light of appropriate wave length, then chemically treated with developers to remove exposed resist material, leaving behind the microsurface topography in the resist representing the information requiring replication. The glass substrate and the resist information on its surface comprise the resist master. These masters are costly, quite fragile and are damaged easily by handling.

It is the job of manufacturing to make relatively low cost, durable copies of this master surface.

Molding has long been the common mass production technique for disks in the the phonograph record industry. Since there is a wealth of experience to draw upon in the areas of precision molding and in precision mold electroforming, there has been an obvious bias towards molding methods when planning for mass production of optical disks.

2. Metallization of resist masters

As stated earlier, the resist master surface must be made electrically conductive in order that electrolytic processes can be used to produce the metal negative. Usually a thin film of Silver or Nickel is vacuum deposited onto the resist master's surface to accomplish this. Wet chemical silvering has also been used, but that process usually requires chemical pretreatment with alkalis that can damage the resist surface. In any case, vacuum deposition works well and deposits have the advantage of being very thin and reflective making testing of the resist master possible before electroforming if required.

3. Preparing the metallized resist master for electroforming

Once a conductive film has been established on the master's surface, electroforming can begin under proper conditions. The metallized master is placed in an electroforming cell - usually on a cathode fixture designed specifically to hold the resist master. The cathode fixture makes electrical connection to the metallized layer and rotates the master in the cell. Connection to the metallization layer is often made at a center hole. This type of connection serves as a mechanical holder and electrical contact. Some systems use masters with no center hole. Various novel connection methods can be suggested in this case such as edge contacts and back contacts. Proper electrical contact is very important. The greater the contact area, the better. This allows for the widest distribution of current over several connectors and helps reduce the chances of burning of metal film from the master surface during subsequent electroforming.

4. Pre-plate

When the master is securely fastened, mechanically and electrically, to the cathode plate, the pre-plating electroforming cycle can be started. Pre-plating is basically very careful, very slow electroforming. The initial layer of Nickel metal is deposited onto the metallized resist master surface in this stage of the process.

The picture shows a Polyform precision disc electroforming system which is equipped to handle pre-plating electroforming as well as higher speed electroforming on disks up to sixteen inches in diameter. Other system may use separate pre-plating equipment. But with Polyform equipment pre-plating electroforming of the metallized resist master can be accomplished in the same vessel as the high-speed electroforming that will follow.

Pre-plating must be started very slowly. This is to prevent burn-off of the metallized layer at the point or points of contact, and alos to establish a finely-grained deposit of Nickel at the interfacing plane of master and electroform.

Typically the electroforming will be started at 0.3 ampere. This condition continues for approximately fifteen minutes as Nickel gradually builds up on the surface and around the points of contact. The Nickel adds to the conductor on the surface and so the current can be automatically raised gradually.

In the pre-plating process, Nickel deposits slowly on all the metallized surfaces of the resist master.

5. Electroforming

After pre-plating, sufficient Nickel has been deposited on the metallized resist master to make it a reasonably reliable conductor for electroforming current. High speed processing is now possible. After pre-plating and before higher speed electroforming commences, an edge masking ring is placed on the master. This ring prevents further build-up of heavy Nickel on the edge of the master that would make removal of the electroform from the substrate difficult. The masking ring has "O" Rings or other seals to stop-off the plating bath from edge and back.

The masking ring in place, electroforming can now be started. The process rate is determined by the quantity of current supplied to the electrode system. Generally, optical disk matrixes are electroformed at a rate well below the potential speed level. Usually, the automatic power supply of the electroforming system is programmed to gradually raise the plating current as process time progresses. Electroforming continues as the programmed current rises until the desired plate thickness is obtained. This thickness averages 12 thousandths of an inch for optical disk molds.

A normal electroforming program for plating current may begin slowly and gradually ramp up from a lower plateau of 50 amperes per square foot to an upper plateau of 125 amps per square foot or more. These rates not only help complete the electroforming quickly but also establish two zones of Nickel in the deposit with differing metallurgical properties that compliment each other. For example, the zone deposited at lower amperage may be slightly stressed compressively while the higher speed deposit may be slightly tensily stressed. The resultant concellation of stresses produces an unstressed composite mold plate.

At the end of the cycle, the power supply system is programmed to shut off automatically, lift the cathode out of the bath, and reset for the next plate.

The masking ring is removed, the resist master with its interfacing Nickel metal negative is disconnected from the rotary cathode holder, and the Nickel plate is gently pried up from the master's surface.

When the Nickel is removed, with it comes the Silver (Nickel or Gold) metallized layer. This layer is now metallurgically bonded to the electroform.

Up to this stage of production, we have the resist master, which has been virtually destroyed by the separation process, and the silver-faced negative Nickel electroformed replica of the original.

It would be very easy at this point to clean off the traces of resist adhering to the metal negative and use it to press many positives. If this is done, however, wear or damage on the negative would necessitate a new mold be provided and we would have to start all over again with a new resist master. That would be very costly indeed.

Instead we will opt to produce many generations of subsequent metal positives and negatives by electroforming, using the first metal negative as a permanent mandrel or metal master. In this way we can, through electroforming, make at least one metal positive from the first metal negative, and from that permanent metal positive (called a Mother) produce many new metal negatives called Stampers or Sons. The Sons can be used as molds to press hundreds or thousands of plastic optical disks. If the Sons wear out or are damaged, they are scrapped and others can be made from the permanent Mother or positive. No costly recutting of a resist master is required. This generation process "tree" is very common in phonograph record manufacturing and in compact digital audio disc manufacturing.

The electroforming processes used to produce each generation are basically the same, although the pre-plating process is only required for metallized resist masters.

V. Problems and Remedies

Now, with these basic process descriptions behind us, I address some special problems and special solutions associated with optical disk mold electroforming.

Electroformed optical disk molds must be exact negative replicas of a resist master substrate. Normal electroforming will replicate the information or microsurface topography exactly, but as we move away from the interfacing surfaces of master and electroform, major changes commonly materialize that can yield molds totally unsuitable for precision dis c manufacturing. Extraordinary control methods are used to correct or compensate for such problems.

The basic problems I'll discuss are:

1) Flatness,

2) Internally stressed molds, and

3) Roughness on backs of molds.

1) Flatness - The optical memory disk must be flat to within a very few microns. Obviously, flat disks cannot be molded with anything but flat electroformed molds.

The laws of electricity dictate the distribution of metal as electroforming takes place. Plating occurs faster in areas of high current density or areas of lowest electrical resistance. Since we are working with a disk shape, it can easily be seen that the areas of least resistance to flow of electricity on a disk's surface will be the edge where most of the material is located. Since most of the current flows around the perimeter of the disk in the electroforming cell, it holds that the current density, and hence the rate of plating, will be greater in these areas. This results in uneven distribution of Nickel along the cross sectional radius of the disk with the bulk of the metal depositing around the edge of the disk. This is true no matter where the electrical contact is made on the mandrel disk.

Now, if we were to use such a disk mold with its dog-bone cross section, it would yield a distorted optical disk. The mold must be flat if the disk is to be flat.

The obvious solution to producing flat electroformed molds is to make the electrical resistance equivalent at all points across the surface - in spite of the edge effects mentioned earlier.

This is most easily affected by increasing the resistance of the cell between the cathode and anode around the edge with a baffle or shield, which is roughly circular in shape. The shield's opening is smaller than the cathode, so it adds resistance around the circumference. The distribution is optimized in this fashion.

Other things effect flatness, especially when we are considering flatness to plus or minus three microns tolerance. At optical disk tolerance levels, plain circular baffles have not been consistantly successful probably due to the nonlinearity of the current distribution from center to edge of the disk. Lamniscate shapes have proven useful as have hearts and stars.

At optical disk tolerance standards, the degree of bath agitation and speed of cathode rotation have proven to be second order effects. My work on flatness has shown that for best results one must keep agitation mild and diffuse, and cathode rotational speed low with the cathode mandrel fully submersed in the bath. Use of a lamniscate-shaped opening in an electrode shield to compensate for the edge effects is also highly effective. With these conditions optical disk molds can be produced flat to plus or minus three microns consistantly at high, medium or low current densities.

2. Internal stress in metal molds

Sulfamate Nickel electroforming chemistry is specifically formulated to produce stress-free (or at least low-stressed) deposits of Nickel. The Sulfamate Nickel process is extremely sensitive to contamination by organic impurities and metallic ions which, if present, even in trace amounts, will greatly increase the internal stress of the electroformed deposits.

Stress in disk mold electroforms manifests as warped plates which tend to spring slightly away from the substrate in a tensile stress situation or curl slightly inward towards the mandrel in a compressively stressed plate. Both types of stress are undesirable.

A good rule to remember with Sulfamate Nickel baths used for optical disk electroforming is not to add anything but water and sulfamic acid on a regular basis. Any additives designed to enhance performance generally will decompose and act as contamination.

Removal of bath impurities responsible for inducing stress can require time-consuming, messy batch treatments or worse. There are some stress inducing contaminants, such as Ammonia or Sulfate, that are not only indicative of stress but are also the sure sign that bath chemistry is not functioning properly and that serious trouble-shooting is required.

3. Roughness

Rough backs on electroformed disk molds are a major source of rejected metal parts and, if undetected, a major cause of rejected disks. Roughness comes in a variety of forms, ranging from a grainy or sandy texture on the back of an electroformed mold, to a surface pocked by relatively large nodules.

Like other quality problems in electroforming, there is more that one cause for roughness. Basically, the sandy or grainy texture on the back of an electroformed mold is caused by a chemical inbalance in the system, resulting in low efficiency. A common cause of this phenomenon is a passive anode system. Passive anodes have many causes. Certain types of anode material are prone to passivity. They include electrolytic chips and carbonyl pellets which are classically very pure, and hence relatively insoluble representatives of the Nickel anode materials list. These anodes are popular with some due to their relatively low sludge content. They are not worth the trouble in this application.

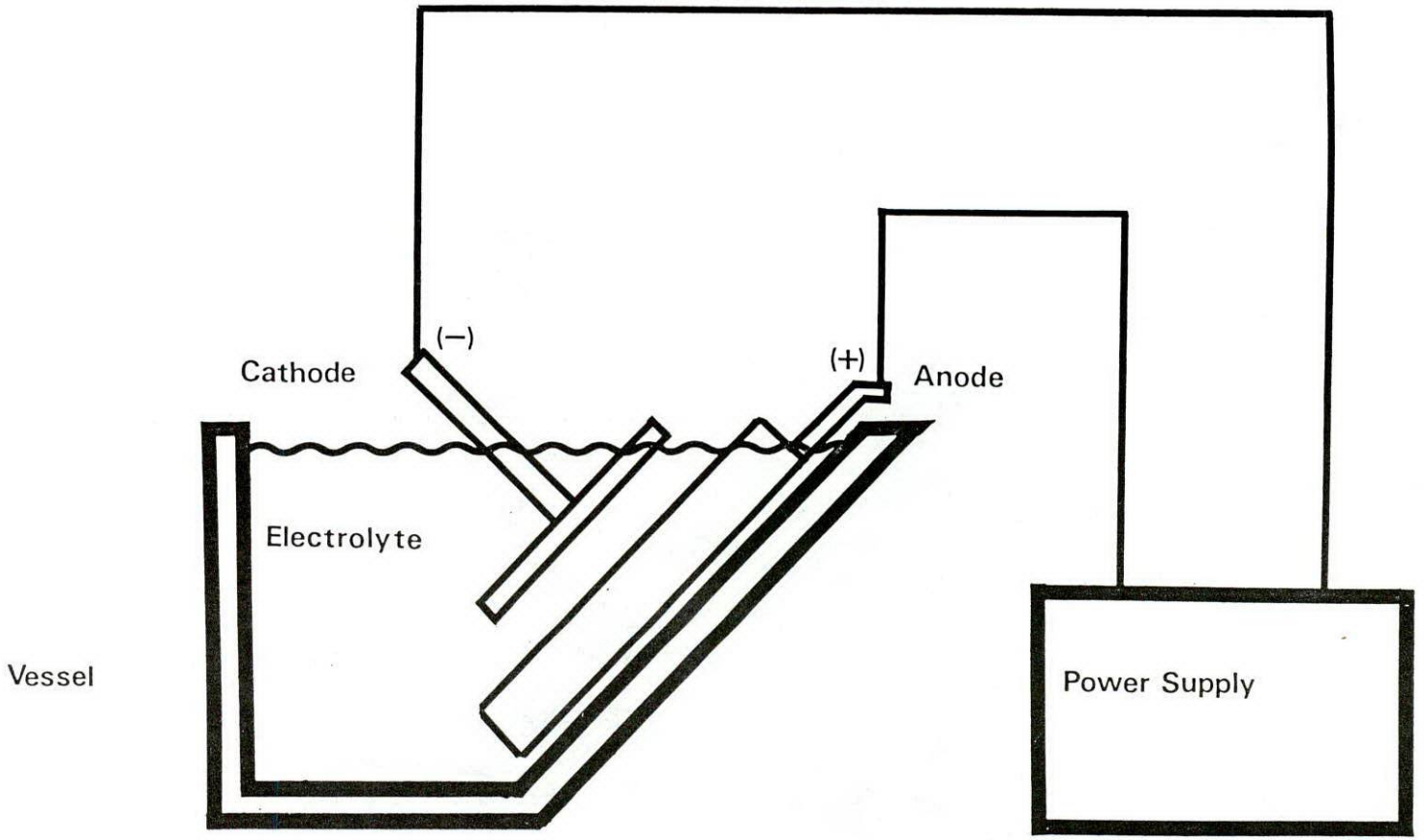
Remedies for this situation include adding chloride or bromide to the bath to accelerate anode dissolution or simply a switch from low-sludge, pure materials to sulfur-depolarized Nickel. Sulfur Nickel is more soluble but it produces an undesireable sludge by-product during electroforming. Particles of this sludge, if not properly contained or removed can adhere to cathode surfaces and nucleate larger nodular growths.

Anode bags over Titanium anode baskets are used to contain sludge. In addition, fine filters are used to remove sludge particles that do escape along with other suspended solids that find their way into the bath wich are potential sources of nodule nucleation.

In state-of-the-art electroforming systems, a submicronic, absolute filtration system designed to filter the entire bath around ten times per hour are employed to keep the bath free from solids and the rough backs to a minimum.

As expected, cleanliness is the key virtue to be observed in optical mold electroforming. But I'm sure it is obvious to you that with all these wet ambient conditions, pre-cleaning and rinsing opportunites, it's a lot nicer than other parts of the process.

More important than strict clean-room habits are strict Q.C. of raw material purity, filter maintenance and reliance on user friendly, automated equipment systems to monitor process parameters.



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D-4

Electroforming Session D

New Developments in Electroformed Nickel-Base Structural Alloys

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NEW DEVELOPMENTS IN ELECTROFORMED NICKEL-BASE STRUCTURAL ALLOYS

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Abstract

Difficulties in forming and joining wrought superalloys such as Inconel 718 for structural assemblies for elevated temperature use often result in numerous weld joints where mechanical properties are degraded by heat-affected zones. Thicker sections are needed to compensate for strength reduction. The substitition of electroformed (EF) alloys of equivalent strength in the required service temperature range would simplify fabrication and possibly reduce weight -- both factors being of great significance in manufacture of many aerospace components. The selection of EF Ni-Mn alloy from candidates including EF Ni-Co and EF Ni-Co-Mn is discussed together with development of this material to a point where mechanical properties are competitive with age hardened Inconel 718 at 20° to 149°C. Mechanisms to account for the performance of EF Ni-Mn are postulated. Some problems to be resolved in applying this material to electroforming of complex hardware shapes are discussed.

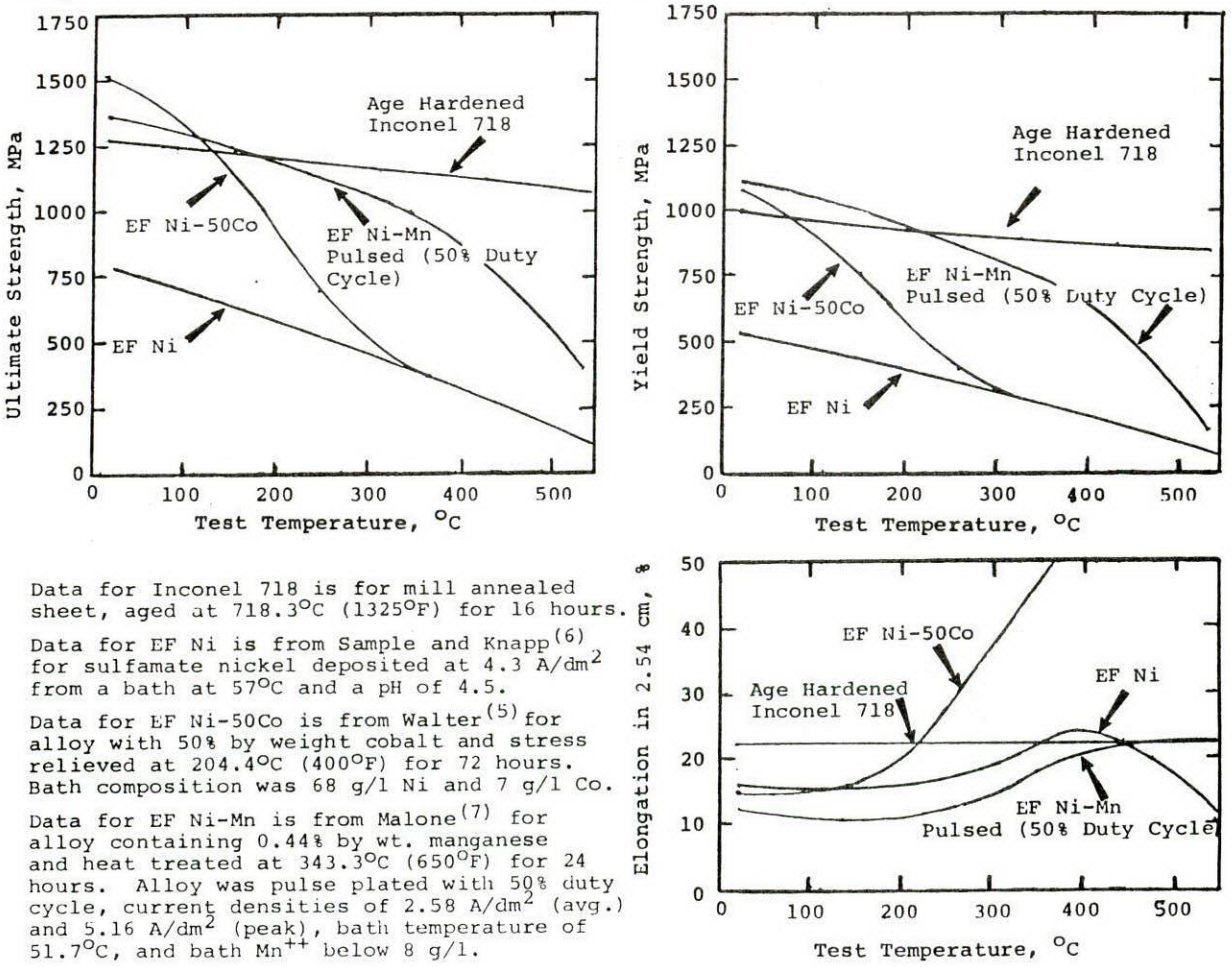
Introduction

The properties of electrodeposited alloys are of particular interest because they frequently have certain enhanced properties -- often they are stronger, have finer grain structure, or are harder than the parent metals. They must possess better properties for a particular application than a pure (unalloyed) electrodeposit to compensate for the increased difficulties involved in operating the alloy plating process.

Nickel as deposited from the low-stress sulfamate bath has been almost universally accepted as the material for electroforming regeneratively cooled propulsion devices for space vehicles and high energy laser components where good mechanical properties at temperatures to 538°C (1000°F) are often desired. However, nickel electrodeposits lose strength rapidly as temperature increases, and the ductility deteriorates within certain temperature ranges. Several electroformable alloy systems have been reported in the literature or developed at Bell Aerospace Textron and characterized to a point where practical hardware application may be considered. These alloy systems are Ni-50Co, Ni-50Co-Mn, and Ni-Mn. Bell's studies have been primarily with the latter two systems. Results of extensive studies of the electrodeposited Ni-Co system are available in the literature.

Ni-Co and Ni-50%Co Systems

Brenner[1] notes that codeposition of nickel and cobalt follows a process of the anomalous type which is characterized by the peculiarity that the less noble metal (cobalt) deposits preferentially. Endicott and Knapp[2] performed the first extensive study of the effects of plating parameters and bath composition on Ni-Co mechanical properties, microstructures, and response to thermal treatments. McFarlen[3] reported results from the first comprehensive study of elevated temperature mechanical properties of EF Ni-Co. Dini, Johnson, and Helms[4] determined that cobalt content and stress increased with electrolyte agitation. They were in agreement with other investigators that best mechanical properties were obtained with a cobalt content of 40 to 60 percent by weight. Walter[5] established that best mechanical properties of this alloy were obtained with a cobalt content of about 50 percent by weight and a stress relief at 204.4°C for 72 hours. His data was used to plot the typical mechanical property test curves for EF Ni-50%Co at various test temperatures as shown in Figure 1.



Data for Inconel 718 is for mill annealed sheet, aged at 718.3°C (1325°F) for 16 hours.

Data for EF Ni is from Sample and Knapp[6] for sulfamate nickel deposited at 4.3 A/dm^2 from a bath at 57°C and a pH of 4.5.

Data for EF Ni-50Co is from Walter[5] for alloy with 50% by weight cobalt and stress relieved at 204.4°C (400°F) for 72 hours. Bath composition was 68 g/l Ni and 7 g/l Co.

Data for EF Ni-Mn is from Malone[7] for alloy containing 0.44% by wt. manganese and heat treated at 343.3°C (650°F) for 24 hours. Alloy was pulse plated with 50% duty cycle, current densities of 2.58 A/dm^2 (avg.) and 5.16 A/dm^2 (peak), bath temperature of 51.7°C, and bath Mn^{++} below 8 g/l.

Figure 1. Mechanical Properties of Inconel 718 and EF Alloys at Various Test Temperatures

From Figure 1 it is evident that mechanical properties of EF Ni-50%Co are excellent until a test temperature of about 150°C is reached. At higher temperatures the ultimate and yield strengths degrade rapidly. Barrett[8] suggests that EF Co can exist in the hexagonal-close-packed (HCP) and face-centered-cubic (FCC) states while EF Ni is usually in the FCC state. From the binary alloy phase diagram for nickel-cobalt[9], Figure 2, it is noted that a peritectic region exists around the e' area in the lower left corner. The e' region consists of cobalt rich HCP cell structures while the peritectic region is composed of mixed HCP and FCC cells in the crystalline lattice.

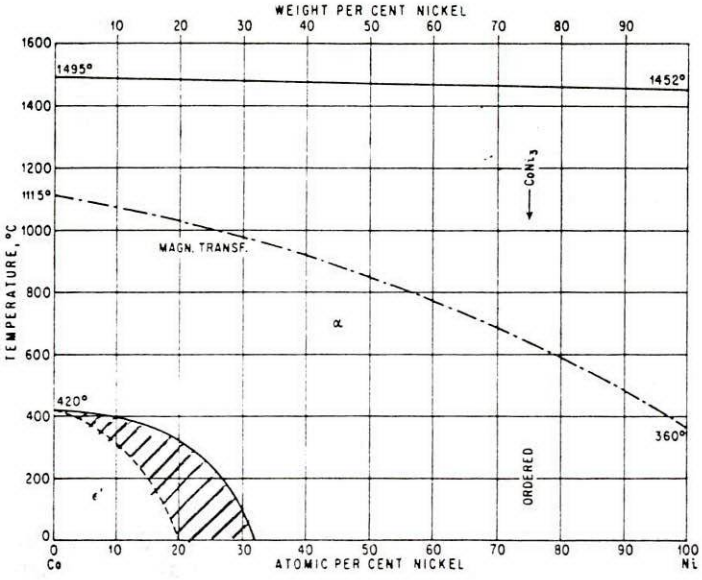


Figure 2. Ni-Co Alloy Diagram

Malone[10] has considered the rapid loss of strength of EF Ni-50%Co with higher temperature as due to the allotropic change of HCP cobalt rich lattice cells to mixed HCP and FCC cell structures. Upon cooling, not all of the HCP cells are recovered. Since HCP structures impart higher material strengths, it is not surprising that the alloy strength dimenishes as temperature excursions into the peritectic zone (shaded area of Figure 2) occur. The allotropic changes occurring in this temperature region might also explain why EF Ni-Co alloy can be stress relieved at very moderate temperatures such as 204.4°C (400°F). Compared with conventional EF Ni from a sulfamate electrolyte, EF Ni-50%Co (stress relieved) has superior mechanical properties from 20°C to about 300°C. At higher test temperatures the strengths of the two materials are similar, but the ductility of the alloy is superior.

Ni-Co-Mn Systems

Stephenson[11] attempted deposition of an alloy of nickel, cobalt, and manganese in an effort to obtain an electroform of high hardness. They reported no mechanical property data for the material but stated that it started to anneal at 315°C (600°F). They found that only a trace of manganese was present in the deposit and abandoned the investigation.

Initial studies by Malone[12] confirmed Stephenson's findings that less than expected amounts of manganese were included in the deposit when cobalt was present in the bath. He explained

this as possibly due to different abilities of nickel and cobalt to share 3d electrons with other transitional series metal ions. Ernst and Holt[13], in their studies of codeposition of molybdenum with iron group metals, described possible reasons for increased molybdenum concentrations in the alloy as one substituted iron group metals in the order: nickel, cobalt, and iron. The abilities of these ferromagnetic elements and their row neighbors to share unpaired electrons is shown in Table I.

TABLE I - DISTRIBUTION OF THE OUTER ELECTRONS IN THE FIRST ROW OF THE TRANSITION ELEMENTS

		OUTER ELECTRONS			
ELEMENT	TOTAL	4s	+3d	-3d	Unpaired 3d
Cr	6	0.6	2.7	2.7	0
Mn	7	0.6	3.2	3.2	0
Fe	8	0.6	4.8	2.6	2.2
Co	9	0.7	5.0	3.3	1.7
Ni	10	0.6	5.0	4.4	0.6
Cu	11	1.0	5.0	5.0	0

* The 3d level can accommodate 10 electrons per atom, 5 with a plus (+) spin and 5 with a minus (-) spin. Electrons generally fill up the +3d levels first and then go into the -3d levels. The unpaired electrons which produce ferromagnetism result because the -3d electrons cancel an equal number of +3d electrons.

From Table I it is noted that cobalt should be able to provide about three times as many unpaired 3d electrons as nickel. One would expect this electron sharing to be primarily with hydrogen atoms due to their small size and presence of one unpaired electron. It may be possible for covalent bonding to occur at the cathode surface where cobalt atoms can each hold 1.7 hydrogen atoms and nickel atoms can hold 0.6 hydrogen atoms. Since manganese has a reduction potential that is very high with respect to the iron group metals, one would not expect it to codeposit with nickel or cobalt. To explain why it will deposit, it has been thought that hydrogen enters into the reduction reaction to decrease the reduction potential of manganese. Since nickel can not hold hydrogen as well as cobalt, it would appear that less hydrogen would be available to assist manganese reduction when cobalt is present. This postulation is supported by the fact that electrodeposited cobalt and cobalt alloys contain far more hydrogen than does nickel. This absorbed hydrogen (possibly in the form of metal hydrides) and the mixed HCP and FCC lattice cells probably account for the high internal stresses found in EF Ni-Co and Ni-Co-Mn.

Bell's interest in manganese additions to EF Ni-50%Co alloys was to produce a thermally stabilized microstructure that would improve the mechanical property performance of EF Ni-Co at

temperatures above 204.4°C (400°F). Using a nickel-cobalt sulfamate bath operated at 48.3°C, a nickel metal content of 63.6 g/l, a cobalt content of 2.6 g/l, a manganese content higher than the cobalt content, and pulse plating with an average current density of 3.23 A/dm^2 at a duty cycle of 33 percent, a specimen of EF Ni-Co-Mn was made which contained 67.2 percent by weight nickel, 32.7 percent by weight cobalt, and 0.22 percent by weight manganese. This material was heat treated at 371.1°C (700°F) for 24 hours and tested at 260°C (500°F). A comparison of mechanical properties of this material with those of EF Ni-50%Co at a test temperature of 260°C is found in Table II. The manganese appears to contribute to a stronger material -- even with a lower cobalt content.

TABLE II - A COMPARISON OF MECHANICAL PROPERTIES OF EF Ni-50%Co AND EF Ni-32%Co-Mn AT 260°C (500°F)

Material	Heat Treatment	Ultimate Strength, MPa	Yield Strength, MPa	Elongation % in 2.54 cm
EF Ni-50%Co	204.4°C, 72 Hours	700	448	26
EF Ni-32%Co-Mn	371.1°C, 24 Hours	1033	865	13

Further studies are required with the EF Ni-Co-Mn system in an effort to determine how the presence of manganese affects microstructure and mechanical properties. It is not clear as to the mechanism for strengthening. A disadvantage exists in that very high heat treating temperatures are required to restore useful ductility when manganese content exceeds 0.25 percent by weight.

Ni-Mn Systems

Brenner[14] notes that manganese has been codeposited with iron, nickel, cobalt, zinc, tin, and tungsten. The codeposition with the iron group metals has received the most attention. He states that most of the manganese alloy plating systems belong to the regular type -- that is, codeposition is characterized by the deposition being under diffusion control where the effects of plating variables on the composition of the deposit are determined by changes in the concentration of metal ions in the cathode diffusion layer and are predictable from simple diffusion theory.

The potential of EF Ni-Mn for elevated temperature applications was not realized until Stephenson[11] reported the results of his investigation of nickel deposits containing low contents of manganese from a sulfamate bath. His electroforming bath contained 80 g/l of nickel, 30 g/l of manganese, and 30 g/l of boric acid. Bath temperature was varied from 32°C to 60°C, and current density effects were studied in the range of 2.1 to 8.1 A/dm^2 (20 to 75 ASF). Brittleness and stress cracking occurred in nearly all deposit containing over 0.6 percent by weight manganese. For a sound deposit, Stephenson reported some elevated temperature test data as shown in Table III.

TABLE III - MECHANICAL PROPERTIES OF NICKEL-MANGANESE DEPOSITS AT ELEVATED TEMPERATURE

Test Temperature °C	Average Ultimate Strength MPa	Average Ultimate Strength ksi	Average Elongation in 5.08 cm, %	Average Hardness R_c
20	1234.2	179	5.4	39
93	1137.7	165	4.0	37
204	896.4	130	5.6	36
316	682.6	99	18.0	37

Stephenson concluded from his studies that the percentage of manganese in the deposit decreased with temperature, increased with current density increase, and was relatively unaffected by changes in the electrolyte pH.

Dini and Johnson[15] investigated EF Mi-Mn from a sulfamate bath containing 1 to 5 g/l manganese. They were investigating means to improve high temperature ductility in EF nickel and noted that Stephenson had obtained excellent ductility at temperatures as high as 400°C (750°F) with as much as 5000 ppm of manganese in the deposit. Manganese is known to be a sulfur scavenger and is alloyed in most wrought nickels to prevent hot shortness at high temperatures. They produced samples with no manganese, with 700 ppm manganese, and with 1800 ppm manganese for test at 22°C and 538°C in the "as deposited" condition, after heat treating at 538°C for one day, and after heat treating at 538°C for one week. They concluded that adding 700 ppm of manganese affected neither yield nor ultimate strengths while adding 1800 ppm manganese increased both of these properties at high temperature.

Wearmouth and Belt[16] investigated the addition of manganese to nickel deposits produced from electrolytes containing organic stress reducing agents. Such deposits without manganese contain abnormal amounts of sulfur which makes them susceptible to catastrophic embrittlement on exposure to elevated temperatures. They found that EF nickel containing over 0.1 weight percent manganese did not experience catastrophic embrittlement on heat treatment.

Using a production sized electroforming facility at Bell Aerospace Textron, Lictenberger[17] investigated the effects of current density and bath temperature on the codeposited manganese content and mechanical properties of specimens not heat treated. His findings, Figure 3, indicated that manganese content of the deposit increases exponentially with increasing current density and decreases with increasing bath temperature. The electrolyte in this study contained less than 2 g/l of manganese. Lichtenberger attributed the decrease in manganese content with increase in bath temperature as due to the lowering of the deposition overpotential with the increasing temperature. From his test data in Figure 4 it is indicated that as little as 0.19 weight percent manganese in EF nickel very significantly improves the

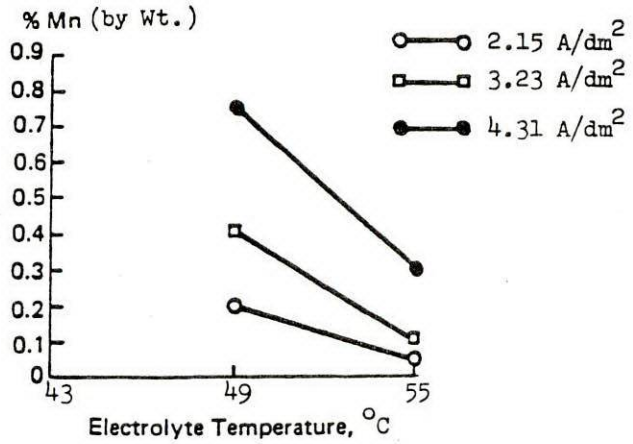


Figure 3. Manganese Concentration in Codeposits as Functions of the Electrolyte Temperature and Current Density

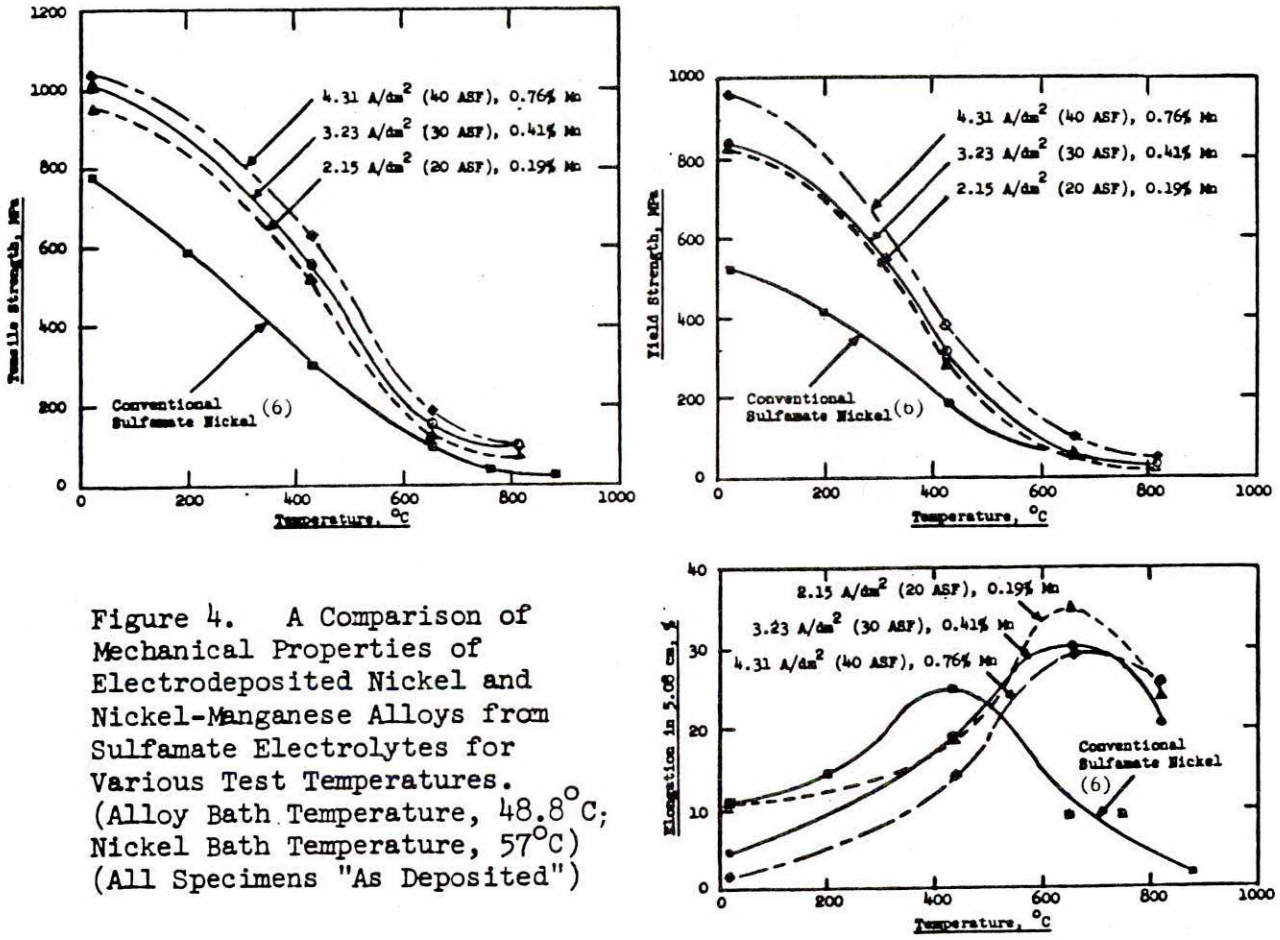


Figure 4. A Comparison of Mechanical Properties of Electrodeposited Nickel and Nickel-Manganese Alloys from Sulfamate Electrolytes for Various Test Temperatures. (Alloy Bath Temperature, 48.8°C; Nickel Bath Temperature, 57°C) (All Specimens "As Deposited")

mechanical strength of EF nickel over a wide temperature range. As the test temperature is increased beyond 400°C (750°F), it is evident that chemical and metallurgical changes are taking place which result in improved ductility performance. Much of this improvement may be attributed to manganese forming a relatively inactive phase of manganese sulfide and preventing the

formation of a mobile liquidus phase of nickel sulfide which wets intergranular surfaces to cause brittle failure.

Malone continued the studies started by Lichtenberger and expanded the investigation to include effects of heat treatments on elevated temperature mechanical properties and the influence of pulse plating on the performance of EF Ni-Mn alloys. All of these studies were conducted in a sulfamate bath containing 74 to 80 g/l of nickel and 1 to 5 g/l of manganese. Bath temperature ranged from 45.6° to 52.2°C (114° to 126°F). Boric acid was present at a concentration of 30 to 35 g/l. Bath pH was maintained between 3.9 and 4.3. Typical EF spacimen size was 11.125 cm by 20.625 cm, and thicknesses ranged from 0.167 to 0.185 cm. Electroforming was performed on stainless steel flat mandrels housed in shield boxes to control current distribution uniformly without producing any edge nodules. Elevated temperature testing employed a quartz tube muffle furnace surrounding the narrow test section of the tensile test bars. The test bar temperature was measured by an attached thermocouple within the gauge marked section. Once temperature was achieved, it was held at this temperature for at least 5 minutes before stressing

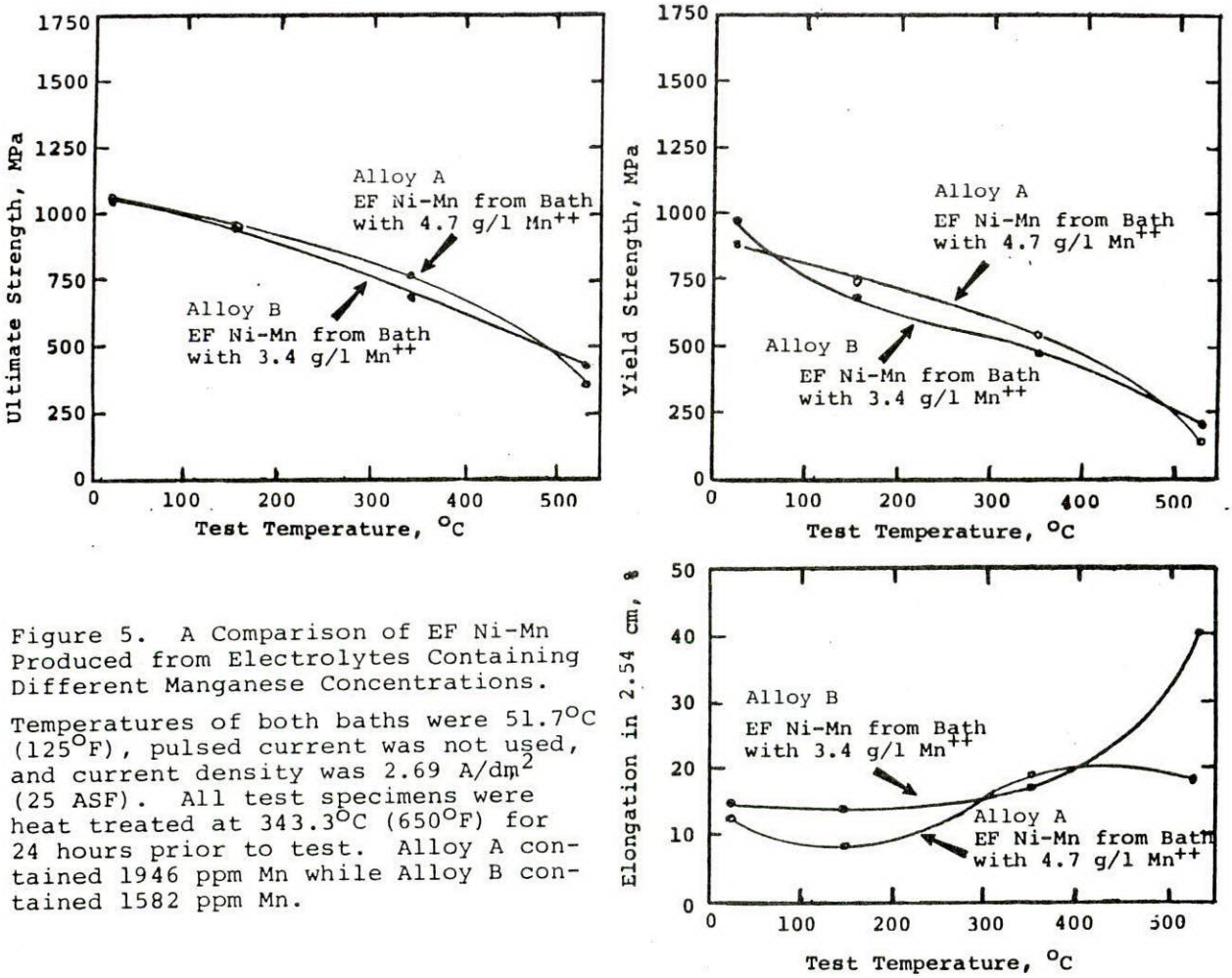


Figure 5. A Comparison of EF Ni-Mn Produced from Electrolytes Containing Different Manganese Concentrations.

Temperatures of both baths were 51.7°C (125°F), pulsed current was not used, and current density was 2.69 A/dm^2 (25 ASF). All test specimens were heat treated at 343.3°C (650°F) for 24 hours prior to test. Alloy A contained 1946 ppm Mn while Alloy B contained 1582 ppm Mn.

the test bar.

Figure 5 shows mechanical property data for two specimens from electrolytes of different manganese concentration -- all other parameters being nearly the same. Although Alloy A had 1946 ppm Mn and Alloy B had only 1582 ppm Mn, there is little difference in ultimate and yield strengths for the two samples. Differences are noted in ductility with the Alloy B sample with less manganese showing better elongation.

A comparison of EF Ni-Mn alloys produced from electrolytes of like composition and similar plating parameters -- except for bath temperature -- are shown in Figure 6 where mechanical properties over a range of test temperatures are plotted. Alloy B from the higher temperature bath contained 1582 ppm Mn while Alloy C from the lower temperature bath contained 3637 ppm Mn. Despite this great difference in manganese content, the two alloys do not show a significant difference in mechanical properties. It is surprising to note that the Alloy B with lower Mn content actually shows slightly better ultimate strength over most of the range of test temperatures.

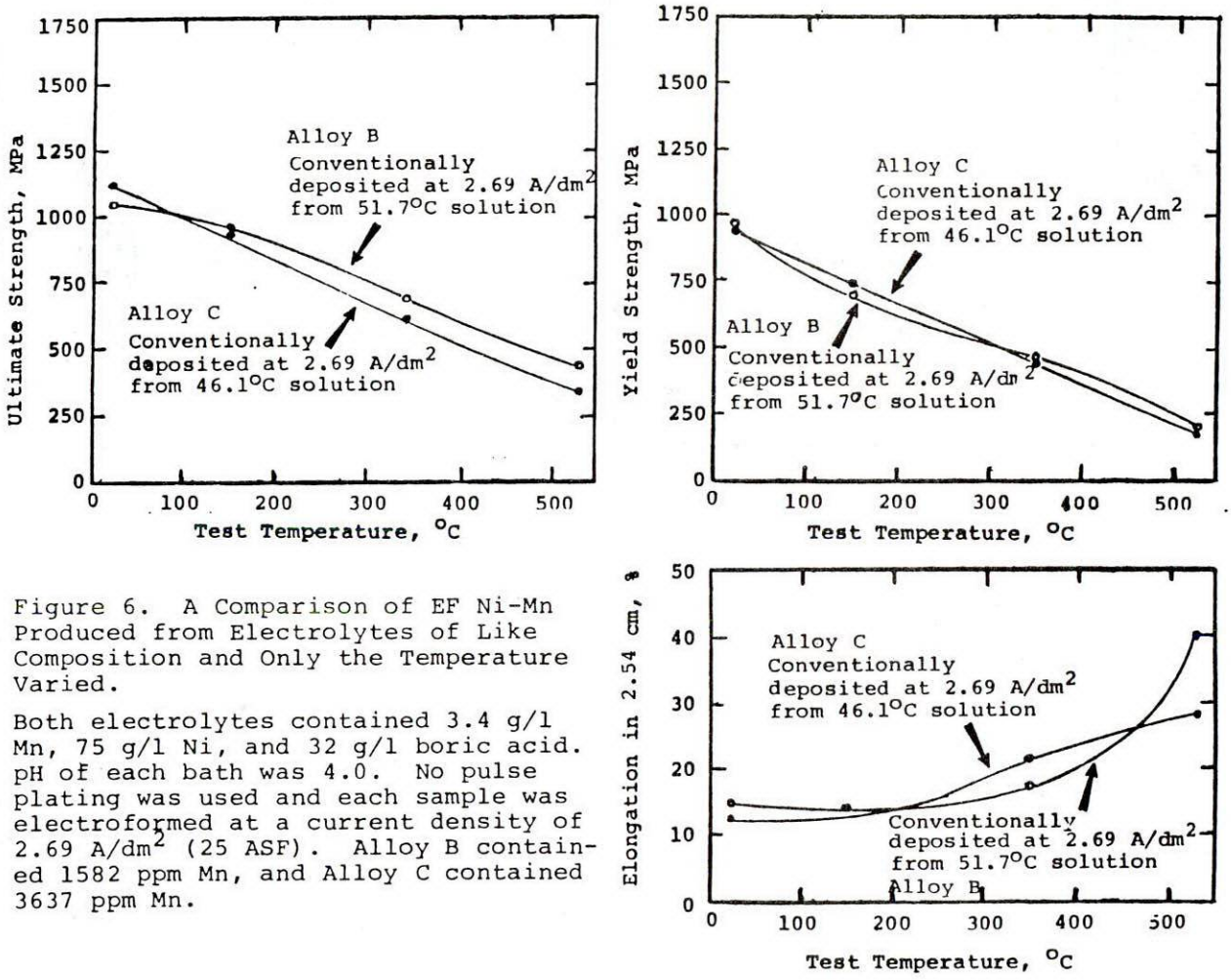


Figure 6. A Comparison of EF Ni-Mn Produced from Electrolytes of Like Composition and Only the Temperature Varied.

Both electrolytes contained 3.4 g/l Mn, 75 g/l Ni, and 32 g/l boric acid. pH of each bath was 4.0. No pulse plating was used and each sample was electroformed at a current density of 2.69 A/dm^2 (25 ASF). Alloy B contained 1582 ppm Mn, and Alloy C contained 3637 ppm Mn.

When pulsed deposition is applied to electroforming nickel-manganese alloys, improvements in mechanical properties are obtained. This is shown in Figure 7 where performances of conventional EF Ni, conventionally deposited EF Ni-Mn, and EF Ni-Mn pulsed at duty cycles of 50 and 67 percent are compared. Pulsing at duty cycles of less than 50 percent will usually result in even higher ultimate and yield strengths; however, the ductility is adversely affected -- often to the point where test bars can not be machined without cracking the alloy. This problem can be overcome by heat treatment, but the heat treatment must be more severe as the pulse duty cycle is decreased below 50 percent. It appears that best combination of ductility and tensile strength is obtained with a positive duty cycle (i.e.- a duty cycle with longer "on" time than "off" time). It has also been noted that higher stress distortion of the electroformed alloy occurs when pulse duty cycles of less than 50 percent are used. From Figure 7 it is observed that the manganese content of the alloy increases as the pulse duty cycle decreases from 100 percent (a 100 percent duty cycle is actually conventional dc plating without pulsing).

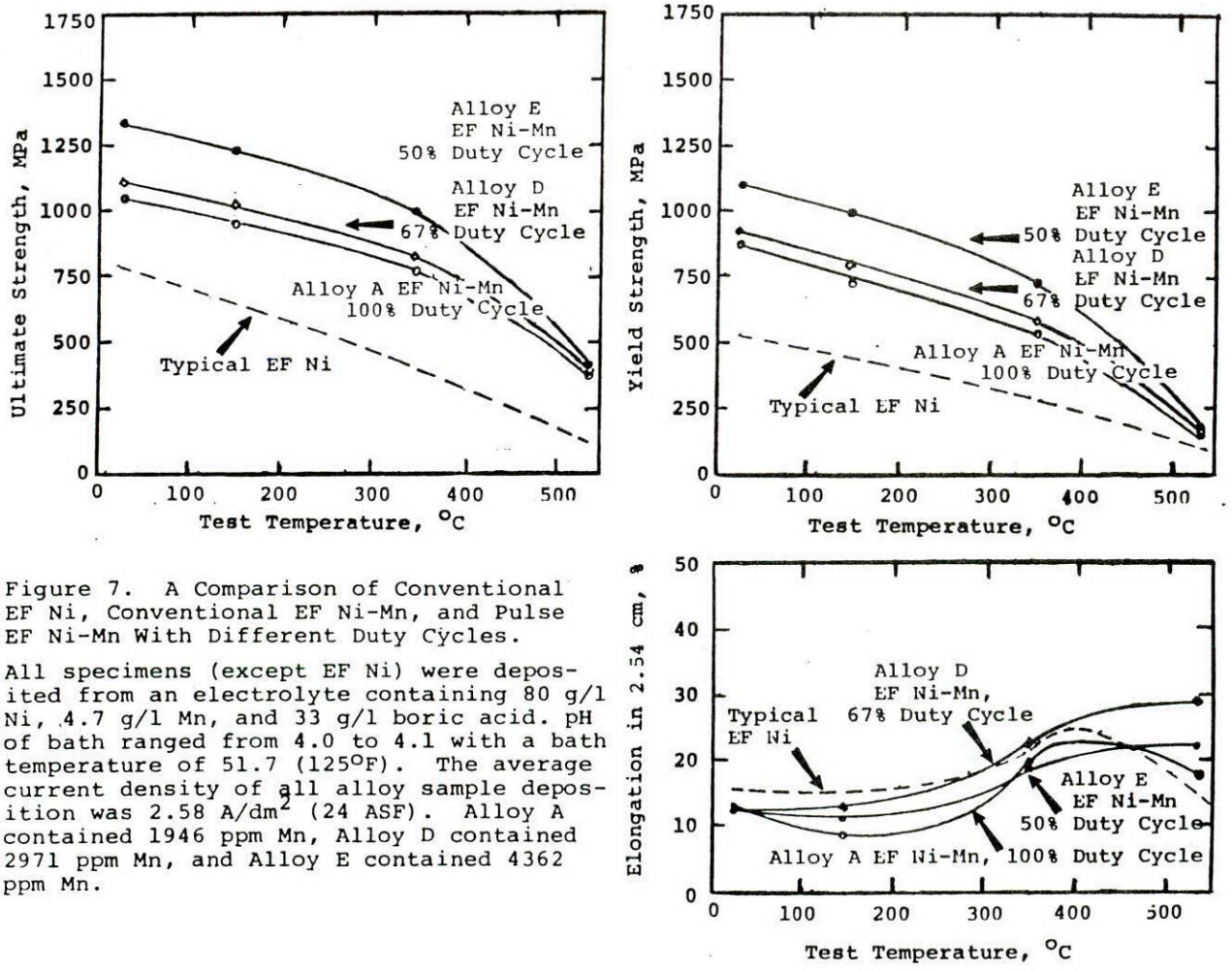
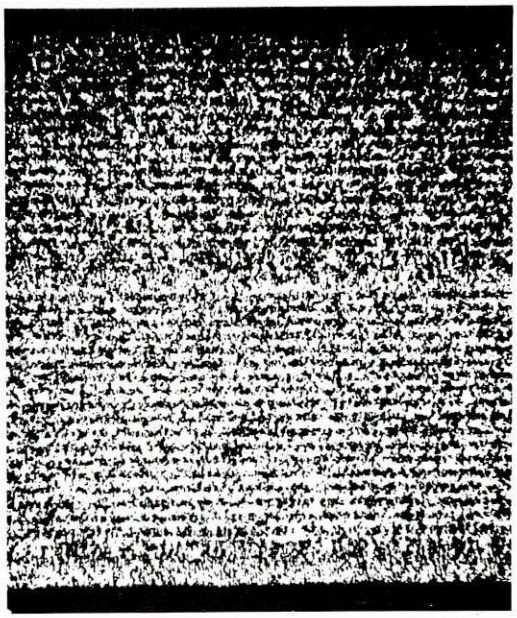


Figure 7. A Comparison of Conventional EF Ni, Conventional EF Ni-Mn, and Pulse EF Ni-Mn With Different Duty Cycles.

All specimens (except EF Ni) were deposited from an electrolyte containing 80 g/l Ni, 4.7 g/l Mn, and 33 g/l boric acid. pH of bath ranged from 4.0 to 4.1 with a bath temperature of 51.7 (125°F). The average current density of all alloy sample deposition was 2.58 A/dm^2 (24 ASF). Alloy A contained 1946 ppm Mn, Alloy D contained 2971 ppm Mn, and Alloy E contained 4362 ppm Mn.

Under certain pulse plating conditions -- particularly where high peak current densities exist -- the EF Ni-Mn alloy will exhibit a banded microstructure. This banding does not disappear when moderate heat treatments are applied. Heat treating seems to make the banding even more distinct. Figure 8 illustrates this banding, before and after heat treating, in a sample of EF Ni-Mn alloy containing 2975 ppm Mn.



Alloy NMR-21A 50X

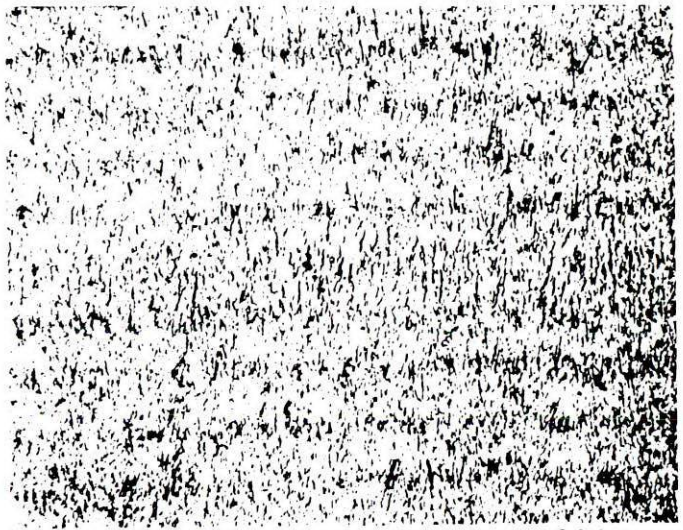


Alloy NMR-21A 200X

Illustrations above and to the left are of "as deposited" Ni-Mn alloy pulse plated at a duty cycle of 50 percent, an average current density of 2.69 A/dm^2 (25 ASF), and a peak current density of 5.38 A/dm^2 (50 ASF).



Alloy NMR-21A 50X



Alloy NMR-21A 200X

Illustrations above and to the left are of the same alloy shown in the top photomicrographs after heat treating at 343.3^{o}C (650°F) for 24 hours.

Figure 8. Banding in Microstructure of EF Ni-Mn

Upon heat treating the alloy described in Figure 8, it was noted that ductility improved as would be expected. However, the yield strength increased as shown in Table IV. On many pulse plated examples of EF Ni-Mn, it has been found that the ultimate strength also increases. The effect is believed to be similar to that of age-hardening in certain wrought metals.

TABLE IV - MECHANICAL PROPERTY CHANGES SIMILAR TO AGE-HARDENING ENCOUNTERED IN HEAT TREATED EF NICKEL-MANGANESE ALLOY

Specimen Identity	Manganese Content, PPM	Heat Treatment	Ultimate Strength, MPa	Yield Strength, MPa	Elongation % in 2.54 cm
NMR-21A	2975	As Deposited	1289	958	8.2
		343.3°C, 24 Hr.	1308	1078	10.7
NMH-07	2971	As Deposited	1047	733	11.0
		343.3°C, 24 Hr.	1119	929	12.0

In electroforming very thick alloys, it is critical that bath and pulse deposition parameters be selected to assure adequate ductility in the "as deposited" condition. Although the alloy will be heat treated to restore required ductility, high stress and brittleness from the massive buildup can cause internal cracking that can not be corrected by heat treating. Figure 9 illustrates an example of such defects in a specimen 1.27 cm thick bonded to a copper substrate.

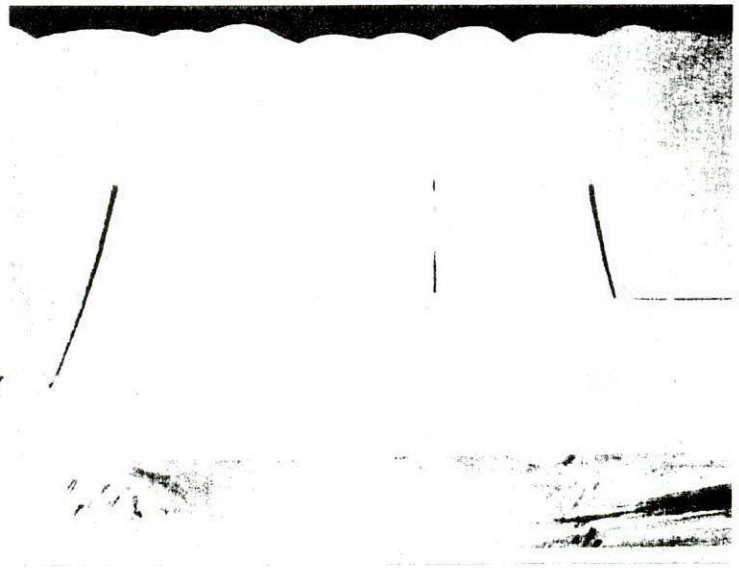


Figure 9. Cracks in Thick EF Ni-Mn Alloy

To explain the behavior of EF Ni-Mn it is necessary to account for the fact that very little manganese in the alloy results in a significant impact on mechanical properties and a high resistance to recrystallization and grain growth at temperatures that would cause major microstructural changes in conventional EF nickel. Theoretically, manganese should not codeposit with most metals due to the high reduction potential required (1.18 volts). It will deposit with iron group metals by a mechanism suspected to involve 3d electron sharing by the iron group metal

with hydrogen. The hydrogen (possibly monatomic) at the cathode surface may act as a reducing agent to lower the highly negative reduction potential of manganese and codeposit it with the iron group metal. Since nickel holds hydrogen much less strongly than cobalt (as shown in Table in Table I), it would be assumed that more hydrogen would be free to catalyze the manganese reduction. Theory and actual happenings agree at this point due to the fact that more manganese codeposits with nickel than with cobalt from electrolytes of similar starting manganese concentrations.

Raising the bath temperature should improve diffusion of manganese ions through the diffusion layer. It should also increase the activity of hydrogen atoms held by nickel so that many are released to collide with other monatomic hydrogen atoms and form hydrogen molecules which leave the electrolyte without assisting in manganese reduction. In actual practice it was found that increasing bath temperature reduces manganese content in the alloy.

Increasing the electroforming current density increases the overvoltage which increases the rate of reduction of hydrogen ions at the cathode surface. As more hydrogen is available for electron sharing (capture) by the reduced nickel atoms at the cathode surface, it would be expected that more reduction of manganese ions could take place as is the actual case. When the plating mode employs pulsed current there is a null period which permits diffusion of nickel, manganese, and hydrogen ions into the catholyte layer. As current (and voltage) increase to the pulse peak and back down to the null, there is a continually varied amount of atomic hydrogen being generated at the cathode surface. This variation would be expected to result in a similar variation of manganese being reduced and codeposited. This supposition seems to have support in actual practice where low pulse duty cycles are attended by high peak current densities and high peak voltages (overpotentials). Resulting EF alloys exhibit unusually high ultimate and yield strengths which can only be attributed to atomic layers of higher than usual manganese content.

To construct a theory for why EF Ni-Mn alloys exhibit such unusual mechanical properties with so little manganese present, it is necessary to examine the binary phase diagram for this material, Figure 10[18]. With pulsed deposition it is reasonable to assume that nickel and manganese can atomically (or molecularly) exist in various stoichiometric combinations such as NiMn, Ni_2Mn, or Ni_3Mn. According to Lasserre and Reynaud[19], Ni_2Mn is unstable and decomposes with heat to form NiMn and Ni_3Mn. The NiMn lattice cell is face-centered-tetragonal, and the Ni_3Mn cell is face-centered-cubic. Since the EF nickel matrix is composed of FCC cells, the random imposition of the

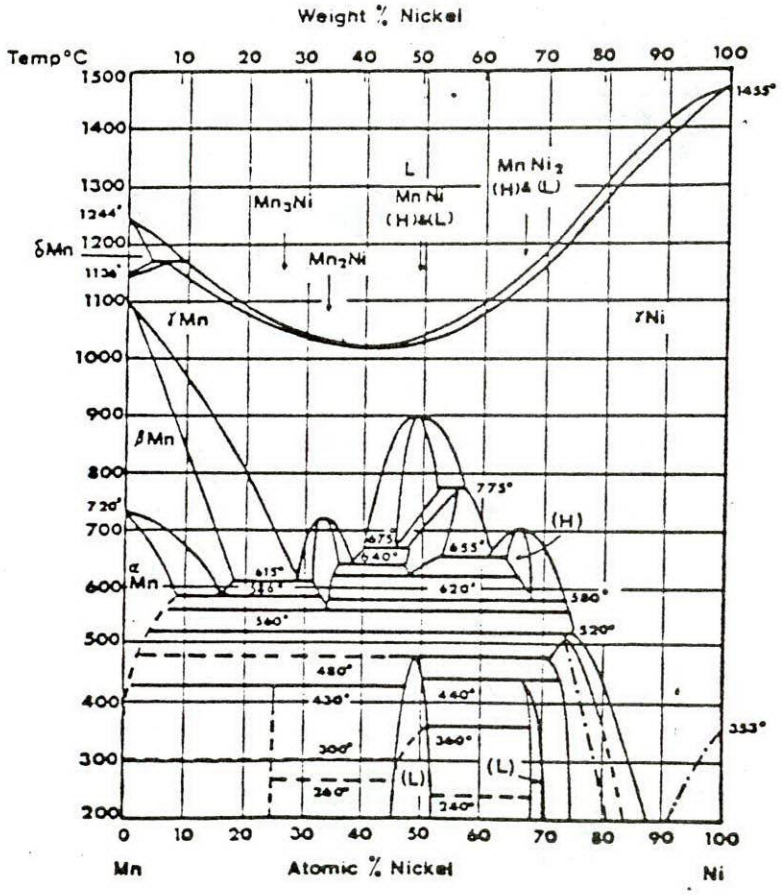


Figure 10. Ni-Mn Phase Diagram

face-centered-tetragonal NiMn cells generates a misfit and results in a lattice distortion. Many preferred slip planes become blocked by the FCT cell configuration so that dislocation entanglements may be possible. This fosters retention of fine grain sizes by impeding dislocation movement across grain boundaries during heat treatment and results in high ultimate and yield strengths while ductility is low. Heating the alloy moderately starts recovery in the lattice structure. Outgassing of hydrogen, oxygen, and nitrogen occurs, as well as possible atomic reordering. This relieves stress and improves ductility, but it does not significantly affect the dislocations present. This heating decomposes any Ni_2Mn present to increase the amount of face-centered-tetragonal (FCT) NiMn and primary slip paths are further inhibited to increase the yield stress needed to cause plastic deformation. This might explain why both yield strength and ductility are simultaneously improved by moderate heat treatment.

The ability for EF Ni-Mn alloy to demonstrate excellent mechanical properties to 538°C and to resist significant grain growth in braze cycles to 900°C and higher may be explained by the peritectic regions for NiMn (50% Ni) where stability of the FCT

NiMn cell exists to about 640°C. Beyond this temperature the high temperature version of NiMn exists which is believed to be body-centered-cubic (BCC). Mixed cell configurations would thus be maintained to at least 900°C. Stabilization of these cells in an FCC nickel matrix is suspected to exert a beneficial effect on mechanical properties over a wide temperature range such as actually observed from tests on EF Ni-Mn alloys.

Conclusions

EF Ni-50%Co, EF Ni-Co-Mn, and EF Ni-Mn alloys can be produced with mechanical properties superior to conventional EF Ni over a range of application temperatures. Some of these alloys are even competitive with certain superalloys such as Inconel 718 over a limited temperature range. EF Ni-50%Co has outstanding mechanical properties over a temperature range from cryogenic to about 260°C (500°F); at higher temperatures the mechaniacl properties are similar to those of EF Ni. EF Ni-Co-Mn has good mechanical strength over a range of temperatures slightly higher than EF Ni-50%Co, but the ductility is low. EF Ni-Co-Mn has great resistance to microstructural changes and heat treatments to 538°C (1000°F) may be necessary to restore suitable ductility. EF Ni-Mn can be produced with a wide variety of manganese contents and related mechanical properties. The alloy can be heat treated to improve mechanical properties. It has mechanical properties competitive with those of Inconel 718 at temperatures to 204.4°C (400°F). It is greatly superior to EF Ni over all temperatures investigated to 538°C (1000°F). It exhibits better mechanical strength than EF Ni-50%Co from about 150°C to 538°C.

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E-1

Environmental II
Session E

Waste Treat or Recovery?
An Introduction to Resource Recovery

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WASTE TREAT OR RECOVERY?
AN INTRODUCTION TO RESOURCE RECOVERY

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The first point that we have to accept is that there are no magic solutions to waste treatment problems. We have, however, developed a practical approach that can bring effluent contamination levels down to a point where you will meet local discharge limitations, possibly with no conventional treatment.

Our corporate philosophy in the field of waste treatment is twofold: Recover valuable plating chemicals rather than destroying valuable plating chemicals; and, Complement recovery techniques with non-sludge generating techniques.

We have found that the ion-exchange and the electrolytic processes are the most viable, complementary techniques available. Some inplant changes need to be made in order to allow you to accommodate ion-exchange. The changes we suggest emphasize waste reduction at the tank to reduce the loading on the ion-exchange resin in order to maximize the time between removal or regeneration.

These changes will provide you with additional benefits compared to the use of conventional treatment technologies. First, you will have less floor space taken up with treatment equipment. Second, you will have a much lower capital investment in equipment. Third, you will reduce your water and sewer use bills.

This presentation will outline the process of cleaning up your waste streams. I must preface it by saying that there is really only so much you can do with these techniques. They are not the complete answer to all your problems, but they are simple, inexpensive, and they can be most effective.

The generally accepted approaches to waste treatment (Fig.1 & 2) can be divided into destruct technologies and recovery technologies. I'm sure you are all familiar with them; you have read enough articles on what they can do and what they can't do.

Your waste streams should be segregated. There are three reasons why you should segregate your lines:

1. Efficient treatment -- if you put everything together, you get an average treatment where pH is a factor, and you can't recovery any metal values.

2. You get much more economical recovery.

3. To isolate chelates, which would make treatment processes totally inoperable.

Figure 3 suggests how to segregate waste lines. The point to make about streams that do not require treatment is that regulatory authorities don't like to see you use non-contact water to dilute your process water. So, if you take a sample that includes degreaser, air-conditioning, or other such non-contact water, they expect you to prorate the analysis as though it were not being diluted. One answer, of course, is to reuse cooling water through your rinses. Now it is process water, and you have the advantage of its dilution effect even though it probably is not a significant factor.

You must consider the effect of cooling water flow on waste treatment equipment capabilities.

You can put an ion-exchange system at the end of each plating tank. If you put it at the end-of-the-pipe, you aren't going to get anything back. After regeneration, you will have a mixed waste, and most studies say that mixed wastes are simply not an economical source for recovering metal values.

Figure 4 is an EPA slide showing schematically what a conventional destruct system looks like. You can surmise that:

1. It can be very complicated.
2. It takes up a lot of room.
3. It probably costs a lot of money.
4. It requires some pretty good people to run it.
5. You are losing the chemicals that you are having to destruct.
6. You are adding destruct chemicals.
7. You are generating a sludge.

Destruct technologies are really not the way that you want to go. We are not saying that they don't work, but if nothing more, you are creating a sludge which is hazardous. Who needs it? There soon may be no land fills. Try to avoid sludge if at all possible!

A critical point to emphasize is that when you mix metal-bearing waste solutions and use alkaline precipitation with lime, hydroxide or carbonate, all metals don't precipitate

completely at the same pH. So, if you have a mixed stream, you have a problem. You have to use an average pH. Many times the levels that you can attain by doing this are not quite low enough. You can use Sulfide Precipitation (Fig.5), which results in much lower residual metal ion concentrations. However, notice the top right-hand corner of Figure 5 which shows for comparison the hydroxide performance. How many of you realize that if you raise your pH too high, many precipitated metals go back into solution?

No matter what approach you take to waste treatment, you can at all times implement water-use reduction -- even if only to save the dollar value of wasted water and sewer use charges.

You can minimize your dragout volume. I will go over that very briefly with you a little later to show you the methods that can be used.

You can implement chemical recovery. In the conventional recovery techniques, you either return a concentrated solution to the tank, destruct this concentrate, or recover metals from a concentrate using electrolytic methods.

You can also use integrated treatment (Fig.6). This is a destruct technology where dragout generally goes downstairs where it is treated and the cleaned solution is sent back upstairs for reuse in rinses.

Resource Recovery means you return materials unchanged directly to the tank from which they were dragged out. It is important to consider that while you can plate out metals from dragout solutions, a gallon of dragged out nickel solution, worth approximately $4.70, contains about 10 oz. per gallon of nickel. If nickel metal is selling for $3 a pound, and you can get $3 a pound for recovered nickel, you're only recovering about 60% of the value of that dragged out gallon of solution. The question about returning impurities to the bath is settled by improving bath maintenance or increasing carbon treatment/electrolytic purification frequencies as necessary.

Water-use reduction (Fig.7) is accomplished by common sense approaches. There is only one thing that rinsing does for you -- it reduces the impurities on a plated piece to the point where you can progress to the next step and get a satisfactory product. Why use more water than you have to?

I am sure that you've already implemented a lot of these. for those who haven't thought of every one, let's cover them briefly:

Flow Control Valves -- platers like to open their water valves full. Put a flow control valve on each water line and know your flow.

Aeration of Rinses -- whether you pump the rinses, bring air agitation in, or use a syphon breaker, the more agitation you get, the more effective is your rinsing.

Countercurrent/Counterflow Rinsing is accepted by just about everybody today as the smartest way to go. Figure 8 shows water coming into a single stage overflowing rinse tank. That is the way it was for years and years. Figure 9 shows a double counter-flow rinse tank where the same amount of water used in the single rinse tank now feeds two rinse tanks. So, you have two for the price of one.

Figure 10 shows water flows required for each gallon of dragout to attain ten parts per million in the final rinse. The numbers are very striking. You can reduce 60-85% by going to a double counter/current rinse and 90-97% by going to a triple. Most people feel that anything beyond a triple is really not buying you anything. That is up to you whether you can afford the extra labor of going to four. Four is better than three, but can you afford the extra step productionwise?

Conductivity Controllers -- These devices allow water to flow into the rinse tank when the water is dirty, and shut water off when the rinse is clean. That is the only reason you have running rinses -- because the water is dirty. If the water is clean, why have pure water continually flowing. It doesn't make sense at all. If you can reuse cooling water, that's great because it is water you have paid for, and it can do a second job.

Rinse Timers -- When work enters the rinse, the operator just hits a switch, water flows for a fixed time, and that is that. That is not quite as sophisticated as a rinse controller, but it works. You can limit your water usage and get good rinsing.

You can recirculate treated rinses if you have a backlog of treated rinse. You can have this water in a holding tank and pump it back.

Open-ended Hoses -- If any of you have had a tank overflow when somebody is filling it at the end of the day, you know the problem. If you use a spring-loaded hose nozzle, you eliminate potential problem.

Don't wash down spills. Use an absorbent material. Save an awful lot of water. You are still going to have to wash down at the end of the day to remove stagnant water that lays under the floor boards. However, if you have a spill, there is no sense in doing anything except using an absorbent material.

Check your tanks and make sure that they are not leaking; you can lose a lot of solution. In the days of water shortages they used to warn about, "One drop per minute" from dripping faucets. It is the same thing with a plating tank.

Minimizing Dragout Volume (Figure 11)-- If you can keep solution in the tank, it isn't a pollutant, and you don't need waste treatment. What you can't keep in will need to be cleaned up by some conventional technique(s).

If you rack a part properly so that it doesn't drain onto the part below, drainage will be more effective.

Drip Timing -- Figure 12 shows that if you can fit it into your production cycle, a 15 second drip time will remove all your solution that is going to drain off.

You can use non-ionic wetting agents, which will not contribute any foreign ions to your plating bath. This will reduce surface tension and reduce the amount of dragout on every part that is withdrawn from a plating tank.

You can put drain boards between the tanks to keep solution off the floor and returned to tanks.

You can remove your parts slowly and smoothly. If you withdraw them slowly, you'll find that you have much less dragout than when you pull them out quickly.

Fog rinses and airknives generally lend themselves more to automatic plating than to rack plating and recover a good amount of dragout.

Rack maintenance -- Many people lose solution because their racks are falling apart. You can also ruin baths due to cross contamination caused by defective racks.

If you can use a higher bath temperature, you will reduce the viscosity and reduce the dragout. With most nickel tanks it doesn't make much difference if you raise the temperature unless you have big parts that flash dry and stain as you pull them out.

Use lower concentration baths if you can. You have seen the low nickel baths that cut the nickel concentration during the days of the energy shortage when you had to go to lower operating temperatures on your baths.

I have seen some dragout figures published by EPA, typically, 1.5 gallons per 1,000 sq.ft. My experience indicates that the figures can be closer to 4 gallons per 1,000 sq. ft. for rack plating and even higher for barrel.

Figure 13 shows dragout data from a large plating shop at the end of one shift. I think they are impressive because they show graphically the performance of dragout tanks.

On the rack nickel the figures in parentheses mean that the two nickel tanks, each with two dragouts, were followed by a common Dragout #3 and Dragout #4. Contaminent level came down to 1.5 parts per million in the fourth common nickel tank.

From the rack copper data you can see that having four dragouts brought copper contamination down to half a part per million.

Now we are going to cover the final items, namely the recovery techniques that we have found to be successful. We, of course, have addressed the conventional recovery technologies. They are all fine; they all work, but they have a price; whether it be in manpower, energy, space, or sludge.

In addition, some conventional recovery techniques (Electrolytic, Ion-Exchange, and Carbon Adsorption) recover only part of the value of the dragged out solution. Brighteners, wetters, chemical additives, and metal fabrication charges are not recovered.

With Resource Recovery you return all of the material values that you paid for. Implementation of an effective reclamation program requires:

1. Dragout tanks on all contaminating processes. Dragout is returned to the operating tank automatically to replenish evaporation.

2. Warm and/or acidified rinses (or fog spray) to effectively remove contaminants from parts.

3. A closed-loop counterflow rinse to feed back to the dragout tank.

4. The use of some technique to reduce bath volume of room temperature baths. These include: forced evaporation, aeration, or a combination of tank overflow and evaporation.

These techniques reduce and can eliminate the need for conventional waste treatment. In those instances where the above techniques alone cannot keep up with contaminants, electrolytic techniques can be added to the dragout(s), and ion-exchange can be added to the closed loop counterflow rinses.

With attention to dragout from acid processes, it is often possible to avoid pH adjustment of an effluent stream.

FIGURE 1

CONVENTIONAL DESTRUCT TECHNOLOGIES

1. ALKALINE PRECIPITATION
2. SULFIDE PRECIPITATION
3. CYANIDE OXIDATION
4. CHROMIUM REDUCTION
5. BOROHYDRIDE PRECIPITATION
6. STARCH XANTHATE
7. FKJA FORMALDEHYDE PRECIPITATION
8. CHELATE DESTRUCT

FIGURE 2

CONVENTIONAL RECOVERY TECHNOLOGIES

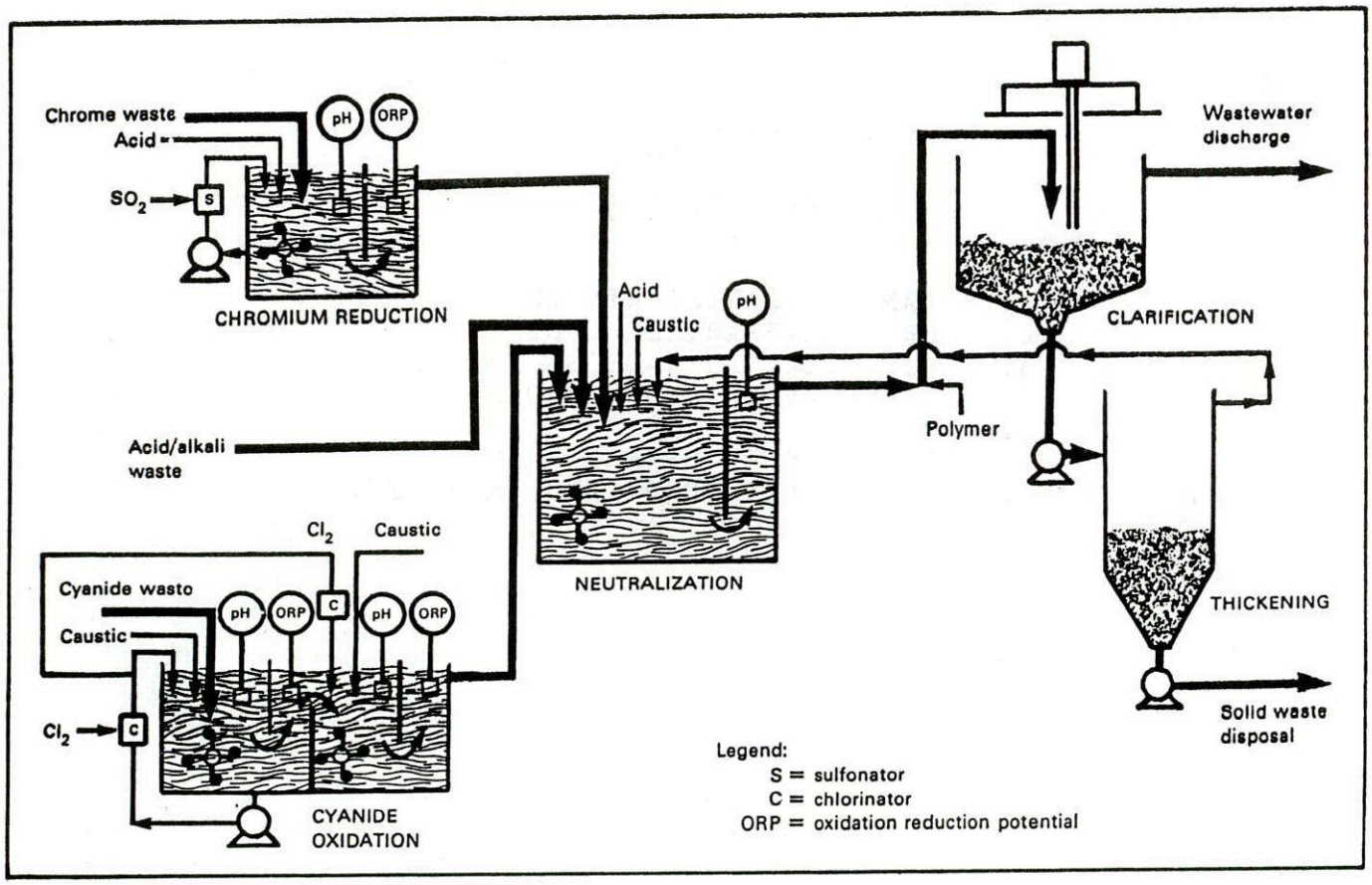
1. ELECTRODIALYSIS
2. REVERSE OSMOSIS
3. EVAPORATIVE RECOVERY
4. ELECTROLYSIS - DC/PULSE PLATE
5. CARBON ABSORPTION
6. ION-EXCHANGE

FIGURE 3

STREAM SEGREGATION

1. CYANIDE-BEARING RINSES
2. CHROMIUM-BEARING RINSES
3. ACID-ALKALI NON-CHELATED RINSES (NON-CYANIDE, NON-CHROME)
4. CHELATED RINSES
5. STRONG DUMPS OF EACH ABOVE
6. STREAMS NOT REQUIRING TREATMENT

FIGURE 4



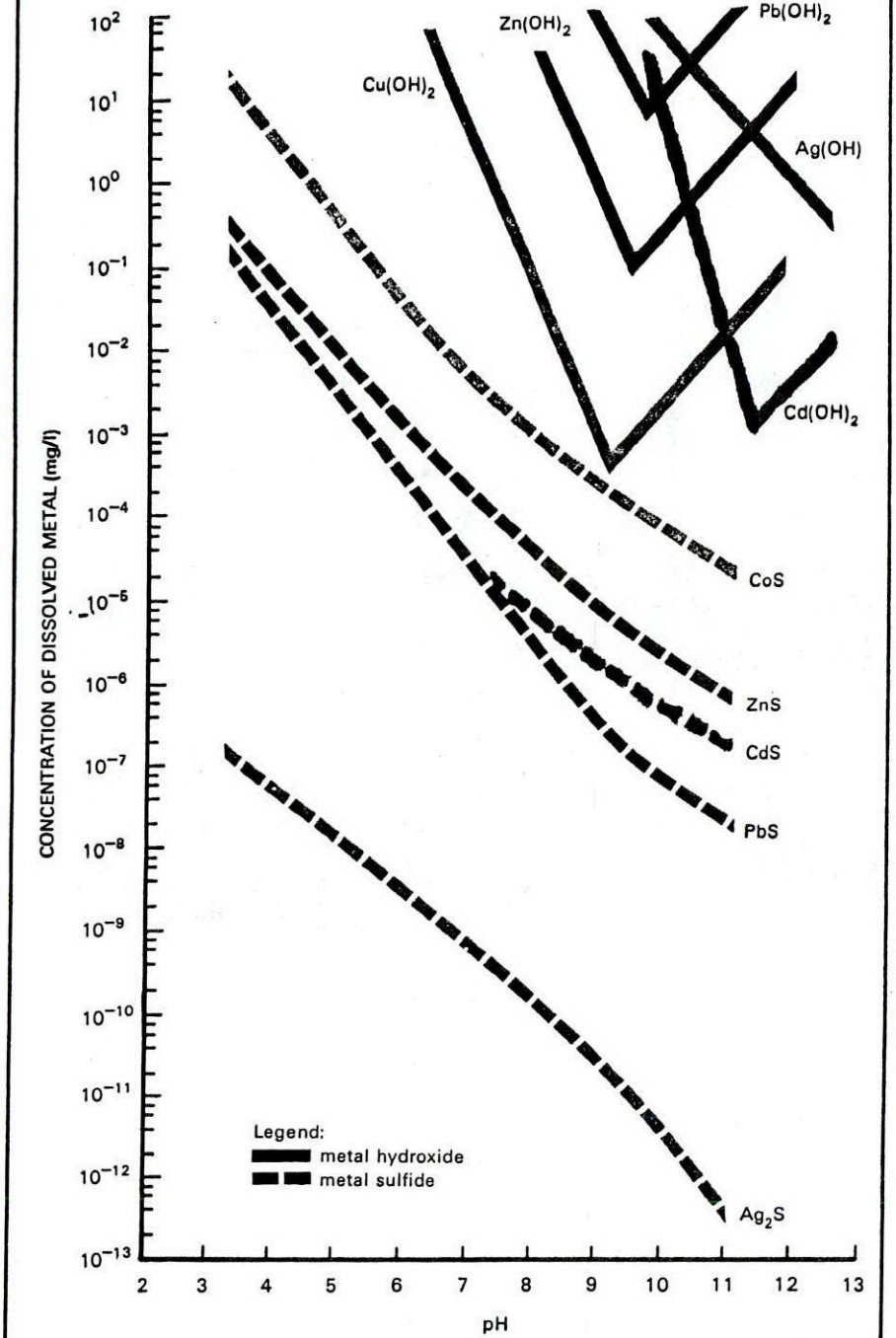
Electroplating Industry Conventional Wastewater Treatment

REPRODUCED FROM
ENVIRONMENTAL REGULATIONS AND TECHNOLOGY

EPA 625/10-80-001, AUGUST 1980, p. 13.

FIGURE 5

Solubilities of Metal Hydroxides and Sulfides as a Function of pH



Note.—Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modern Alkaline Cooling Water Treatment," in *Industrial Water Engineering* (p. 31), Jan.-Feb. 1973.

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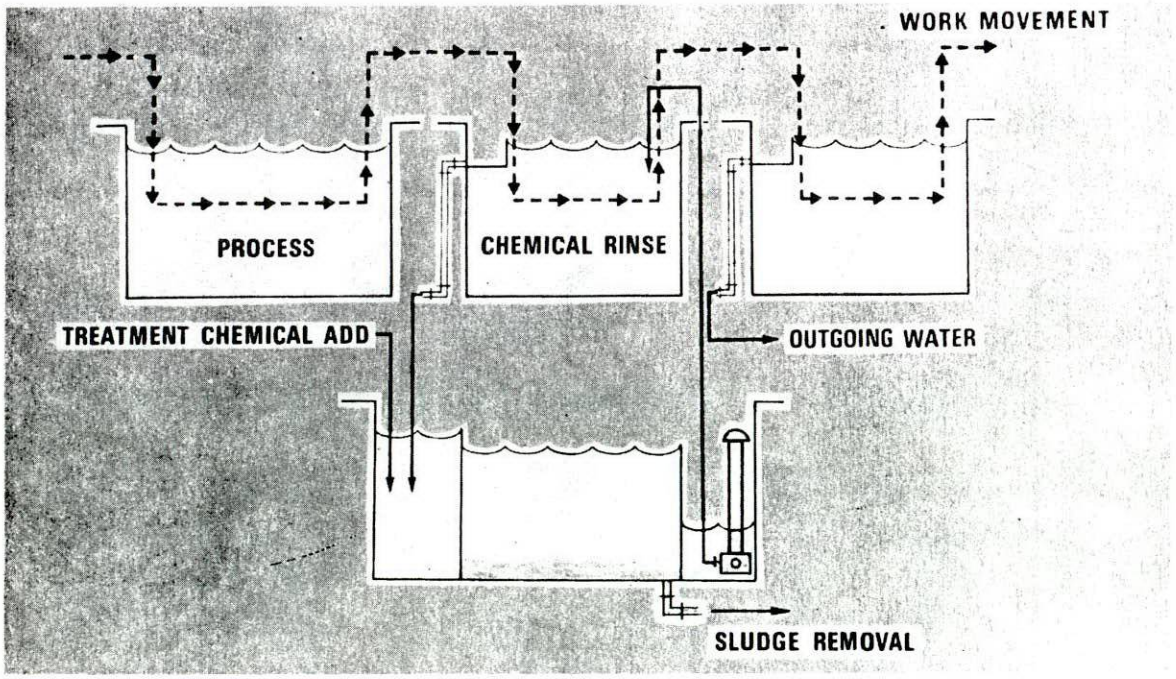
CONTROL AND TREATMENT TECHNOLOGY FOR THE METAL FINISHING INDUSTRY
EPA 625/8-80-003, AUGUST 1980, p. 3

FIGURE 6



Integrated chemical rinse.

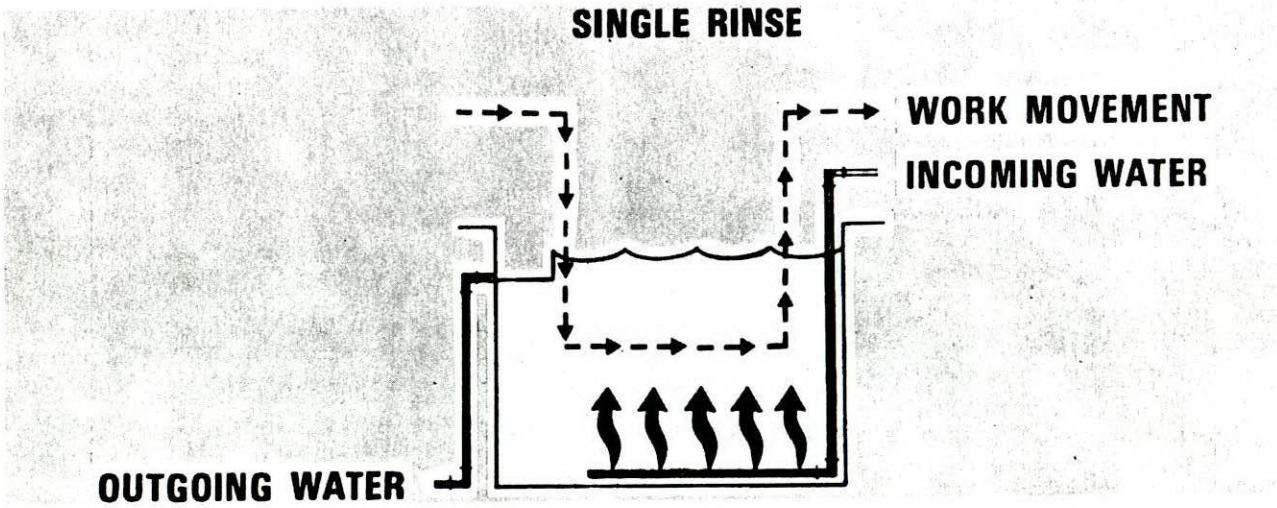
REPRODUCED FROM:
IN PROCESS POLLUTION ABATEMENT -- UPGRADING METAL FINISHING FACILITIES TO REDUCE POLLUTION
EPA 625/3-73-002, JULY 1973, p. 30.

FIGURE 7

WATER USE REDUCTION

- FLOW CONTROL VALVES
- AERATION/AIR AGITATION/PUMPING
- COUNTERCURRENT RINSING
- CONDUCTIVITY CONTROLLERS
- REUSE COOLING WATER
- RINSE TIMER
- RECIRCULATE TREATED EFFLUENT
- REUSE ACID RINSES AFTER ALKALINE CLEANERS
- NO OPEN-ENDED HOSES (SPRING-LOADED HOSE NOZZLES)
- CLEAN UP SPILLS WITH ABSORBENT - NO WASHDOWN
- INSPECT FOR LEAKING TANKS, VALVES, ETC.

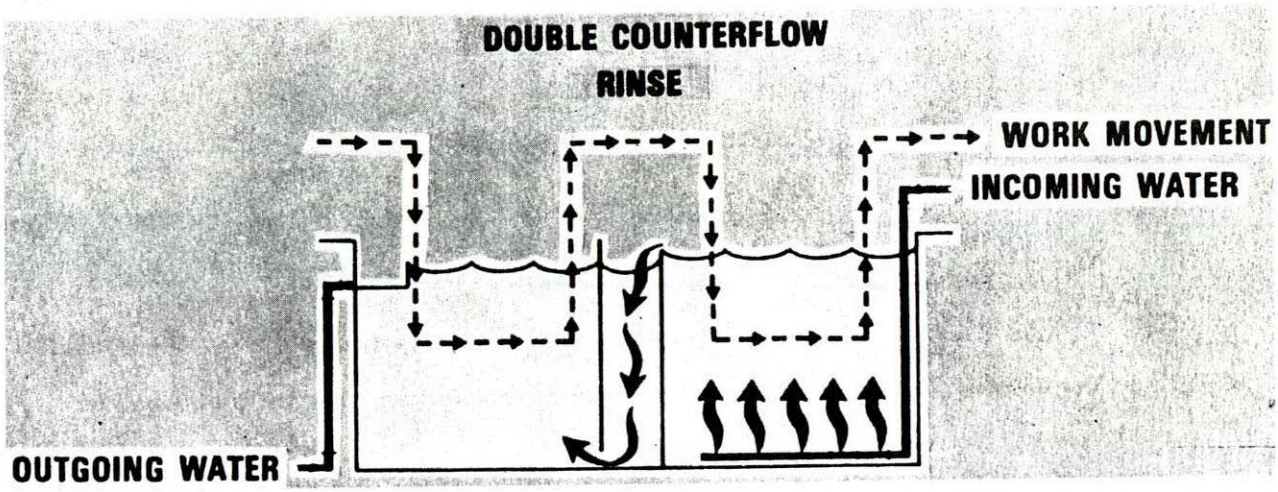
FIGURE 8



REPRODUCED FROM:
IN-PROCESS POLLUTION ABATEMENT, UPGRADING METAL-FINISHING FACILITIES TO REDUCE POLLUTION

EPA 625/3-73-002, JULY 1973, p. 27.

FIGURE 9



REPRODUCED FROM:
IN-PROCESS POLLUTION ABATEMENT, UPGRADING METAL-FINISHING
FACILITIES TO REDUCE POLLUTION
EPA 625/3-73-002, JULY 1973, p. 27.

FIGURE 10

REDUCTION OF FLOW

IN MULTIPLE RINSE TANKS

RINSE RATIO	PERCENT REDUCTION OF FLOW NO. OF TANKS		
	1	2	3
10	0	68	80
100	0	90	95
1,000	0	97	99
10,000	0	99	99.8

FIGURE 11

MINIMIZING DRAGOUT VOLUME

- PROPER RACKING
- DRIP TIMERS
- WETTING AGENTS
- DRAIN BOARDS
- REMOVE PARTS SLOWLY
- FOG RINSES
- RACK MAINTENANCE
- INCREASED BATH TEMPERATURES
- LOWER CONCENTRATION BATHS

FIGURE 12

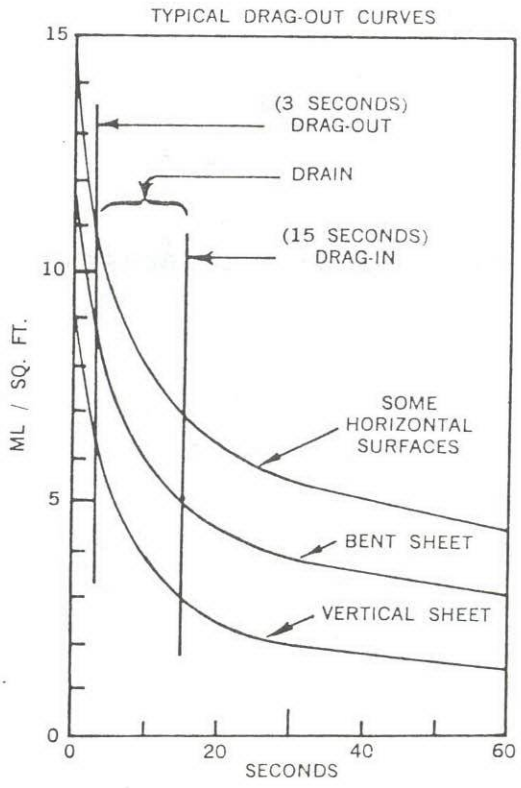

TYPICAL DRAG-OUT CURVES
15
10
5
0
ML / SQ. FT.
(3 SECONDS)
DRAG-OUT
DRAIN
(15 SECONDS)
DRAG-IN
SOME
HORIZONTAL
SURFACES
BENT SHEET
VERTICAL SHEET
0
20
40
60
SECONDS

FIGURE 13

DRAGOUT DATA

BARREL NICKEL

D.O. #1 . . . . . 12,800 mg/l Ni
D.O. #2 . . . . . 4,040 mg/l Ni

RACK NICKEL

D.O. #1
1,100 mg/l Ni . . . . 1,640 mg/l Ni
D.O. #2
220 mg/l Ni . . . . . 368 mg/l Ni
COMMON D.O. #3
70 mg/l Ni
COMMON D.O. #4
1.5 mg/l Ni

BARREL COPPER

D.O. #1 . . . . . 6,100 mg/l Cu
D.O. #2 . . . . . 1,720 mg/l Cu

RACK COPPER

D.O. #1 . . . . . 740 mg/l Cu
D.O. #2 . . . . . 110 mg/l Cu
D.O. #3 . . . . . 18 mg/l Cu
D.O. #4 . . . . . 0.4 mg/l Cu

E-2

Environmental II
Session E

Recovery of Metals from Effluents by High Efficiency Air Agitation Electrowinning

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RECOVERY OF METALS FROM EFFLUENTS BY HIGH EFFICIENCY AIR AGITATION ELECTROWINNING

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INTRODUCTION

Although it has been recognized only relatively recently that the electrowinning process could be employed for the recovery of metals from wastewaters, the basic process is well established. Electrorefining, a process closely related to electrowinning, was introduced about a hundred years ago. Today, practically all of the world's copper (approx. 8,000,000 metric tons/year) is electrorefined. Although copper electrowinning is by far the most common, other metals such as zinc, nickel, cadium are also electrowon to a significant extent.

Electrowinning and electrorefining, have traditionally been carried out on a very large scale. An average copper refinery producing 500 tons per day of copper utilizes approximately 200,000 m^2 of total electrode area. This corresponds to about 50,000 anodes and 50,000 cathodes suspended in about 1500 tanks occupying a total floor area of about 6000 m^2 By way of comparison, a typical effluent stream is very much smaller, perhaps yielding less than 0.01 tons per day of metal.

The primary limitation of electrowinning technology for effluent recovery is that the traditional design does not lend itself to the treatment of low metal concentrations. Solution metal concentrations in conventional electrowinning operations are usually in the order of 30-50 g/L while most effluent streams contain less than 10 g/L and frequently less than 1 g/L.

Because of the large size of commercial electrowinning and electro-refining installations for primary metals production, the depressed market conditions of metals and because of the rather conservative philosophies of the industry, recent developments in cell design, which would improve performance and extend the operating concentration range of the process,

have not been exploited. Because of the smaller size of effluent applications it is feasible to incorporate the latest cell design innovations to alleviate the concentration limitation of the process.

THE ELECTROWINNING PROCESS.

In electrowinning, metal is deposited from solution onto cathode blanks by application of a direct electrical current according to equation (1). In a competing reaction, hydogen ions are reduced to gaseous hydrogen according to (2). As the concentration of metal ions in solution is lowered the potential of (1) approaches that of (2) and the majority of the current is consumed by the hydrogen evolution process.

Oxygen evolves simultaneously from insoluble anodes, according to equation (3).

$$Cu^{++} + 2e^{-} \longrightarrow Cu^{0} \qquad (1)$$

$$2H^{+} + 2e^{-} \longrightarrow H_2 \qquad (2)$$

$$H_2O \longrightarrow 1/2\,O_2 + 2H^{+} + 2e^{-} \qquad (3)$$

For the most part, electrowinning cells utilize a basic design comprising alternating flat sheet cathodes and anodes. As metal is plated onto the cathode, the stagnant liquid film adjacent to the cathode surface tends to become depleted in metal. The current density, which determines the rate of metal deposition, must not exceed the rate at which metal ions diffuse through this film to the cathode. If the current density is too high, the concentration of metal ions in the film will be excessively depleted producing a condition known as "concentration polarization". This results in an adverse effect on the current efficiency as well as the quality of the deposit, as a result of hydrogen evolution.

Concentration polarization tends to promote the growth of minute surface imperfections in the deposit in the following manner. The mass transfer to the tips of these imperfections protruding into or through the diffusion film is greatly improved compared with smooth parts of the cathode (see Fig. 1). The low concentration polarization at these tips compared with the rest of the cathode disturbs the uniformity of the current distribution and

results in increased current density on these imperfections.

The allowable or *critical* current density is determined by two principal factors:

1. the concentration of metal ions in the bulk of the solution
and

2. the thickness of the film.

With conventional electrowinning designs employing flat plate electrodes, the maximum allowable current density for high quality deposits is impracticably low below a concentration of about 10 g/L. The rule of thumb for conventional electrowinning (referred to as the "capability index" is a current density (in amps/ft^2) of about 0.5 to 0.7 times the copper concentration in g/L [1,15]. Meyer [2] for example, reported the efficiency of deposition as a function of Cu concentration and current density. He also described the quality of the deposit.

Table 1 - Copper Electrowinning with no agitation [2]

concentration [Cu](g/L)	current density (A/dm^2)	current efficiency	deposit quality	capability index
10	0.54	99	good	0.50
4	0.52	41	spongy	1.21
4	0.26	99	good	0.61
1	0.54	41	poor	5.00
1	0.08	93	good	0.75

There are basically two different design approaches to extending the operating concentration range of the electrowinning process. The first approach accepts the fact that low current densities must be employed at low concentrations and counteracts this by using cathodes with high effective surface areas such as porous beds of conductive particles or fibres [3,4]. The second approach seeks to increase the allowable current density by reducing the thickness of the diffusion film.

A major practical consideration in the selection of a novel cell design is the form in which the final metallic product is obtained. Designs employing flat plate cathodes produce an easily harvested sheet of metal

which is marketable. High surface area cathode designs usually produce a metal product which must be further processed to achieve marketability. This is a serious limitation to the high surface area approach, particularly where larger quantities of metal are involved. In addition, the complexity of any particular cell design and the anticipated problems associated with its operation must be seriously weighed against its relative advantages in performance.

One way of decreasing the cathode film thickness is to agitate the electrolyte by recirculating the solution at a high velocity past the cathode, parallel to the surface [5,6]. Published data indicates that a capability index of approximately 1.1 can be achieved at copper concentrations below 10 g/L at 21°C with this cell[7](see Figure 3). This is approximately twice that reported by Meyer with no agitation, a significant improvement.

HIGH EFFICIENCY AIR AGITATION

Another well known agitation technique is air agitation. Air agitation is employed extensively in the electroplating industry. Kennocott Copper, at one time the largest U.S. copper producer, sought a means of reducing electrowinning plant costs for processing the relatively dilute leach liquors characteristic of low grade copper ores. A development program that extended through the 1970's yielded a patented electrowinning cell design based upon a new high efficiency air agitation (HEAA) scheme [8]. A uniform curtain of fine air bubbles is directed across the face of the cathode which reduces the thickness of the diffusion layer of liquid adjacent to the cathode and dramatically increases the rate of mass transport to the cathode from the bulk liquid. This reportedly allowed deposition of metal at current densities which are high in relation to the metal concentration, while producing metal of excellent purity and mechanical integrity. Extensive testing on laboratory and pilot plant scale indicated that this cell design could increase the electrowinning capability index to 3-5 ASF/g/L. Most of this work was conducted on copper electrowinning applications at metal concentrations in excess of 10 g/L. Table 2 shows some typical results. These results can be compared to conventional electrowinning cells which operate at concentrations of 30-50 g/L and current densities of 1.96 amps per dm^2 (21 ASF).

Ettel[9] made a detailed comparison of various agitation schemes including the electrolyte recirculation method and a well designed air agitation system. Assuming one wanted a three-fold increase in mass transfer over natural convection, he calculates that the power required for agitation by electrolyte recirculation would be about 10 times higher than for air sparging. He concluded that the most effective approach was air agitation.

Ettel's work at INCO, utilizing a similar air agitation scheme to Kennecott's, yielded comparable results. One experiment conducted at Cu= 2 g/L (see Table 2) obtained a capability index of approximately 4, which is almost *four* times that of the electrolyte recirculation cell!

Based upon this data it is evident that the air agitation technique has a lot of potential in treating dilute solutions. It was felt, however, that more testing was required with the HEAA cell to better determine its utility in treating solutions at metal concentrations of less than 10 g/L.

Table 2 - Published Data: Copper electrowinning with air agitation

	#1 [10]	#2 [9]
Cu concentration (g/L)	32	2
current density (A/dm^2)	15.2	0.806
acid concentration (g/L)	171	5
temperature	63.°C	N/A
voltage	2.8	N/A
capablility index	4.4	4

CELL DESIGN

Although, as discussed above, very few innovations in electrowinning cell design have been exploited in the primary metals industry, this does not mean that there have not been any developments in the field. A number of these improvements were incorporated into the HEAA cell design to supplement and complement the air agitation.

Cathode size

Most commercial electrowinning cells used in the primary metals industry

employ "standard" cathodes measuring approximately 1m x 1m. Given the much smaller size of effluent applications, it was felt that smaller cathodes, which if necessary could be removed by hand without the aid of a crane, would be more appropriate.

Close anode/cathode spacing.

Conventional cells typically employ cathode/anode spacing of about 5 cm (2 inch). This was reduced to about 2.5 cm (1 inch). Closer anode to cathode spacing reduces the "IR" voltage drop across the cell, resulting in lower energy consumption and improves agitation[9]. It also allows for a reduction in the overall size of the cell for a given cathode area requirement.

Non-retentive cathode blanks.

Metal is deposited on permanent stainless steel cathode "blanks" from which it can be easily stripped. The design of the cell is such that non-conductive edge stripping, to prevent the edges of the deposit on each face from joining, is **not** required. Special treatment of the cathode blank surface with parting agents is also **not** required. Removal of metal from cathodes can be done on a individual basis by manually lifting each cathode from the cell, or a crane can be employed to simultaneously remove the entire cathode inventory for more efficient, high production processing.

Lead/calcium alloy anodes.

A patented lead/calcium alloy[11] is employed for the anodes for sulfate systems. This results in the production of a very high purity deposit. The excellent physical characteristics of this alloy extend anode life considerably. Anodes are soldered to the copper crossbars to ensure fault free electrical contact. Since occlusion of anode corrosion products is a major contributor to cathode lead impurities, the use of these more stable anodes results in the production of purer copper[12].

Figure 2 shows a commercial **HEAA** cell designed for treating dilute solutions. This unit contains 22 cathodes each containing 56 dm^2 (6 ft^2) for a total of 1230 dm^2 (132 ft^2) of cathode area.

While the potential increase in performance with air agitation is sub-

stantial, the design remains fairly simple, yields deposits which can be readily harvested and marketed and maintains a basic similarity to the traditional design, upon which a wealth of practical experience and data has been accumulated over many years of commercial scale operation.

EXPERIMENTAL

It was decided to perform testing on full sized cathodes, because of the misleadingly good cathode quality and high current density capability obtained with smaller cells that had been reported in comparison tests[13]. The cell employed for the tests utilizes a single cathode with approximately 56 dm^2 of total area (both sides) and incorporates the above design features. One anode is employed on each side of the cathode. Figure 3 shows the test cell along with a spare cathode.

Electrolyte was circulated continously between the cell and a small reservoir. The total electrolyte volume was approximately 130 L. Cooling coils were installed in the reservoir to maintain the temperature at approximately 25°C. Runs were conducted over periods of time ranging from 2-16 hours to deposit sufficient metal so that deposit quality could be established. Concentrated copper sulfate solution was metered to the cell to maintain the copper concentration as constant as possible over the duration of the run. A sulfuric acid concentration of apporoximately 1M was obtained in the electrolyte at all times.

Table 3 - Test Results: Copper electrowinning with air agitation

	#1	#2	#3	#4	#5
[Cu] (g/L)(avge)	.125	.54	.81.	1.95	10
$[Cu]_i$ (g/L)	.1	.5	1.05	2.0	9.4
$[Cu]_f$ (g/L)	.15	.58	0.55	1.9	10.5
CD (A/dm^2)	.0538	.269	0.321	.936	5.38
CD (ASF)	0.5	2.5	5.11	8.7	50
voltage	NA	1.2	1.2	1.5	NA
avge. cap. index	4.0	4.62	3.7	4.5	5
run time (hr)	4	2	16	4	3
current eff.(%)	56%	>99%	95%	93%	91%
depost quality	smooth	smooth	smooth	rough	rough

DISCUSSION OF RESULTS

Results for five different runs, ranging in copper concentration from 0.1-10 g/L, are summarized in Table 3. These runs correspond to the maximum current density at a given concentration of copper for which an acceptable deposit was obtained. The deposit produced in runs 1-3 was very smooth and adherent. It is possible that the current density could have been increased somewhat and still been acceptable. The deposit produced in runs 4 and 5 was somewhat rough, but adhered firmly to the substrate and although possibly not acceptable for commercial copper production, was considered acceptable as saleable scrap material. Under the latter conditions the current density was probably approaching the upper limit.

The copper concentration fluctuated somewhat during run 3. Considering the extended length of this run (16 hours), the cell operated at the lower range of copper concentration for a considerable length of time towards the end of the run, during which time the deposit was presumably good, since the final deposit was smooth. It could then be stated, with some justification, that the capability index for this run was as high as 5.45 for this run.

The lower current efficiency (56%) for run 1 should be noted. The increased tendency for hydrogen evolution is undoubtedly a result of the increased cathode potential as a result of the very low copper concentration (0.1 g/L) along with the high (1M) hydrogen concentration.

The capability index obtained was approximately 4 throughout the concentration range of 0.1-10 g/L. This compares favorably with the previous published air agitation results summarized in Table 2, at least one of which was conducted under much more favorable, high temperature conditions (63°C). It is almost four times that of the electrolyte circulation system, and eight times that of a cell with no applied agitation!

No attempt was made to study the effect of temperature on capability index although the higher diffusion rates realized at elevated temperatures would undoubtedly have a very significant positive effect. Published data with the electrolyte recirculation cell[7] indicates that increasing the temperature from 21°C (70°F) to 60°C (140°F) allows a four and one

half fold increase in current density. A comparable effect could be experienced with the HEAA cell.

Figure 3 summarizes the results obtained in this study as well as published results with the electrolyte recirculation system and no applied agitation. Note that the temperature for the electrolyte recirculation system was slightly lower (21°C) than for the HEAA tests (25°C). No temperature data is available for the non-agitated data, but it is presumed they were obtained at room temperature.

Under the conditions of run 4 at Cu= 2 g/L, the energy conumption is calculated as 1.37 kwh/kg copper, assuming a 100% rectifier conversion efficiency.

APPLICATION

An excellent application of the HEAA cell is recovery of metal values directly from metal finishing rinsewaters. Normally the cell would be installed in a bypass arrangement on the first rinse tank following the plating bath (i.e. the dragout tank). Spent electrolyte from the cell would overflow back to the rinse tank and be recirculated on a continuous basis through the cell (see Fig. 4). For some applications (e.g. nickel) it is necessary to provide continuous pH adjustment of the rinsewater to counteract the generation of acidity at the anodes. For applications where anions other than sulfate are present, it may be necessary to substitute other anode materials such as precious metal clad titanium for lead alloy, which corrodes in chloride and other media. For cyanide plating rinsewater, as an added benefit, some of the cyanide would be destroyed at the anode by oxidation.

The HEAA cell can be advantageously applied in conjunction with an ion exchange system as shown in Fig. 5. Effluent solution containing a very low concentration of metal (e.g. Cu<1 g/L) is passed through a cation exchange column to yield a barren solution containing less than 1 mg/L. Sulfuric acid elution of the cation exchanger yields a metal sulfate solution containing typically 10-40 g/L of metal. This eluate flows to the electrowinning cell which plates the metal down to a concentration of about 1 g/L or below and simultaneously liberates an equivalent amount of sulfuric acid. The sulfuric acid solution yielded by the electrowinning cell can then be neutralized or in some cases be reused by the cation exchanger

for subsequent regenerations.

Since it is not possible to electrowin nickel below a pH of about 2, it is necessary to continuously neutralize the acid that is generated during electrowinning with sodium hydroxide. As a result, the acid cannot be recycled to the cation exchanger. If a metal selective chelating resin is employed, however, the spent electrolyte can be combined with the dilute effluent stream feeding the ion exchanger to recover the residual nickel. The chelating resin will selectively recover the residual nickel, rejecting the sodium (see Fig. 6).

An important advantage of the combined ion exchange/electrowinning configuration is that by employing sulfuric acid regeneration of the ion exchanger, the cell sees only sulfate solution, despite the fact that the original metal source may contain other anions. This eliminates the need for exotic anode materials when dealing with corrosive anions such as nitrate or chloride. It is possible, for example, to take a bleed from a cupric chloride etch, remove the copper by cation exchange and electrowin copper from the sulfate electrolyte eluted from the ion exchanger.

Metallic salt byproduct solution produced by an acid purification unit (APU) employing a sorption resin operating on a metal etching and pickling operation can also be treated by electrowinning (see Fig. 7)[15]. For example, when operated on sulfuric acid/peroxide baths for brass or copper etches, the APU produces a byproduct containing 20-40 g/L copper. This can be readily reduced to about 1 g/L or below by HEAA electrowinning and then discharged to a conventional precipitation type waste treatment system to obtain compliance.

Further work is now underway investigating performance of the HEAA electrowinning cell for recovery of zinc and other metals from a variety of different types of dilute effluent solutions

ECONOMICS

To evaluate the economics of the HEAA process, consider a simple case of recovering copper from the first rinse following an acid copper plating bath. If this rinse were held at Cu=2g/L, energy consumption would be 1.37 kwh/kg. Considering a rectifier conversion efficiency of 50% this

would represent about 2.74 kwh/kg. Base on a power cost of $0.04/kwh, the operating cost would be $0.11 /kg ($0.05 per lb). The current value of number one grade scrap copper is about $1.21 /kg ($0.55/lb). The direct savings, excluding labor, to run the recovery system would then be about $1.10/kg ($0.50/lb).

The alternative to recovery would be precipitation, and sludge disposal. Assuming the cost of sludge disposal is $400 per ton and that the sludge has been dewatered to 40% $Cu(OH)_2$, there would be an additional savings of $2.27/kg ($1.03/lb) in sludge disposal costs. The labor saved in operating the sludge dewatering equipment would more than compensate for the labor in operating the recovery system. The total savings would then be about $3.37 per kg ($1.53/lb)

The 1230 dm^2 (132 ft^2) cell shown in Figure 2 could recover 869 g/h of copper when operated conservatively at Cu=2 g/L, 0.65 A/dm^2 (6 ASF) and 93% current efficiency. Over 6000 h/y (5 d/w, 24 h/d, 250 d/y) the system would recover 5214 kg of metal, netting a saving of $17,571 annually.

The cost of the recovery system, including cell, rectifier, pump and other accessories, would be approximately $53,000. The payback on the initial capital investment would therefore be 3.0 years, a figure normally considered acceptable. The economics of recovering more concentrated solutions or more valuable metals would obviously be more attractive.

SUMMARY

The HEAA electrowinning cell provides an effective means of electrowinning metals from dilute solutions, typical of those associated with effluent streams. High quality deposits are easily harvested in a convenient sheet form which can be readily marketed for a premium price.

The efficient operation of the cell is such that equipment size may be reduced by a factor of approximately eight over conventional non-agitated electrowinning systems, and by a factor of four over competitive electrolyte recirculation systems.

The economics of the process indicates that a rapid return on capital investment may be achieved under certain circumstances.

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Figure 1: Growth of Imperfections

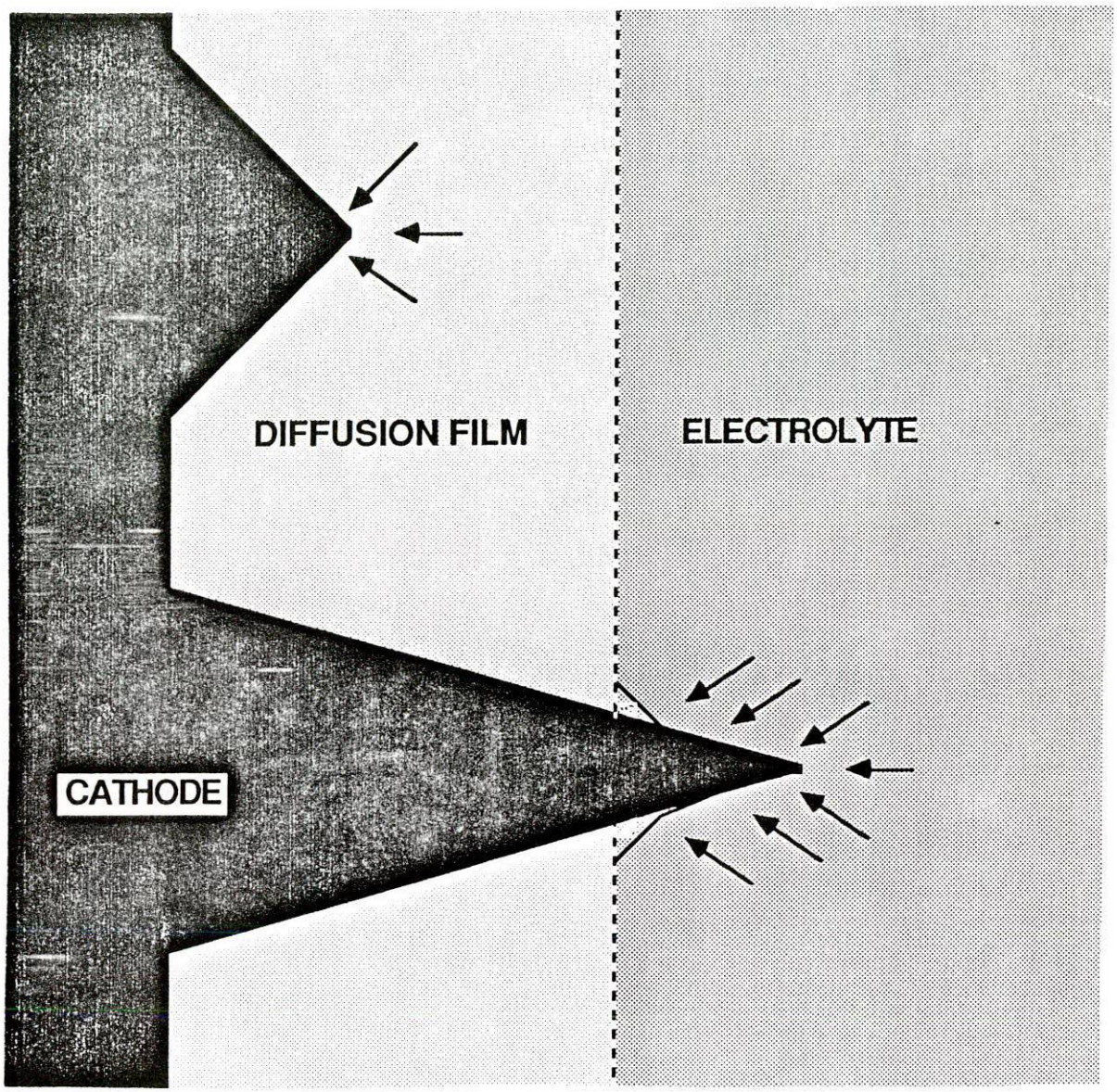


Figure 2: Commercial 1230 dm^2 (132 ft^2) HEAA Electrowinning Cell

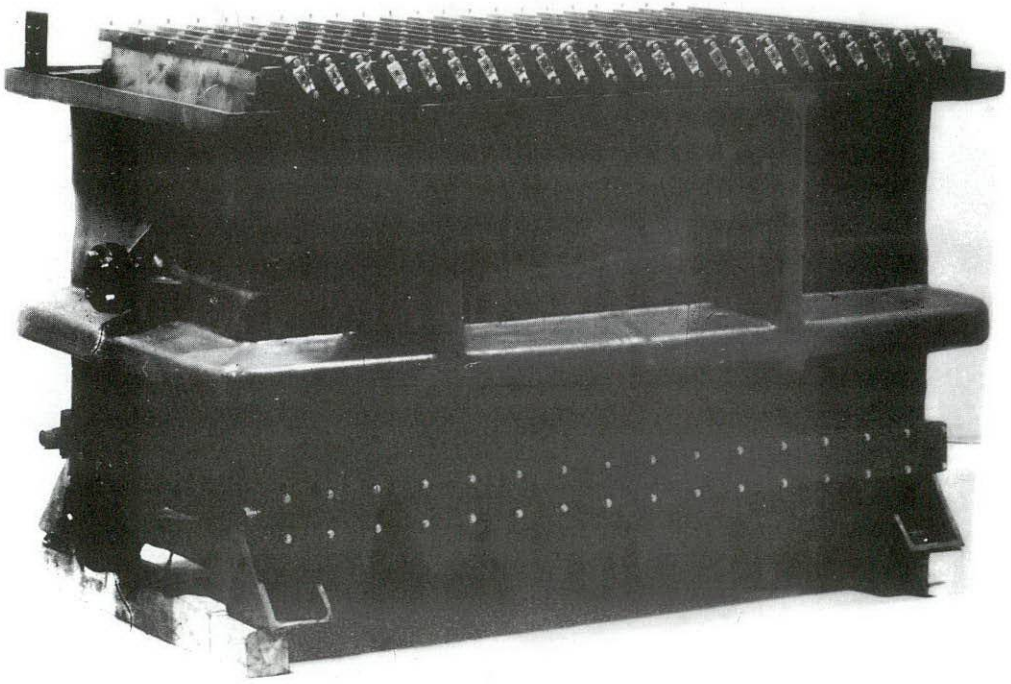


Figure 3: Laboratory HEAA Test Cell

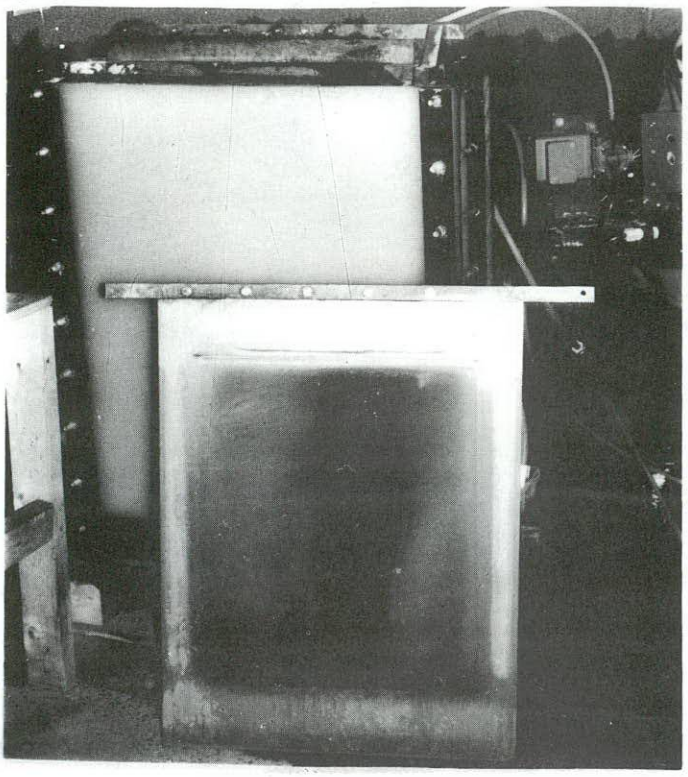


Figure 4: Electrowinning Cell Performance

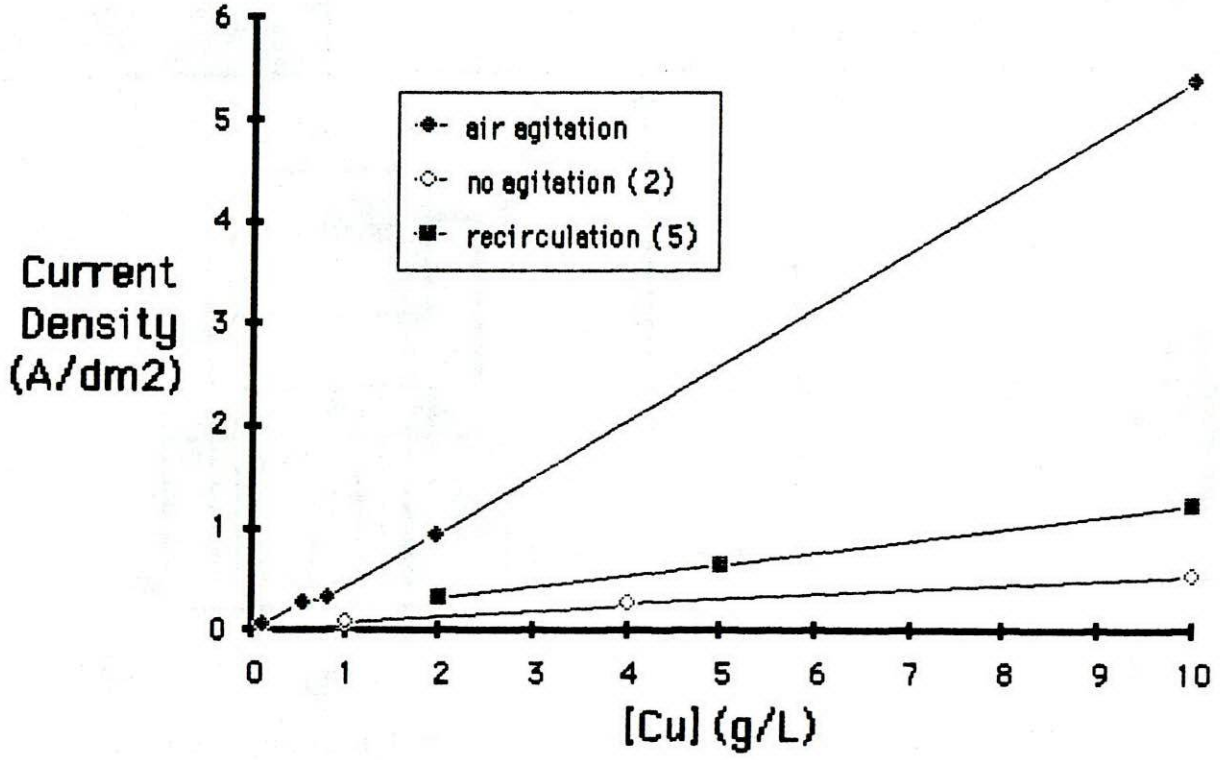


Figure 5: Electrowinning Rinsewater Recovery System

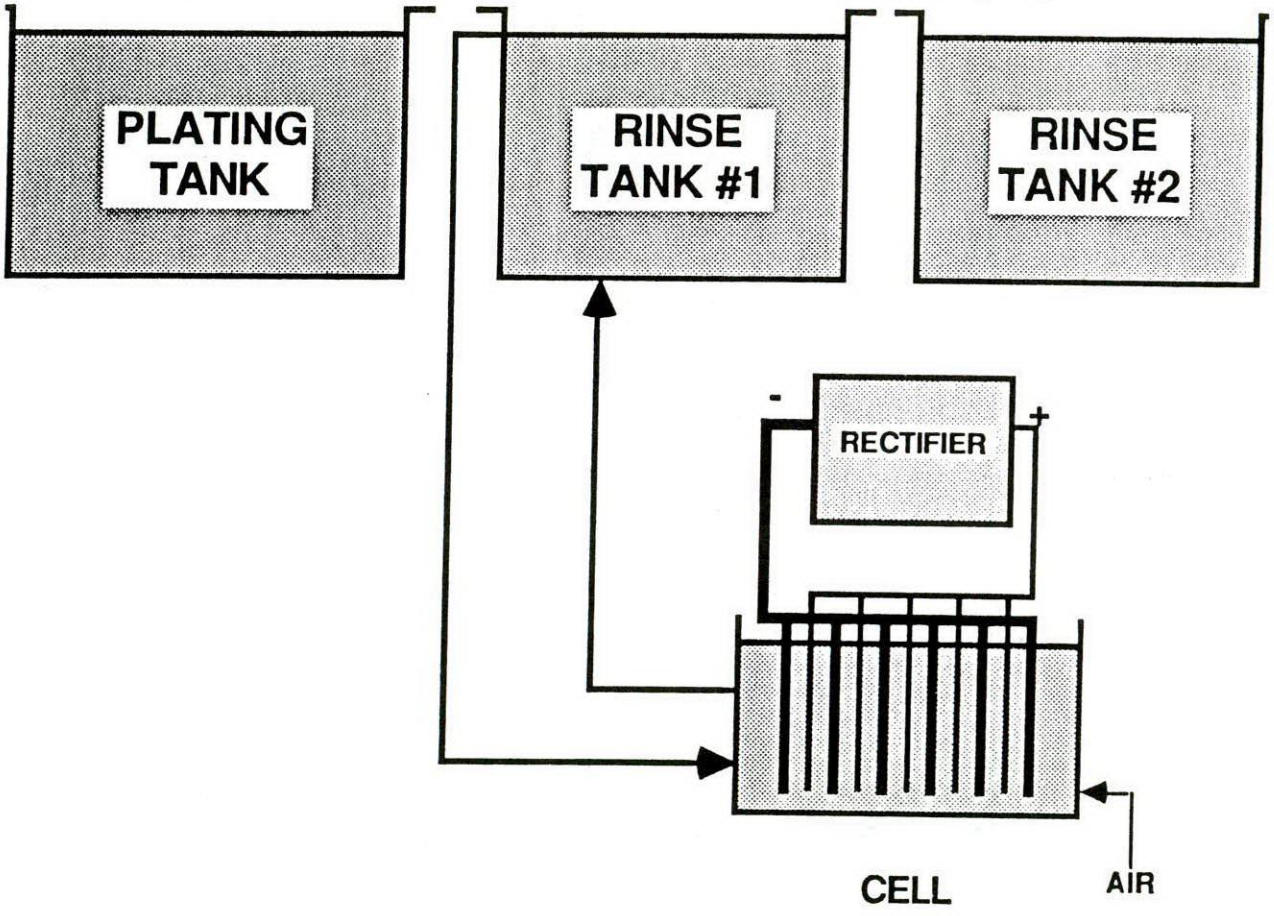


Figure 6: Ion Exchange/Electrowinning Recovery System

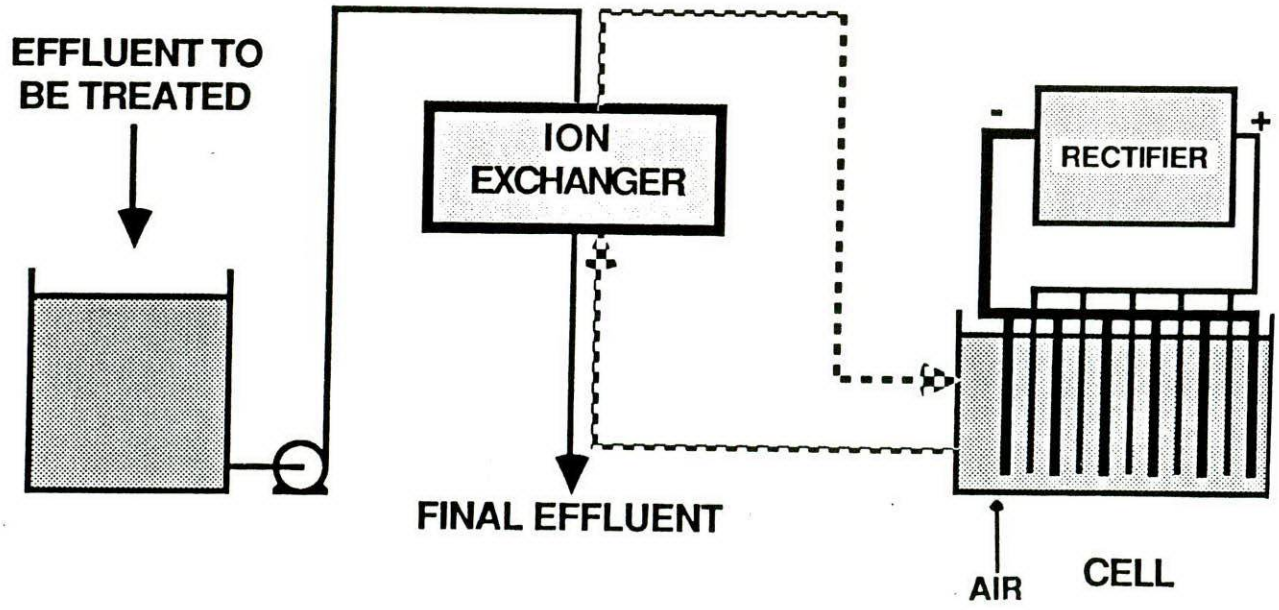


Figure 7: Chelating Ion Exchange/Electrowinning Recovery System

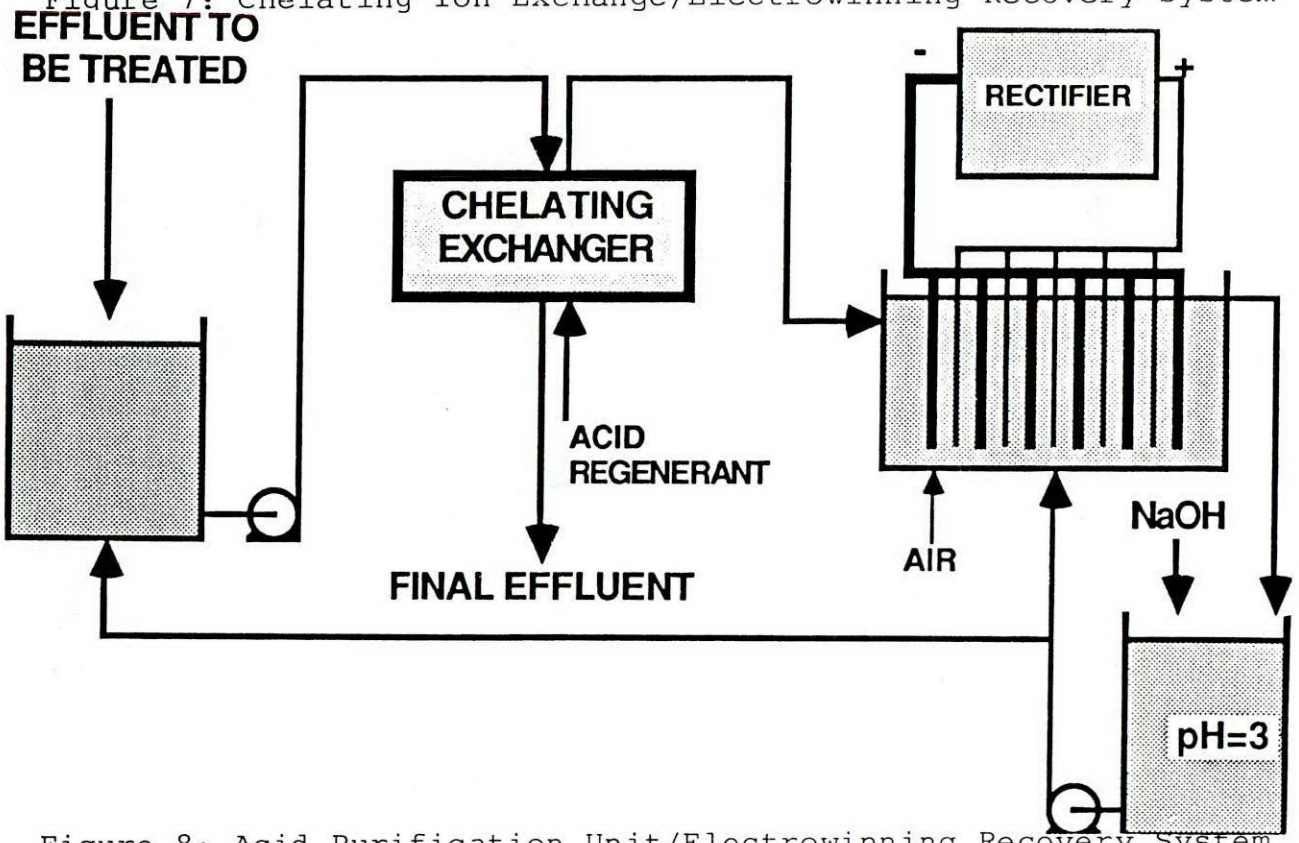
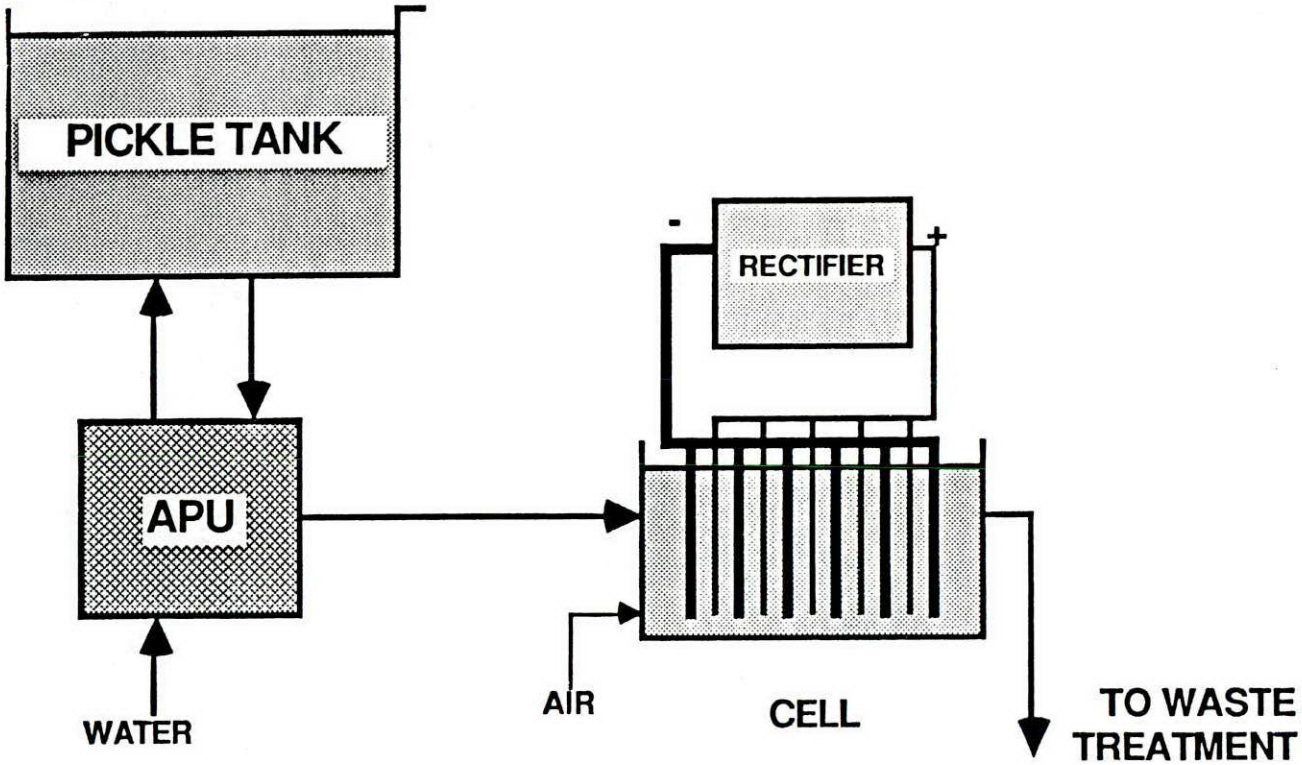


Figure 8: Acid Purification Unit/Electrowinning Recovery System



E-3

Environmental II
Session E

Recovery of Nickel Salts By Electrodialysis Reversal Process

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RECOVERY OF NICKEL SALTS BY ELECTRODIALYSIS REVERSAL PROCESS

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ABSTRACT

Benefits of utilizing Electrodialysis Reversal (EDR) process in recovery of valuable plating chemicals from rinse waters are described in this paper. Expensive metal salts such as nickel sulfamate, chloride, and sulfate are no longer being lost to conventional hydroxide precipitation. The EDR metal recovery system offers a short-time pay-back in capital investment, low operating cost, and minimum operator attention. It also indicates that an efficient recovery process can turn environmental problems into economic opportunities.

INTRODUCTION

The electrodialysis (ED) process was introduced in 1952[1] as a new method of desalting sea water and brackish water based on a physical principle rather than the boiling of water and condensation of steam. The electrodialysis process is an electrochemical separation process in which ions are transferred through a pair of ion selective membranes from a less concentrated to a more concentrated solution as a result of the flow of direct electric current.

From 1954 to 1970[2], the classical ED systems were operated with the transfer of dissolved ions in one direction only. Problems with membrane fouling such as concentration polarization, scale, slime, and undesirable organic build-up were found to be troublesome. Addition of acids, polyphosphates, or similar agents were used extensively in an attempt to control calcium salts scale. However, the practice of chemical addition was relatively ineffective whenever there was poor flow distribution caused by poor channel design or local blockages from slime, silt, or debris build-up.

The Electrodialysis Reversal (EDR) process is a basic improvement in scale control without continuous addition of descaling or complexing agents. The EDR process achieves cleaning and descaling of electrodialysis membrane surfaces by periodic reversal of the direct current flow through the ED membrane stack, and by a simultaneous interchange of diluting and concentrating streams. Figures 1a and 1b depict the simplified EDR process diagram and schematic respectively.

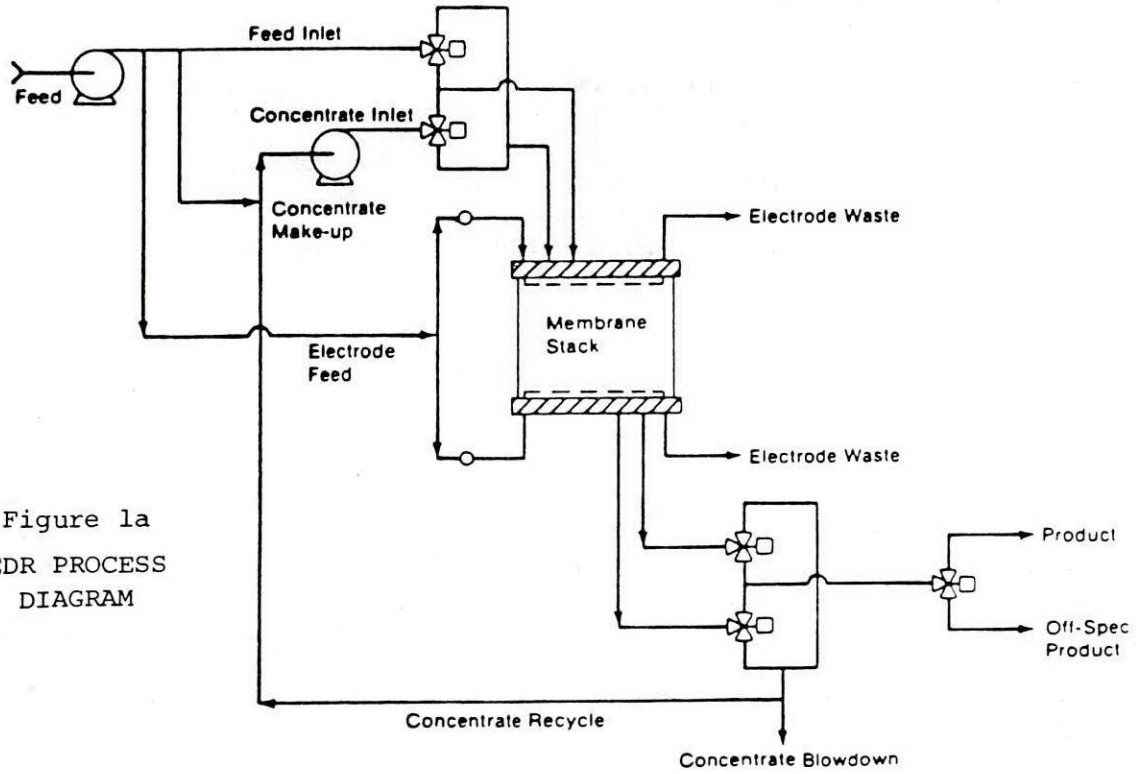


Figure 1a

EDR PROCESS DIAGRAM

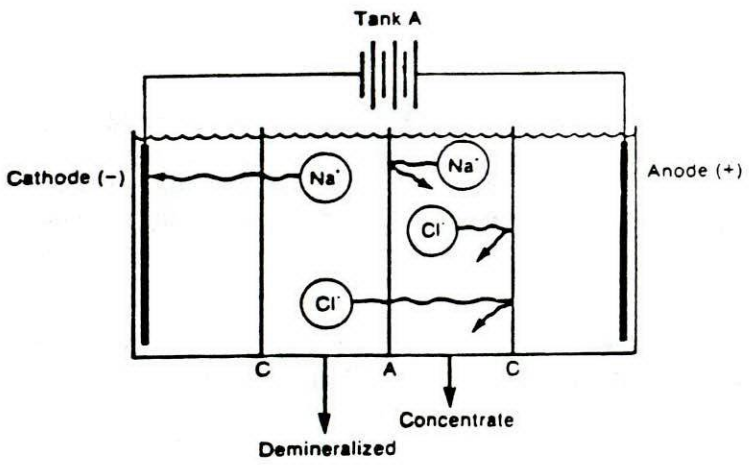
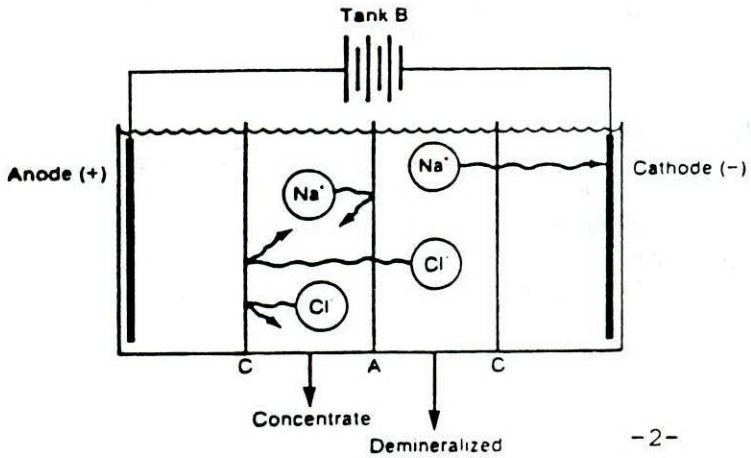


Figure 1b

EDR SCHEMATIC



The polarity reversal principle has been applied successfully in many large commercial units. Today, the largest operating EDR unit is the 6 MGD plant used for demineralizing Tigris River water for a major refinery in Baghdad, Iraq. The success of the EDR process resulted in the design and sale of standard EDR plants ranging in capacity from 500 to 1 million gallons per day. Over 1,400 EDR plants are in use around the world.

Applications of the EDR process range from desalination of brackish water[3] to process water treatment for in situ mining[4], industrial water treatment[5], quality water for safety rest area[6], ponds[7], and deionization of printed wiring board process water[8]. Recently, the EDR process is being used to recover nickel salts from rinse water in nickel plating operation.

EDR NICKEL RECOVERY PROCESS

The early work on unidirectional ED for recovery of nickel salts from rinse water was published in 1972 by Trivedi and Prober[9]. A more comprehensive program conducted by the Ford Motor Company is reported by Marcovac and Heller et. al.[10][11]. Later on, ED is reported in some instances to be used commercially in recovery of nickel salts from rinse water[12]. Today, however, this use of ED is not wide spread due to the following reasons:

- Costs for plating chemicals are considered as raw materials costs and the normal practice has been to pass these costs along to customers.
- Platers have had the impression that electrodialysis systems are less reliable than conventional hydroxide precipitation, evaporation or ion exchange systems.
- Until recently, disposal costs associated with sludge and wastewater effluents have been relatively minor.
- Platers have not been cognizant of the magnitude of cost savings that can be achieved with an effective metal recovery system.

Now having accumulated two years of pilot testing and an additional year of commercial operation with outstanding performance results, EDR systems are available to turn plating waste problems into plating operation profits.

Solving Plating Waste Problems

Consider the case of a large manufacturer of houseware products in the north central area of the U.S. Under environmental pressure to reduce nickel and wastewater effluent discharge levels, the company investigated evaporation, ion exchange, and reverse osmosis prior to selecting an EDR system for its inherent advantages over the other methods. The EDR system was installed to solve a plating shop waste problem.

Based on a reported nickel loss due to dragout of approximately 4,100 lbs per year, the plating operation benefits in four ways as a result of the EDR installation. First, approximately 2,300 gallons of generated nickel hydroxide sludge is eliminated by using the metal recovery system, saving the disposal cost of $6,000 per year. This is based upon an average cost across the nation of $700 per ton of sludge at 35% solids. If long hauling distances are involved, the savings could be greater. Second, there is a reduction of

40,000 gpd in the volume of rinse water waste effluent. By utilizing the metal recovery system, the rinse water requirement for the first running rinse tank is drastically cut. In the involved metropolitan area, basic water and sewerage charges for industry cost $1.17 per thousand gallons. This amounts to over $12,000 per year savings in water charges. Note, however, for an electroplater a surcharge may be involved for the plant effluent arising from its toxicity to anaerobic sewage treatment plants. This cost is not included in these economics. Third, an estimated 4,053 pounds of nickel per year is recovered which, at an average cost of $1.30 per pound for nickel salts, results in a savings of over $21,000 per year. The last benefit is reduced chemical consumption to treat the water , which amounts to a reduced caustic usage of approximately 5,800 pounds per year which, at a cost for caustic in 55 gallon drums of $66 per drum, amounts to an annual savings of $1,100.

The total of these four areas is an annual savings of $40,100. Using a budget price of $50,000 for the EDR Metal Recovery System, the payback on the north central plant is estimated at 2.6 years. Economic calculation are presented in Table 1.

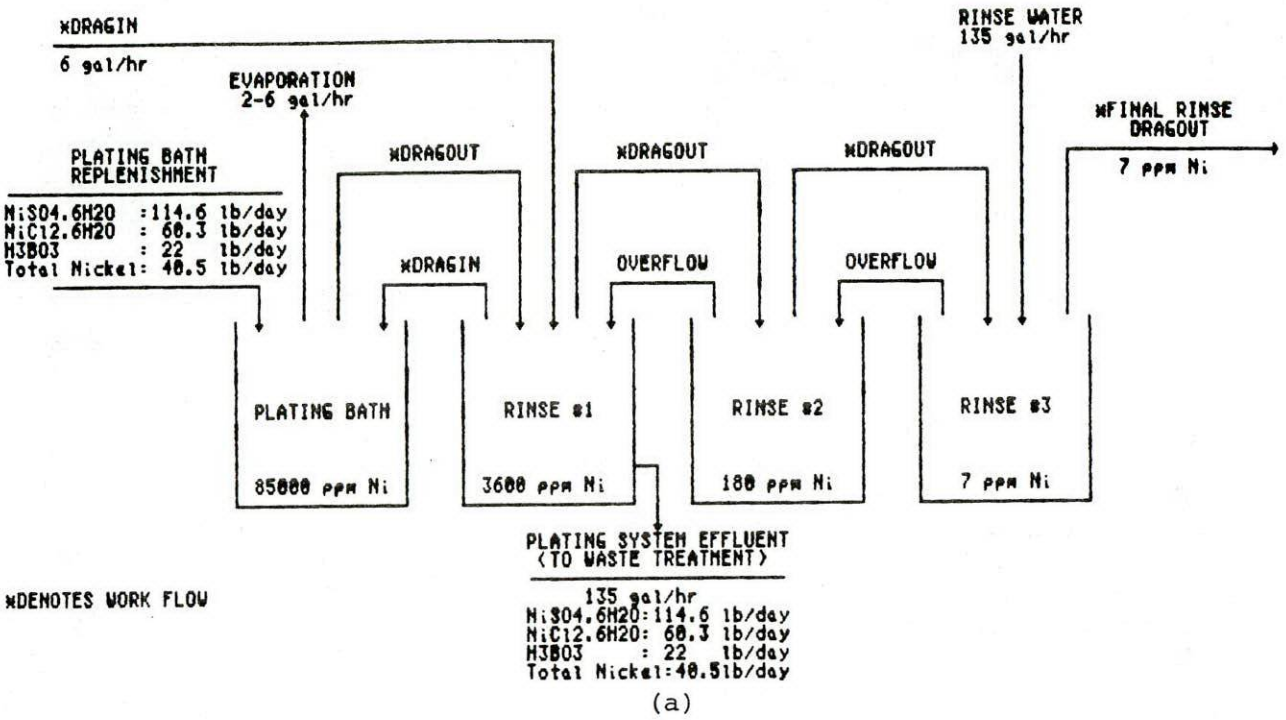
Increasing Plating Operation Profitability

Consider the case of a leading job shop plating operation along the Atlantic Seaboard. The plant, which had been recently modernized, was equipped with a sophisticated waste water treatment system with chrome reduction, cyanide destruction, hydroxide precipitation with clarifier, filter press and cake drier. Although the plant was in conformity with all existing environmental regulations, the owners were aware that total nickel losses due to automatic barrel dragout represented approximately 80 to 100 pounds per day as nickel metal. After investigating recovery options, the owners chose to install an EDR system to recover nickel plating salts that otherwise were being lost via rinse water effluent.

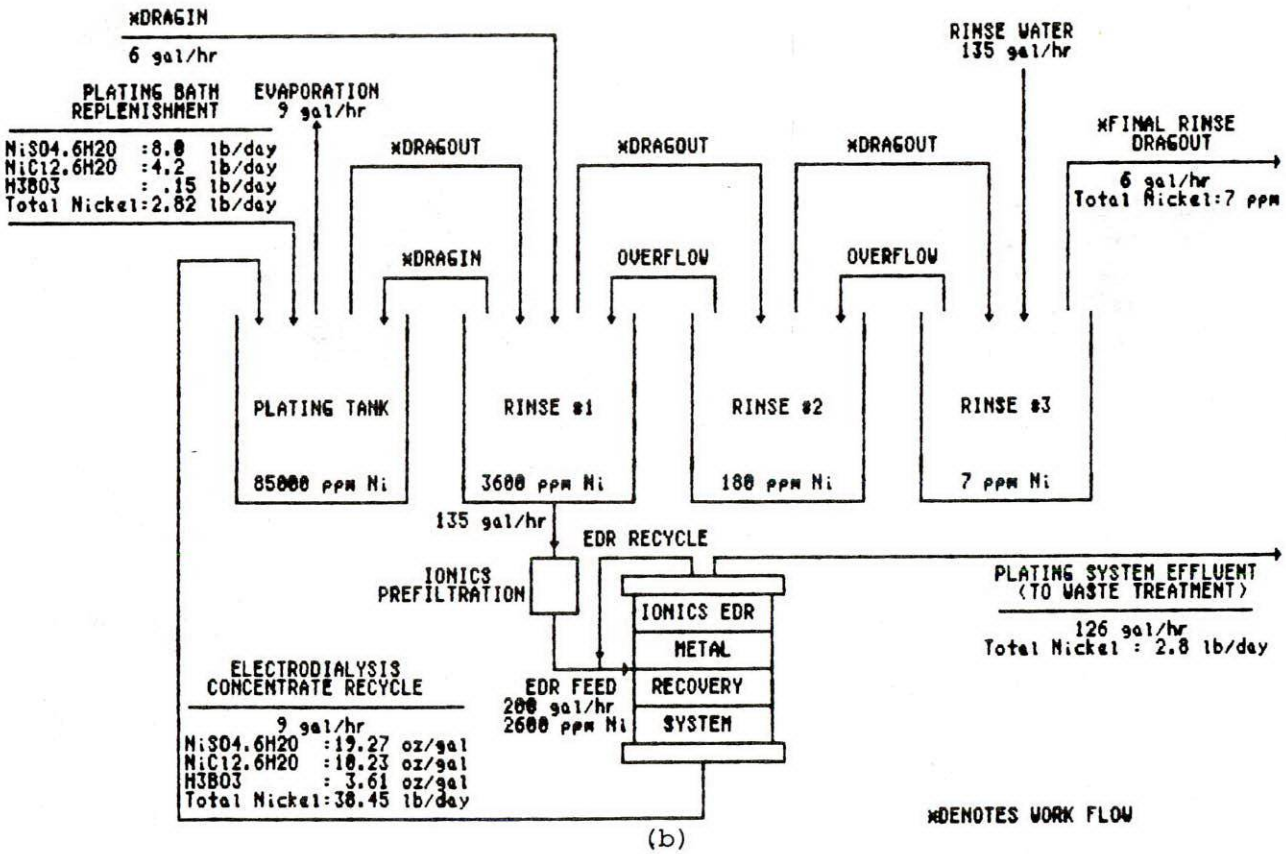
As a result of this installation, the plant profitability improves in three ways. First, annual costs for purchased plating chemicals are reduced by approximately $110,000, based on nickel sulfate at $1.10 per lb., nickel chloride at $1.40 per lb., and boric acid at $0.41 per lb. Second, annual costs for sludge disposal are reduced by $6,600, based on sludge disposal costs of $250 per ton at 95% solids. Third, annual costs for water treatment chemicals are reduced by $2,200, based on 50% sodium hydroxide solution at $0.90 per gallon.

The total of these three areas represents an annual reduction in operating costs of $118,800, a savings which can be used to improve operating profitability or can be passed on to customers to maintain competitive pricing.

Using a budget price of $100,000 for the EDR metal recovery system, the payback on the Atlantic Seaboard plant is estimated at 1.7 years. Details for the plating operation and economic calculations are presented in Figures 2a and 2b and Table 1 respectively.



(a)



(b)

Figure 2: Simplified Flow Schematics of One Nickel Plating Line at a Leading Job Shop on The Eastern Seaboard

TABLE 1

ECONOMICS OF ELECTRODIALYSIS REVERSAL PROCESS FOR NICKEL SALT RECOVERY FROM PLATING RINSE WATER

Items	North Central Plant	Eastern Seaboard Plant
1. Installed Cost		
. Equipment	50,000	100,000
. Installation, labor and materials	1,500	1,500
. Total	51,500	101,500
2. Annual Operating Cost (Estimated)		
. Labor, 100 hours/year @ $10/hour	1,000	1,000
. Maintenance @ 2½% of investment	1,250	2,500
. Raw Materials		
Filter Cartridges	750	1,000
Membrane Replacement (1)	3,000	6,000
. Electricity ($0.05/KWH)	750	1,500
. Total	6,750	12,000
3. Annual Fixed Cost		
. Depreciation, 10% of investment	5,150	10,150
. Tax and Insurance, 1% of investment	515	1,015
. Total Fixed Cost	5,665	11,165
4. Total Cost of Operation	12,415	23,165
5. Annual Savings		
. Plating Chemicals	21,000	110,000
. Sludge Disposal Cost (2)	6,000	6,600
. Water Treatment Chemicals	1,100	2,200
. Water Usage	12,000	--
. Total	40,100	118,800
6. Net Savings (annual savings - (operating + fixed cost))	27,685	95,635
7. Net Savings After Tax 48% Tax Bracket	14,397	49,730
8. Average ROI (%) (net savings after tax/total investment)	27.9	49.0
9. Cash Flow From Investment (net savings after tax + depreciation)	19,547	59,880
10. Payback Period = Total Investment/Cash Flow	2.6	1.7

(1) assuming 2 year membrane life

(2) @ 35% solids for North Central plant and @ 95% solids for Eastern Seaboard plant

IN CONCLUSION

The EDR system is unique in providing the automated self-cleaning process which results in prevention of scale formation on the membrane surfaces. With EDR technology, fouling and frequent cleaning operations associated with classical ED and other membrane systems are virtually eliminated. The EDR system offers the benefits of reliability, low operating cost, minimum operator attention, and short-term payback in capital investment.

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E-4

Environmental II
Session E

Low Cost Recovery

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LOW COST RECOVERY

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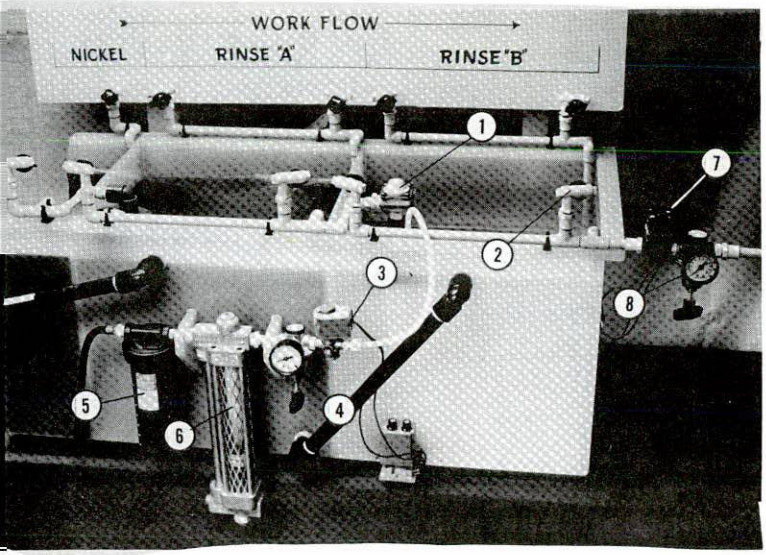
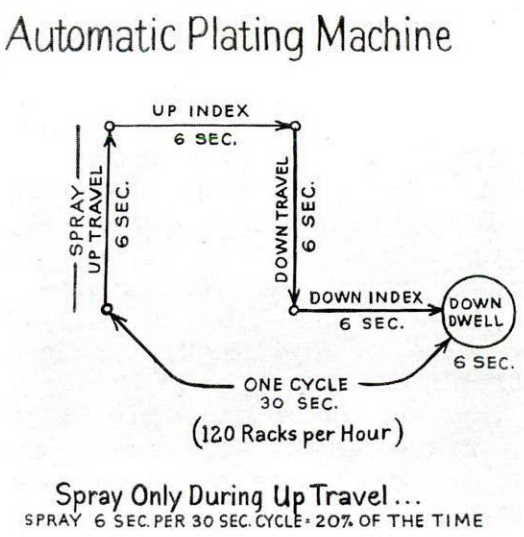
In most plating shops, drag-out is the single greatest cause for expense with regards to chemical consumption and waste treatment cost. Through the years our industry has spent countless thousands of dollars in treating perfectly good chemicals which in turn have to be replenished by newly purchased chemicals. It is paramount that our industry recognize that "a rinse tank is nothing more than a diluted plating tank". It has the same chemicals and in the same proportions as the plating tank. The only difference is a matter of concentration. This paper deals with the concept of returning the dragout back to the plating tank in a cost effective and simple method. We concentrate in two areas:

1. Minimize the amount of rinse water required to adequately rinse plated parts.
2. Maximize the amount of headroom available in the plating tank to accomodate the return of these dragged out chemicals.

MINIMIZE RINSE WATER

To accomplish this first part, we utilize what we call "Pulse Spray Counterflow Rinsing".* Most rinse systems involve adding fresh water to the second rinse tank and allowing this relatively clean water to counterflow through an external pipeline into the first rinse tank where it becomes contaminated in the more contaminated rinse tank. This cleaner rinse water of the second rinse tank can be used far more effectively by counterflowing it through a spray system where it rinses off the more contaminated rinse water of the first rinse, resulting in much less carryover of contamination. This method of rinsing (Fig 1) allows you to accomplish five very distinct rinse operations with only two rinse tanks. You have the spray rinse upon exiting from the nickel tank, spray rinse on exiting from Rinse Tank A and spray rinse upon exiting from Rinse Tank B in addition to the two normal submerged rinses A & B.





For maximum spray rinsing effectiveness, spray must occur only during the vertical exit of the part from the plating or rinse tank. Figure 2 shows the movement sequence of an automatic plating machine. The sprays are triggered only during the 6 sec. up travel and are off during the up index, down travel, down index, and down dwell. The sprays are therefore on for 6 sec. of a 30 sec. cycle or 20% of the time. This allows for a high instantaneous spray flow rate for effective spray rinsing with a low average rinse water flow. All rinse water movement between tanks occurs through the sprays and only during the up motion of the machine. Referring to Fig.1, the movement of water from Rinse Tank B to Rinse Tank A is effected by the air powered pulse pump (1) located in Rinse Tank B. This pulse pump feeds the spray nozzles (2) located over Rinse Tank A. Triggering the pulse pump is an air solenoid valve (3) activated by the control system of the automatic plater. Also required is a pressure regulator (4) to control spray intensity. The system operates on shop air introduced into an oil coalscing filter (5) followed by a MICRO polishing filter (6) which has a colormetric indicating replaceable cartridge. The only fresh water introduced into the rinsing system comes through a water solenoid valve (7) and is also activated by the control system of the automatic plating machine. This fresh water is fed through the spray system located over Rinse Tank B. The water in Rinse Tank B is pumped by the air pump located in Rinse Tank B through the spray nozzles over Rinse Tank A. The water in Rinse Tank A is simultaneously pumped by a second air pulse pump located in Rinse Tank A through the spray nozzles over the plating tank. Therefore all the rinse waters introduced into the rinse system ends up in the plating tank along with the dragged-out chemicals, thereby closing the loop. This method of rinsing has proven to be so effective that it provides the same degree of rinsing with three gallons of water per 100 sq.ft. that with normal counterflow rinsing would require 15.6 gallons per 100 sq.ft. (Figure 3).

PULSE SPRAY COUNTERFLOW RINSING

Water required for comparable rinsing of 100 square feet

Single Rinse "A" only	*500 gal.*
Separate water feed to "A" & "B"	*30.6 gal.*
Water feed to "B" & counterflow to "A"	*15.6 gal.*
Water feed to "B" & pulse spray counterflowed to "A" and to process tank	*3 gal.*

Figure 4 refers to a company located in Tennessee which operates a Full Automatic plating machine 24 hours/day at 120 racks per hour with 6.6 sq.ft. of surface area per rack. This results in 800 sq.ft. of surface area being plated per hour. Operating at 120 racks/hour is a 30 sec. cycle time and in this case they have a 6 sec. lift. The "Pulse Spray Counterflow Rinse" occurs only during this 6 sec. vertical lift. The sprays therefore operate but 1/5 of the time, and therefore allow for an instantaneous spray at five times the average flow rate. They have four 0.5 GPM spray nozzles on each rinse tank. They spray at a 2 GPM rate 20% of the time for an average flow rate of 0.4 GPM. This is but 24 gallons of fresh water per 800 sq. ft. or 24 gallons per hour. This is only 3 gallons/100 sq. ft. of surface area as shown earlier. The three jars shown contain solutions from this automatic plater. The first jar contains the nickel plating solution with a nickel concentration of 11.2 oz/gal. As the work rises



from this tank, it is sprayed down with water from Rinse Tank A where the Nickel content is 0.48 oz/gal. As the work rises from Rinse Tank A, the work is sprayed down with the rinse water from Rinse Tank B which has a nickel metal content of 0.03 oz/gal. Upon exiting from Rinse Tank B, the work is sprayed down with fresh water. This results in near perfect rinsing with only two rinse tanks and using only 24 gal/hr of fresh water.

To accomplish total recovery we must return this 24 gal/hr of rinse water to the Nickel Tank which, under normal conditions, is incapable of accepting this volume due to inadaquate head room.

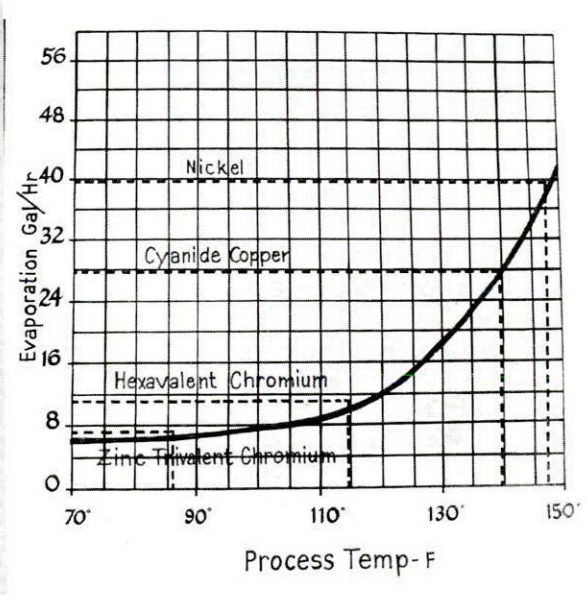
MAXIMIZE HEADROOM

To generate headroom in the process tank, we suggest the use of an atmospheric evaporator because they are inexpensive, effective and simple, requiring very little maintanence.

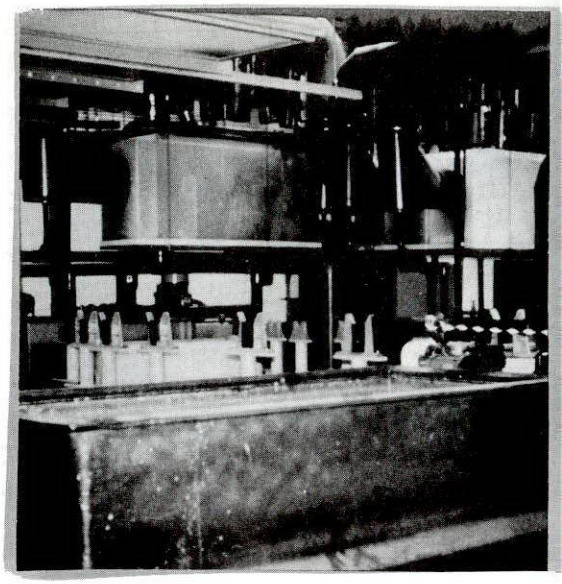
Unsaturated air will absorb moisture from wet surfaces. As the relative humidity drops the rate of evaporation increases. The evaporator creates headroom in the process tank by taking advantage of airs ability to absorb water from the process solution while leaving the valuable salts behind. Depending upon relative temperatures, hot air may warm the process solution and conversely evaporation, which produces a refrigerating effect, cools the solution. Conditions which favor evaporation are: hot air, dry air, hot solution, and high air flow.

Figure 5 shows approximate evaporative rates that can be expected from a fairly small evaporator. Be mindful, however, that this curve is strictly an approximation of evaporative rates to be expected and actual numbers could be less or greater depending upon the atmospheric conditions.

Single effect evaporation requires about 8,000 BTU/gallon of water evaporated. To supply this energy, the evaporator pulls heat from the process solution. In order to make the evaporator more economical to buy and operate, we use equipment the plater already has on hand but is under utilizing. For example when sizing a boiler for a nickel plating line, most of the boiler capacity is to provide energy for a 3 hour heat up. During operation, most of this heat capacity is unused and therefore available for evaporation. By taking advantage of this on hand capacity, the company saves the capitol expense of extra heat generating equipment and actually utilizes his boiler more efficiently with the higher steam demand. With this approach, the evaporator offers a lot of performance with a small price tag.

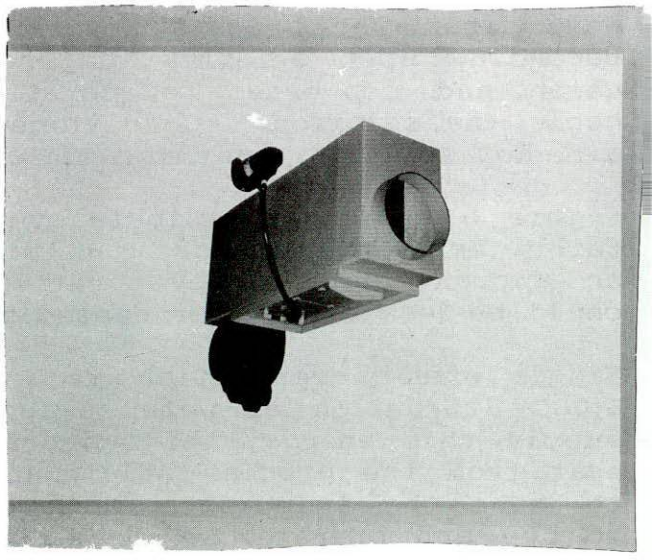


Evaporation of a pure salt solution will produce a pure water vapor while leaving the salts behind in solution. If there are volatile components in the solution, as is sometimes the case in plating processes, these components could enter into the vapor phase, thereby becoming a component of the discharged air. As a general rule of thumb, the air discharged from the evaporator is approximately of the same quality as the air immediately above the plating tank. A toxic tank requiring fume scrubbing may require similiar treatment of the air being discharged from an evaporator. Common practice for tanks with existing ventilation is to use this system to draw air through the evaporator in lieu of using a blower. (Figure 6)



EVAPORATIVE EQUIPMENT

The atmospheric evaporator (Fig.7) is a rather simple flow through device where the process solution is pumped and sprayed over packing to maximize the contact between solution and air. Typically the unit would be located at a higher elevation than the process tank it is servicing to allow for gravity flow return. It is imperative the entire system be chemically compatible with the process solution which it is servicing. Materials of construction such as PVC, polyethylene, and polypropylene are very commonly used in the plating industry.



Other areas of consideration are:

1. Horizontal air discharge to prevent condensation from running back into the evaporator.

2. Randomly oriented packing which continously redistributes the fluid flow to prevent channeling and plugging.

3. Non-atomizing spray nozzles which minimize foaming and provide good fluid distribution.

4. Vertical mist eliminators to provide the best draining of coalesced droplets

5. Easy accessibility to the interior without having to dismantle the ducting.

6. Blower separated from the spray compartment to keep corrosive solution away from the blower.

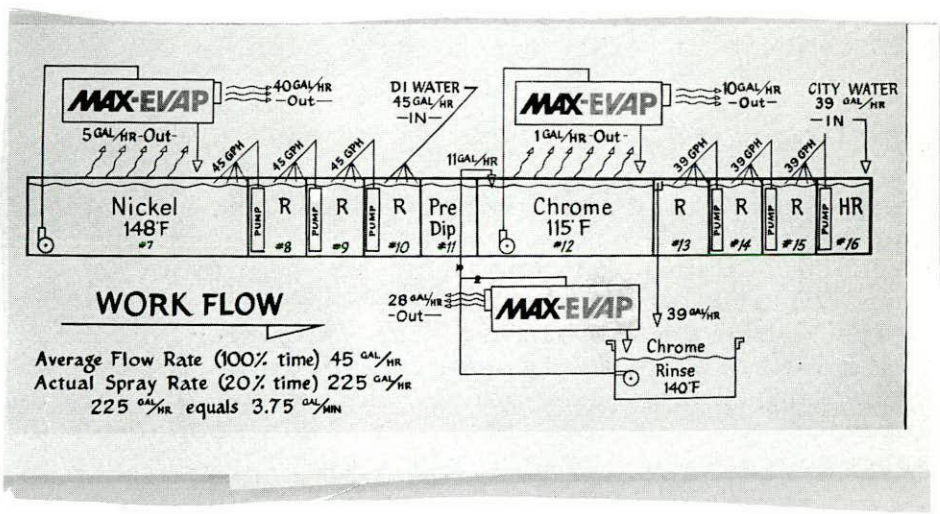
The evaporator allows the plater to recover some or all of his dragged-out plating chemicals. Any degree of recovery, partial or total, will result in reduced waste treatment costs as well as savings on plating chemicals.

CLOSING THE LOOP

Referring to Fig. 8, you can see how easy it is to obtain a closed loop system when dealing with a process that is elevated in temperature such as nickel. At 148°F, the anticipated evaporative rate is approximately 40 gal/hour (Fig. 5). Coupling this with normal tank evaporation of approximately 5 gal/hour results in a total evaporative loss from the nickel tank of 45 gal/hour. This allows for the addition of 45 gal/hour of rinse water to the Nickel Tank. This 45 gal/hour is added at Tank #10 by way of a water solenoid valve actuated by the machine to spray during uplift only. Because the spray occurs only 20% of the time, the instantaneous spray flow rate is 5 times the 45 gal/hr or 225 gal/hr which equals nearly 4 gpm. By locating a spray nozzle at each of the four corners of each rinse tank, each nozzle will spray at approximately 1 gpm for 6 seconds every 30 seconds. This results in excellent rinsing with only 45 gal/hour of fresh water being introduced into the system which when "Pulse Spray Counterflowed" to the Nickel Tank will totally close the loop.

When applying this system to a low temperature process we must take a slightly different approach. The evaporative rate of low temperature processes is not sufficient to sustain an adequate rinse water return directly to the process tank by way of the "Pulse Spray Counterflow Rinse" system. Because of this evaporative deficiency it is necessary to incorporate a heated side tank (Fig.8 Chrome System). This example indicates an average rinse water flow requirement of 39 gal/hr. The evaporative rate of a 115°F Chrome bath is about 10 gal/hour (Fig.5). We must therefore have secondary evaporation from the system if we are to accomplish a closed loop condition. This is achieved by overflowing Rinse #13 into a side tank, and by heating the side tank to 140°F, we can expect an evaporative rate of approximately 28 gal/hr. which will reduce the 39 gal/hr. average rinse flow rate to 11 gal/hr. This can now be returned to the Chrome tank to offset the 1 gal/hr. of natural evaporation and the 10 gal/hr. by the evaporator.

In addition to closing the loop, in this case, we also cool the chrome solution which will reduce mechanical refrigeration requirements. The evaporation of 10 gal/hr. represents over six tons of refrigeration.



AREAS OF CONCERN

There is an old saying amongst platers,"Dragout is a platers best friend". This is because dragout limits the build up of harmful contaminents in the plating bath. As we go from partial to total recovery, contaminents may build to harmful levels that must be dealt with. When recovering bright nickel, for example, it is desirable to use deionized rinse water to prevent the build up of calcium and magnesium. Should this occur, however, it can be removed with a flouride treatment.Sodium, while a potential problem has never proven harmful despite many years of total recovery. Experience has shown sodium leveling off at approximately 20,000 ppm. In some operations, organic contamination could be a problem with total or partial reclaimation. This has been readily controlled with increased carbon filtration and routine additions of hydrogen peroxide to the nickel plating bath. The rinse water system may also on occasion require carbon filtration and/or the addition of small amounts of formaldehyde to prevent white wash in the chrome plate due to organic films or biological growths on the surface of the nickel plate.

In recovering hexavalent chrome, care should be taken to avoid the build up of metallic ions such as nickel, copper, iron, zinc, and trivalent chrome. These may be dealt with by using a cation exchanger on the rinse water prior to returning them to the chrome plating tank.

Recovery of cyanide plating baths may result in the build up of carbonates. The normal methods of removing carbonates are by freezing them out in the winter time or precipitating them out by using barium cyanide or calcium oxide.

In the case of cyanide zinc plating it is customary to preceed the plating operation with a Muriatic acid pickle. This will result in chlorides being dragged into the cyanide zinc process tank which with a closed loop system would build to an intolerable level. The chloride ion is converted at the steel anode basket to chlorine which attacks the steel baskets, cooling coil, brightner system, and sodium cyanide only to return again to the chloride ion and repeat its destructive cycle while never being eliminated from the system. In view of this, we recommend the acid ahead of the cyanide bath be a sulfate based material rather than chloride. This would require the operator to strip his parts and danglers off the plating line. Sulfate being dragged into the cyanide zinc will simply build to a point where it will "freeze out" along with the carbonates as necessary.

APPLICABILITY

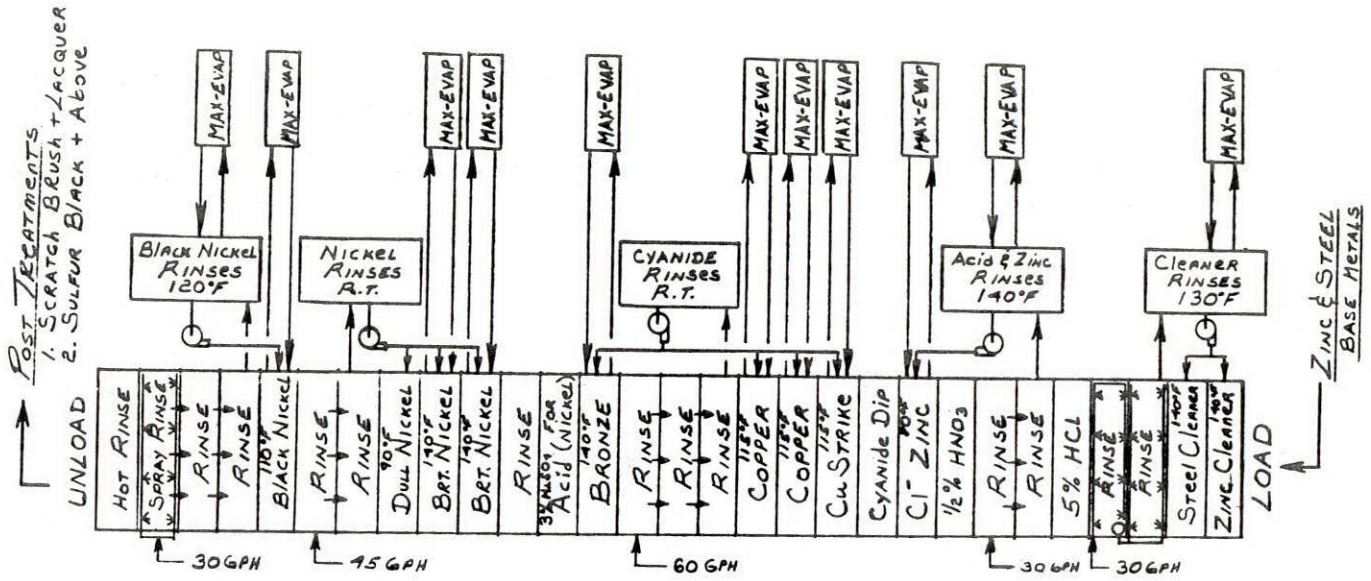
Many laboratory tests have been run on Acid Chloride zinc and Alkaline Non-cyanide zinc processes. The tests involved first running an "AS-IS" hull cell panel on the plating solution. A 300 ml sample of solution was then diluted to 600 ml and heated to 160°F with air agitation for 48 hours while maintaining the solution volume at 600 ml. Thereafter, the volume was allowed to evaporate down to the original 300 mls at which time a second hull cell panel was run. In all cases, this second panel was inferior to the original but was capable of being restored to original appearance with a small addition of brightner.

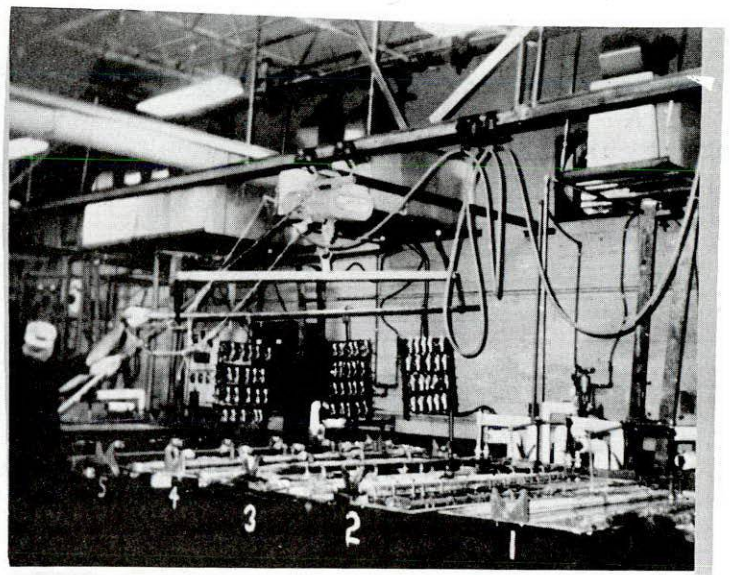
When we close the loop we are treading in unchartered waters and there is a certain risk factor involved. Our industry has been well aware of various treatments involving carbon, hydrogen peroxide, potassium permanganate, and electrolytic dummy plating, which allow us to remove most contaminents should they build to a detrimental level.

There are yet many problems to be experienced and answers to be resolved but, generally speaking, with a little forsight and ingenuity these problems can be avoided or corrected with a minimum amount of expense and effort.

INDUSTRIAL APPLICATIONS

Figure 9 shows the schematic layout of a plant located in Virginia which manufactures casket hardware. This company does not have a sewer line but simply a septic tank for their lavatories. EPA gave them a November, 1985 deadline to stop using an outdoor unlined lagoon for their plating department discharge. They have no waste treatment facilities and the only way they could remain in operation was by using the evaporative reclaim system as shown in the schematic. They have incorporated "Pulse Spray Counterflow Rinsing" and 14 evaporators into their system, (Fig.10 & Fig.11), allowing them to totally close the loop on all rinse waters including the cleaner and acid rinses. The Cleaner and Acid dumps are treated monthly on a batch basis.





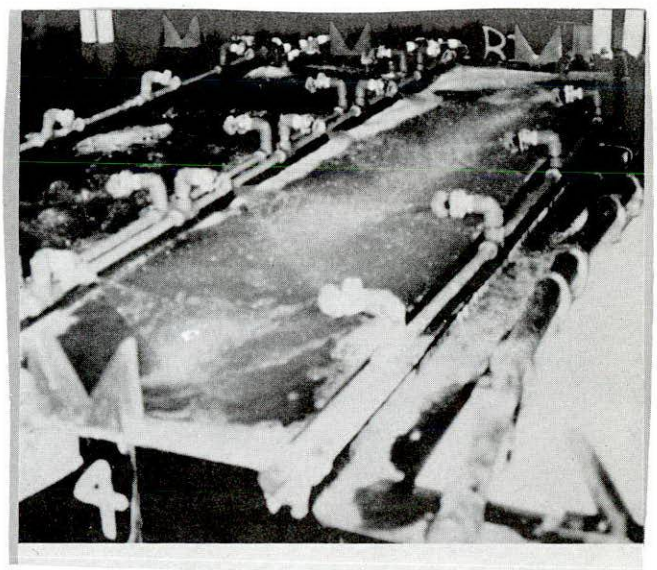
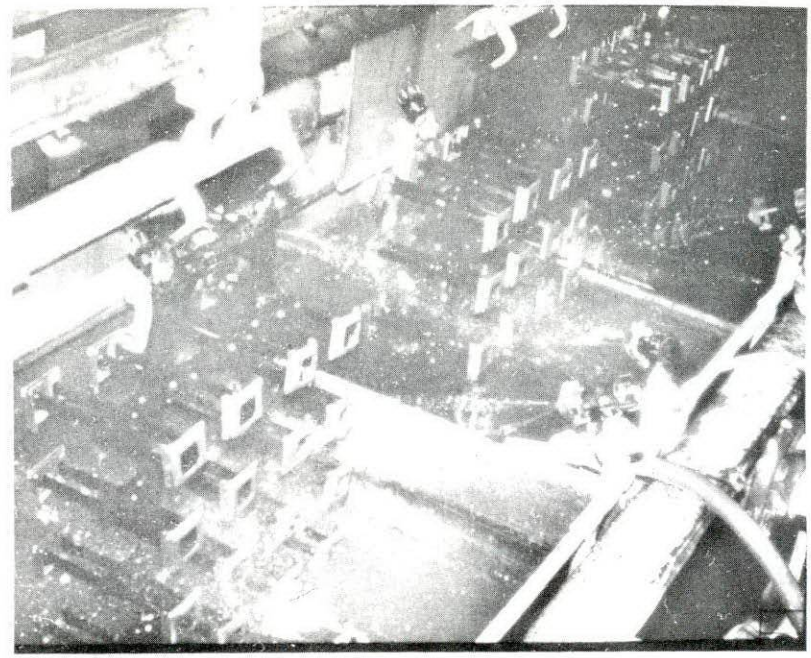


Figure 12 shows a small full automatic nickel chrome plating machine which operates at 106 transfers/hour plating satin nickel and chrome on automotive hardware. There are three nickel rinses and five chrome rinses. By using "Pulse Spray Counterflow Rinsing" and evaporative recovery, their water bill on this machine has fallen from $1,100.00/month to $85.00/month. The final rinse tanks show nickel at 5.6 ppm and chrome at 5.0 ppm. They have no waste treatment system yet the local EPA official recently told the owner they have the cleanest shop he has ever seen.



Clearly "Pulse Spray Counterflow Rinsing" enables the plater to reduce the volume of rinse water required without sacrificing quality of rinsing.

Since 1980 we have located near 200 evaporative units throughout industry on such processes as acid chloride zinc, cyanide copper, hexavalent chrome, trivalent chrome, nickel and acid copper.

CONCLUSION

"Pulse Spray Counterflow Rinsing" and atmospheric evaporators provide a very simple yet effective system for reducing or eliminating waste treatment while saving chemicals. The simplicity of this concept can be easily understood by both plater and maintanence people alike. The owner of a business will experience in most cases, a two to six month payback on investment.

As an industry we have been extremely wasteful of our resources, and if we are to remain viable, healthy, and competative we must become more cost effective to off set the new technology in powder coating, electrophoresis and other organic finishes. We must develop and perfect improved methods of reclaimation bearing in mind that: "A rinse tank is but a diluted plating tank", comprised of perfectly good reusable chemicals.

DON'T WASTE IT -- USE IT !!

E-5

Environmental II
Session E

Groundwater Treatment Aspects Of Remedial Action Plans for Electroplaters/Metals Finishers

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GROUNDWATER TREATMENT ASPECTS OF REMEDIAL ACTION PLANS FOR ELECTROPLATERS/METALS FINISHERS

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Introduction

Groundwater contamination assessment and clean-up has become a high priority on the agenda of environmental protection. The enactment of federal Superfund legislation has been followed by activity on the state and local levels to address contaminated sites not in the scope of federal cleanup efforts. Guidelines for development and implementation of remedial action at hazardous waste sites have been incorporated as part of the National Contingency Plan (NCP) which provides procedures and protocols for all cleanup activities associated with federal Superfund sites. The purpose of the NCP is to establish standardized methods for hazardous waste site activities to ensure that the cleanup activities deal adequately with issues of environmental protection, cost effectiveness and technical feasibility of applied treatment technologies, and protection of the health and safety of site workers and the general public. The NCP concepts have been largely adopted by State Agencies for use in non-Superfund site cleanup activities such as industrial groundwater contamination studies.

The manufacture of printed circuit (wiring) boards and electronic components as well as the surface finishing of various base materials requires the use of chemicals that, when spent, must be properly disposed of. Federal and state hazardous waste agencies currently regulate disposal practices for these chemicals. Unfortunately certain past legal disposal options, such as the pretreatment of industrial wastewater and discharge to waste lagoons may require remedial action to restore the groundwater. In other cases, the corrosive nature of many of the chemicals utilized by the industry caused floor slab and sewer pipe line damage with subsequent contamination of the soil and water under the site.

The potential impact of these contaminants is evaluated by the risk assessment process. The effect of contaminants on the human population and the environment is assessed, with mechanisms of exposure and potential exposure levels investigated relative to the toxicity of individual identified contaminants. Depending on the findings of this risk assessment and the regulatory review process, removal of the contaminants may be required.

In the two case studies presented herein certain groundwater pumping, treatment and disposal alternatives were chosen as the remedial action plan. This paper will update earlier case histories presented by our firm at the 7th Annual AESF/EPA Conference.

CASE STUDY 1

Introduction

Site 1 involves the release of wastewater from a facility engaged in electroplating of electronic components. The facility is located on a six-acre site in an area of light industry bordering on a residential area of condominiums and single family dwellings.

Problems at the facility including wastewater discharge violations and visible signs of wastewater leakage into the soil were the subjects of inspections by the municipal sewer authority and the local Board of Health in 1980 and 1981. In 1983, suspected soil contamination from a leaking wastewater conveyance pipe was verified by soil testing conducted by the owner of the site, which indicated contamination of the soil with metals, cyanides, acids, and volatile organic compounds (VOCs) such as 1,1,1-trichloroethane. The state environmental agency hazardous waste division was notified of the evidence of a release to the environment, and the agency ordered a complete site assessment to be conducted. The site assessment activities were initiated in January, 1984.

Inside the facility, corrosion in the wastewater conveyance trench system was discovered to have allowed leakage of wastewater to the soil below. Contaminated soil beneath the trenches was excavated and disposed as a hazardous waste along with the corroded concrete lining the trenches. This action was taken outside the framework of a Remedial Investigation/Feasibility Study, an action agreed upon by the owner and the regulating agency as a positive and expedient resolution of the problem. The action was taken at the request of the owner to allow an on-going renovation of the building interior to proceed on schedule.

Site History

A site history was compiled to identify past and present chemical usage and waste handling and disposal practices. Existing analytical results on samples of soil and groundwater, wastewater discharge monitoring reports, hazardous waste hauling invoices, and raw materials purchases were incorporated, rumors were heard of drums containing hazardous waste being buried on-site and other information which would be useful in planning a site sampling and analysis plan, as well as providing a preliminary basis for designing a site safety plan.

Field Investigation Activities

Geophysical survey techniques were employed on the site prior to additional sampling efforts in order to provide information about the subsurface geology, the depth to water table, contaminant distribution, and the presence of buried waste drums. Seismic refraction, electrical resistivity, electromagnetic induction, and ground penetrating radar were used to study the site. The data gathered from the geophysical surveys was used to plan the construction and installation of groundwater monitoring wells and to help locate the wells in

areas of probable contaminant occurrence. No evidence of buried waste drums was found and the issue of buried drums was of no further concern.

The field investigation included installation of nine groundwater monitoring wells including one well intended as a background well, located upgradient of the site groundwater flow and at a distance of 170 feet from the facility (Refer to Figure 1). Hydrogeological observations were made to determine soil permeability and other groundwater flow characteristics. Soil and groundwater samples were collected from the well installations and analyzed for a range of test parameters based on the site history. VOCs were the major contaminants of concern, reaching a maximum of 91,000 parts per billion, 1,1,1-trichloroethane, for example, in the groundwater. Other contaminants of significance in the groundwater included cadmium, copper, nickel, sulfate, and fluoride.

Data Interpretation/Risk Assessment

The major contaminant source was found to be leaking underground wastewater collection sumps, with lesser contributions from other sources such as leaking wastewater conveyance pipes and trenches. The wastewater was introduced into a fine sand and silt material that was found to be the predominant soil type above bedrock. The fine grained material limited movement of the contaminants in both the horizontal and vertical directions. It was estimated that very limited off-site migration of contaminants could have taken place, given the calculated rates of travel (approximately four feet per year) and the 20 year period over which the facility had been operating and using chemicals. Movement of contaminants through the underlying aquifer was the only avenue of migration of contaminants away from the site, since the contaminants were not located near the surface and could not be picked up by surface run-off. The nearest receptors in the path of groundwater flow from the site were a group of private water supply wells located approximately 1,700 feet downgradient of the site. The major risk associated with the contamination at Site 1 was degradation of the aquifer water quality that could render the local water supply wells unusable.

Groundwater Recovery and Disposal

Selection of remedial action alternatives began with the decision to recover contaminated groundwater from the aquifer for treatment. The alternatives for groundwater recovery included deep wells with submersible pumps and well point systems for use at shallow depths. While most of us are familiar with deep wells utilizing submersible pumps, a well point system should be explained. This system consists of a group of closely spaced wells connected by a header pipe. A central pump can be used for the entire well point system depending upon the depth, volume pumped and soil permeability. Spacing between well points usually ranges from 2 to 6 feet with flow rates usually less than 5 gpm. In comparison, higher capacity deep wells can be spaced at a greater distance due to their increased drawdown of the aquifer.

Further information for selection of the recovery method was provided in this area by the construction at the site of a groundwater recovery well which was used to perform a pump test to evaluate the response of the aquifer to ex-

tended pumping. The results of this test indicated that deep wells would be more efficient in collecting groundwater on the site than a shallow well point system. A total of four wells would be required to effectively contain the contaminated groundwater and collect it for treatment.

Before considering alternatives for treatment of the recovered groundwater, it was useful to explore the range of possibilities for disposal of the treated groundwater, since the method of disposal would have an effect on the level of treatment required. The three alternatives for disposal of treated groundwater were: use as process water, with final treatment and disposal to the municipal sewerage system; discharge to surface water; and on-site recharge of the aquifer.

Process use and discharge to the sewerage system was attractive from the standpoint of decreased water supply costs and the relatively less rigorous discharge standards imposed by the sewer authority, but was limited by the process water quality requirements and the limited volume that could be recycled versus the amount of groundwater to be recovered for treatment. Discharge to surface water required the most exacting treatment to meet stringent aquatic toxicity standards.

On-site recharge was selected as the most feasible method of disposal. Through proper placement of recovery wells and the recharge system, the treated groundwater could be recycled in a closed loop system, which offered the possibility of soil flushing to extract contaminants which might otherwise be left in the soil. The closed loop concept was also favored by the regulatory agency and would allow initial discharge of treated groundwater at levels exceeding the groundwater quality standards, provided that groundwater quality standards would be met at some point before system shutdown.

Groundwater Treatment

Alternatives for groundwater treatment were considered in three parts; metals, VOCs, and anions such as fluoride and sulfate. Alternatives for metal removal included chemical precipitation followed by conventional sedimentation and granular filtration, and chemical precipitation followed by ultrafiltration. The ultrafiltration alternative was chosen because an existing on-site wastewater pretreatment system utilizing ultrafiltration technology became available for use in groundwater treatment. This approach afforded the advantages of cost effectiveness and ease of implementation while providing acceptable metals removal. A treatability study was performed on a representative sample of contaminated groundwater to assess system performances and effluent quality results. Using lime addition to a pH of 9.5 s.u., the following results were obtained:

Metal	Influent, mg/L	Effluent, mg/L	Groundwater Quality Standard, mg/L
Nickel	20	0.1	0.63
Copper	18	0.1	1.0
Cadmium	0.06	0.003	0.01

Air stripping and granular activated carbon (GAC) were considered as alternative treatment technologies for VOC removal. Both treatment methods were feasible from the standpoint of being able to achieve the desired VOC removals. Operationally, GAC required periodic regeneration of the carbon bed, requiring on-site regeneration equipment or hauling the carbon to an off-site facility. The potential for VOC breakthrough as the carbon approaches its capacity for adsorption requires careful monitoring of the effluent. Air stripping however, provides relatively constant removal performance with minor operation and maintenance requirements, and no associated residual waste disposal costs. Quantities of VOCs that would be discharged into the air from the equipment were not significant and state air regulatory authorities approved of the operation. For these reasons, air stripping was chosen for VOC removal at Site 1.

Removal of the anionic components of the groundwater, sulfate, fluoride, chloride, and nitrate, required the likely use of reverse osmosis or ion-exchange, at significant increases in treatment system equipment costs and operating and maintenance requirements. Estimation of the dilution effects that would be achieved during the groundwater recovery/recharge cycle however, indicated that without treatment, the anions would be reduced to groundwater quality standard levels or below, and that no adverse effects on groundwater quality would occur. Should operating data indicate this is not the case, removal would be required.

Remedial Action Plan Design

The final remedial action plan consisted of four major elements: groundwater recovery wells, chemical precipitation/ultrafiltration, air stripping, and treated groundwater recharge. Following approval of the conceptual design by the regulating agency and public review through the mechanism of the groundwater discharge permit process, implementation of the remedial action plan was initiated.

Final design parameters for the groundwater recovery wells and the recharge system were developed from previously obtained pump test data and permeability testing conducted on-site. Groundwater recovery was achieved with four wells extending into bedrock with a combined design pumping rate of 80 gallons per minute (gpm). Treated groundwater would be recharged to the site through a leaching trench with an area of 3,600 square feet, 420 feet in length.

The air stripper design was completed using data obtained during a pilot test conducted on-site. The final air stripping design specified a 4 foot diameter stripping tower with 11 feet of packed height, with recirculation of the groundwater through the tower for multiple-pass treatment capability. The maximum volume/volume air to water ratio was 150:1 at 80 gpm. The overall design removal efficiency was 99.91%.

Operating Results

This section will be distributed and discussed at the 73rd Annual AESF Technical Conference and will be based on actual operating results from the second quarter of 1986.

CASE STUDY 2

Site Conditions

The site described in Case Study 2 occupies an area of 270 acres, 100 of which are developed with buildings, parking and storage areas, etc. The facility operations include printed wiring board production. A number of VOC spills occurred in the developed area, beginning about 1957. Trichloroethylene was the principal contaminant found at the site. VOC contamination in the groundwater was measured at levels as high as 250,000 parts per billion (ppb) in an area of 3 to 4 acres, with a total area of about 60 acres exhibiting VOC levels of 100 ppb or greater.

The overburden soil is separated from bedrock by a relatively impermeable layer of glacial till, forming two aquifer systems. Leakage of VOCs into the lower bedrock aquifer was influenced by the presence of industrial water supply wells at the site, causing a downward flow component of the groundwater from the overburden to the bedrock.

Remedial Action

Remedial action at the site was concerned with preventing off-site migration of VOCs and removal of VOC from the groundwater. As in Case Study 1, groundwater pumping and treatment was chosen as the preferred remedial action. Disposal alternatives for treated groundwater included process use, direct discharge to the municipal sewerage system, and on-site recharge. The presence of naturally occurring iron concentrations of up to 35 parts per million (ppm) in the groundwater would require iron removal as part of the treatment system if the process reuse alternative was selected. Discharge to the municipal sewer was selected as the most cost-effective alternative.

The groundwater recovery system was designed to withdraw groundwater from the overburden and bedrock aquifers with two separate well systems to prevent further downward migration of VOC contaminated groundwater into the bedrock aquifer. It was determined that such migration would increase the time required to complete groundwater renovation. The overburden recovery system was designed as a shallow well point system composed of 24 well points. An existing deep well was selected for groundwater recovery from the bedrock. The total design withdrawal rate of groundwater from the well systems is 160 gpm.

As in Case Study 1, air stripping was selected as the treatment alternative for VOC removal. Final design of the air stripper was based on a pilot study conducted at the site. The desired VOC effluent concentration for discharge of treated groundwater to the municipal sewer was 50 ppb, total VOCs. The specified system, for a design flow of 160 gpm, was a two tower system in series. Each tower was 3 feet in diameter with a packed height of 24 feet and a removal efficiency for trichloroethylene of 99.5 per cent per tower at a volume/volume air to water ratio of 100:1.

Summary

Two remedial action case studies have been presented that illustrate the remedial action process as conducted by site owners. In both cases, the remedial action process, from site investigation through implementation was conducted over a period of approximately 2-1/2 years. Investigation of the site hydrogeology and contaminant distribution accounts for a large proportion of project duration, but it is time well spent. Complexity is the rule rather than the exception when describing site hydrogeology, and insufficient data will inevitably result in inadequate design and excessive cost impacts. The stepwise approach to remedial action as described herein is intended to ensure that both the technical and economic aspects of a project are properly addressed so that a successful result is achieved.

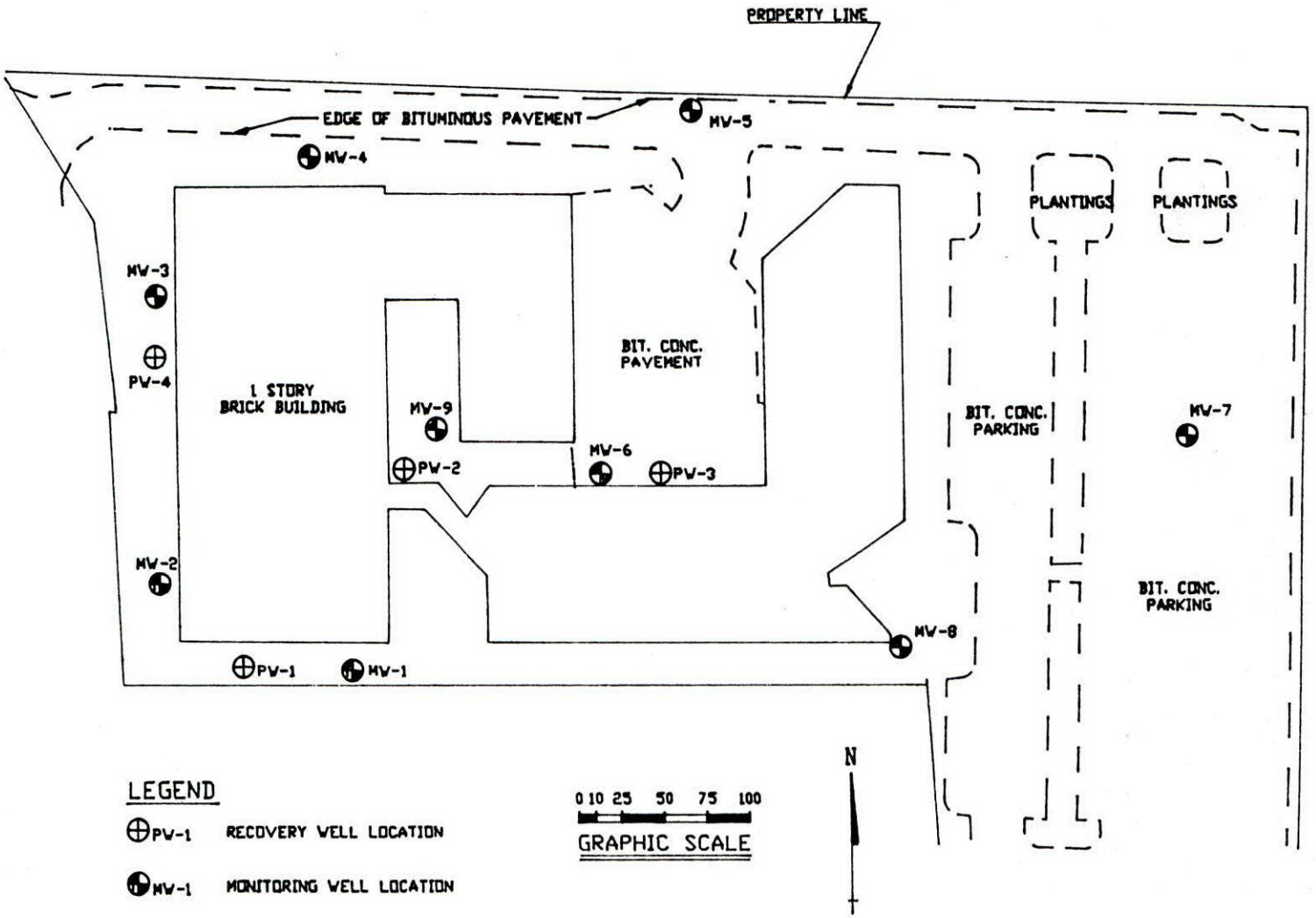

FIGURE 1. SITE PLAN CASE STUDY 1

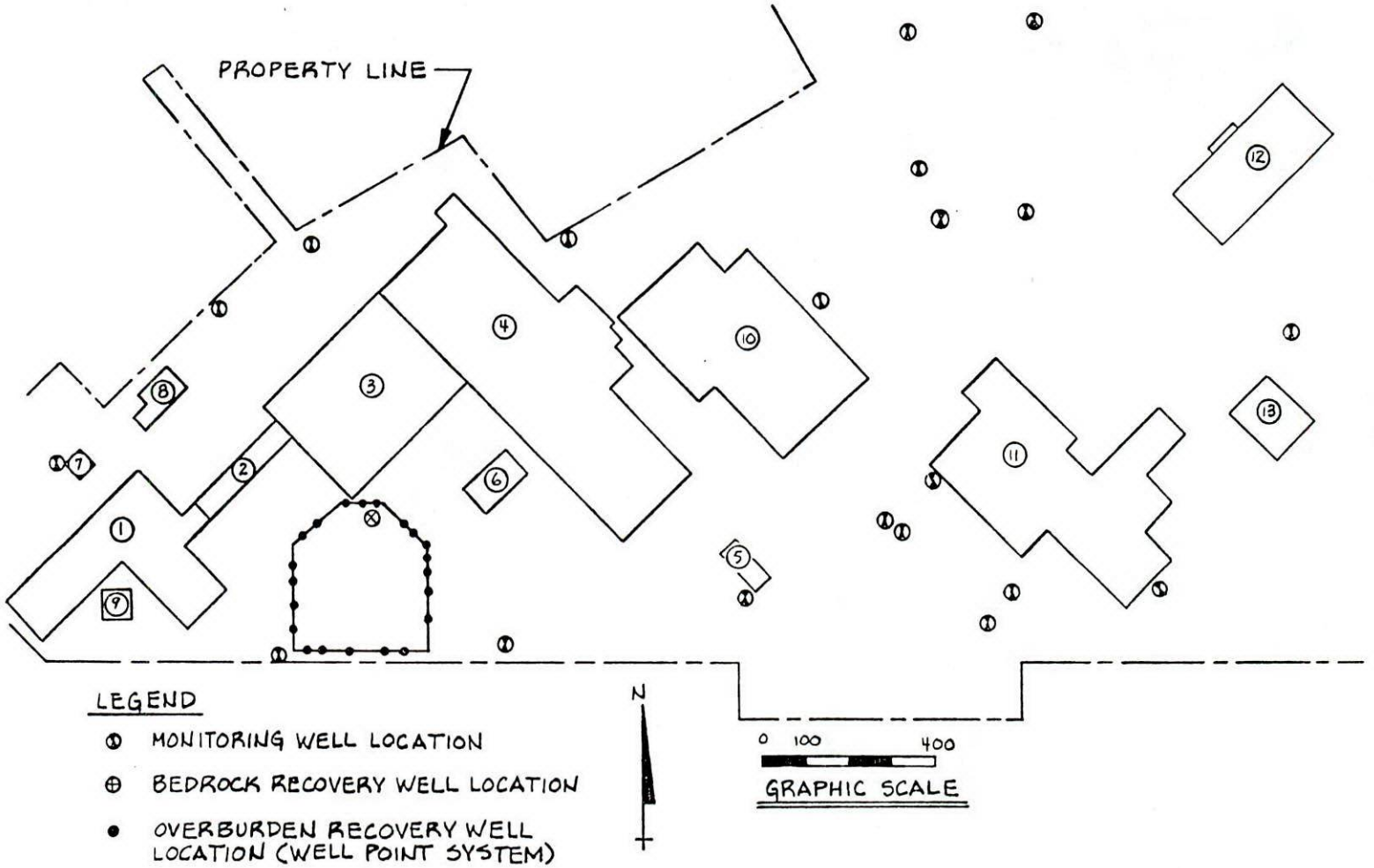

FIGURE 2. SITE PLAN CASE STUDY 2

F-1

General Interest Session F

An Investigation of the High Speed Plating of Nickel. I. The Research Plating Machine

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AN INVESTIGATION OF THE HIGH SPEED PLATING OF NICKEL I. THE RESEARCH PLATING MACHINE

by

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Introduction

In our continuing investigation of high speed plating (HSP) systems, it was decided to study the high rate electrodeposition of nickel. Previous work was carried out in an air pressure flow system (APFS)(1,2) which required a volume of solution greater than 100 L (26 gal) to operate. Although this system could accept full-size, production parts for plating studies, it was not convenient for research in plating.

For research studies, smaller operating volumes are desirable particularly if the chemicals studied are expensive. Small test samples could not be researched in the large machine, and therefore, the current densities were limited by the size of the rectifier. By using a flow-channel fixture, much higher solution flow rates should be reached.

This report describes in detail the smaller HSP APFS machine which was designed and built for plating research programs. It will be referred to as HSPII.

Machine Construction

As before (1,2), the principle of operation is based on driving the solution from one reservoir tank with compressed air, through the flow channel fixture, to a second empty reservoir tank. When the second tank was filled, the solution flow was reversed by solenoid-operated valves controlled by an electronic timer.

A photograph of HSPII is presented in Fig. 1 where the essential parts of the system are indicated. The volume of the reservoir tanks is 20 L and the temperature of the experiment is controlled by the heat exchanger over a range from 52 to 72°C. Since the air pressure was varied between 2 and 4 x 10^2 kPa, the solution flow rate through the channel could be varied from 5 to 10.5 m/s. In the experiments with Ni, the applied voltage ranged between 5 and 11 V resulting in a current density range of 1.09 to 3.3 A/cm^2.

The flow channel fixture is shown in Fig. 2 and consists of upper and lower sections made of lucite. When clamped together with the bolt wing-nut assembly, it is sealed with the O-ring. The anode was cut from a Ni bar with a cross sectional area of 6.45 cm^2 and mounted in the middle of the channel (34.3 x 2.54 x 0.21 cm) machined in the lower section of the fixture. This anode was adjustable so that it could be maintained flush with the floor of the channel during the plating operation. Copper test samples (2.54 x 2.54 x 1.59 cm) were mounted in the upper section with a set screw, flush with the upper surface. After the fixture was clamped in place, the gap between anode and cathode was 0.21 cm.

Procedure

Before the weighed copper sample was mounted in the fixture, it was degreased, and the cleaning procedure was continued by a one minute electrolyte flow in the plating fixture under open circuit conditions. The copper sample was then plated under a give set of experimental conditions for one minute. Afterwards the cell was opened and the plated copper sample reweighed to obtain the weight of the Ni deposit. The number of coulombs passed during the plating operation was determined with an electronic coulometer from which the current efficiency for metal deposition could be obtained.

The electrolyte investigated was a 1/2 Watts bath with the following composition: Nickel sulfate ($NiSO_4 \cdot 6H_2O$), 165 g/L; Nickel Chloride ($NiCl_2 \cdot 6H_2O$), 22.5 g/L; Boric Acid (H_3BO_3), 18.5 g/L. Measurements were made at three temperatures, 52, 66 and 72°C and at three solution flow rates, 5, 7.5 and 10 m/s over a current density range from 0.5 to 3 A/cm^2.

Results

In Fig. 3, the deposition rate of Ni in μm/min is plotted against the current density at three temperatures and three flow rates. The current efficiency for metal deposition as a function of the current density is given in Fig. 4.

From these data, the most obvious effect is the linear increase in deposition rate with increasing current up to a critical point after which a precipitous drop in deposition rate occurs in all cases. In the increasing linear range, the nickel deposit is sound and semibright with good adhesion. Beyond the critical current density, the deposits were mottled with irregular black and green patterns as noted in Fig. 5. The black smut was easily wiped off to reveal a smooth layer of Ni underneath.

It was found that the flow rate must be >1 m/s before HSP of Ni can take place. It is observed in Fig. 3 that the critical point is shifted to higher current densities with increasing flow rate. The negative slope of the curves for current densities greater than the critical point is generally lowered with an increase in flow rate.

With increases in temperature, higher deposition rates can be obtained before the critical point is reached. At 72°C, Ni was deposited at a rate of 40 μm/min with a current efficiency of 62% when the flow rate was 7.5 m/s. Presently, it is not possible to make measurements at temperatures greater than 72°C because the solution flow sensor contains a PVC paddle wheel which cannot withstand temperatures greater than 72°C for extended periods of time. The quality of the Ni deposits in the initials linear range at higher temperatures is very good.

References

1. M. A. LaBoda, Surf. Technol., 11, 91 (1980); U.S. Pat., 4,111,761 (1978).

2. M. A. LaBoda, A. H. Holden, and J. P. Hoare, J. Electrochem. Soc., 127, 1709 (1980).

Figure Captions

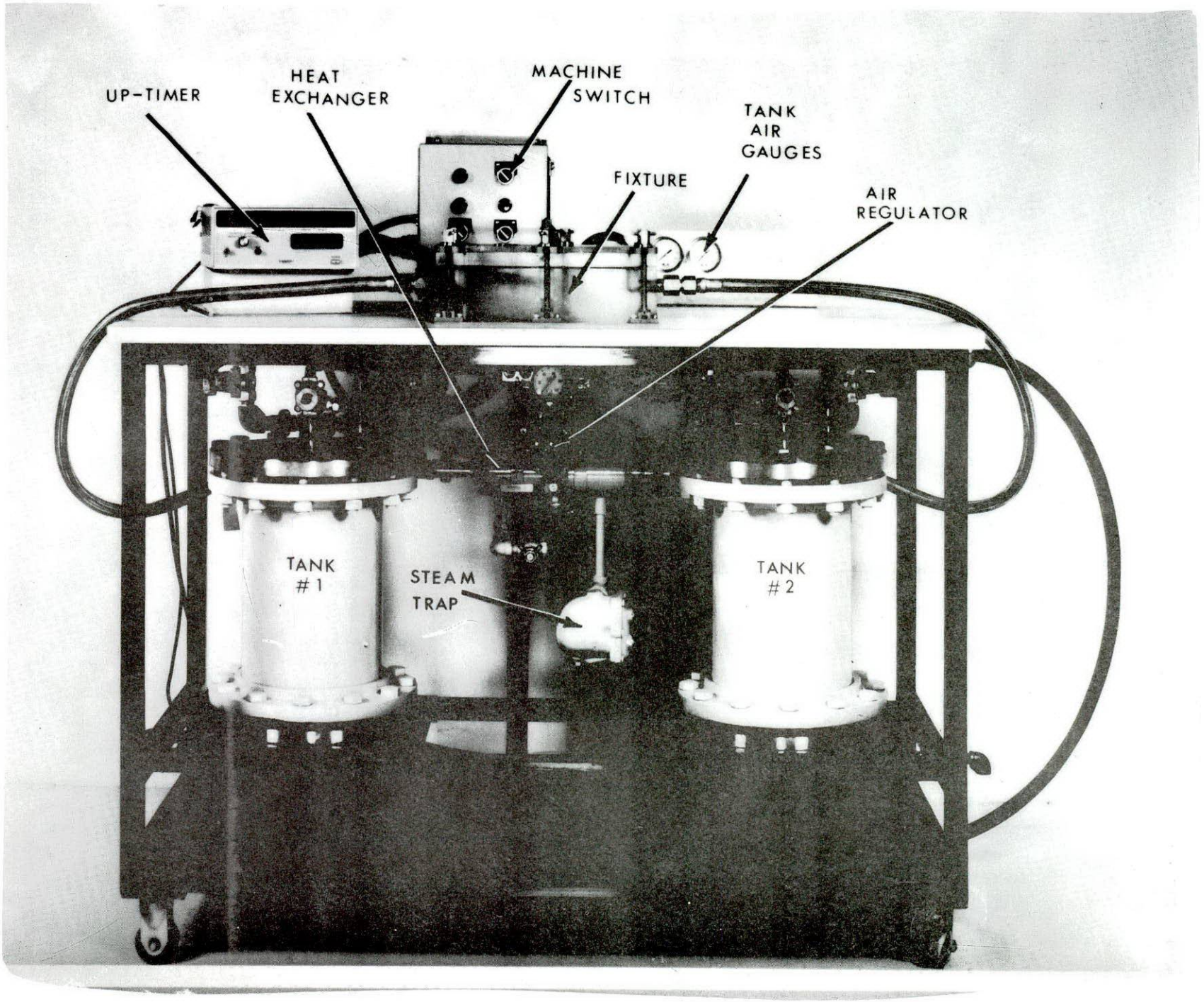
Fig. 1 The HSPII system shown without rectifier.

Fig. 2 The HSPII fixture in the open position.

Fig. 3 The depositions rate of Ni from a half-strength Watts both on a Cu substrate as a function of the current density for three values of both the temperature and solution flow rate.

Fig. 4 The cathode current efficiency for the system in Fig. 3 as a function of the current density.

Fig. 5 Typical green and black patterned Ni deposits obtained on Cu samples at high current densities beyond the critical current density.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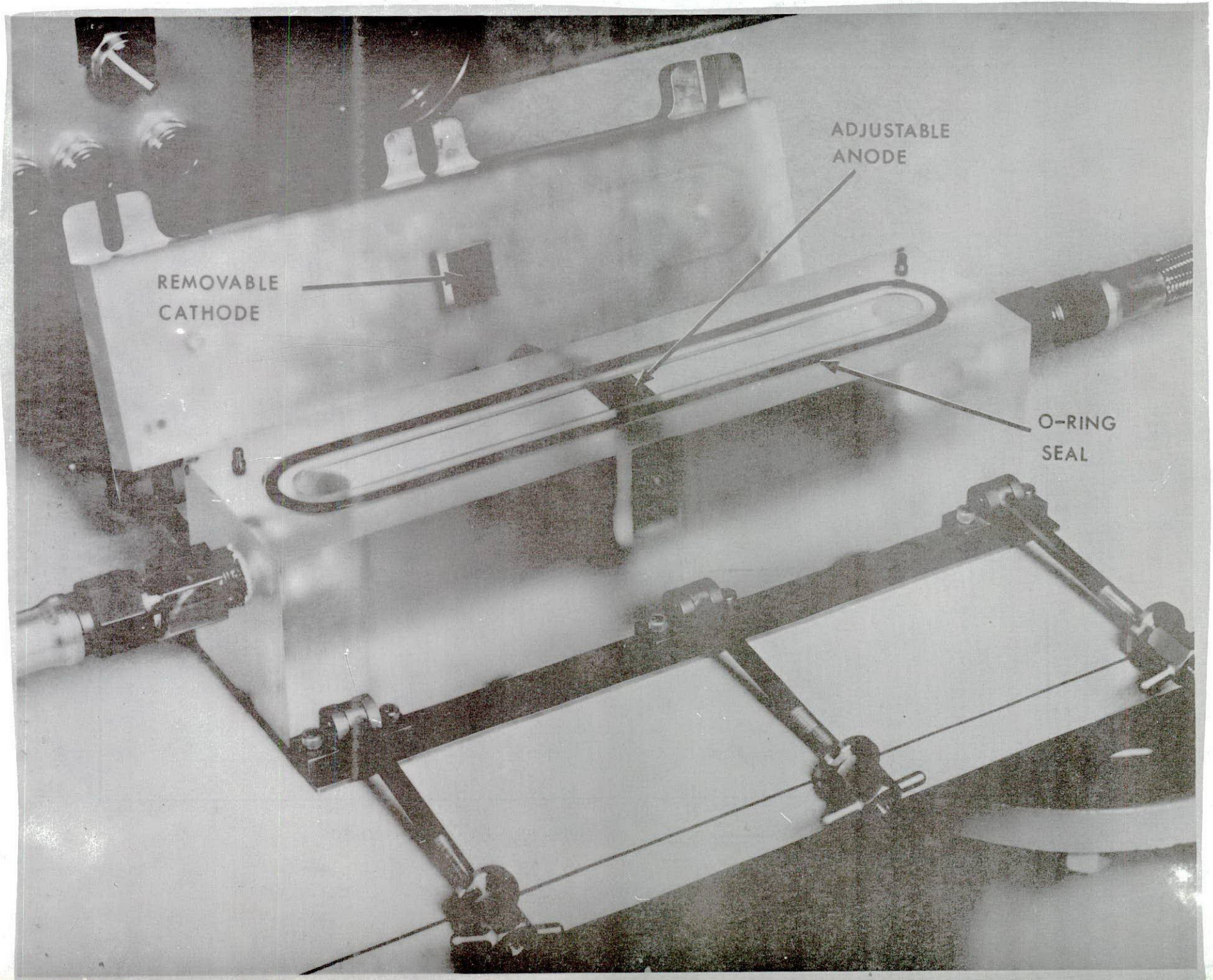
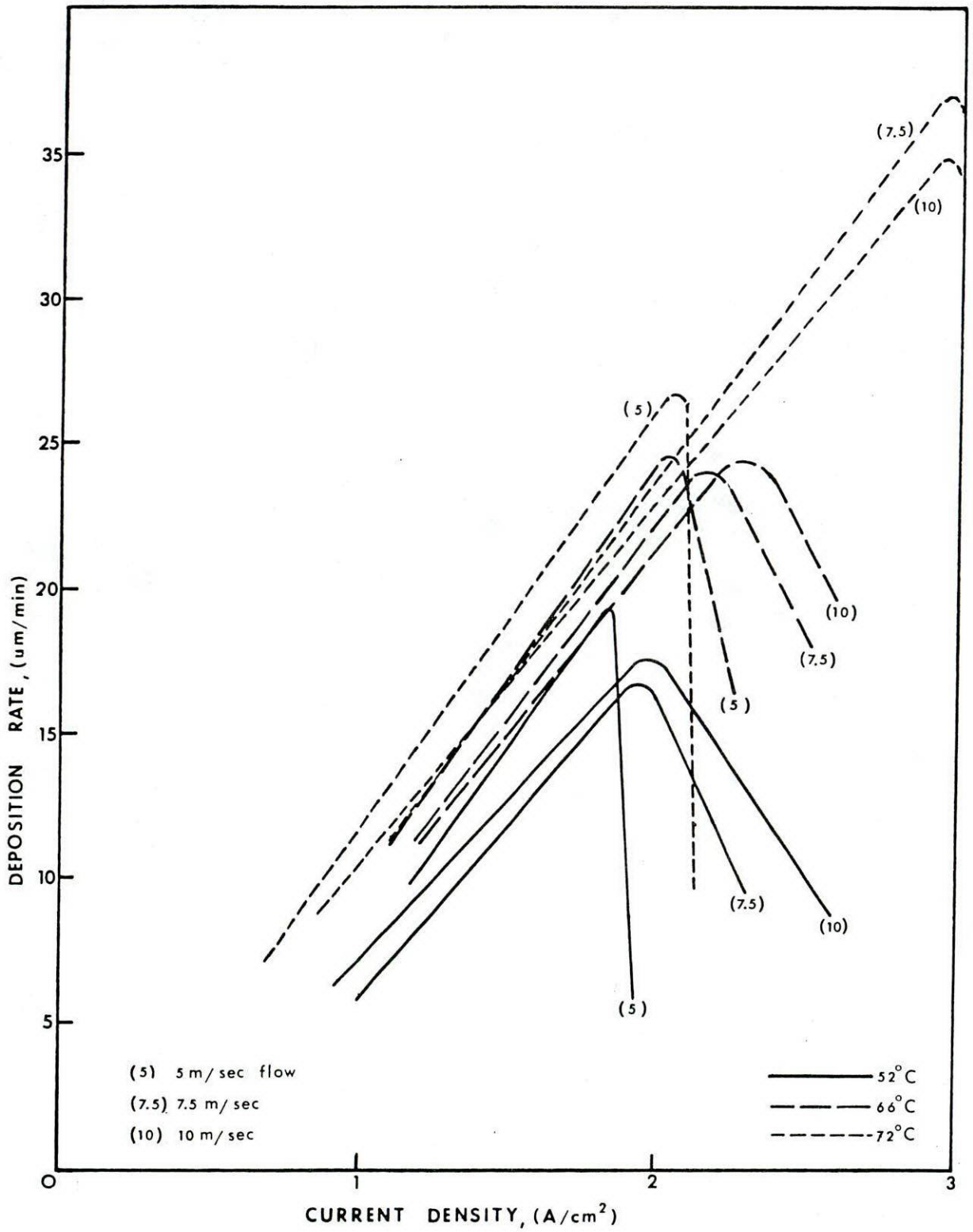
HEAT EXCHANGER
MACHINE SWITCH
TANK AIR GAUGES
FIXTURE
AIR REGULATOR
TANK #1
STEAM TRAP
TANK #2


ADJUSTABLE
ANODE
REMOVABLE
CATHODE
O-RING
SEAL


DEPOSITION RATE, (um/min)
CURRENT DENSITY, (A/cm²)
0
1
2
3
5
10
15
20
25
30
35
(5) 5 m/sec flow
(7.5) 7.5 m/sec
(10) 10 m/sec
52°C
66°C
72°C
(7.5)
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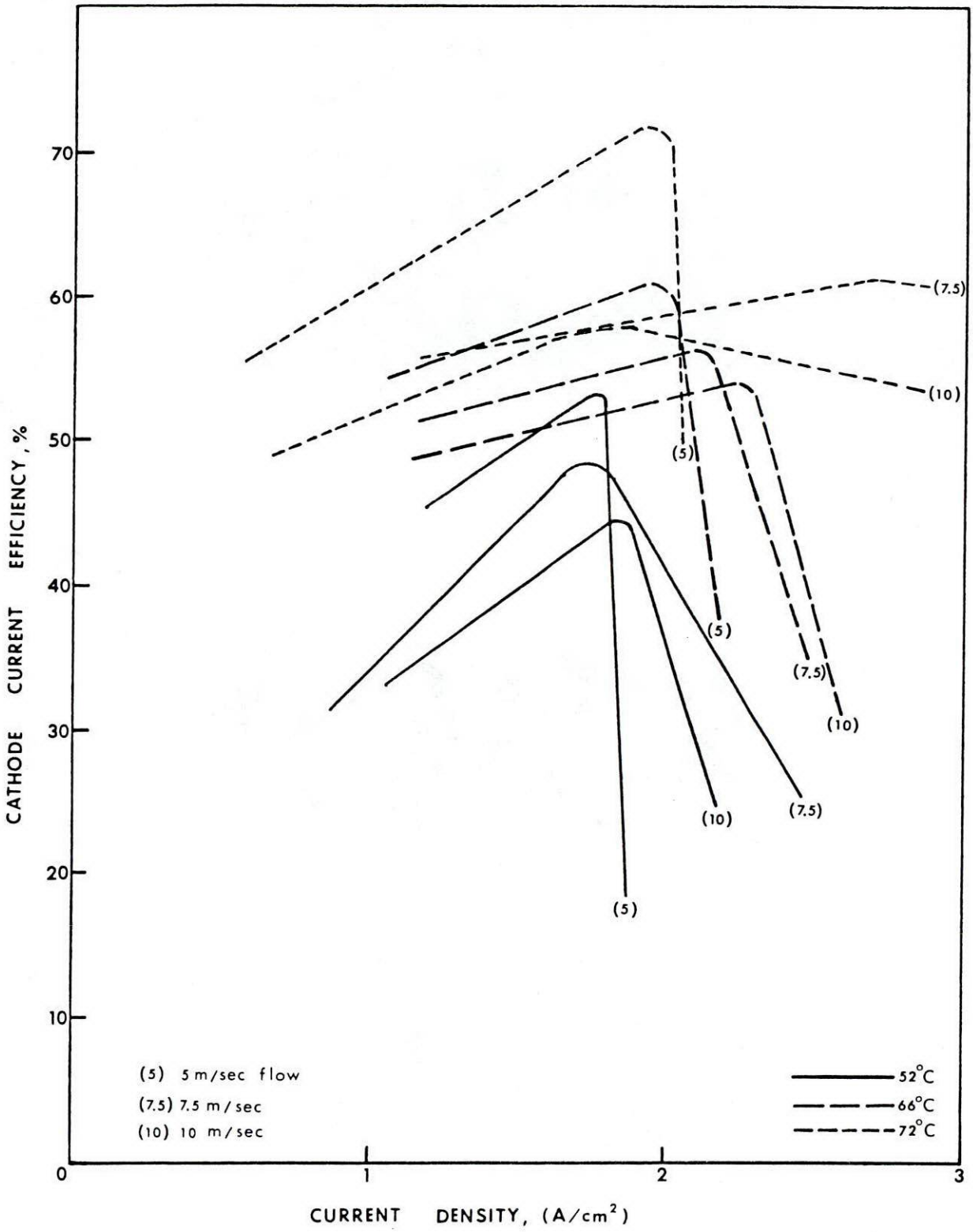
CATHODE CURRENT EFFICIENCY, %
70
60
50
40
30
20
10
0
1
2
3
CURRENT DENSITY, (A/cm²)
(5) 5 m/sec flow
(7.5) 7.5 m/sec
(10) 10 m/sec
52°C
66°C
72°C
(7.5)
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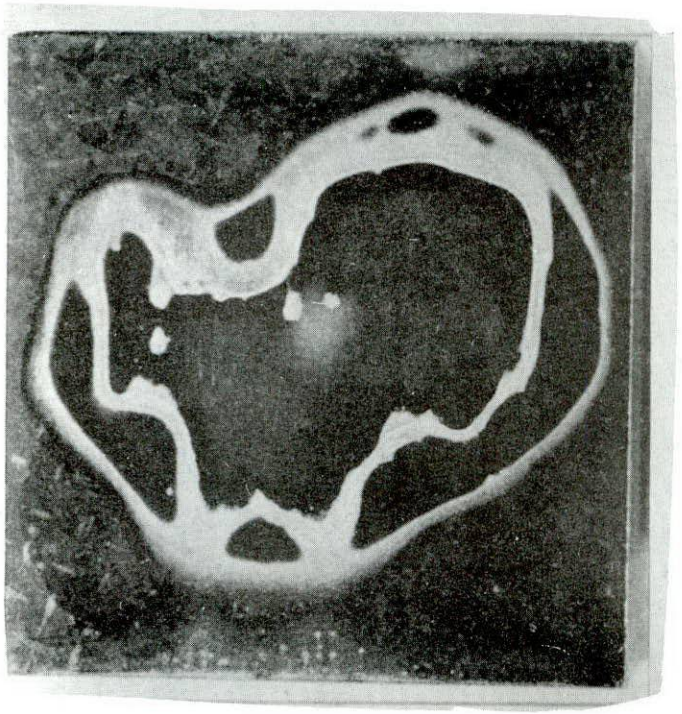

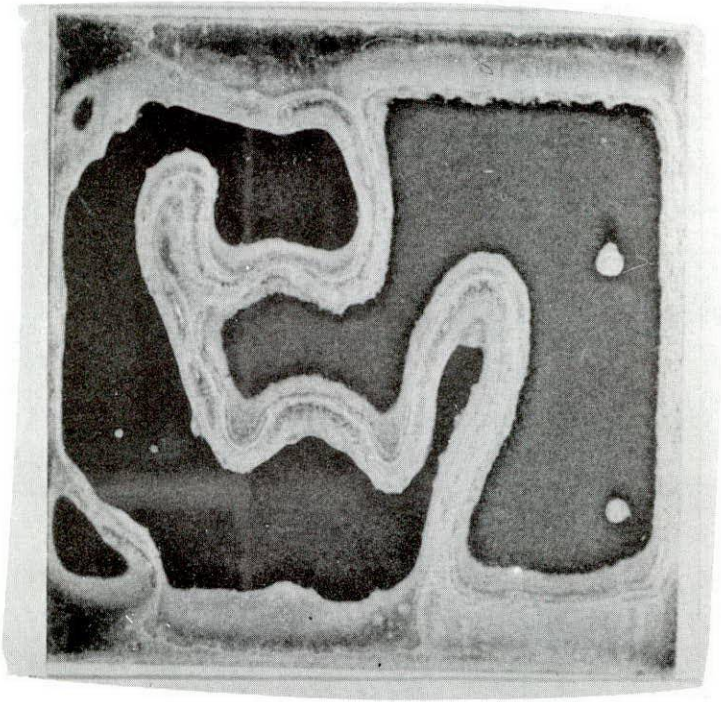

F-2

General Interest Session F

An Investigation of the High Speed Plating of Nickel. II. Mechanisms

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AN INVESTIGATION OF THE HIGH SPEED PLATING OF NICKEL. II MECHANISMS

by

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Introduction

When nickel was deposited at high rates (20-40 μm/min) from a half-strength Watts bath in the high speed plating (HSP) machine known as HSPII, the deposition rate increased with the current density until a critical value was reached after which it unexpectedly dropped abruptly to significantly lower values (see Part I). In contrast, the rate of deposition of chromium from chromic acid solutions in the HSP machine increased linearly with current density up to the highest rates studied without deviation from linearity [1].

To understand this surprising behavior of nickel, a study of the electrodeposition of Ni on a Pt substrate was undertaken using steady-state polarization and cyclic voltammetric techniques.

Platinum was chosen as the substrate rate metal because it is relatively inert and its electrochemistry is well know [3]. The results of this investigation are described in this report.

Experimental

The test micro-electrodes were small beads (about 0.12 cm in dia) melted at the ends of Pt (99.99% pure) wire in an oxygen torch and cleaned by heating white hot in a burning H_2 jet followed by quenching in concentrated nitric acid. After three of these test electrodes (for duplicate runs) were potted in polyethylene so that only a hemisphere is exposed, they were mounted in the test side of a two-compartment, Teflon cell [2]. In the reference side connected to the test side by a glass frit, a saturated calomel reference electrode (SCE) was placed. After the cell was filled with the electrolyte of interest, it was sealed with molten polyethylene.

Solutions were made with triply distilled water from an all quartz still and with reagent grade chemicals. Polarization measurements were made in 0.6M $NiSO_4$ solution and in half strength Watts bath (165 g/L $NISO_4 \cdot 6H_2O$ + 22.5 g/L $NiCl_2 \cdot 6H_2O$ + 18.5 g/L H_3BO_3) at ambient temperatures (24 ± °C).

Steady-state polarization measurements were made by increasing the applied constant current in steps. Before the current was changed to the next step, the steady-state potential was recorded as determined by the trace on a strip-chart recorder (less than one mV change per minute). The cyclic voltammogram was determined by sweeping the potential from a lower to an upper limiting value at constant rate and recording the current with an X-Y recorder. In each case, the potential was cycled between the potential limits until a steady-state trace was obtained. Then, the voltammogram was recorded. All potentials are reported against the SCE unless noted otherwise.

Results

Steady-state polarization curves at constant current and for increasing current density from open circuit conditions are plotted in Fig. 1 for Pt in N_2-stirred 0.6M $NiSO_4$ solution and in Fig. 2 for Pt in N_2-stirred half strength Watts bath. Various sections of the curves are designated by the letters.

During polarization of Pt in 0.6M $NiSO_4$ (Fig. 1), if the circuit were opened at current densities in plateaus A or B, the open circuit potential shifted to the original rest potential of 510 ± 10 mV. At this point when the Pt test bead was removed from the cell and analyzed with Auger Electron Spectroscopy (AES), only Pt was detected and Ni was not present. If, however, the polarization of the Pt electrode was carried into plateau C or D before the circuit was broken, the open circuit potential came to rest at -460 ± 10 mV. In this case, AES detected only Ni indicating that a thick layer of Ni was deposited on the Pt electrode. This potential is close to that given [4] for the Ni/Ni^{+2} couple, -257 mV vs. NHE (-502 mV vs. SCE).

The rest potential for Pt in half strength Watts bath is also 510 ± 10 mV. When the polarizing circuit was broken in the A-plateau, the potential recovered to the 510-mV value. Once the system was polarized into the B-plateau and beyond, the open circuit potential came to rest at the negative value, -460 mV, associated with the Ni/Ni^{+2} potential.

Figure 3 contains the family of curves generated by increasing the lower limit in 50 mV steps of the cyclic voltammogram obtained on Pt in N_2-stirred 0.6M $NiSO_4$ at a potential sweep rate of 100 mV/s. The trace for each increase in the potential range over which the potential was scanned is noted by the small numerals and the major current peaks are noted by the large Roman numerals. The direction of scanning is indicated by the arrows. Similar, voltammetric data are recorded in Fig. 4 for Pt in N_2-stirred half strength Watts bath.

Discussion

As soon as the polarizing circuit is closed in Figs. 1 and 2, the potential falls at the lowest current densities studied to the steady-state values in

Section A. A line is drawn with a slope of 0.030 to show that the data in Section A are consistent with this slope. The Tafel slope for hydrogen overvoltage on Pt in acid solution is 0.030 [5]. Consequently, the electrode process in plateau-A is the reduction of H^+ ion to molecular H_2.

Additional evidence for this conclusion is found in the data of Fig. 3. As the lower limit is increased from -300 to -600 mV, the height of peak IV_H increases. The electrode process corresponding to I'_H is the evolution of H_2 on Pt and IV_H is the oxidation of H_2 on Pt. With increasing cathodic potential more H_2 is evolved. Between -600 and -700 mV, the height of IV_H decreases because some of the current is consumed in forming a thin epitaxial layer of Ni which is complete at II'_H and corresponds to region B in Fig. 1. Above -750 mV a thick coating of Ni is laid down and the substrate is no longer a Pt surface but a Ni surface. In Fig. 3, IV_H disappears and a new peak II_H appears which is the oxidation of H_2 on a Ni surface. At potentials above -800 mV (thick Ni layers corresponding to Section C in Fig. 1), II_H develops a shoulder, I_H. This effect may indicate that two types of sites exist on Ni for the oxidation of H_2. Finally, anodic dissolution of the Ni layer deposited in II'_H and III'_H takes place in the tail designated as III_H.

A visual inspection was made of Pt electrodes for which the polarization was stopped at various points along the curve in Fig. 1. The surface of those electrodes polarized only in region A had the bright whiteness of Pt. Since a very thin, strained, epitaxial Ni film is easily removed at open circuit (rest potential ~500 mV), the electrodes polarized only in the B region also had the bright white appearance of Pt. Those electrodes polarized into region C had a smooth surface with the yellowish cast of Ni (rest potential ~ -450 mV). When polarized at high current densities in region D, the electrode was covered with a black coating which was easily brushed away to expose a smooth yellowish white layer of Ni. Therefore, with increasing current density on Pt in 0.6M $NiSO_4$, H_2 is evolved first after which a thin, strained, epitaxial layer of Ni similar to that observed on copper [6] is laid down. Then, a thick layer of Ni is deposited. At high current densities, a black smut is deposited on a relatively smooth layer of Ni.

The steady-state polarization curve obtained on Pt in half strength Watts bath in Fig. 2 exhibits a number of linear regions. A line with a slope of 0.130 which is found for the overvoltage for Ni electrodeposition [7,8] is drawn in Fig. 2 to show that the data in Sections A and D are consistent with such a slope. In A then, the thin epitaxial layer is deposited. Support for this conclusion is obtained from the data in Fig. 4. These cyclic voltammograms exhibit only one peak, II_H, on the anodic going trace which corresponds to the oxidation of H_2 on a Ni surface. As the lower limit of the potential sweep is increased, the amount of H_2 oxidized in II_H increased but is much smaller (note potential scales) than in Fig. 3. Peaks for the H_2 reaction on Pt are missing because the Pt electrode becomes covered with a Ni layer before H_2 can be evolved. As a result, the hysteresis noted in Fig. 3 is absent in Fig. 4. This behavior difference is

traced to the addition of boric acid in the Watts bath. Boric acid acts as a catalyst for the deposition of Ni [9] which lowers the overvoltage of the Ni reaction. In this way, boric acid masquerades as a buffer by suppressing the evolution of H_2 which alters the pH at the metal-solution interface.

Similar to the interpretation of the data in Fig. 1, a thin epitaxial layer of Ni is deposited in A before H_2 is evolved in agreement with the literature [10] stating that Ni deposition from Watts baths is nearly 100% efficient. In B, the Ni layer becomes thicker and its surface is rougher than that of bright Pt (roughness factor of 2 [11]). This causes the surface area to increase, and at C, the curve doubles back in a negative resistance region because the true current density is less than the apparent. Once these area changes have reached a constant value, the linear region of Ni overvoltage resumes in region D. Visual inspection of these deposits discloses a yellowish white layer of Ni. As in Fig. 1, a black smut is deposited on the Ni layer at high current densities in region E.

From these data it is possible to account for the abrupt drop in the Ni deposition rate at a critical current density during the HSP of Ni described in Part I.

The narrow gap between the anode and cathode in the HSPII machine allows very high currents to be drawn without excessive iR loss. With the high rate of solution flow through this gap, the temperature in the gap can be controlled and depletion of reactants in the gap is prevented by the continuous influx of fresh solution into the gap. Consequently, in Fig. 5 the deposition rate of Ni increases linearly with increasing current density up to the critical point. The rate of H_2 evolution also increases with the current density. Eventually, the rate of H_2 evolution becomes so great that the pH in the vicinity of the cathode reaches a value large enough that the solubility product for $Ni(OH)_2$ is exceeded. Under these conditions, $Ni(OH)_2$ begins to precipitate onto the cathode surface. At this critical current density, Ni can no longer be deposited in a smooth coherent layer and the depositions rate falls off.

The presence of the precipitated $Ni(OH)_2$ deposits on the cathode surface interfere with the uniform electrolyte flow over the electrode surface causing swirls and eddys. This nonuniform solution flow in turn produces the varied patterns of green $Ni(OH)_2$ and black finely divided Ni deposits pictured in Fig. 6. As seen in Fig. 5, the critical current density for the deposition-rate fall-off occurs at higher values of the current density with increasing flow rate. The higher flow rate sweeps the precipitate out of the gap and shifts the critical point to higher current densities where a higher concentration of precipitate can accumulate in the gap and disturb the uniform flow of electrolyte. This sweeping-out effect may also account for the deceleration in the rate of Ni deposition with increasing flow rate at current densities beyond the critical value.

In all cases as noted in Fig. 5, the rate of Ni electrodeposition increases with increasing temperature. From the data in Fig. 5, it is concluded that,

although the increased temperature increases both the rate of Ni deposition and H_2 evolution, the increase in the Ni rate is greater than that for the H_2 rate for a given jump in temperature. As a result, it requires a higher current density to be reached before H_2 evolution is great enough to produce the required change in pH to cause precipitation of $Ni(OH)_2$ near the cathode. This maybe understood in terms of current efficiency for metal deposition. With an increase in temperature for a given current density and flow rate, more current is consumed in Ni deposition than in H_2 evolution. As noted in Fig. 7 for every case, the current efficiency for Ni deposition increases with temperature. This occurs at the expense of H_2 evolution thus delaying the critical point to higher current densities.

In the case of the high speed plating of chromium [1], chromic acid baths are so acidic that they are very good buffers in themselves. Therefore, in the studies undertaken, a current density was never reached where the pH could be increased by H_2 evolution to a point where the solubility of $Cr(OH)_3$ would be exceeded. For these studies, the rate of Cr deposition increased monotonously with increasing current density.

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Figure Captions

Fig. 1 Steady-state galvanostatic polarization curve obtained on Pt in N_2-stirred 0.6M $NiSO_4$ solution.

Fig. 2 Steady-state galvanostatic polarization curve obtained on Pt in N_2-stirred half-strength Watts bath.

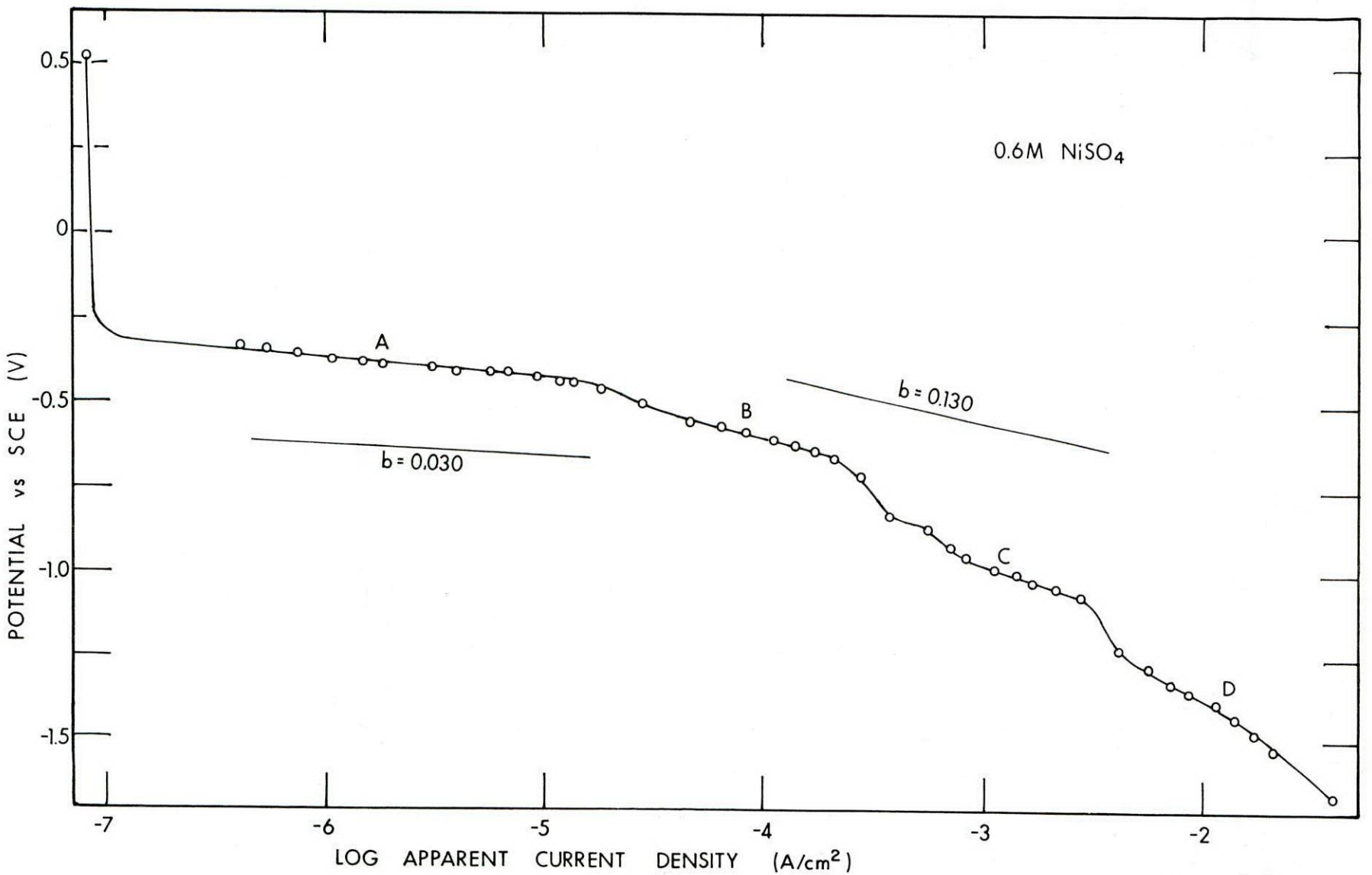
Fig. 3 Family of cyclic voltammograms obtained on Pt in N_2-stirred solution swept from -900 to 800 mV at a rate of 100 mV/s as a function of the potential of the lower limit; numerals index sequence of curves.

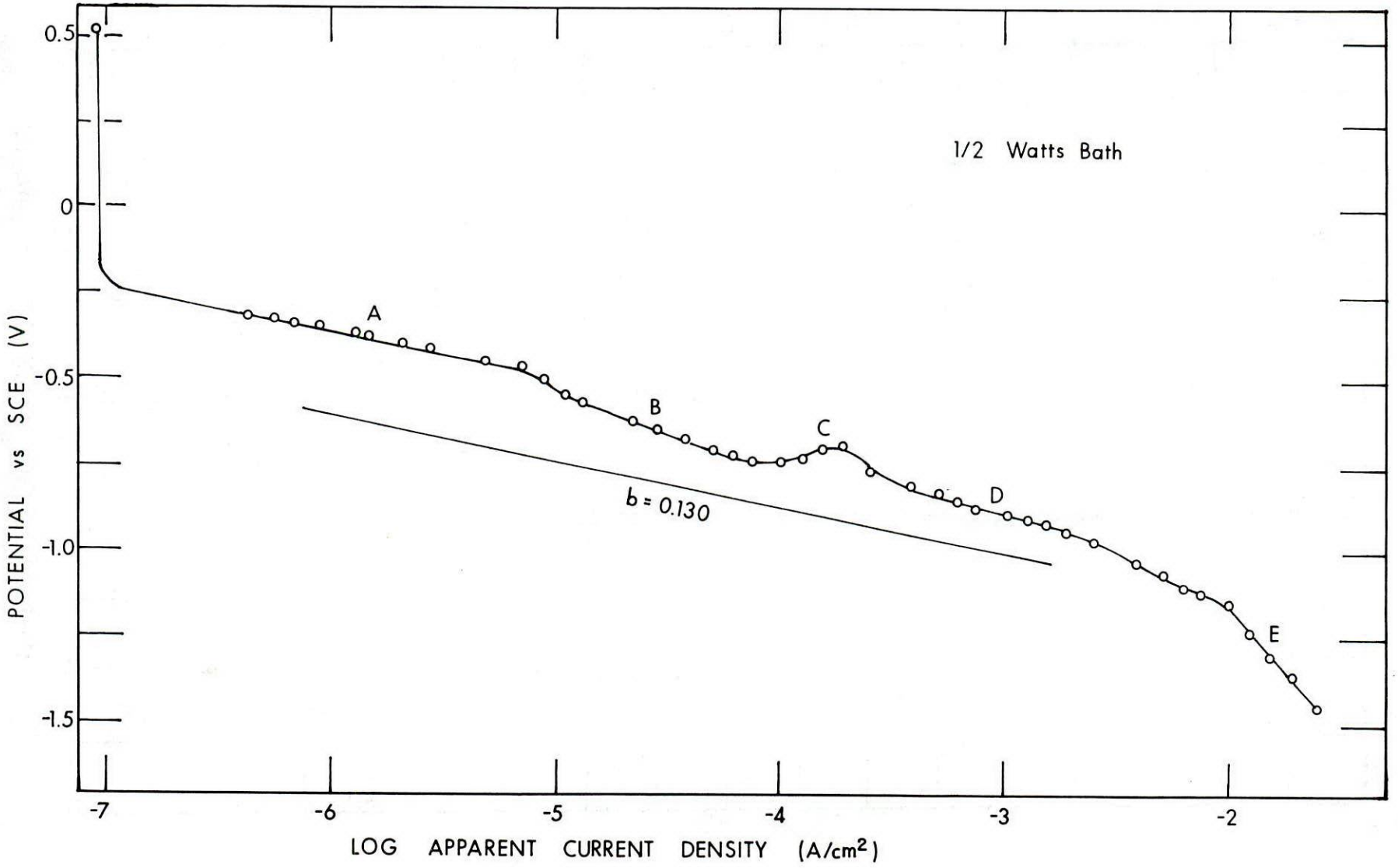
Fig. 4 Family of cyclic voltammograms obtained on Pt in N_2-stirred half-strength Watts bath swept from -1100 to 500 mV at a rate of 100 mV/s as a function of the potential of the lower limit; numerals index sequence of curves.

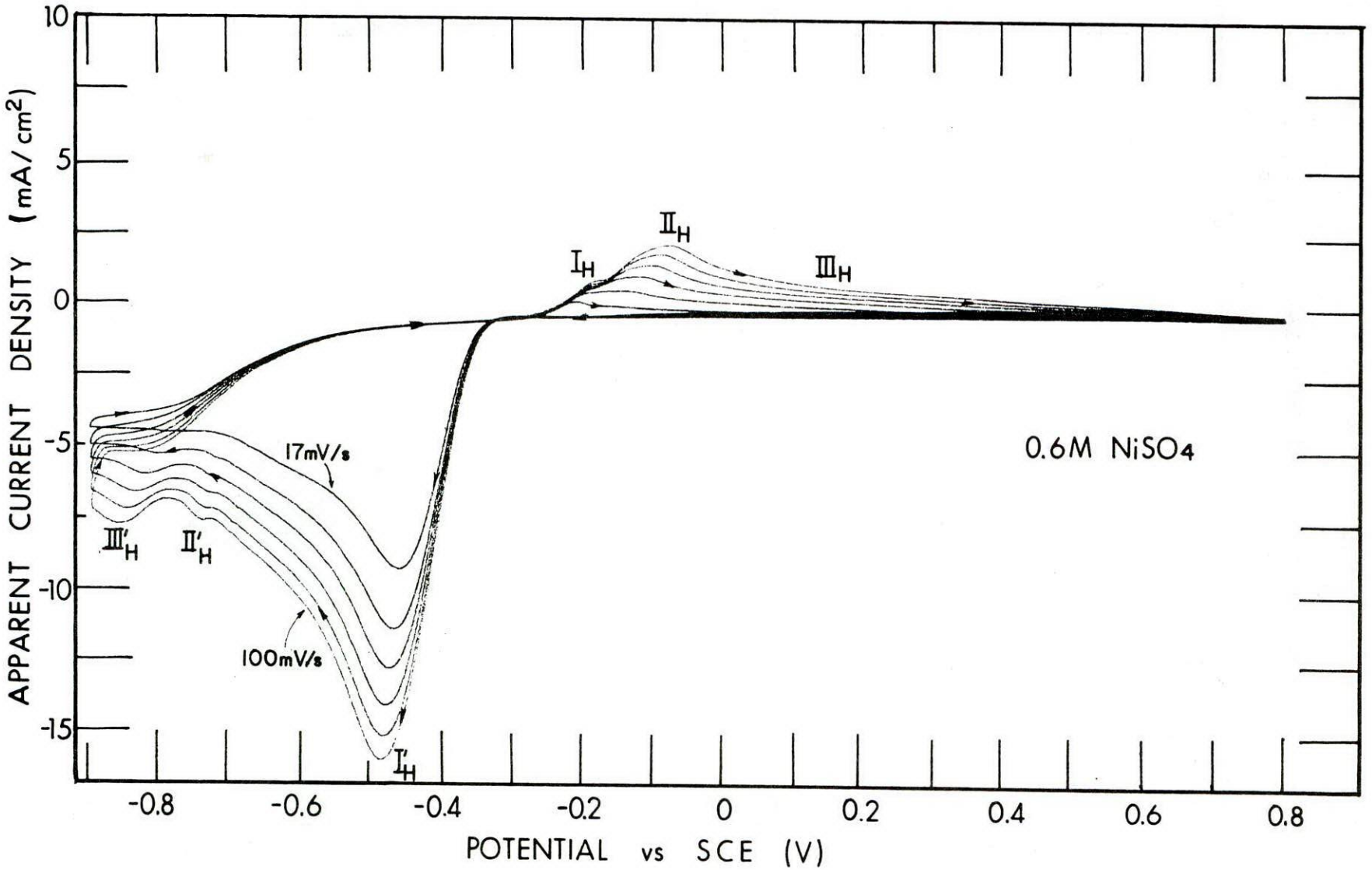
Fig. 5 The deposition rate of Ni from a half-strength Watts bath on a Cu substrate as a function of the current density for three values of both the temperature and solution flow rate.

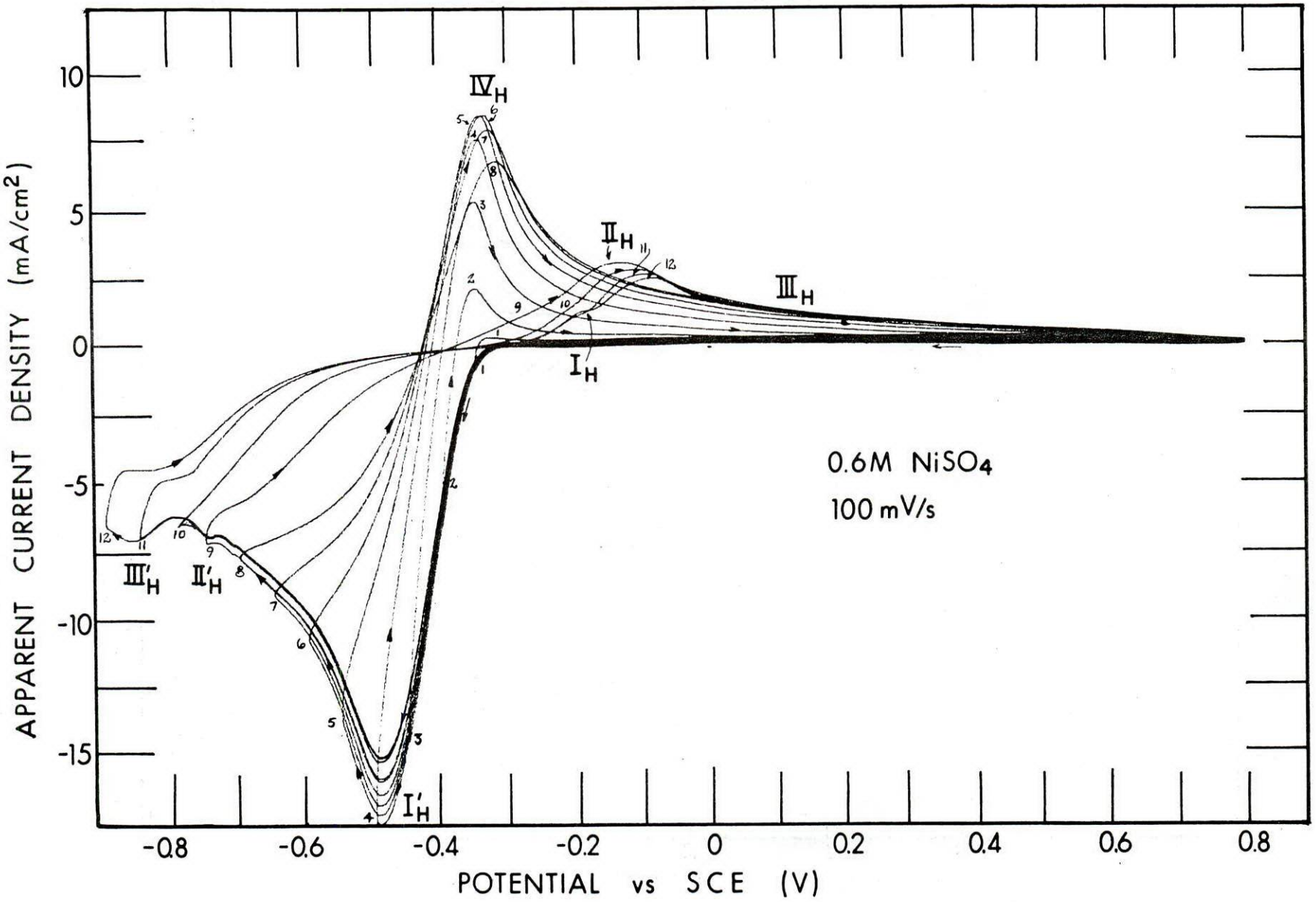
Fig. 6 The cathode current efficiency for the system in Fig. 5 as a function of the current density.

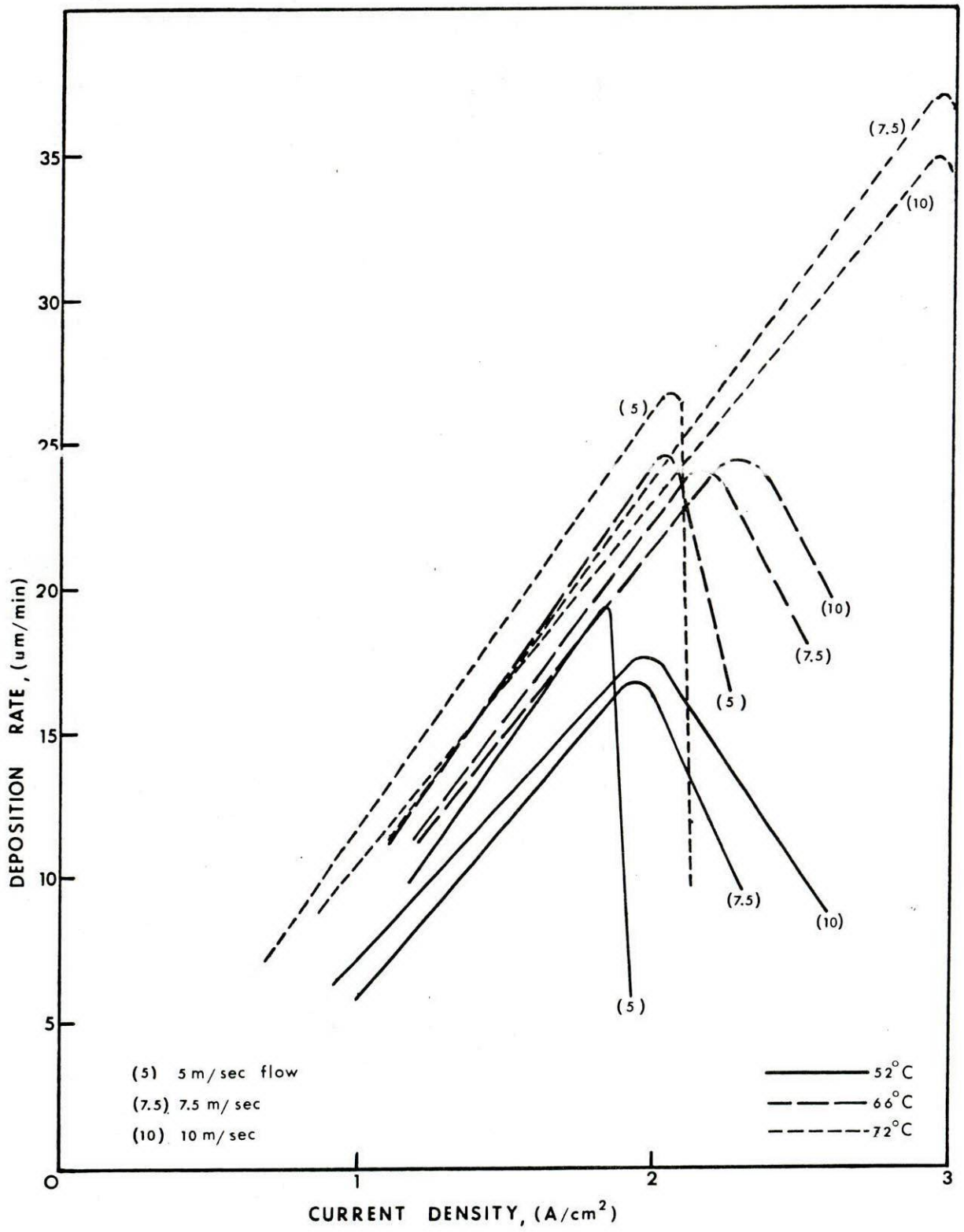
Fig. 7 Typical green and black patterned Ni deposits obtained on Cu samples at high current densities beyond the critical current density.

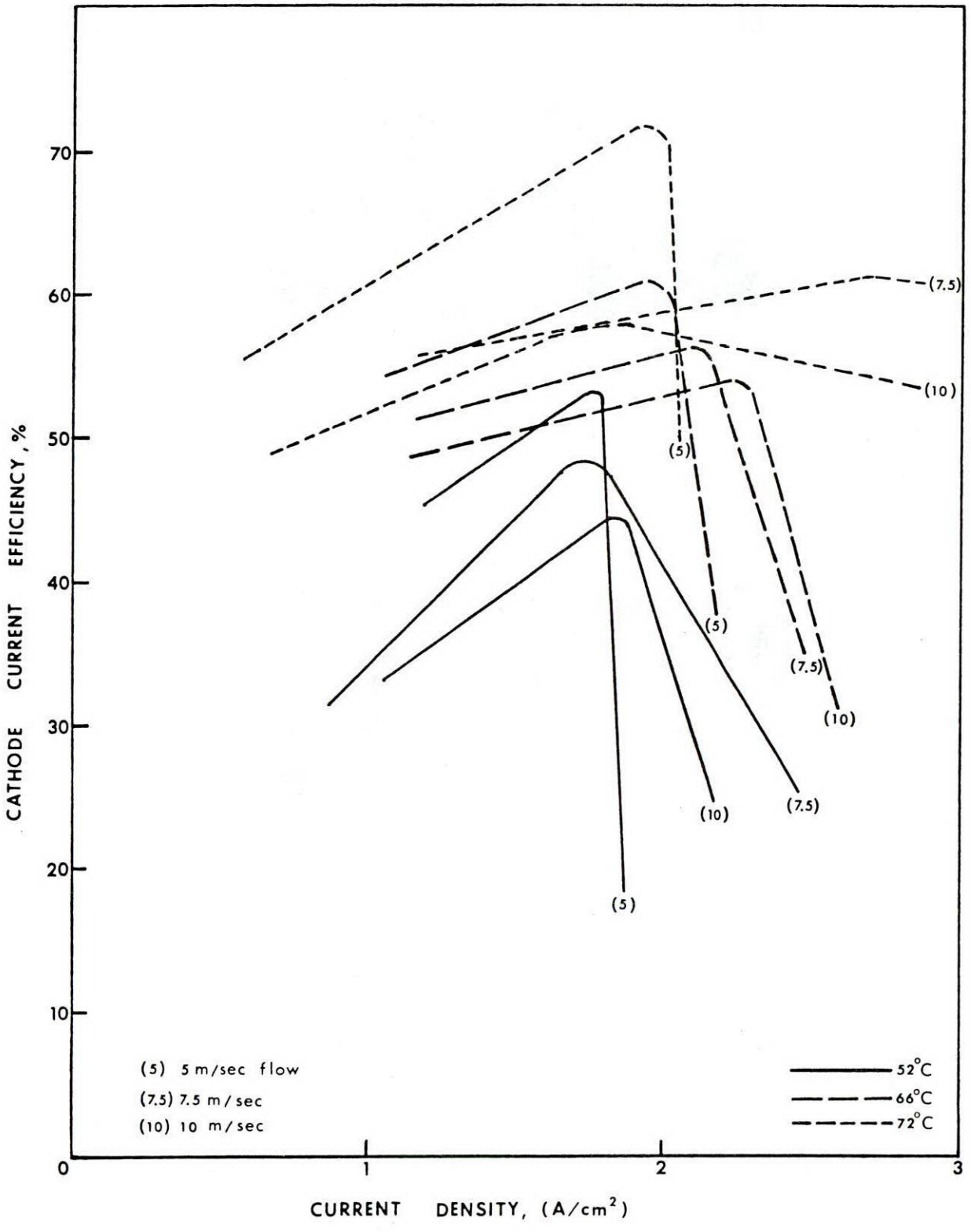

0.6M NiSO4
A
B
C
D
b = 0.030
b = 0.130
0.5
0
-0.5
-1.0
-1.5
POTENTIAL vs SCE (V)
-7
-6
-5
-4
-3
-2
LOG APPARENT CURRENT DENSITY (A/cm²)

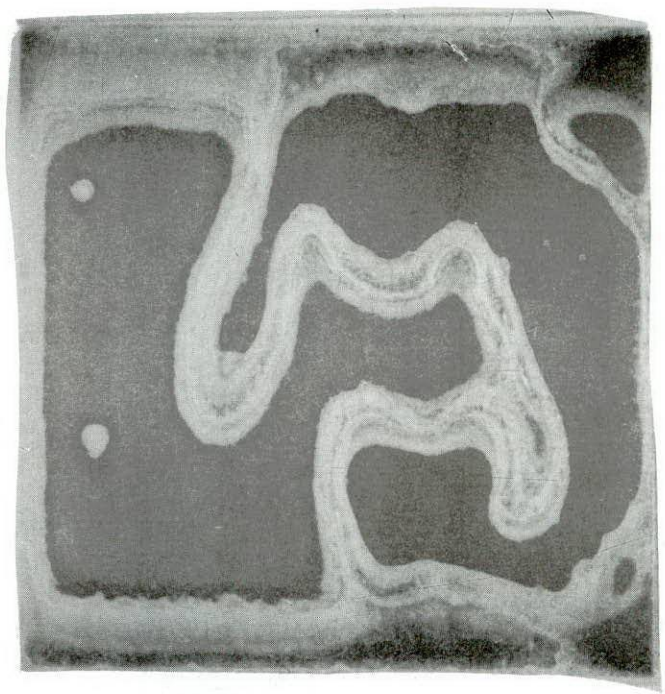

1/2 Watts Bath
A
B
C
D
E
b = 0.130
0.5
0
-0.5
-1.0
-1.5
-7
-6
-5
-4
-3
-2
POTENTIAL vs SCE (V)
LOG APPARENT CURRENT DENSITY (A/cm²)

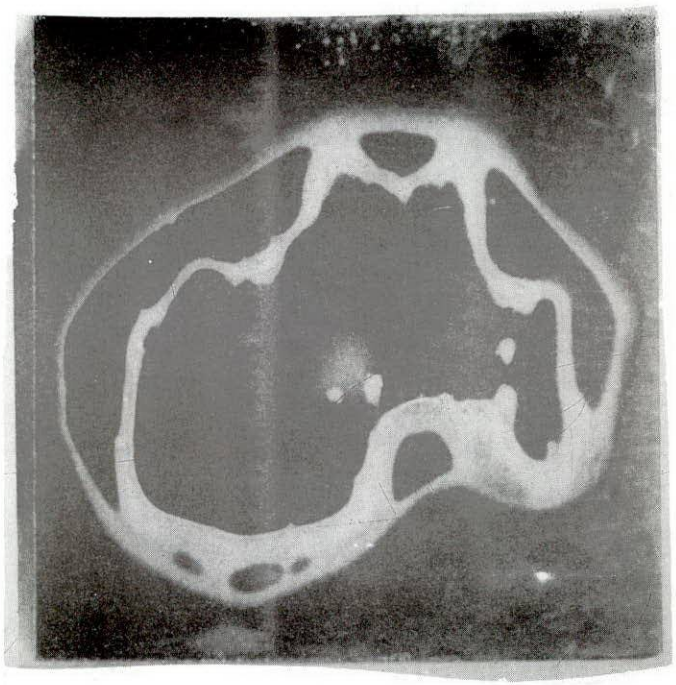

10
5
0
-5
-10
-15
APPARENT CURRENT DENSITY (mA/cm²)
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
POTENTIAL vs SCE (V)
II_H
I_H
III_H
17mV/s
100mV/s
III'_H
II'_H
I'_H
0.6M NiSO4


APPARENT CURRENT DENSITY (mA/cm²)
10
5
0
-5
-10
-15
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
POTENTIAL vs SCE (V)
IV_H
II_H
III_H
I_H
III'_H
II'_H
I'_H
0.6M NiSO4
100 mV/s


DEPOSITION RATE, (um/min)
CURRENT DENSITY, (A/cm²)
0
1
2
3
5
10
15
20
25
30
35
(7.5)
(10)
(5)
(10)
(7.5)
(5)
(7.5)
(10)
(5)
(5) 5 m/sec flow
(7.5) 7.5 m/sec
(10) 10 m/sec
52°C
66°C
72°C


CATHODE CURRENT EFFICIENCY, %
70
60
50
40
30
20
10
0
1
2
3
CURRENT DENSITY, (A/cm²)
(7.5)
(10)
(5)
(5)
(7.5)
(10)
(5)
(10)
(7.5)
(5) 5 m/sec flow
(7.5) 7.5 m/sec
(10) 10 m/sec
52°C
66°C
72°C





F-3

General Interest Session F

Tensile Properties of Electrodeposited Nickel-Cobalt

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TENSILE PROPERTIES OF ELECTRODEPOSITED NICKEL-COBALT

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ABSTRACT

The tensile properties of electrodeposited nickel-cobalt were determined as a function of test temperature -196 to 649°C (-320 to 1200°F) and heat treatment conditions. Long-duration, 204°C (400°F), heat treatment increased the as-deposited strength and ductility of this alloy so that ambient and cryogenic tensile properties equal to those of high-strength nickel-base alloys were obtained. The high strength of EDNi with 40 to 60 weight percent cobalt results from its extremely fine grain size. Testing and heat treating at >260°C (500°F) reduces the effectiveness of grain boundaries as barriers to plastic deformation. It is postulated that this reduction is mainly the result of the reduction of grain boundary area internal stresses. Grain boundary deformation or creep dominates at 482°C (900°F), at which tempera-temperature the alloy is superplastic. Superplastic deformation of electro-deposited alloys enables production of complex shapes by combining preform-preforming by electrodeposition and final forming of the internal structure by superplastic deformation.

INTRODUCTION

The available literature on electrodeposited nickel-cobalt (EDNi-Co) indicates that this alloy group is much stronger than EDNi. The optimum tensile properties of EDNi-Co occur (Ref. 1) between 40 and 60 wt% Co, where it is approximately 2-1/2 times as strong as EDNi. Despite the high strength of EDNi-Co, it has had limited application because of difficulty controlling the deposited composition (Ref. 1-2) and because of low ductility, 2 to 8% elongation (Ref. 1-4). Walter (Ref. 5) showed that composition control of EDNi-Co alloys can be obtained through elimination of Co ion depletion by maintaining adequate electrolyte flow at the cathode, while the electrolyte Ni ion and Co ion concentrations are maintained by separately controlled Ni and Co anodes. Attempts (Ref. 1-4) to improve the tensile properties of EDNi-Co by heat treatment produced significant improvements of ductility but with substantial strength reductions. These investigators limited their studies to ambient temperature tensile properties although there are important cryogenic and elevated temperature applications for high-strength electrodeposited alloys. This paper addresses the tensile properties of EDNi-Co with respect to its ambient, cryogenic, and elevated temperature tensile properties and the influence of heat treatment on these properties.

In this paper, the EDNi-Co composition will be designated in terms of weight percent cobalt. An alloy composition of 45 wt% Co is designed as EDNi-45Co. An alloy range of 45-50 wt% Co is designated as EDNi-45/50Co.

PROCEDURE

Experiments were performed in a 378-L (100-gal) tank. The anode baskets were hung at the sides of the tank, and the cathode was suspended from a rod extending across the middle of the tank. The anode circuit consisted of titanium baskets filled with cobalt chips and of titanium baskets filled with sulfur-depolarized nickel chips. The nickel and cobalt anodes were controlled by separate rectifiers previously described (Ref. 5). The cathode was a flat 1.9 x 1.9 dm (7.5 x 7.5 in.) plate in a plexiglass-shield box. Electrolyte flow impingement was supplied by showerhead flow nozzles located approximately 2.54 cm (1 in.) from the cathode surface. The flow was perpendicular to the cathode surface. Cathode rod agitation was used to distribute the electrolyte flow across the deposit surface.

The electrolyte was Ni-Co sulfamate containing about 75 g/L of Ni+Co and 12 to 20 Ni/Co weight ratio and with boric acid buffer and a wetting agent.

The tensile properties were obtained from plate specimens machined from 0.23-cm (0.090-in.) thick deposits, and cylindrical specimens with 0.635-cm (1/4-in.) diameter reduced sections machined from >1.27-cm (1/2-in.) thick deposits. The 1.27-cm thick plates were deposited on both sides of 0.066- to 0.076-cm nickel EDNi-Co substrates. These thin Ni-Co substrates were initially produced by deposition onto stainless steel panels without prior activation for easy stripping. All reported data are averages of either duplicate or triplicate tests.

Internal stress measurements were performed using the GE internal stress cell technique in which EDNi-Co was deposited onto thin copper strips and the stresses analyzed as cantilever beam displacements. Prior to performing the measurements, the stress cell was modified to provide electrolyte flow past the copper substrates to prevent cathode composition polarization.

RESULTS AND DISCUSSION

The tensile properties of EDNi-Co are listed in Table 1 for cylindrical specimens and Table 2 for plate specimens. The plate specimens were somewhat stronger but had about the same overall ductility as the cylindrical specimens. The higher strength of the plate specimens is somewhat unexpected because of the lower Co content (40 wt% Co for plate and 53/55 wt% Co for cylindrical) of the plate specimens.

Heat treatment significantly improved the properties

Table 1. Ambient Temperature Tensile Properties of EDNi-53/55Co Cylindrical Specimens

HEAT TREATMENT			STRENGTH, MPa (ksi)		DUCTILITY	
°C	(°F)	HOURS	YIELD	UTS	% EL	% RA
—	—	—	1062 (154)	1634 (237)	10	31
204	(400)	4	1110 (161)	1565 (227)	15	49
204	(400)	124	1124 (163)	1538 (223)	16	62
260	(500)	50	1007 (146)	1400 (203)	15	61
316	(600)	25	1020 (148)	1303 (189)	15	67
371	(700)	4	958 (139)	1096 (159)	18	63
482	(900)	4	758 (110)	807 (117)	38	67
649	(1200)	4	476 (69)	662 (69)	50	69

Table 2. Ambient Temperature Tensile Properties of EDNi-40Co 0.23 cm (0.090 in.) Plate

HEAT TREATMENT			STRENGTH, MPa (ksi)		DUCTILITY	
°C	(°F)	HOURS	YIELD	UTS	% EL	% RA
—	—	—	1131 (164)	1765 (256)	20	18
204	(400)	10	1172 (170)	1600 (232)	18	33
399	(750)	4	958 (139)	1055 (153)	27	55

of both the cylindrical and plate specimens. The most noticeable effect was for long-duration heat treatment at 204°C (400°F). This heat treatment produced a small but significant improvement of ambient temperature yield strength and increased the ductility by a factor of 1.5 as measured by both elongation (EL) and reduction of area (RA).

The strength and ductility improvement for long-duration 204°C heat treatments is likely due to evolution of hydrogen accompanied by some reduction of the internal tensile stresses developed during depositon. The 124-hr, 204°C heat treatment was based on the estimated duration required to remove hydrogen from the metal. Confirmation hydrogen analysis was, however, not performed. Removal of hydrogen and reduction of internal stresses would improve ductility but not the strength. The strength improvement was comparatively small but significant and repeatable. A mechanism which would improve the strength is impurity (other than hydrogen) migration to the grain boundaries.

Higher temperature anneals at 260 to 371°C (500 to 700°F) decreased the strength without a further gain of ductility. The high strength of EDNi-Co is due to its fine grain size and the inhibiting effect of grain boundaries to slip propagation into adjoining grains. Grain size of the EDNi-Co specimens was $< 0.1\ \mu m$ as determined by transmission electron microscopy. Recrystallization or grain growth was not observed after the heat treatments performed below 649°C (1200°F), yet these produced significant yield strength reductions.

These yield strength decreases were likely caused by grain boundary changes that reduced their effectiveness as dislocation barriers. One such change would be reduction of the internal stress associated with grain boundaries either as an elastic strain field or dislocation network around the grain boundaries, allowing easier transport of slip across the boundaries.

Table 3 contains the results of internal stress measurements performed on EDNi-Co deposits. The internal stress varies with deposit thickness, current density, and electrolyte flow. As described previously (Ref. 5), the cobalt content of the deposit depends on adequacy of electrolyte agitation for maintaining Co^{++} deposition. The lower internal stresses measured without electrolyte flow are thus due to lower deposit Co contents. On this basis, the internal stress for EDNi ~50% Co was about 110 MPa (16 ksi) tensile for deposits thicker than 0.005 mm (0.2 mils). The lower internal

Table 3. Stress Measurements of EDNi-Co Deposited on 0.18 cm Copper (Electrolyte: 65 g/L Ni, 6.2 g/L Co)

INTERNAL TENSILE STRESS, MPa (ksi)						
1.08 A/dm^2 0.0033 mm DEPOSIT	1.16 A/dm^2 0.005 mm DEPOSIT	2.15 A/dm^2 0.0066 mm DEPOSIT	3.23 A/dm^2 0.0099 mm DEPOSIT	4.3 A/dm^2 0.013 mm DEPOSIT	>4.3 A/dm^2 >0.013 mm DEPOSIT	COMMENTS
95 (13.8)	112 (16.2)	81 (11.8)	86 (12.5)	79 (11.5)	47 (6.8)	NO ELECTROLYTE FLOW
188 (27.2)	157 (22.8)	131 (19.0)	110 (15.9)	113 (16.3)	91 (13.3)	ELECTROLYTE FLOW
92 (13.4)	46 (6.6)	50 (7.2)	23 (3.4)	33 (4.8)	45 (6.5)	STRESS INCREASE BECAUSE OF ELECTROLYTE FLOW

stress obtained for a thicker deposit at current density >4.3 A/dm^2 (40 asf) is probably the result of inadequate electrolyte flow for this current density. Thus, the internal stress is substantial in the as-deposited material, and the heat treatment effects are probably related to reduction of these stresses.

Reduced effectiveness of grain boundaries for inhibiting plastic deformation was observed by Thompson and Saxton (Ref. 6) for EDNi. Figure 1 shows Thompson and Saxton's results on EDNi together with Wilcox and Clauer's (Ref. 7) results on cold-drawn nickel. The abscissa for EDNi is the grain diameter and for cold-drawn nickel is the dislocation cell diameter. It is seen that the yield strength increases with decreasing grain size according to the Hall-Petch relationship (Ref. 8)

$$\sigma_y = \sigma_o + kd^{-1/2}$$

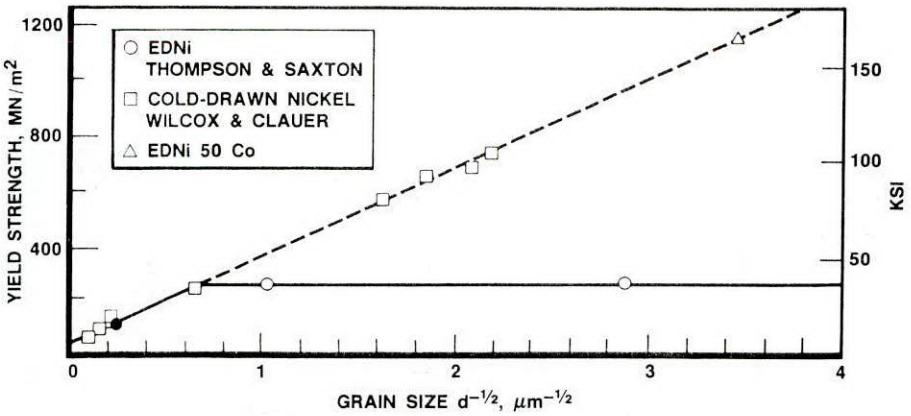
where

σ_y = yield strength

σ_o, k = constants

d = average grain diameter

It is seen that below a certain microstructural size (<0.2 μm diameter), grain size changes in ED nickel had only a small effect on the yield strength. On the other hand, the dislocation cell size continued to strongly influence the yield strengths for grain diameters as small as 0.2 μm. Thompson and Saxton suggested that the very small yield strength dependency on fine-grain EDNi is because the unrecrystallized grain boundaries are likely to be quite pure and are, therefore, potential sites for dislocation generation. On this basis, a correlation was shown between the shallow Hall-Petch slope in EDNi and shallow slopes obtained by others for high-purity metals. Grain boundary impurities lock dislocation generation sources in the grain boundaries. Intergranular slip is then dependent upon transport of slip bands, originating within the grains, across the grain boundaries, which forms the basis for the Hall-Petch relationship.



NOTE: FILLED SYMBOL REPRESENTS 875 K HEAT TREATMENT;
HALF-FILLED SYMBOL, 575 K HEAT TREATMENT;
OPEN SYMBOL, AS-PLATED MATERIAL

Fig. 1. Dependence of Yield Strength in EDNi on Grain Size

Shown in Fig. 1 is a point representing the yield strength of as-deposited EDNi-50Co (1100 MPa YTS, 0.08 μm grain size). The point lies on the wrought nickel extrapolation of the Hall-Petch relationship. The reduction of yield strength of EDNi-Co with nonrecrystallization heat treatments is consistent with producing stress-free grain boundaries in high-purity EDNi-Co.

As a consequence of the effectiveness of EDNi-Co grain boundaries for inhibiting slip band transport, the ambient temperature properties of EDNi-40/60Co are essentially the same as that of the nickel-base superalloys. Table 4 lists the minimum ambient temperature properties of annealed wrought Ni, EDNi, EDNi-40/60Co, and Inconel 718. Inconel 718 is a common high-strength, wrought nickel-base alloy that obtains its strength through age-hardening heat treatments that produce extremely small coherent precipitates.

Table 4. Minimum Ambient Temperature Tensile Properties of Electrodeposited and Wrought Nickel Alloys

MATERIAL	STRENGTH, MPa (ksi)		DUCTILITY	
	YIELD	ULTIMATE	% ELONGATION	% REDUCTION AREA
ANNEALED, WROUGHT Ni*	138 (20)	483 (70)	50	70
EDNi	414 (60)	621 (90)	16	50
EDNi-40/60Co	965 (140)	1379 (200)	12	40
INCONEL 718	1034 (150)	1241 (180)	12	15

*NOMINAL PROPERTIES

Microstructures of EDNi, EDNi-Co, and Inconel 718 are shown in Fig. 2. The EDNi microstructure consists of columnar grains aligned in the deposit or thickness direction. These grains are much finer than recrystallized equiaxed grains of annealed wrought Ni and this accounts for the higher strength of EDNi over that of annealed wrought Ni.

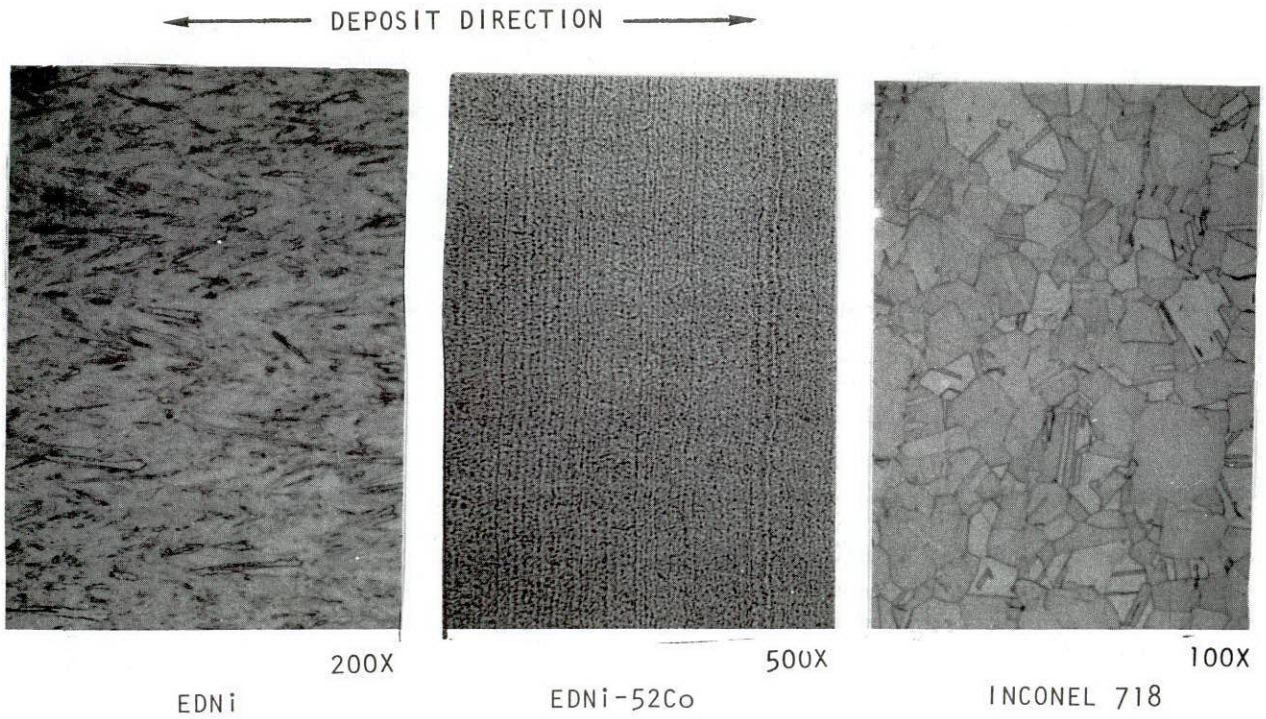


Fig. 2. Optical Microscopy of As-Deposited EDNi and EDNi-52Co and Solution-Treated and Aged Inconel 718

The as-deposited microstructure of EDNi-Co appears to be composed of finely spaced layers. The most likely explanation of these striations is that they represent composition gradients. Microprobe analysis, however, indicated only minor chemistry (approximately ± 1 wt% Co) variations across the deposit thickness. It is, however, possible that even these small compositional variations could produce a striated-appearing microstructure. Over 10,000X magnification would be needed to resolve the fine grain size (<0.1 μm) of EDNi-Co microstructure.

The microstructure of Inconel 718 consists of fairly large equiaxed grains with small intergranular carbides to inhibit elevated-temperature creep deformation, and age-hardening precipitates that require transmission microscopy to resolve. At ambient temperature, the strength achieved by the very fine EDNi-Co microstructure is equivalent to age-hardening strengthening of nickel.

Unfortunately, the strength of EDNi-Co decreases relatively rapidly with increasing temperature as shown in Fig. 3. As will be discussed below, grain boundary sliding or creep becomes important at about 482°C (900°F). The rapidly decreasing strength of EDNi-Co with increasing temperature is the result of decreasing effectiveness of the grain boundaries for inhibiting slip. One way to improve the elevated temperature properties of EDNi-Co would be the addition of a third element to form a dispersion of stronger second-phase grains in the microstructure.

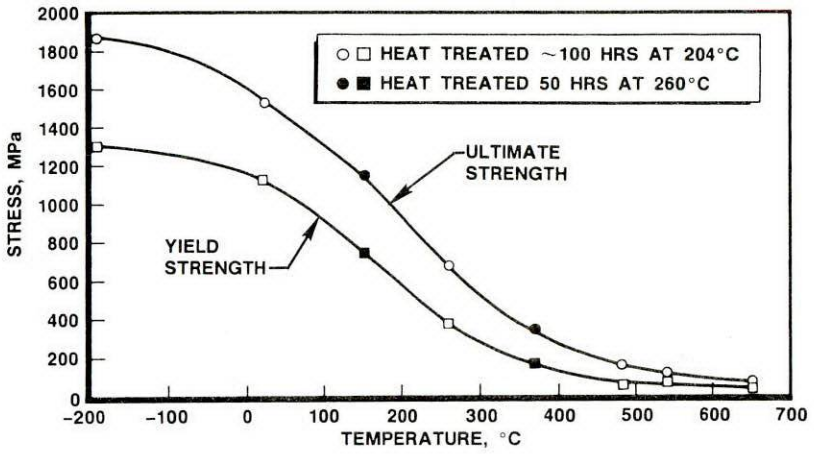


Fig. 3. Average Tensile Strength of EDNi-45/56Co

Table 5 contains results on the influence of heat treatment on the 260°C (500°F) tensile properties of EDNi-Co. Heat treating at temperatures above 260°C improved the 260°C yield strengths of cylindrical and plate specimens. This strengthening was certainly not expected in light of the reduced ambient temperature strength experienced by heat treating. The reason for this elevated temperature strengthening through heat treatment is not known but may be related to impurity migration to the grain boundaries during the heat treatments.

Table 5. Influence of Heat Treatment on the 260°C (500°F) Tensile Properties on EDNi-Co

SPECIMEN TYPE	COMPOSITION % Co	HEAT TREATMENT			STRENGTH, MPa (ksi)		DUCTILITY	
		°C	(°F)	HOURS	YIELD	UTS	% EL	% RA
CYLINDRICAL	54	204	(400)	108	372 (54)	676 (98)	28	55
		371	(700)	4	434 (63)	710 (103)	28	67
		427	(800)	4	448 (65)	662 (96)	32	68
PLATE	40	204	(400)	10	393 (57)	669 (97)	40	60
		399	(750)	4	483 (70)	621 (90)	51	67

The elevated-temperature ductility of EDNi-45/56Co is shown in Fig. 4. A ductility peak occurred at 482°C (900°F) where EDNi-Co exhibits superplastic behavior.

Superplasticity results from grain boundary sliding and requires a very fine grain size or a large grain boundary area. Figure 5 shows a specimen tensile tested at 482°C and having 280% elongation over the central area of the 3.175-cm (1-1/4-in.) long reduced section. Optimization of the temperature and deformation rate has not been performed, and significantly greater elongation may be obtainable on this electroformed alloy. The specimen shown in Fig. 5 was pulled under standard ASTM loading conditions (0.05 cm/cm min from yield to fracture) at 482°C, and did not fail because of travel runout of the tensile testing machine. The specimen was then cooled to room temperature, reheated to 482°C, and pulled to failure again under standard ASTM

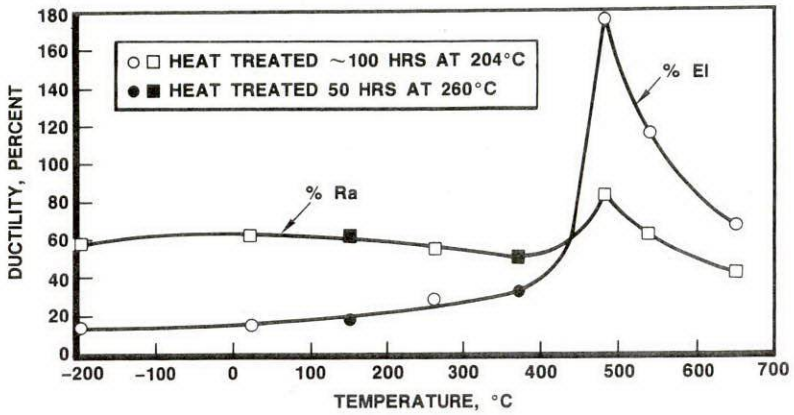


Fig. 4. Average Tensile Strength of EDNi-45/56Co

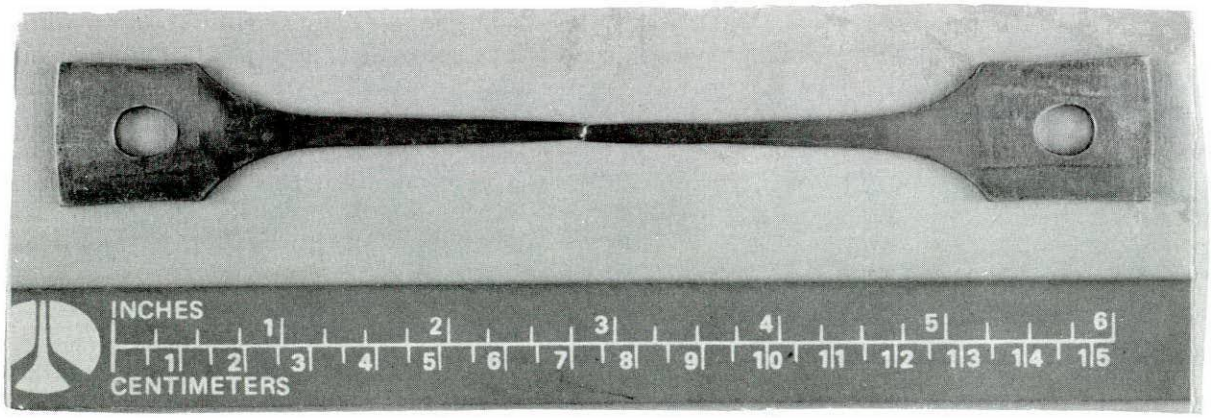


Fig. 5. Superplastic Deformation in EDNi-45Co
280% Elongation at 482°C (900°F)

loading conditions. A second specimen from the same panel was tested to failure during a single-pass and had 166% elongation.

Commercial production of parts by superplasticity is usually accomplished by expanding superplastic metal sheets into a die cavity at optimum temperature and deformation rate conditions using differential gas pressures. This is then often followed by diffusion bonding two superplastic deformed plates together to form three-dimensional shapes. The ability to produce electroformed superplastic material increases the versatility of the superplastic fabrication process. This is because superplastic forming of electrodeposited alloys would involve preshape formation by electrodeposition followed by final shaping by superplasticity into a preshaped mold. Electroforming the preshape would eliminate the need for a final diffusion bonding processing operation. It can be visualized that internal channels or passages can be produced through electrodeposition leaving intentionally unbonded areas for final superplastic enlargement of internal cavities.

CONCLUDING REMARKS

Excellent ambient and cryogenic tensile strengths and ductilities are produced through long-duration 204°C (400°F) heat treatments. Substantial strength reductions accompanied increased ductility with higher temperature heat treatments. The high strength of EDNi-40/60Co is the result of its extremely fine grain size. It is theorized that the 204°C heat treatment evolved absorbed hydrogen and reduced internal stresses to increase both strength and ductility. Higher temperature heat treatments produced sufficient reduction of the dislocation grain boundary network to reduce the slip-inhibiting effectiveness of the grain boundaries. Similarly, the tensile strength of EDNi-Co decreases rapidly with increasing temperature because of the reduced slip-inhibiting effectiveness of the grain boundaries.

Grain boundary deformation or creep dominates at 482°C (900°F), and superplastic deformation occurs for EDNi-40/60Co at this temperature. Combining preshape formation by electrodeposition and final shaping by superplastic deformation adds a new dimension for fabricating complex shapes and internal channeling.

ACKNOWLEDGMENT

Appreciation is extended to W. T. McFarlen who initiated and provided technical assistance during the program and to Cecil Rhodes of the Rockwell International Science Center for performing the transmission electron microscopy and for his assistance in preparing this manuscript. Acknowledgment is also extended to Dr. R. P. Jewett for his review of the manuscript.

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F-4

General Interest Session F

Plating on Polyacetal

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Plating on Polyacetal

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1. Abstract

In Japan, ABS resin (acrylonitrile-butadiene-styrene resin) comprises approximately 85% of the total consumption of basis materials for plated plastics. The remainder are engineering plastics such as polyacetal, nylon, noryl (modified PPO) and PBT (polybutylene terephthalate).

Unlike with ABS resin, the plating of polyacetal (a crystalline polymer) does not require chromic acid and is thus free from environmental pollution problems such as necessitate waste water treatment. Moreover, it is both excellent in adhesion and highly reliable. For these reasons, polyacetal is used as a plated material in a wide variety of fields.

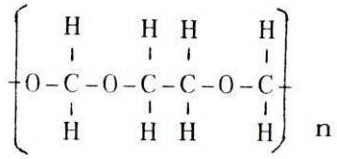
2. Introduction

Polyacetal, a material excellent in chemical and physical properties, such as antifatigue quality and anticreep quality, is widely used as a substitute for metals.

Although it had long been studied, the plating of polyacetal was difficult to industrialize owing to poor adhesion. However, a new method of plating using slightly modified polyacetal has recently been developed, making such industrialization possible.

The following two are representative polyacetal products available in Japan.

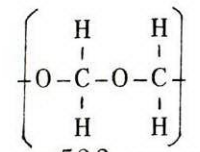
* Copolymer type
  1) Duracon (MP-01)
  2) (Polyplastics Co., Ltd.)



* Homopolymer type

1) Tenac PT300

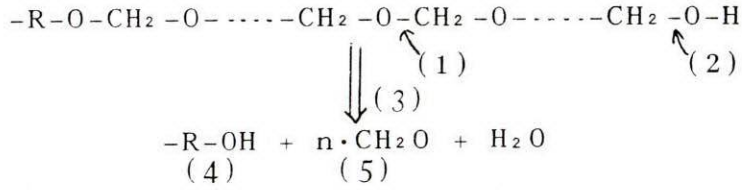
2) (Asahi Chemical Industries Co., Ltd.)



n=500 or average

In initiating the study on the plating of polyacetal, our idea was that etching be performed as a pretreatment to provide sufficient adhesion, that is, polyacetal is decomposed by treatment with both acid and alkali solutions. The anticipated reaction process is as follows :

Typical reaction mechanism



(1) Decomposed with acid and water

(2) Decomposed with acid and alkali

(3) Etching

(4) (Decomposed polymer)

(5) (Resulting formaldehyde)

3. Experimental Methods, Results and Discussion

Plating

Polyacetal, a polymer of formaldehyde molecules, is decomposed using both an acid solution and an alkali solution to form a rugged surface, resulting in high adhesion between base material and deposit. The plating process is shown in Table 1.

Annealing

Compared to other resins, polyacetal is more likely to generate internal stress when it is formed or molded. Such internal stress, if residual, will cause cracking during plating treatment, and the article will be damaged. Annealing is recommended as preventive of this phenomenon; temperature and time are important factors in this treatment.

Through various experiments, the following method proved the best :

As shown in Fig.1, the article to be plated is first annealed at approx. 150°C for 1 hour and then at 90~95°C for 1 hour. It is then left at room temperature to cool. It should be noted that rapid cooling from high temperature (150°C) to room temperature is undesirable.

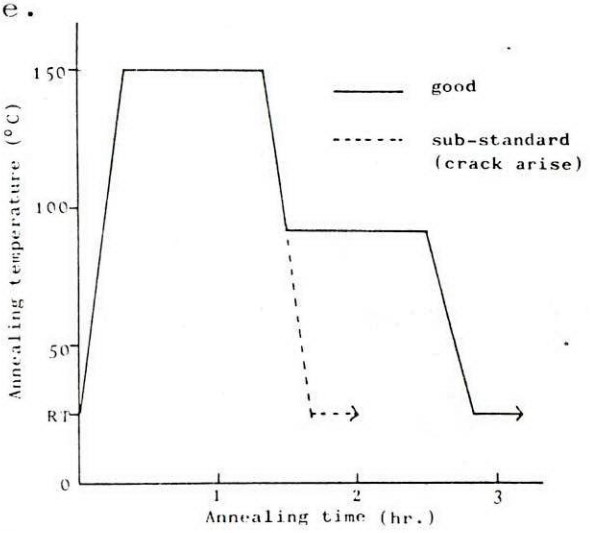


Fig.1 Annealing of the molded article

Relationships between etching bath types and adhesive strength

Using three types of baths (H_3PO_4, HCl-H_2SO_4, H_2SO_4-H_3PO_4), acid etching was performed, and then alkali treatment; adhesive strength data obtained are shown in Figs.2 through 4 respectively. Adhesive strengths obtained were 1.0 Kg/cm² with H_3PO_4 bath, 2 Kg/cm² with HCl-H_2SO_4 bath, and 3.8 Kg/cm² with H_2SO_4-H_3PO_4 bath.

Peeling test method

As in the previous plating process, articles to be used as samples, after electroless nickel-plating, were plated with acid copper to an approx. 50 μm thickness, dried at 80°C for 2 hours and then cooled.

Measurement instrument : Autograph SD-100-C, Shimazu Corp.
Sample size : 5 cm × 8 cm × 0.3 cm

Changes in resin surface conditions due to etching

Polyacetal forms a rugged surface when subjected to etching treatment. Fig.5 show scanning electron microscopic photos of treated resin surfaces.

Plating process of polyacetal

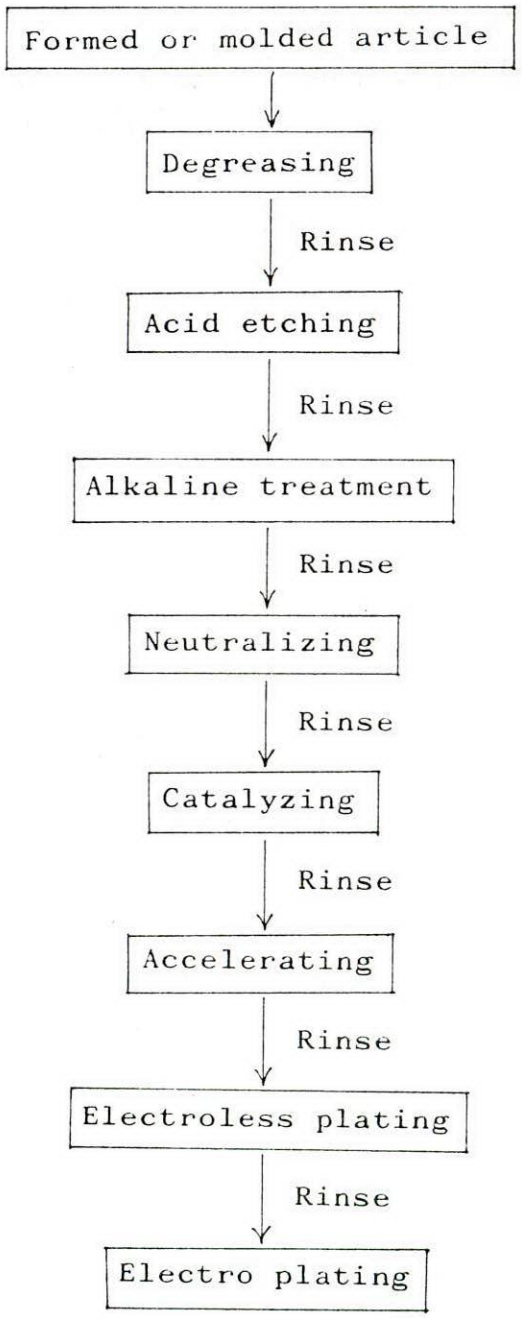


Table 1

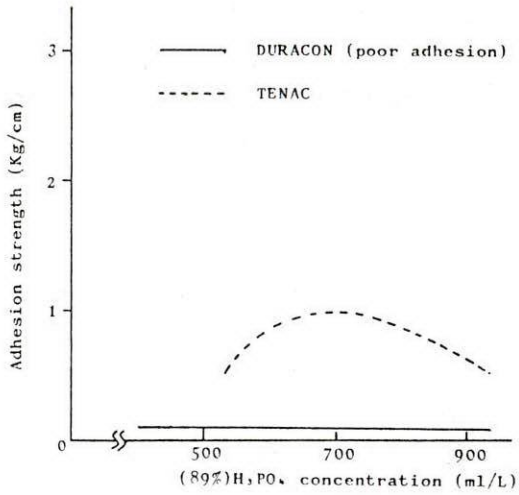


Fig.2 H_3PO_4 bath (60°C, 15 min.)

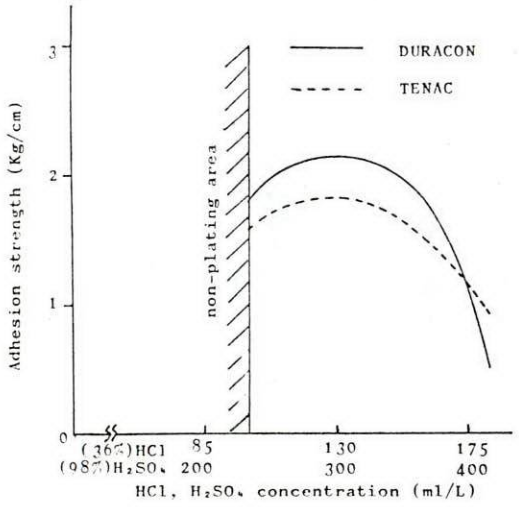


Fig.3 HCl-H_2SO_4 bath (25°C, 20 min.)

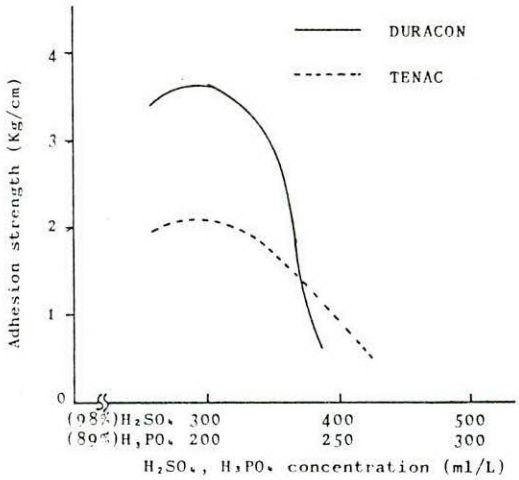
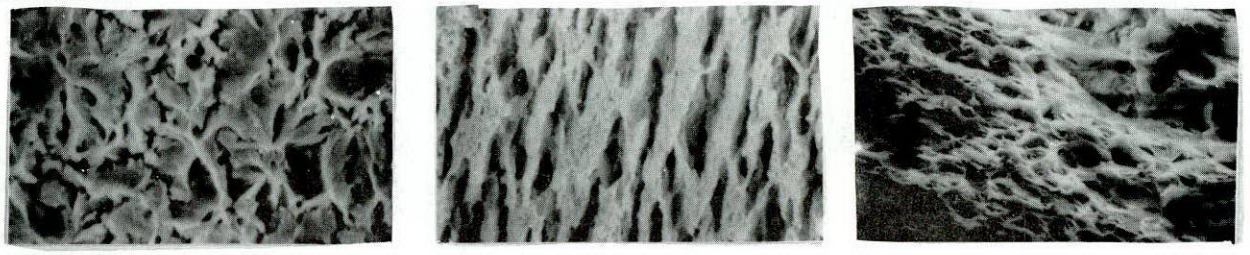


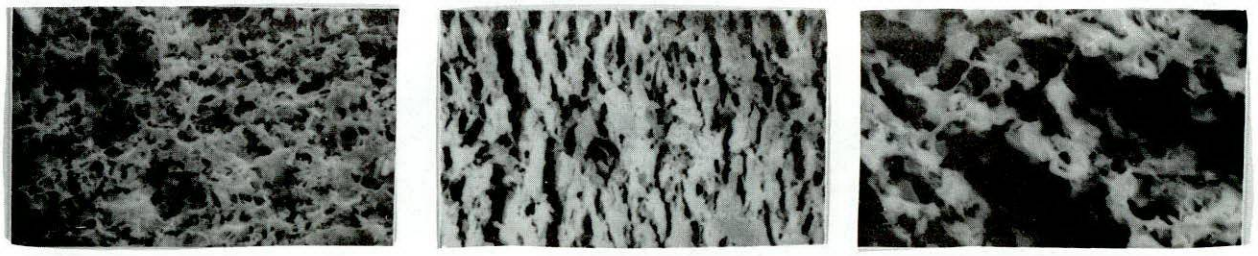
Fig.4 H_2SO_4-H_3PO_4 bath (40°C, 7 min.)

DURACON



A B C

TENAC



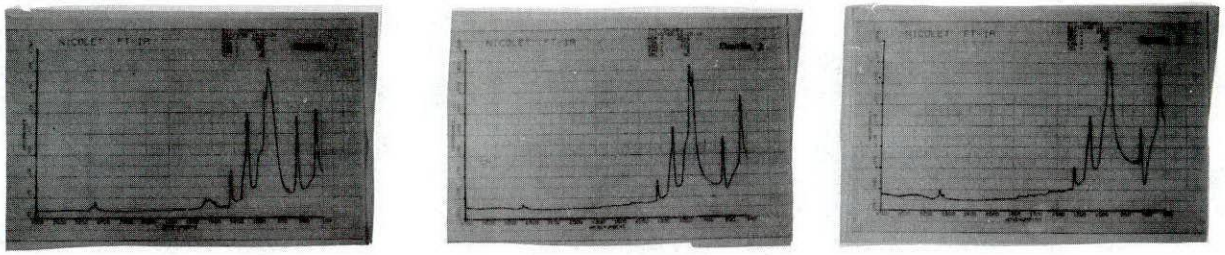
A B C

Fig.5 SEM photos of polyacetal surface after etching (× 3,000)

A: H_3PO_4 bath 89%H_3PO_4 700ml/L, 60°C, 15min.
B: HCl-H_2SO_4 bath 36%HCl 130ml/L + 98%H_2SO_4 300ml/L, 25°C, 20min.
C: H_2SO_4-H_3PO_4 bath 98%H_2SO_4 300ml/L + 89%H_3PO_4 200ml/L
40°C, 7min.

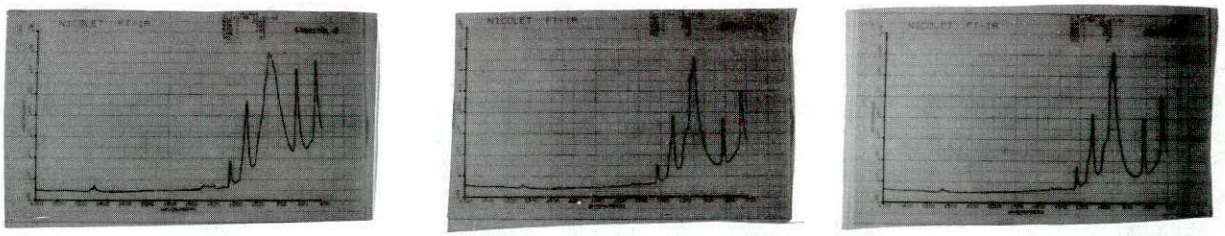
Based on the fact that hydrophilicity had been imparted, it was inferred that some chemical changes had also occurred. To prove this, surface conditions were examined by fourier transform infrared spectrophotometry as well; results are shown in Fig.6. It was expected that groups OH^-, CO^- or COO^- were produced on the resin surface through etching treatment. But as the results of mesurement, those could not be found and there were no difference between base material and various treated surface. Further, there we also no difference between copolymer and homopolymer.

DURACON



A B C

TENAC



A B C

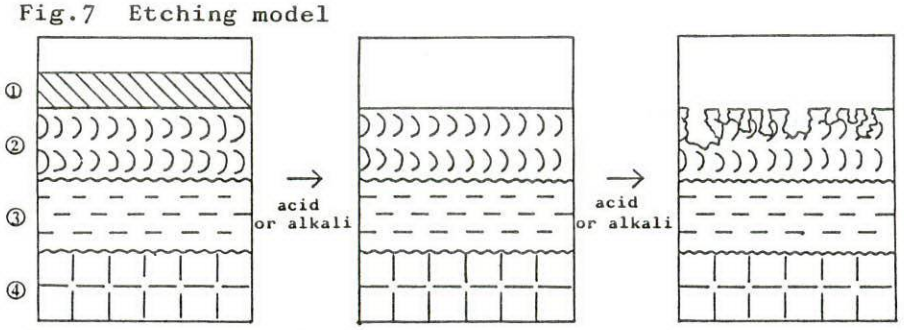
Fig.6 Fourier transform infrared spectrum of polyacetal surface

A: base material
B: surface after acid etching HCl 130ml/L + H_2SO_4 300ml/L 25°C, 20min.
C: surface after acid etching (B) → alkaline etching NaOH 100g/L, 60°C, 10min.

4. Conclusions

Plating adhesive strength on polyacetal resin is improved to 2.0~3.8 Kg/cm^2 by treating the base material resin with an etching bath liquid (H_3PO_4, HCl-H_2SO_4 or H_2SO_4-H_3PO_4). Etching models are shown in Fig.7.

Fig.7 Etching model



① amorphous layer ② semi-crystal layer ③ small spherulite layer
④ large spherulite layer

The most suitable etching condition of plating on polyacetal is shown as follows :

Copolymer

$HCl-H_2SO_4$ bath: HCl 130ml/L + H_2SO_4 300ml/L 25°C, 20min.

$H_2SO_4-H_3PO_4$ bath: H_2SO_4 300ml/L + H_3PO_4 200ml/L 50°C, 7min.

Homopolymer

$HCl-H_2SO_4$ bath: HCl 130ml/L + H_2SO_4 300ml/L 25°C, 15min.

$H_2SO_4-H_3PO_4$ bath: H_2SO_4 300ml/L + H_3PO_4 200ml/L 40°C, 7min.

Moreover, in case of H_3PO_4 only, good results could not be obtain.

Applications of plated polyacetal

Fig.8 show examples of plated polyacetal products available in Japan.

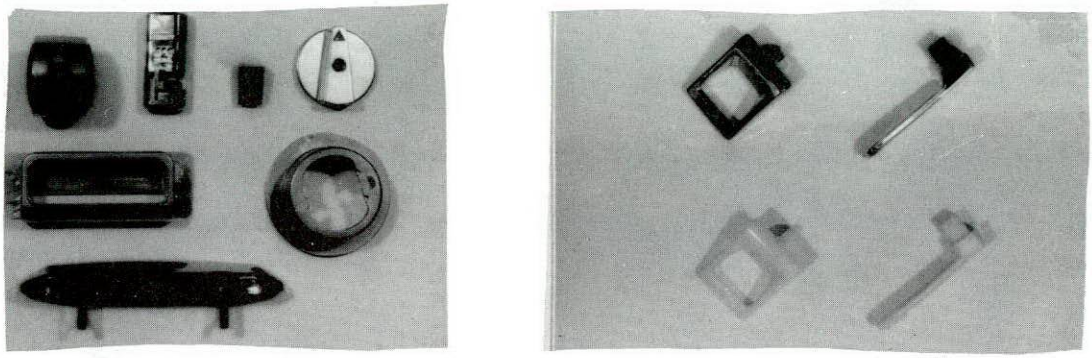


Fig.8 A selection of plated polyacetals

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F-5

General Interest Session F

Corrosion Protection Systems

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CORROSION PROTECTION SYSTEMS

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Introduction:

The importance of electroplated zinc on steel has seen significant increases worldwide over the last few years. Zinc is deposited from acid-, low- to high-cyanide- or non-cyanide alkaline zinc plating solutions, which are run at an average of 1 A/dm² in barrels and up to 120 A/dm² in high efficiency tube- or sheet plating operations. Zinc plated parts oxidize to white rust when exposed to the atmosphere and further to red rust once the anodic protection of the zinc layer has been broken through. To delay the formation of white-rust, immersion type chromate solutions are used, which produce light blue-, black-, yellow-, or olive-chromate coatings over the zinc surface. Corrosion protection of these coatings increases in the order given above. Light-blue and black chromates are used for decorative purposes whereas yellow- and olive-coatings are used on hidden automotive or machine parts or on parts to be subsequently painted or plastic coated. It has become apparent, however, that the combination of zinc and chromate is not enough to provide maximum corrosion protection. Pores, chromate cracks and high temperature influences are examples of problems which cannot be solved by chromate films alone. The following discussion deals with new protection processes, which are placed on top- or are used in combination with commercially available chromate processes.

Protection Processes

Based on the many different demands placed on zinc with respect to appearance and corrosion protection and in view of the many different types of plating equipment used, a number of protective processes are on the market. These protective processes, offered to the plating industry, can be devided into three groups, which we will call Type A, Type B and Type C. Since they differ widely in their usage, their coating characteristics, and their corrosion protection, we will deal with each one in detail and separately.

A typical zinc plating line is as follows: After racking or filling the plating barrels, parts are pre-treated, consisting of soak-, acid-, and electro-cleaning, with rinses between each one of the cleaners. Parts can be plated in either acid-, cyanide-, or non-cyanide zinc solutions. The final post-treatment cycle, consists of two rinses, a chromate and two more water rinses. Protective coatings of Types A, B, and C are applied as part of

this post treatment cycle.

Type A Coating

Usage:

Products of Type A are mainly applied on yellow chromated parts and are used in the last rinse tank, after chromating.

Make-up and Solution Parameters

Make-up :	0,5 - 5 % water solution
pH:	3.0 - 9.0
Temperature:	Room
Immersion Time:	30-60 sec
Analysis:	Possible
Running Costs:	Consumption is very small since the film produced is extremely thin. A new dip solution should be made up, whenever the drag-in of chromate becomes too high.

Advantages:

1. Less rinse water is used by changing the water rinse, following chromating, from a running water rinse to a stationary one. The last rinse tank, containing Type A solution is only periodically changed.

2. An increase of corrosion resistance of chromated parts treated with a Type A product is observed compared to just a chromated one. It can be shown that the maximum increase is about 30 %.

3. The extemely thin coating strengthens adhesion of the yellow chromate film on a zinc surface in its wet state before drying and prevents post passivation or peeling off of the chromate film in prolonged rinses or during carry-over.

4. After drying, parts treated with Type A products have very hard surfaces which feel smooth to the touch.

Type B

Usage:

Type B is an organic coating, which is formed in a solution containing a combination of chromates and resins. The film so obtained consists of chromates combined with resin particles. Parts are plated in the typical sequence of a zinc plating operation, in which the chromating tank is substituted for a Type B coating tank. It is important to notice that water rinses,

following the coating process, will remove any excess coating solution thereby avoiding the collection of resin solution at the edges of the parts, which will show up as dried solids. Drying operation does not require higher temperatures than with regular chromates.

There are two main application for Type B processes:

1. In combination with normal hexa-valent chromating solutions. A picture of two parts, one yellow chromated and the other one treated in a Type B solution, both dried at 80° C, shows that the yellow chromated part is crisscrossed with thin cracks, whereas the part treated in B has no cracked surface. It is obvious that this fact alone will contribute to better corrosion-resistance.

2. The second application of Type B solution is in combination with tri-valent chromating solutions. For several years, chemical suppliers have been offering blue-chromating solutions based on tri-valent chrome, not containing any hexa-valent chrome. These tri-valent chromating solutions can be combined with Type B solutions.

Make-Up and Solution Parameters

Make-up:	3 - 10 % 3 % in combination with blue chromates, up to 10 % in combination with yellow or olive drab chromates.
PH:	About 0.2 units below the pH value recommended in the technical literature for the respective chromate used.
Temperature and Dip time:	As recommended in the technical literature for the respective chromate used.
Maintenance:	Maintenance of chromates as recommended in the technical literature.
Maintenance of Type B product:	Resin B is precipitated, its volume measured,compared with the recommended volume and replenished, accordingly.
Life:	Type B solution can be maintained indefinitly. Life of the combined solution is dependent on the life of the chromate used.

Costs: Maintenance costs are low since consumption consists of resin which is deposited or lost by drag out. This costs will be minimal as compared to the make-up costs of a new solution. It is, therefore, important to use a chromating solution which can be maintained for a long time. This is generally not true for blue chromating solutions.

Waste-Treatment: Waste-treatment causes no problem since the resins can be precipitated out, filtered, and the remaining chromating solution waste-treated.

Deposition Mechanism:

It seems that in a B Type coating, chromate particles and polymerized acrylic resin particles are laying side by side in a homogeneous mixture. While the chromate film is formed -this film is described by Bishop[1] as being a gel of polymeric hydrated chromium hydroxide- the fully polymerized acrylic resin particles, which are dispersed in the solution, will settle with the chromate gel and will so become part of the film structure. Continuous agitation to maintain a homogeneous chromate-acrylic resin mixture is important in order to obtain a homogeneous chromate resin film. Acrylic resins used are completely polymerized and will not require any extended time nor extensive heating for hardening.

Advantages:

Parts treated with Type B solutions have a number of advantages over chromated ones, they are:

1. We compared corrosion resistance of normally chromated production parts against those treated with Type A and Type B. (Salt spray tests were run according to DIN 50021 or ASTM B-117 specifications). Results shown, represent average corrosion values to be expected on production parts and not laboratory findings run at ideal conditions. Production parts run with Type B have about 100 - 150% better corrosion resistance than regular chromated parts. This is true for blue-, yellow-, or olive-drab plated parts.

2. Better corrosion resistance in combination with blue chromates, containing only tri-valent chrome. Manufacturers of these chromates claim at least 24 hours salt spray resistance, tested according to DIN 50021 or ASTM B-117. We checked three commercially available chromating solutions and found that we were only able to obtain approx. 6 hours salt spray to white corrosion. This is totally non-acceptable. If you combine the tri-valent chromating solutions with Type B products,

corrosion resistance of resulting chromate-resin films will increase dramatically. We compared commercially available tri-valent chromate solutions with equivalent combined Type B solutions.

3. Tests have proved that parts exposed to 150° C for one hour did not show any cracks nor a loss of corrosion resistance.

4. We took two parts, the top one yellow chromated, the bottom one treated in a yellow chromate-Type B solution. After using an erasor test on both, the lower part shows less damage to the surface.

5. Acrylic particles in the chromate film decrease surface roughness and make parts more slippery. This is already noticable to the touch.

Type C

Usage

Type C coating processes are the third and final process to be discussed. Type C processes have been on the market for several years. Parts are treated with Type C coatings in the last tank of a plating line. Ideally, this tank should be added to the line. If there is no room, the last rinse tank can be used for this purpose, in which case drag-in of chromates should be kept at a minimum. It is important that parts are allowed to drain for some time, before drying and unloading. Type C processes being offered are water-based solutions or dispersions of partially or fully polymerized acrylates, or acrylate/styrenes to which small amounts of other organic components and/or small amounts of chromates can be added.

Type C solutions can be used in immersion processes as for instance with rack parts. In this case racks are immersed into the treatment solution, whereby immersion time is not important. They can also be used as spray processes in which case racked parts are sprayed with Type C solution as the racks are lowered into and lifted out of the treatment tank. Excess solution is returned to a holding tank to be used, again. This process is the prefered one since it requires only relatively small amounts of Type-C solution and gets the best corrosion protection results. A third application is by sprinkling Type C solution over a plating barrel, or into a centrifuge filled with chromated parts. The excess Type C solution is collected, to be used again.

Make-Up and Solution Parameters

Make-Up: 7 - 40 % water based

PH: 8 - 10

Temperature:	Room
Immersion Time:	10 - 40 sec.
Maintenance:	a) Can be done by measuring the density of the solution and replenishing it, accordingly b) By measuring the solid content by participating the resin, this is the preferred method.
Life:	Type-C solutions can be used indefinitely, providing they are not of the type, which precipitate into a rubbery mass whenever the pH falls below 7.0.
Costs:	Running costs are negligible, since the life of the solutions is indefinite, as mentioned above. Costs are determined by solid content of the solution, viscosity of the solution and configeration of the parts to be treated, which determin the drag out losses to be expected. Consumption Figures of 5 - 15 g Type-C concentrate per m^2 work area have been reported.
Waste Treatment:	Processes, in which resins will precipitate as a rubbery mass, are difficult to waste-treat. Gummy precipitates cling to the tank walls, close up pipes and destroy ion-exchange resins. These processes require waste treatment systems of their own. Waste treatment of processes in which a resin will precipitate in a flocculent form is easy. pH is dropped below 5.0, resins are precipitated, are filtered off and the remaining solution is sent to the regular treatment tank. If some of the precipitated resins are drawn into an ion-exchanger, they can be flushed out without harming the ion-exchange resins.

Deposition Mechanism

Metzger & Schmitz[2] claim that resins used for Type C products should not be completely polymerized, that these resins will cross-link or condense if dried at elevated temperatures, that they will form homogeneous coatings resulting in increased corrosion resistance. They further claim that only the right

selection of temperature and resins will produce optimum corrosion resistance. Newly developed processes contradict these claims and show that completely polymerized resins mixed with other organics and possibly small amounts of chromate will produce coatings, dried at normal temperatures, resulting in the same corrosion protection as claimed by Metzger & Schmitz. Type C products, as described by Metzger & Schmitz, have different properties as compared to the ones using fully polymerized resins. Some of them are worth to be noted:

Type I (Not polymerized resins)	Type II (Polymerized resins)
Can only be used when applied in baskets	No problem with barrel plating when applied in a barrel, basket or centrifuge
Object temperature must be higher than 80° C for at least 2 Min.	Parts can be dried at any temperature recommended for chromates used.
at pH below 7.0, resin will precipitate as a rubbery mass which cannot be used, again.	at pH below 7.0 resin will precipitate in a flocculent form, which can be brought back by raising pH above 7.0.
In waste-treatment gummy precipitates will form, requiring separate treat= ment equipment.	During waste-treatment flocculent precipitates can easily be filtered off.

Advantages:

1. Increase of corrosion protection over 300 % compared to the equivalent chromate.

2. Good temperature tolerance. It can be shown that chromates protected with a Type C coating show little or no change when exposed to temperatures of 150 - 180 °C for one hour.

3. Improvement in colour over yellow chromated parts. Irridescence of a yellow chromate changes to a golden colour, as can be shown. This colour can be called decorative and can be used as such.

4. Added protection against light abrasion which can happen during transportation.

5. Ability to increase adhesion in subsequent lacquering or plastic coating.

Conclsuion:

Today, we have presented three different protective coating systems for zinc plated parts, which change and improve the corrosion resistance of chromated surfaces from 30 to over 300 %. These three coating systems allow a plater to chose that coating system which will guarantee him his required corrosion protection, using his existing zinc plating equipment. Corrosion tests, measured to white rust, are gaining more and more importance; this means that thin zinc coatings, using optimum post treatments, will be called for in the future. This paper has attempted to show that this is possible and has offered practical solutions.

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F-6

General Interest Session F

Restoration of Metal Work On the Philadelphia City Hall Tower

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Philadelphia, PA

RESTORATION OF METAL WORK ON THE PHILADELPHIA CITY HALL TOWER

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Philadelphia, PA

Restoration of the City Hall tower is taking place at an elevation of 337 to 484 ft. The tower is composed of cast-iron plates coated with copper that are attached to a steel framework. The plates will be removed and the loose coating removed prior to electroplating with copper and tin-zinc. Some plates will have to be re-cast. Work on the William Penn statue at 500 ft will also be undertaken.

PAPER NOT AVAILABLE

G-1

Research Session G

The Effect of Chloride and Cadmium Ions on the Relationship Between Structure and Electrochemical Properties of Electrodeposited Copper

AESF Research Project No. 62

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THE EFFECT OF CHLORIDE AND CADMIUM IONS ON THE RELATIONSHIP BETWEEN STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF ELECTRODEPOSITED COPPER

AESF RESEARCH PROJECT NO. 62

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The objective of AESF Project 62 has been to determine what relationships exist between the two groups of data which have resulted from the numerous investigations of electrodeposition. One group of data consists of electrochemical measurements of such parameters as the overpotential, the exchange current density and those resulting from the imposition of current transients. The other group involves the structure and properties of the deposits. In only a few investigations were data from both groups obtained. There are practical reasons for determining if the two groups are related. With the increasing use of plating in sophisticated applications, it has become necessary to monitor the processes more closely in order to maintain the stricter tolerances. The electrochemical parameters lend themselves more readily to being monitored during the plating process while the properties of the deposits are the ones which must be strictly maintained. Controlling the properties during plating therefore depends on knowing the relationships between the two groups of data.

Results of investigations conducted under Project 62 have been presented at two previous Annual Technical Conferences of this Society. In 1983 the presentation dealt with the relationships in additive free plating solutions of the microstructure to the overpotential and the differential double-layer capacitance (DDLC), which is an electrochemical parameter obtained when transients are imposed. The relationships in plating solutions containing an organic addition agent, o-phenanthroline were discussed last year. The effects of the addition to the plating solution of a metallic ion, cadmium and of a negative one, chloride are the principal topics of this communication.

EXPERIMENTAL PROCEDURE

As the experiments were already discussed in the previous presentations(1,2), they are described only briefly. Electropolished, single-crystal copper discs were plated in a solution containing 0.5M copper sulfate and 0.1M sulfuric acid at a current density of 0.2 mA/cm^2. Either a {111} or a {100} crystal plane was parallel to the substrate surface. The deposits had the same orientation as the substrates. Additions of 5×10^{-5}M cadmium sulfate and 6×10^{-3}M cupric chloride, respectively were made to acid-sulfate plating solutions. The effects of the addition of 1×10^{-4}M o-phenanthroline which were not previously reported are also discussed. The plating times were such that there would have been uniform thicknesses varying from 0.01 to 0.5 µm. The overpotential was monitored during deposition. The DDLC was determined from the rise in the magnitude of the overpotential with time at the start of deposition and when a transient was imposed immediately after the current was turned off after the various plating times. The surface structures of the deposits of different thicknesses were examined by transmission electron microscopy using replicas upon which latex spheres had been placed prior to shadowing so that the heights of pyramids, crevices and steps could be

measured.

RESULTS

The variation of the overpotential with deposit thickness is shown in Figure 1 for deposits plated on substrates which had a {100} crystal plane parallel to their surfaces. Previously reported data for deposits plated in the additive-free solution and one containing 1×10^{-5} M o-phenanthroline are included on Figure 1 and on subsequent figures for comparison purposes. It is seen that the magnitude of the overpotential increases slightly when there were additives present in the plating solution and then reaches a steady-state value. The corresponding variation when the substrate surface was parallel to {111} is shown in Figure 2. The magnitude of the overpotential tends to decrease with increasing deposit thickness except in the presence of chloride ions when it increased after a minimum.

The DDLC varied with deposit thickness on {100} planes as depicted in Figure 3. Except for deposition in the presence of chloride ions, the DDLC is seen to increase from different initial values to a maximum when the deposits are about 0.5 μm thick. When o-phenanthroline or cadmium ions were present in the plating solution, the DDLC is seen to decrease continually with increasing deposit thickness over the investigated range. When the plating solution contained chloride ions, the DDLC is seen to stay constant over the investigated thickness range. The results of DDLC determinations when the substrate surface was parallel to a {111} crystal plane are presented as Figure 4. A large difference in the effect of the additives on the variation of the DDLC with thickness is noted. The DDLC does not change with thickness in the presence of o-phenanthroline except when the deposits are very thin. In the plating solutions containing chloride or cadmium ions the DDLC rises sharply with increasing deposit thickness and then tends to level off.

The structures of the surfaces of the deposits when they were parallel to {100} changed with increasing thickness. The structures which developed when 10^{-5} M o-phenanthroline was present in the plating solution were described previously(2). Groove-shaped crevices parallel to <100> directions were observed to have formed at a thickness of about 0.05 μm. The thicknesses at which the structural changes were first observed electron microscopically are also indicated in Figure 3. It is noteworthy that while groove formation was the first structural change when o-phenanthroline was present in the plating solution, pyramids developed when there was no additive. Multi-atom-high layers then developed which tended to sweep over the surface of the deposits from the additive-free and the o-phenanthroline-containing solutions so that at a thickness of about 0.5 μm the pyramids or crevices were only visible at their edges. The effect of increasing the concentration of o-phenanthroline to 1×10^{-4} M on the structure was similar. Crevices developed again which are shown in Figure 5. With increasing deposit thickness, layers formed again and covered the crevices. The layers were thinner than those which had formed when the additive concentration was lower. The edges of the steps were found to lie along <100> directions. The effect on the structure of cadmium-ion additions to the plating solution when the substrate surface was parallel to a {100} plane was similar to that of

o-phenanthroline. Crevices were found to have formed which were overtaken by steps when the deposit thickness was about 0.5 μm.

The structures which developed when chloride ions were present in the plating solution and the substrate surface was parallel to a {100} plane resembled those from the additive-free electrolyte. Pyramids were observed to have formed at a deposit thickness of about 0.05 μm as was the case in the additive-free plating solution. However, in the presence of chloride ions, the pyramids became truncated as shown in Figure 6.

The surfaces of deposits parallel to a {111} crystal plane and plated in the presence of o-phenanthroline or cadmium remained smooth over the studied thickness range of 0.5 μm. This result is the same as was obtained in the additive-free plating solution. In the presence of chloride ions, pits developed at a thickness of about 0.05 μm as also indicated on Figure 4. Pitting was the only structural change observed in the investigated thickness range.

DISCUSSION

The relationship of the overpotential to the structure is based on two factors. As the real area of the deposit surface increases due to the development of pits, crevices or layers from an essentially smooth one, the current density decreases when the plating current is constant. As the magnitude of the potential tends to be proportional to the current density, it should also decrease. The second factor is that the overpotential on different crystal planes is not the same. For example, the magnitude of the overpotential is smaller on {110} than on {100}. The grooved crevices shown in Figure 5 which developed on {100} planes were probably bounded by {110} planes as they were found to lie along <100> directions. So the formation of the grooved crevices should also have resulted in a decrease in the overpotential. Thus the overpotential should have decreased with thickness. However, as seen in Figure 1, the overpotential increased slightly. Therefore, the effect of the additives rather than the structure was the predominant one. When the substrate surface was parallel to {111}, such was probably also the case as the overpotential decreased or increased even when no structural changes were resolved. Apparently, the overpotential is not an effective parameter for monitoring changes in the structure-dependent properties of deposits when additives are present in the plating solution.

The DDLC depends also on the value of the real surface area. It increases when pits, pyramids or grooves develop on an initially smooth surface. When the multi-atom-high layers spread over the surface, its area decreases and the DDLC should do the same. When foreign substances such as the additives used in this study are absorbed on the surfaces of deposits, their effective area decreases and so does the DDLC. Figure 3 shows maxima at the deposit thicknesses at which the grooved crevices formed on {100} planes in the presence of o-phenanthroline or cadmium and at which pyramids were observed in the additive-free plating solution. Adsorption of the additives can account for the continual decrease in the DDLC with thickness. The reason why the DDLC did not change significantly with deposit thickness in

the presence of chloride ions could be that their initial adsorption overshadowed all other effects. The transfer of charges to metal ions initially adsorbed on the cathode surface can also affect the value of the DDLC. This effect could account partly for the different initial values of the DDLC. The small variations of the DDLC with thickness when {111} substrate-surface planes were plated in the solution containing o-phenanthroline seen in Figure 4 corresponds to the lack of resolvable structural changes. The DDLC also did not change greatly after pits had formed in the presence of chloride ions on {111} planes. However, there was no structural change with deposit thickness in the additive-free solution or that containing cadmium while the DDLC increased markedly. The reason may again be adsorption. The existence of a relationship between the DDLC and the structure-dependent properties of electrodeposits appears to depend on being able to assess the effects of adsorption.

The cause of the grooved crevices and pits also appears to be due to preferential adsorption of foreign substances impeding deposition as was previously(2) discussed. An explanation for the formation of pyramids was given by Mirzamaani(3) in his doctoral thesis which was based on Project 62. It was proposed that partially reduced metal ions arrive on the deposit surface at a faster rate than they are able to diffuse to sites where they can be incorporated into the existing structure. These so-called adions would then accumulate and join together to nucleate the pyramids.

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ACKNOWLEDGMENTS

The advice of the members of the Project 62 Committee consisting of Messrs. A. Damjanovic, G. Fisher, D. Hardesty, F. Koch, D. Marx, S. Nakahara, Y. Okinaka, T. Palumbo and M. Paunovic is gratefully acknowledged. We are also grateful for the support of the AESF sustaining membership, Research Board and Board of Directors.

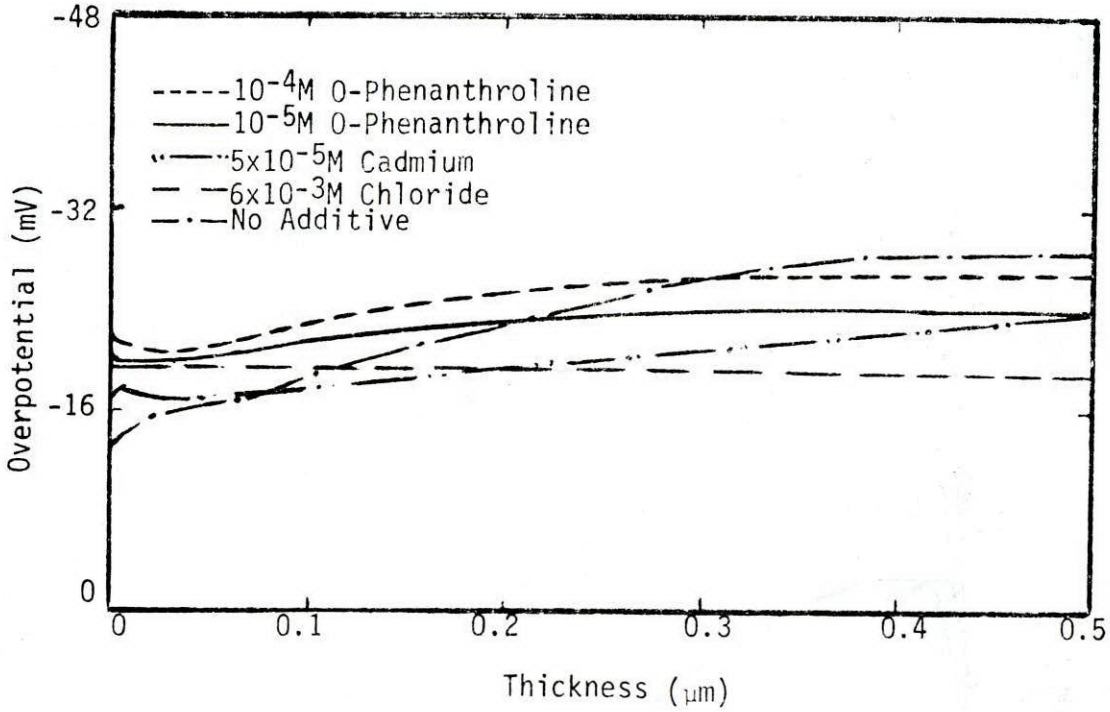

Figure 1 Variation of Overpotential with Deposit Thickness for Deposition on {100} Substrate Planes.

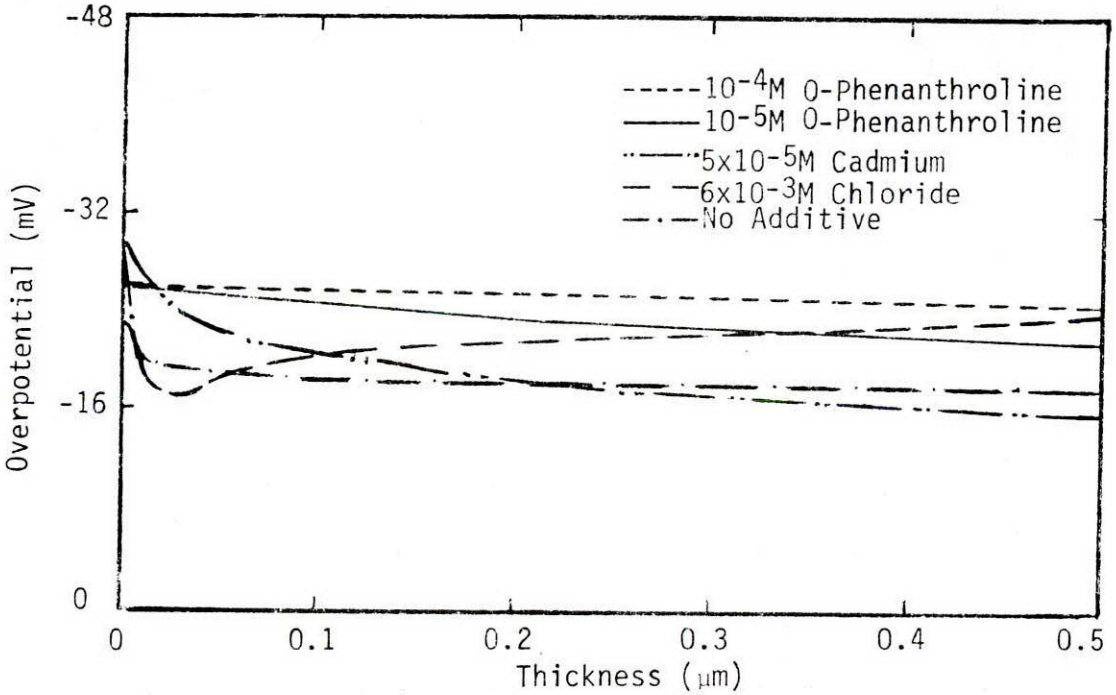

Figure 2 Variation of Overpotential with Deposit Thickness For Deposition on {111} Substrate Planes.

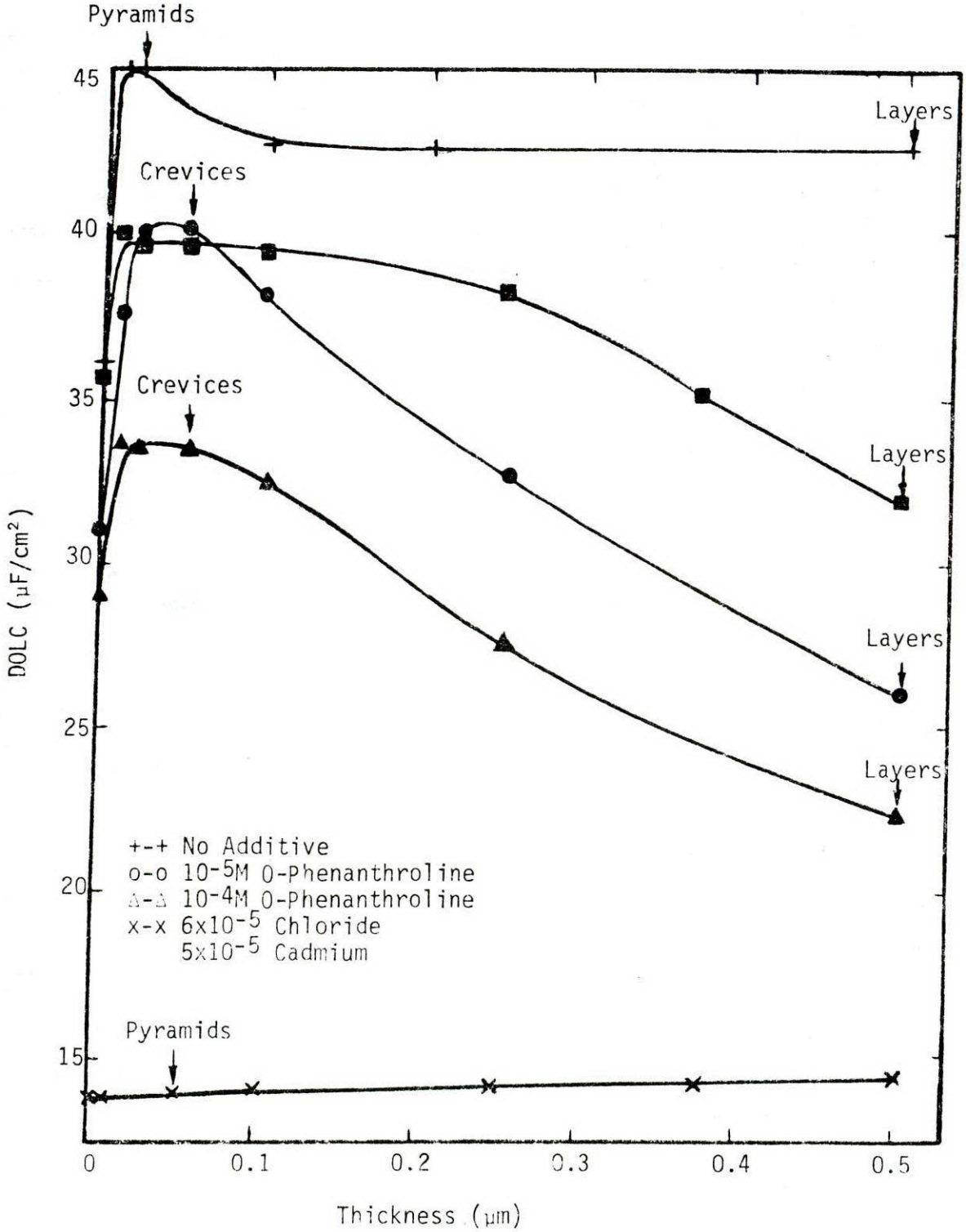

Figure 3 Variation of Differential Double-Layer Capacitance with Deposit Thickness on {100} Substrate Plane.

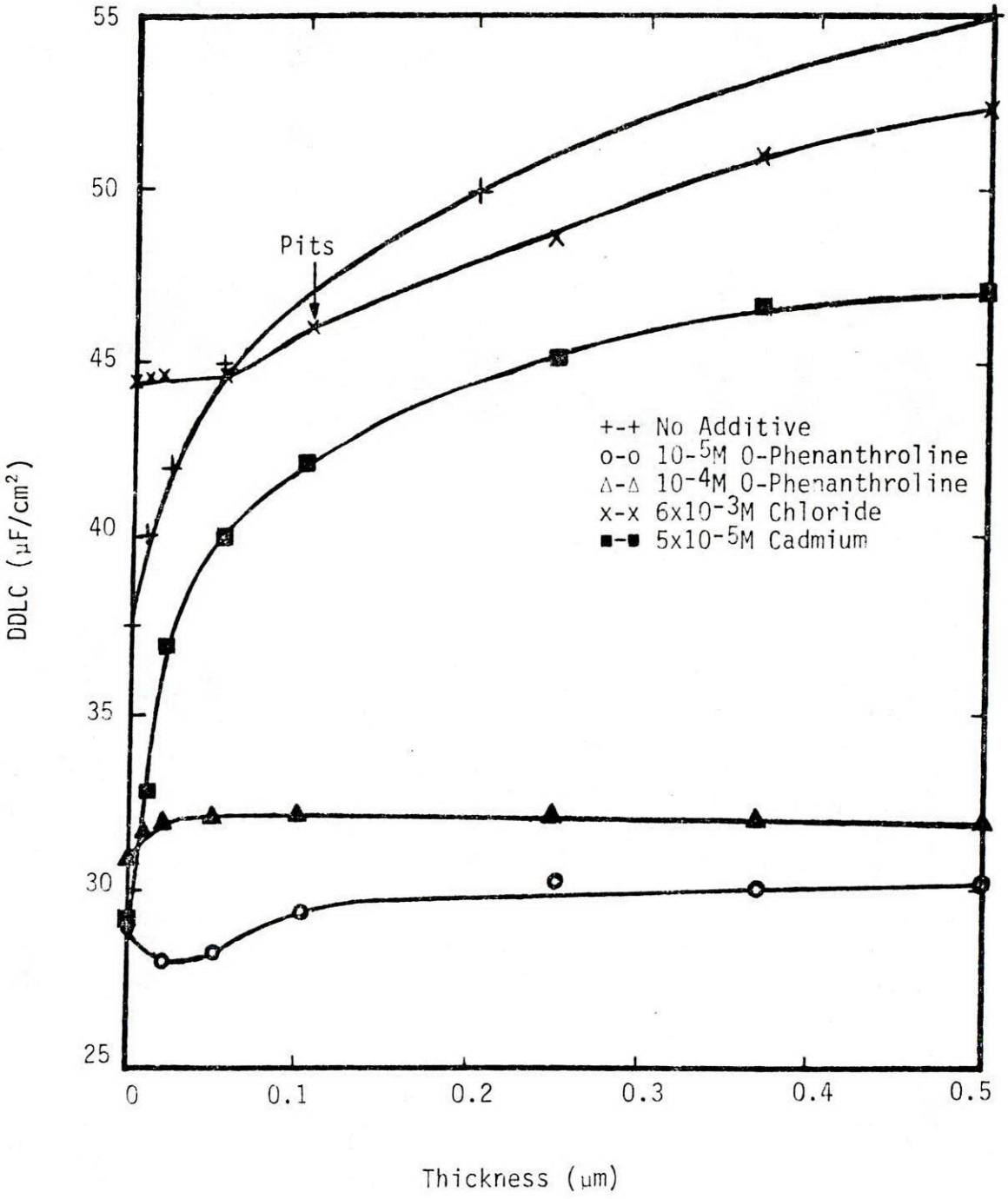

Figure 4. Variation of Differential Double-Layer Capacitance with Deposit Thickness for Deposition on {111} Substrate Plane.

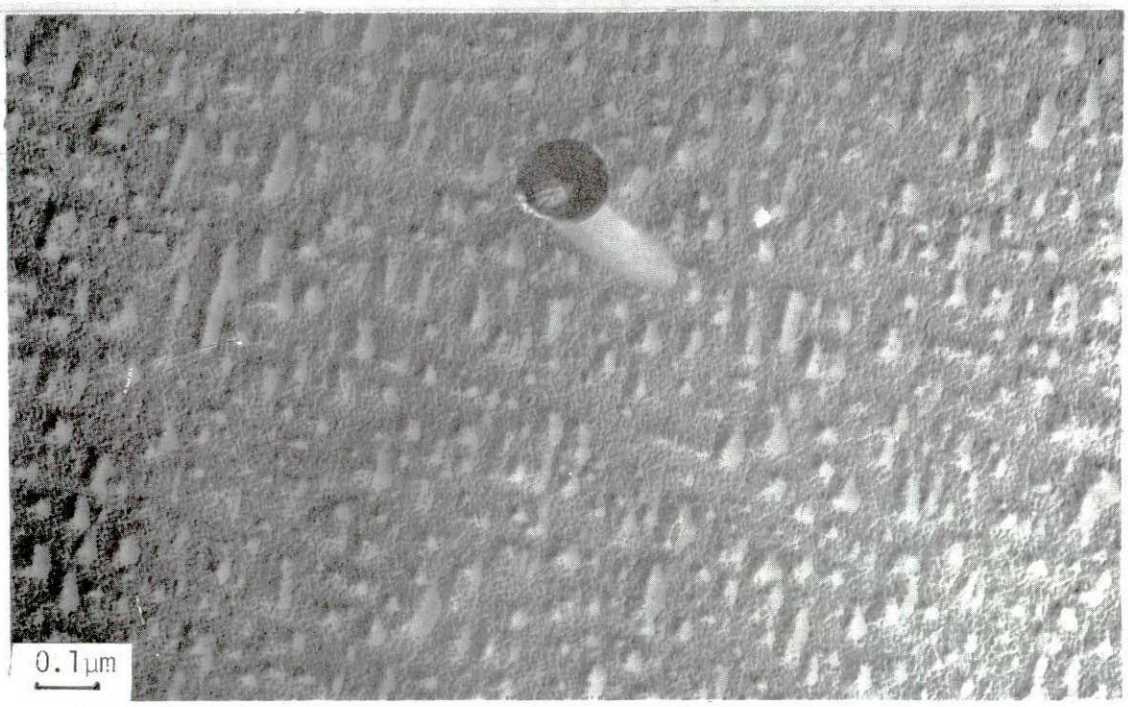

Figure 5: Electron Micrograph of Replica of Copper Deposit Plated on {100} Plane to a Thickness of 0.05 μm in a Solution Containing 10^{-4}M O-phenanthroline.



Figure 6: Electron Micrograph of Replica of Copper Deposit Plated on {100} Plane to a Thickness of 0.25 μm in a Solution Containing $6x10^{-3}$M Chloride ions.

G-2

Research Session G

Photoresponses of Zinc Surfaces: Model Studies as a Basis For an Accelerated Corrosion Test

AESF Research Project No. 65

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PHOTORESPONSES OF ZINC SURFACES: MODEL STUDIES AS A BASIS FOR AN ACCELERATED CORROSION TEST--AESF PROJECT 65

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Abstract

Chromate conversion coatings applied to zinc plated steel are widely used to inhibit environmental corrosion; the purpose of the present work is to investigate the effectiveness of these coatings. Photoexcitation techniques are now being developed, and applied to the above. Thin film gold/zinc/zinc oxide test samples have been fabricated, and the photoresponse of the zinc oxide surface alone is being measured by means of an apparatus designed specifically for this work. These preliminary measurements are necessary to provide a fundamental basis for future work to measure the photoresponse of coated zinc oxide samples. It is anticipated that these studies will clarify the nature of corrosion protection offered by the coatings at a molecular level, and may also lead to a non-destructive test of their effectiveness.

Introduction

ZnO is an n-type semiconductor. The corrosion resistant properties of a ZnO layer with and without an applied chromate coating are believed to be related to the semiconducting properties of the ZnO, or ZnO + coating interfacial systems. Photoexcitation techniques allow various charge transfer currents which flow in such systems to be measured. Measurements taken of ZnO with and without coatings may therefore give an indication of the role of the coatings in inhibiting charge flow, and hence corrosion. Initial photoresponse measurements on the solid state Au/Zn/ZnO samples have been performed, and it is hoped that similar measurements on coated samples may soon be carried out.

In order to develop the concepts applicable to the photoexcitation work it will be necessary to outline the theoretical aspects of charge transfer in photoelectrochemical cells (PEC's); these form the basis for interpretation of all photoexcitation data. Ultimately, the data obtained will be analyzed in terms of semiconductor and band theories to obtain a fundamental understanding of the ZnO + coating layer at a molecular level.

Theory

1. Charge transfer in PEC's.

In a PEC a semiconductor is brought into contact with an electrolyte solution. Equilibration of the Fermi level, E_f, of the former, and the redox potential, E_{ro}, of the latter induces a bias across the semiconductor (1,2,3); this causes band bending and also gives rise to a strong field ($\sim 10^6$ Vm^{-1}) in the depletion region.

If the semiconductor surface is irradiated with light whose energy, $h\nu$, exceeds the band gap, E_g, electron-hole pairs may be generated (h is Plancks constant, and ν is the frequency of the radiation). These charge carriers then migrate under the influence of the electric field. Several possible mechanisms exist for charge flow across the semiconductor/electrolyte interface, including electromigration, tunnelling, and photoemission (4). Of these mechanisms electromigration has been shown to be predominant.

Having crossed the interface, subsequent reactions of electrons and holes lead to the oxidation and reduction of electrolyte species. In the present context such reactions may ultimately lead to corrosion at the interface. Application of an electrically conducting conversion coating to the semiconductor surface provides filled energy states up until E_f, thus offering a barrier for charge flow across the interface which leads to corrosion protection. Analysis of the corresponding photocurrent responses plotted as a function of irradiation wavelength (and hence energy) can identify the adsorbed species and electrolyte ions in the vicinity of the interface.

2. Charge transfer in the present Au/Zn/ZnO solid state system.

The theory for the solid state system differs slightly from that just described for a PEC. The band bending and electric field necessary for charge migration are now provided by applying a variable d.c. bias voltage, V_b, across the Au/Zn/ZnO structure as shown schematically in Fig. 1B. (ZnO is biased positively with respect to Au). The net effect of the bias is to raise the Fermi level, E_{f_2}, of the metallic contact on the ZnO side with respect to that of the Au contact, E_{f_1}, by an amount proportional to the bias, i.e., by eV_b, where e is the electronic charge. Fig. 1A shows the corresponding energy diagram. If a connection is made between the two contacts as shown, a photocurrent will flow in a manner similar to that just described for a PEC when the

oxide is irradiated with light of sufficient energy. In the present system electrons are collected at the Au contact, and injected back into the ZnO conduction band via the corresponding ZnO contact. (Most experimental arrangements employ a chopped light source, and therefore an alternating photocurrent is usually detected).

Finally, it should be mentioned that the ZnO layer must be sufficiently thick such that its resistance is great enough to maintain a suitable bias (up to a few volts) across the Au/Zn/ZnO structure. A lower bound for the oxide thickness is loosely set by the depletion region width which is typically on the order of a few μm.

Experimental

Photocurrent responses in PEC's are small - usually of the order of μA. Modulation and lock-in amplification techniques are therefore necessary for their detection. The apparatus developed for these measurements is described below. Additionally, novel thin film test samples are being used for the present work which are comprised of an (oxidized) zinc electrode vacuum evaporated onto an underlying gold contact electrode, previously evaporated onto an insulating substrate (a standard 3" x 1" glass microscope slide). These Au/Zn/ZnO samples were designed such that good electrical contacts could be made easily to the Zn and ZnO layers. Standard vacuum deposition techniques were employed for sample fabrication which are also outlined below. All evaporations were performed using a Varian VE 10 rotary and diffusion pumped vacuum system at a pressure of $\sim 10^{-5}$ Torr.

Sample Fabrication

(i) Gold Evaporation

A modified evaporation source was used which consisted of the dimple section of a tungsten boat placed in a tungsten filament basket. This source was charged with approximately 500-1000mg of 99.99% pure gold (supplied by Millers) which was then flash evaporated onto the glass slide by resistively heating the source. The gold contact electrodes then formed were of the order of 500-1000Å thick, and their geometries were defined by a shadow mask adjacent to the substrate, held at a distance of ~15cm from the source by means of a table. Stainless steel was used as the material for the masks and table to minimize outgassing. A schematic diagram of the evaporation system is shown in Fig. 2a.

Prior to all evaporations the glass slide, masks, and slide holder were cleaned rigorously by agitating with "micro solution" laboratory detergent in an ultrasonic bath. Additionally, the masks and holder were scrubbed with fine grade steel wool. After thoroughly rinsing in distilled water and drying in a vacuum oven the assembly was placed in the vacuum chamber. Further cleaning was achieved by exposure to a d.c. glow discharge of 500 V d.c. at 150 mA at a pressure of 100 mTorr for 25 min. Overall, this cleaning ensures that the substrate is relatively free from dust, grease, and other contaminants. This is essential for good adhesion of the evaporated films to the substrate.

(ii) Zinc Evaporation

The zinc electrodes were formed by evaporating zinc granules (supplied by Fisher Chemicals, 99.9% pure) using a resistively heated tungsten filament basket source. Approximately 1-2g zinc were used for each evaporation. Once again, electrode geometries were defined by shadow masking.

Diagrams showing the completed geometry for both gold and zinc electrodes, together with a schematic cross section of a sample are shown in Fig. 2b. Electrical contacts were made to the electrodes by means of lightly clamped copper flats as shown in the diagram.

It was mentioned in the theory section that the ZnO layer must have a large enough resistance to maintain a bias of up to a few volts. Therefore, it has been necessary to thicken the oxide, and the approach which has been successfully adopted for this purpose is thermal treatment in air. Junction resistances of freshly completed Au/Zn/ZnO samples (measured between the Au and ZnO contacts) prior to thermal treatment are typically on the order of a few ohms. After baking in a Lindberg "Heavi-Duty" furnace at a temperature of approximately 400°C for a period of several tens of hours (which varied from sample to sample) the junction resistance rose to several hundred ohms, and in some cases a few kohms. (The form of the resistance growth curve resembled that of the charging of a capacitor.) A final value of approximately a few hundred to a few kohms is necessary for the present situation (With a constant bias current of 1mA, and the above junction resistance, a bias of a few volts may be applied across the sample).

Thermally treating the sample will not be necessary if the sample is immersed in an appropriate electrolyte solution, i.e., with a PEC. "Automatic" biasing will be achieved due to the difference in potential between the Fermi level of

the the ZnO, and the redox potential of the electrolyte as discussed before.

2. Photoresponse Measurement System

A block diagram of the experimental arrangement is shown in Fig. 3. A variable d.c. bias with an approximately constant current of ~0.5mA is applied across the sample by means of a 9V transistor type battery and 20 kΩ potentiometer. The sample is then irradiated with pulsed UV light using a 100W Hg vapor lamp and a PAR 125 mechanical light chopper. Beam area adjustments can be made by means of a crudely variable slit. At present, the sample is exposed to the entire spectral output of the bulb (UV, visible, and IR). In future work it would be desirable to use glass optical filters to select particular wavelength bands. Data presented in this report are for the broad band photoresponse of the sample when irradiated by the unfiltered mercury lamp. Using the alternating voltage signal, V_{REF}, from the chopper as a reference, the modulated photovoltage, V_S, developed across the sample is detected by a PAR 5301 high stability lock-in amplifier (LIA). Essentially, the LIA rejects all signals which are not at the chopper frequency and/or are out of phase with it.

Two large (2 μF) ceramic disc capacitors C_1 and C_2 are used to block the d.c. bias from the lock-in amplifier input stage. At 350 Hz (the frequency of the reference signal) the reactance of a 2 μF capacitor is approximately 200Ω, which is sufficiently small to avoid any significant loss of the a.c. photocurrent response.

Finally, the LIA output (a d.c. signal whose magnitude is proportional to the a.c. photoresponse) is plotted as a function of time using a Houston Instruments 200 chart recorder.

3. Photoresponse Measurements

Fig. 4 shows a schematic diagram of the sample irradiation arrangement using the bare 100 W mercury lamp. At present there are no collimation optics. Approximate values for the geometric parameters defined in the figure are given in the insert. The photoresponse was measured for various values of the bulb-sample distance, d, irradiated sample area, A, and applied bias, V_b, appearing across the sample. Other measurements were also carried out to check the effect of previous irradiation on the magnitudes of the photoresponse. In all, six sets of experiments were performed, namely:

(1) Fix d, and measure the photoresponse as a function of A.

(2) Fix A and measure the photoresponse as a function of d.
(3) Fix both A and d, and measure the photoresponse as a function of applied bias, V_b.
(4) Fix both A, and d, and measure the bias across the sample and battery voltage, V_c, as a function of irradiation exposure time.
(5) Measure the photoresponse when the sample is exposed to intermittent light pulses.
(6) Verify that the photoresponse is not affected by slight heating of the sample by the light source.

The purpose of these experiments was to investigate the behavior of fundamental experimental parameters, and also to estimate the optimum working values of these parameters for the present work.

It is clear from the geometry in Fig. 4 that if d is varied when the slit width, W, is fixed, then the irradiated sample area, A, will also very slightly. In practice, for a narrow W (a few mm), and a small range of d (typically from 2 to 9cm), the variation of A was negligible. Collimation optics would be desirable since a constant photon flux at the sample surface could then be achieved. In the data presented later, when a "fixed A" is quoted, this refers to the area measured when d was the minimum, i.e. the sample was as close as possible to the slit (~2 cm in all cases).

Results and Discussion

Fig. 5 shows a typical set of raw photoresponse data plotted as a function of time. These are presented to give some indication of the noise levels that can be expected, and also the general form of the plots. All data were taken with chopped light of frequency 340 Hz ± 10 Hz. These particular data show the effect of varying the irradiation area, A, for a fixed bulb-sample distance, d. For each measurement the bias, V_b, appearing across the sample was set to an arbitrary value less than that corresponding to the ZnO band gap of 3.2 V; in this case V_b was set to 1.6 V. Each curve was obtained after allowing the sample to equilibrate for 30-60 minutes with no photoexcitation.

As can be seen, when the sample is irradiated there is a sharp increase in photoresponse to a maximum value V(max) with a rise time of approximately 1 s. A decay and leveling off is then observed approaching a steady value V(min). When the beam is cut off (not shown here), a sharp decrease to zero is observed which will be discussed later. The difference between V(max) and V(min) values varies from sample to sample and is believed to be due to slight variations in

oxide composition. All the following data were taken from a typical sample. In order to present these data more clearly, the values of V(max) and V(min) are plotted as a function of the experimental variable - in this case A.

1. Sample Photoresponse as a Function of Irradiation Area, A, (Bulb-Sample Distance, d, Fixed)

Fig. 6 shows a set of V(max) and V(min) values plotted as a function of A, with d set at 2 cm. An approximately linear dependence is observed up until A~1 cm^2. (This is what one might expect since the photoresponse is dependent upon the absolute number of UV photons incident on the surface; assuming a uniform photon flux at the surface the number of photoexcitation events should increase linearly with A.) The linear region is followed by an apparent plateau for values of A > 1 cm^2. At present it is not possible to tell whether the plateau is a real effect (e.g. a saturation current is reached), or an artifact of the lighting geometry. As was mentioned earlier, the beam is not collimated, and the intensity distribution over the irradiated area, A, may not be uniform. Therefore the photon flux at the sample surface may not remain constant as A is varied.

It should be remembered that one of the purposes of the present series of experiments was to estimate the optimum working values for A, d, and V_b. It would appear that values of A up to 1 cm^2 are reasonable for the lighting geometry used.

2. Sample Photoresponse as a Function of Bulb-Sample Distance, d, (Irradiation Area, A, Fixed).

Fig. 7 shows the effect of varying d on the photoresponse, with A set to 1.5 cm^2. The arbitrary bias across the sample was set at 1.6 V for each measurement, and once again, an equilibration period of approximately 30-60 minutes was allowed between measurements.

A detailed analysis of these data is not feasible since it is recalled that A is not actually fixed, but increases slightly with d due to the non-collimated beam. Also, a non-uniform photon flux distribution may well exist at the sample surface. Nevertheless, it would appear from the figure that an inverse square law type dependence of photocurrent with d seems to exist.

Note that the value of the photoresponse, V(max), at d=2cm (and A = 1.5 cm^2) of ~6μV is in reasonable agreement with the corresponding value from Fig. 6. This gives some indication of the error bars for the measurements.

3. Sample Photoresponse as a Function of Applied Bias, V_b, (Irradiation Area, A, and Bulb-Sample Distance, d, Fixed).

In this set of experiments, A was set at 1.5cm^2 and d at 2 cm. V_b was then adjusted to the desired value and the raw photoresponse-time curves were recorded. A scan time of 300 s was used to estimate V(max) and V(min) from each curve. After an equilibration period of 5-10 minutes, V_b was readjusted to the next value and the measurements were repeated.

The V(max) values plotted as a function of V_b are shown in Figure 8. (V(min) plots are not shown but have the same form as Fig. 8.) It can be seen from the figure that the photoresponse increases with V_b up until approximately V_b = 2V where a plateau is reached. For $V_b \gtrsim 3V$ (n.b. the band gap energy for ZnO corresponds to 3.2V) a decrease in photoresponse is observed until V_b = 5V when measurements were stopped. Some hysteresis is then observed as V_b is decreased back down to zero. It is believed that the behavior observed in these experiments can be explained in terms of semiconductor and band theories, which will be the subject of future work.

4. Measurment of the D.C. Bias, V_b, Across the Sample and Battery Voltage, V_c, as a Function of Irradiation Exposure Time (Irradiation Area, A, and Bulb-Sample Distance, d, Fixed)

Fig. 9 shows V_b plotted as a function of exposure time, t, for four fixed values of d, namely 2,3,4, and 9cm. In all cases V_b was set initially to ~1.6V, and continuously monitored using a DVM. Time t=t(o) corresponds to the switching on of the beam; at t=1300s the beam was switched off.

All the curves show a decrease in V_b over a period of ~300s, followed by a plateau region until the beam is switched off where a recovery is observed. As one might expect, as d is increased (and consequently the irradiation intensity is decreased) the value of the bias plateau decreases. Carrier depletion phenomena are thought to be the reason for this.

The decay of the battery voltage, V_c, was monitored simultaneously using another DVM during the sample irradiation. A monotonic decay is observed which is independent of sample irradiation and is of the order of .05V over the course of an experimental run (~1300s). Clearly this decay will not significantly affect the bias appearing across the sample which decays by as much as 0.3V during this period.

5. Sample Photoresponse When Exposed to Long (10's of Seconds) Pulses

Fig. 10 shows some typical raw photoresponse data when the beam is switched on and off. The first 8 pulses correspond to the beam being switched on for 50 s, and then off for 50 s. It can be seen that the V(max) value gradually decreases. After a 200 s beam off period the V(max) value shows an increase, or "recovery" (see pulse 9). After another 200s beam off period pulse 10 shows another recovery. Pulses 11-15 are approximately 25 s on, 25 s off, and do not show as great a decrease in V(max) as pulses 1-8.

In summary, shorter pulses with longer duration between pulses do not reduce V(max) values significantly whereas long continuous pulses do. In future work intermittent pulses would be sufficient to detemine whether or not a sample exhibits any photoresponse.

6. Heating Effects

The 100 W mercury lamp was replaced with a 150 W tungsten lamp and repeat measurements were performed. No photoresponse was observed, indicating that any thermally induced transitions had an insignificant effect. (n.b. kT at room temperature is approximately 1/40 eV, where k is Boltzmann's constant, and T is the temperature in Kelvin. An exceptionally high T would be required for kT to be commensurate with the band gap energy.)

Conclusions

1. Photoresponses have been measured in solid state Au/Zn/ZnO samples.

2. Thickening of the zinc oxide layer is necessary in order to maintain a sufficiently large d.c. bias across the sample; thermal treatment is one method of achieving this.

3. The broad band photoresponse varies with bulb-sample distance, illumination intensity and area, as one might expect. The response also varies with the applied bias across the sample, and is diminished in magnitude if the sample has been irradiated previously.

4. The magnitudes of the photoresponses are on the order of μV. Electrical noise contributions must therefore be minimized.

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Acknowledgments

This study was supported by the AESF. Partial funding for the project was provided by the National Science Foundation (PYI award), CPE-8351849, and the University of Akron. The authors wish to acknowledge the guidance provided by the members of the project advisory panel: L. Bill Austin of National Steel, Dave Hardesty of General Motors, George Kline of OMI International, and Karl Korinek of Parker Chemical.

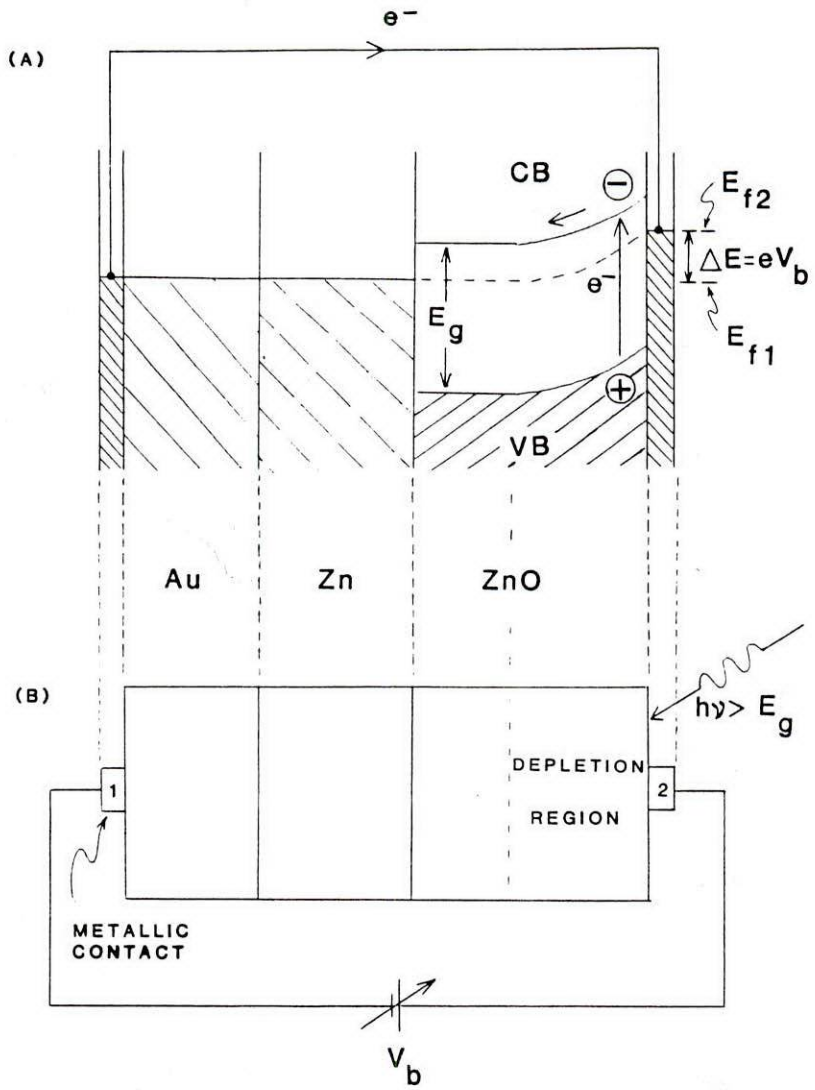

Fig. 1A. Energy band diagram for a Au/Zn/ZnO device for ZnO biased positively with respect to Au.

Fig. 1B. Schematic diagram of a Au/Zn/ZnO device with an applied d.c. bias.

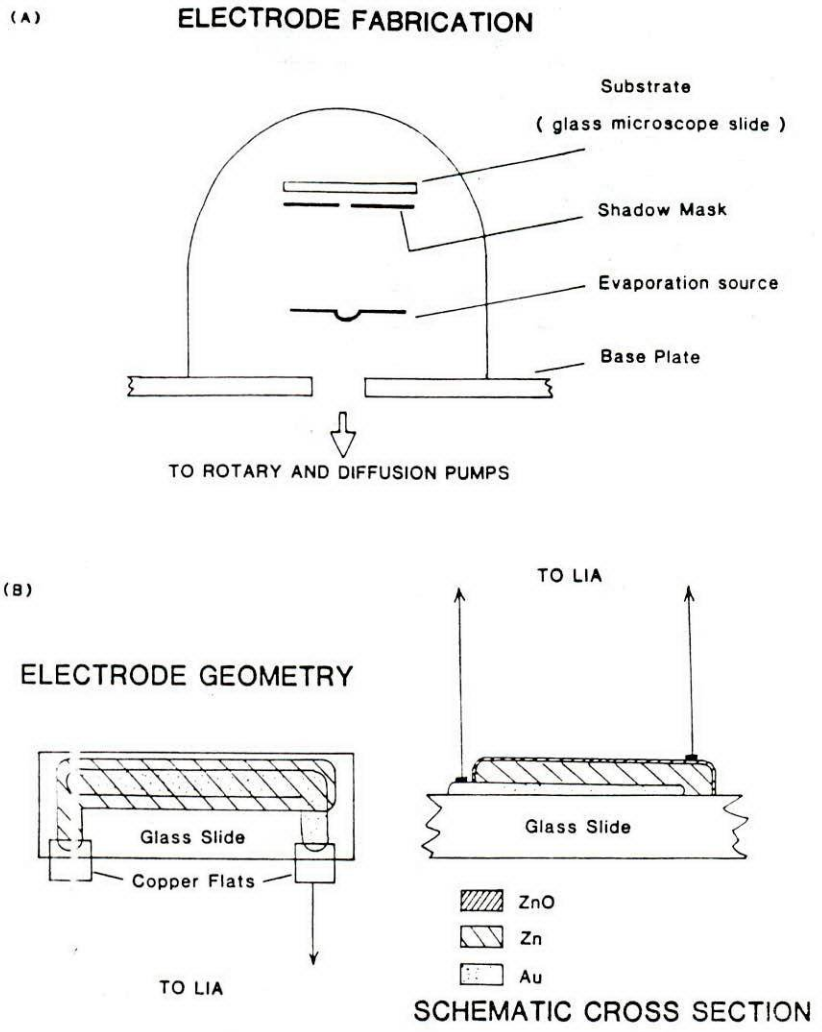

Fig. 2a. Schematic diagram of the vacuum evaporation system.

Fig 2b. Electrode geometry of the completed Au/Zn/ZnO device, and a schematic cross section through one showing where electrical contacts are made.

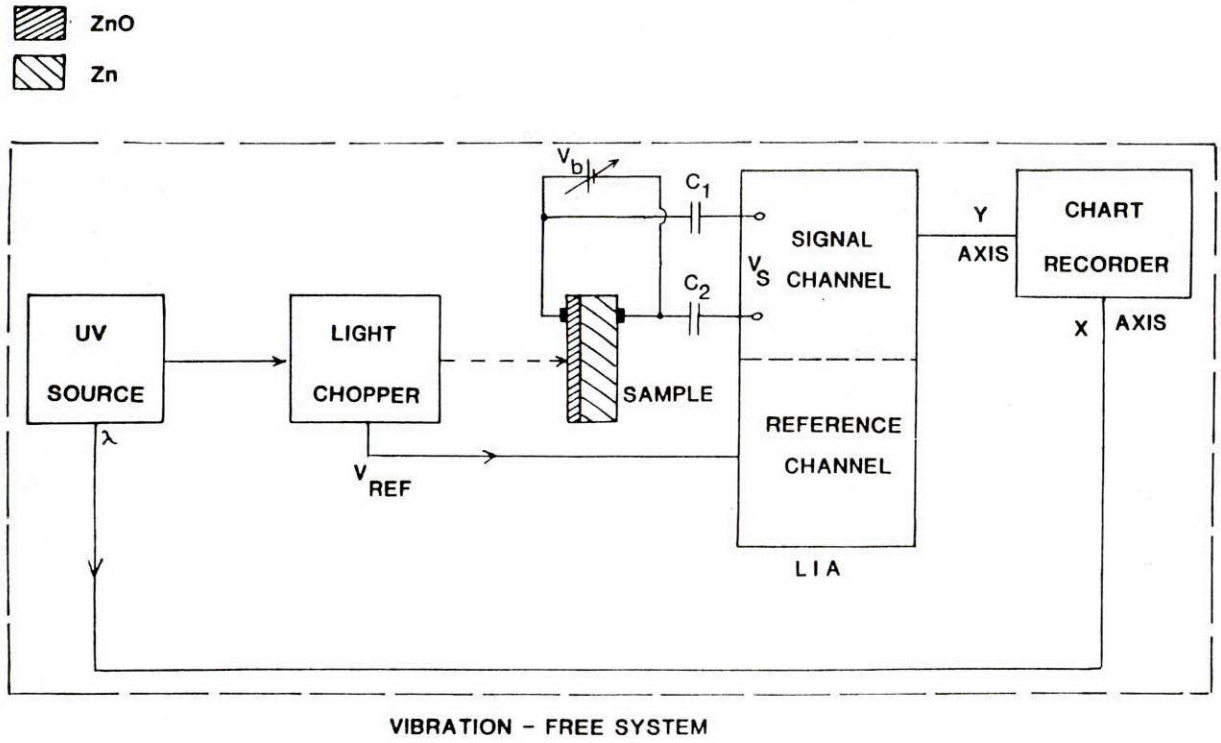

Fig. 3. Block diagram of the photoexcitation experimental arrangement.

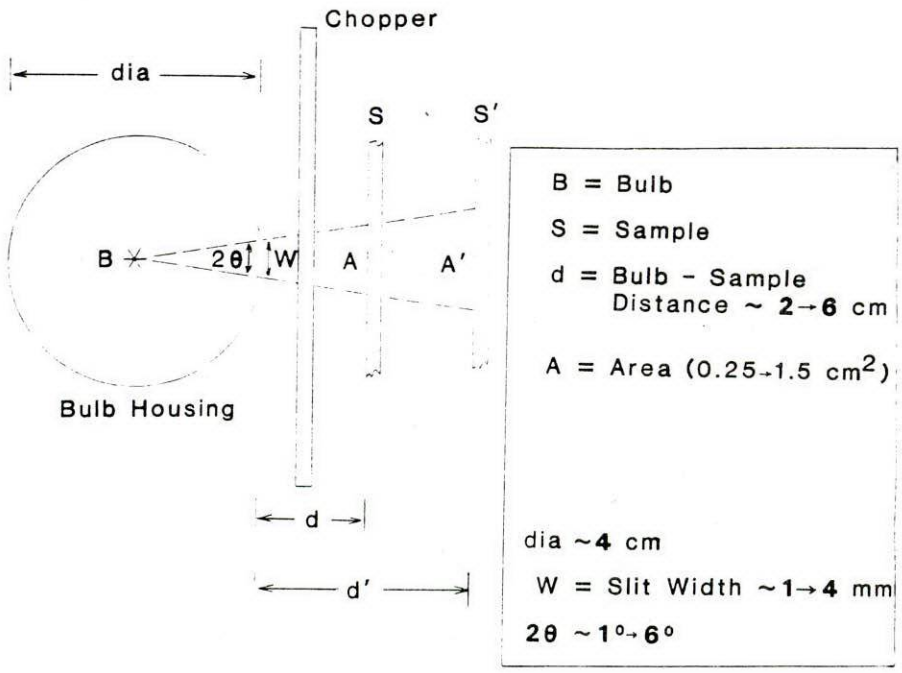

Fig. 4. Schematic diagram of the sample irradiation arrangement with the bare 100 W mercury lamp.

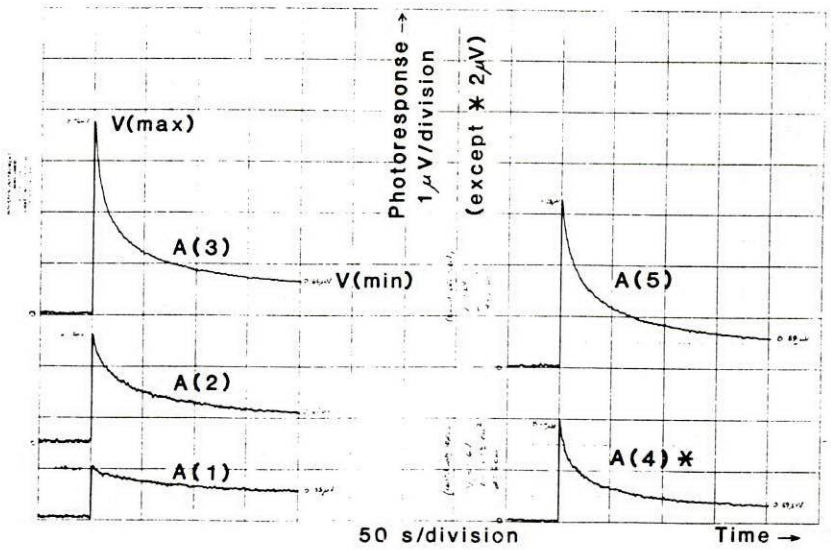

Fig. 5. Typical raw photoresponse-time curves. These particular data show the effect of varying the irradiation area, A, (in cm^2) for a fixed bulb-sample distance (d = 2 cm in this case). The values of A are: A(1) = 0.375, A (2) = 0.75, A(3) = 1.125, A(4) = 1.5, A(5) = 1.5 (repeat).

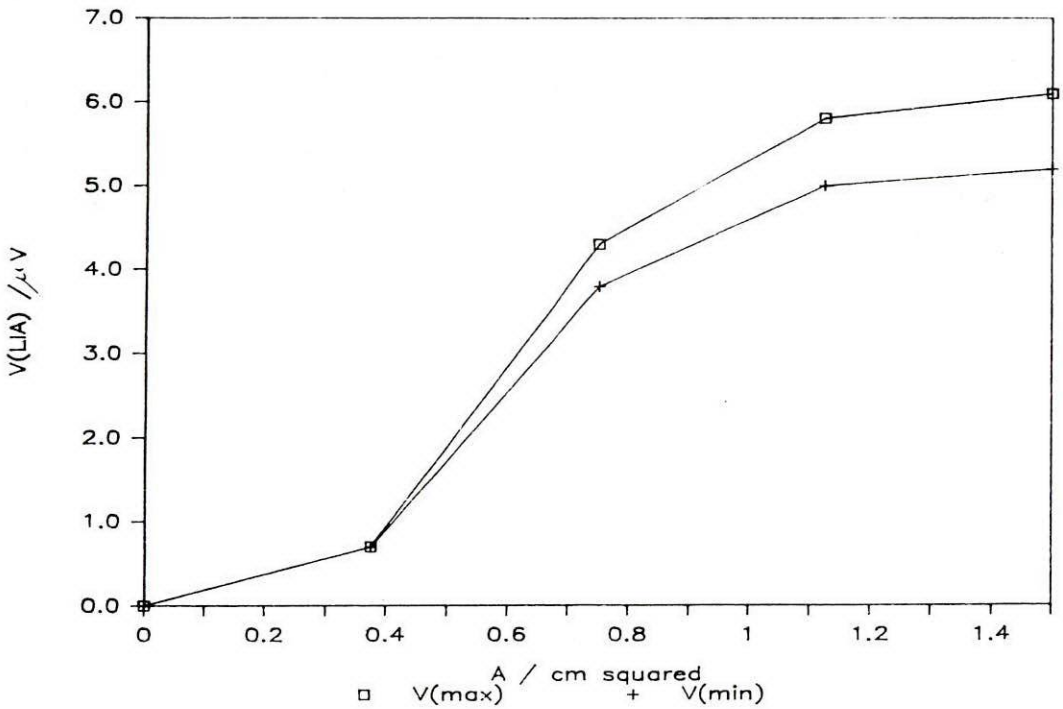

Fig. 6. Sample photoresponse as a function of irradiation area, A, with the bulb-sample distance, d, held fixed at 2 cm. V_b was set at 1.6 V for each measurement. (See text for explanatioin of terms).

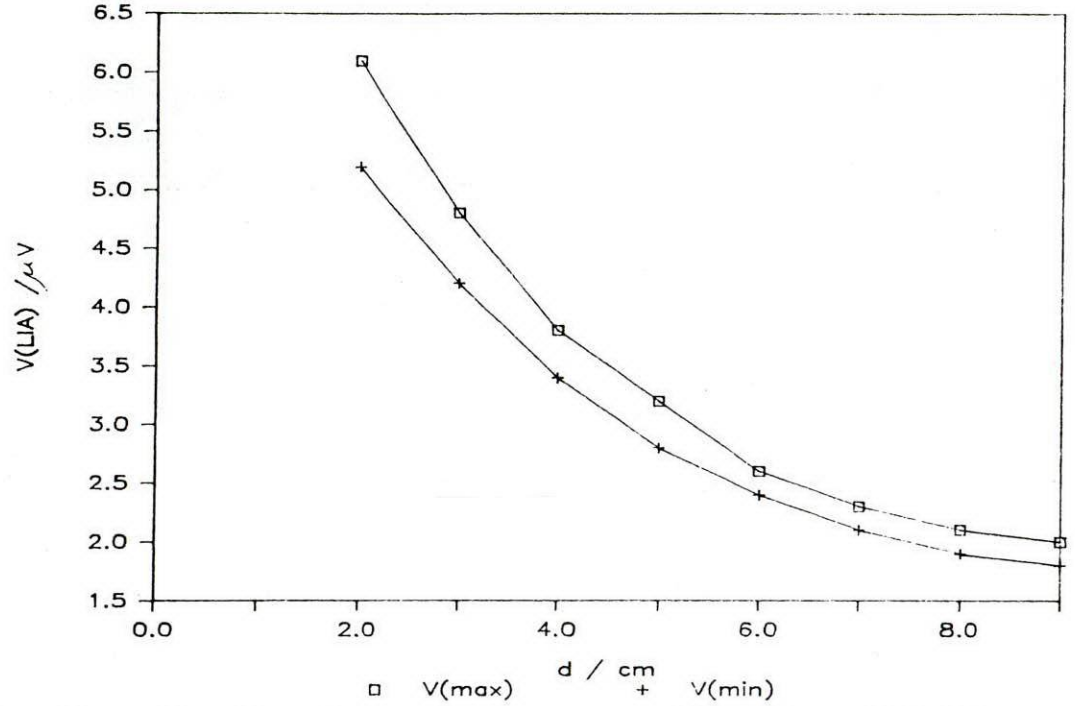

Fig. 7. Sample photoresponse as a function of bulb-sample distance, d, with the irradiation area, A, held fixed at 1.5 cm^2. V_b was set at 1.6 V for each measurement. (See text for explanation of terms).

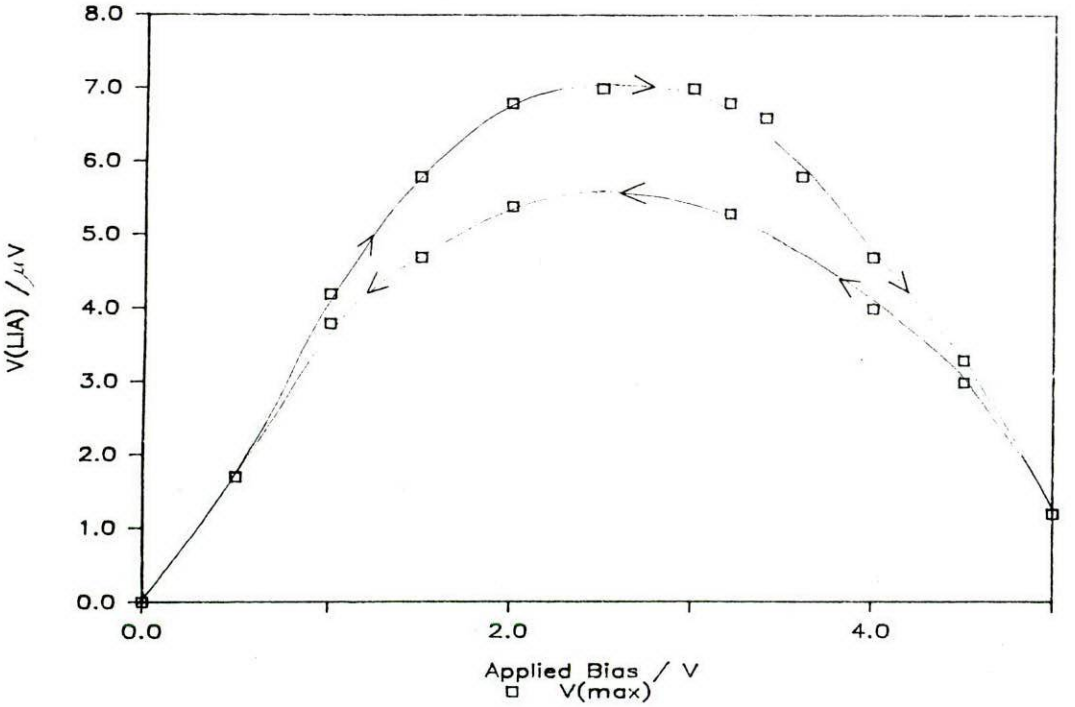

Fig. 8. Sample photoresponse V(max) as a function of applied bias, V_b, with irradiation area, A, and bulb-sample distance, d, held fixed at 1.5 cm^2, and 2 cm respectively. (See text for explanation of terms).

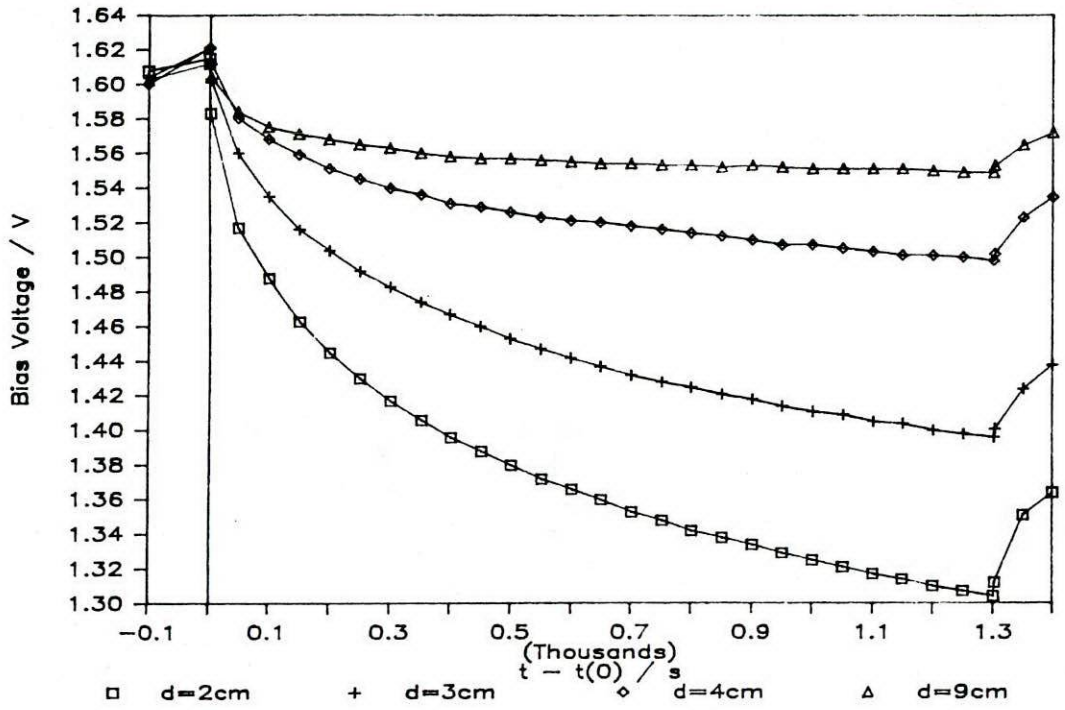

Fig. 9. D.C. bias decay across the sample as a function of irradiation exposure time. (See text for explanation of terms).

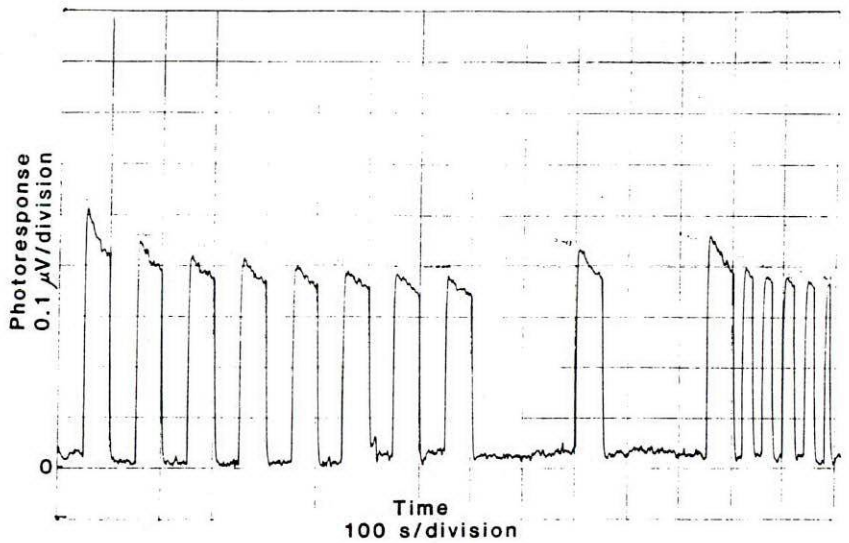

Fig. 10. Raw photoresponse data showing the effect of pulsing. Initially, V_b was set at 1.6 V, A at 1.5 cm^2, and d at 2 cm.

G-3

Research Session G

Adherence of Gas Bubbles To Inclined Surfaces

AESF Research Project No. 66

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ADHERENCE OF GAS BUBBLES TO INCLINED SURFACES

(AESF Project 66)

by Dana Allen
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Pittsburgh, PA

The adhesion of small gas bubbles to metal surfaces was investigated. The solid surfaces were inclined at various angles to the horizontal in order to determine the largest bubbles that would stick to the surface for a particular combination of metal solutions and bubble sizes. Contact angle hysteresis, the difference between advancing and receiving contact angles, was responsible for the adherence of the bubbles. Theory governing the adhesion of the bubbles was verified.

G-4

Research Session G

Low-Temperature Interdiffusion

AESF Research Project No. 67

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Dr. H. W. Pickering
Dr. William R. Bitler
College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, PA

LOW-TEMPERATURE INTERDIFFUSION
(AESF Project 67)

By J. Hyers
Dr. H. W. Pickering
Dr. William R. Bitler
College of Earth and
Mineral Sciences
The Pennsylvania State University
University Park, PA

Results of long-time (two year) and low-temperature (75 to 325° C) diffusion anneals will be reported for Watts nickel/copper, sulfamate nickel/copper, gold/copper, and cobalt/copper. Also, results obtained for the interdiffusion of phosphorus-and boron-containing electroless nickel with copper will be discussed. Because with the latter systems phase reactions take place simultaneously with the interdiffusion and because in all low-temperature diffusion couples other processes such as grain-boundary motion and/or recrystallization can occur along with the interdiffusion, great care must be exercised in interpreting the results of such studies. Some examples taken form the current investigations will be addressed.

G-5

Research Session G

Study of Selective Pulse Plating

AESF Research Project No. 68

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AES PROJECT 68: STUDY OF SELECTIVE PULSE PLATING

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Abstract

This project is concerned with a study on the use of pulse current (PC) to selectively deposit metal onto a localized area of an unmasked cathode. The localized deposition is achieved by directing a small anode toward a large cathode at the desired location, and by applying a large instantaneous pulse current. This paper presents the experimental results obtained with an acid copper sulfate bath. The use of PC on the range of 0.1-10 A/cm^2 greatly improved the localization of copper deposition at the cathode. A PC-control method was used to determine the average potential vs. average current behavior of the copper bath under the pulse plating conditions. It was found that the Wagner number evaluated from the slopes of the polariztion curves could be used as a guidline in the estimate of current distribution in pulse plating.

Introduction

Recently, selective plating (also called spot plating) has received increasing attention in the metal finishing industry because of the high cost of noble metals. This project is concerned with a study of using high pulse current (PC) to selectively deposit metals onto a localized area of an unmasked cathode.

The problem of current and metal distribution in pulse plating has not been well understood. There are contradicting reports in the literature. Sheshadri (1) examined the copper deposits obtained with PC, and concluded that PC reduced grain size and produced more leveled and smoother deposits. Enchev (2) used PC in the electrowinning of nonferrous alloys; he obtained higher quality deposit and higher current efficiency. Chin et. al. (3, 4) found that PC enhanced the nucleation rate and produced more uniform zinc deposits in acid zinc chloride and alkaline zincate solutions. With a pasted zinc battery electrode in a nickel-zinc cell, they (5) found that the superposition of a rectangular PC onto a direct current (DC) during the charging period caused a deeper penetration of current into the porous electrode matrix and more zinc deposits were obtained at the silver current collector grid on the back side of the zinc electrode. Pulse current has

been used in the color anodizing of aluminium(6, 7). The color of anodized aluminium appeared to be brighter with PC because of deeper penetration of metallic dye ions into the micropores of the oxide film on the aluminium surface. Ibl (8) discussed the problem of current distribution in pulse plating. Since the instantaneous current density during pulse plating is usually higher than that in the DC plating, he thought that the primary current distribution would prevail, and the current distribution would be less uniform than that in DC plating. This property appears to be useful in selective plating to localize the metal deposit on an unmasked cathode.

This paper reports some preliminary results of selective pulse plating using an acid copper sulfate bath. The copper deposition is localized by directing a small insoluble anode toward a large unmasked cathode, and by applying a high pulse current on the order of 0.1-10 A/cm^2. The degree of localization is expressed in terms of a ratio of the deposit area to the anode area, and the results are compared to those of DC plating under the similar bath conditions.

Experimental

Figure 1 shows the experimental setup used in this work. The experiments were carried out with a rectangular Plexiglas cell. A yellow brass plate, 5 cm long by 5 cm wide by 0.038 cm thick, was used as the cathode substrate. Suitable grooves were cut on the walls of the cell to support the cathode vertically and to facilitate easy insertion and removal of the cathode. An insoluble lead dioxide circular disk of 0.4cm in diameter flush-mounted on a Teflon sleeve served as the anode. Provisions were made to introduce the anode from one end of the cell and to secure it with its exposed plane parallel to that of the cathode. A saturated calomel electrode located in a Luggin capillary was used as the reference electrode. A thermometer inserted through the cell cover was used to measure the electrolyte temperature.

The standard acid copper sulfate bath consisting of 0.75M copper sulfate and 0.75M sulfuric acid was used for the experiment. The electrolyte was stored in a solution reservoir housed inside a constant temperature water bath. A plastic pump was used to transfer the electrolyte from the solution reservoir to the experimental cell. Purified nitrogen gas was bubbled through the electrolyte before and during the experiment to get rid of dissolved oxygen and to prevent the corrosion of brass cathode during the experiment.

For each run, the brass cathode was polished with 0.3 micron alumina polishing compound and cleaned with water and methanol. It was dried and weighed to 0.1 mg accuracy. The cathode was then electrolytically treated in dilute sulfuric acid before being transferred into the test cell. A constant rectangular PC of known pulse period (on-time plus off-time) and duty cycle (percent on-time in one period) was then applied to the cell from a PC-control circuit (9). A digital data acquisition system using a Commodore PET 4032 microcomputer and accessories was used to monitor the average plating current, average potential drop between the cathode and

reference electrode, average anode-cathode cell voltage, and root-mean-square of the periodic potential components. The wave-forms of applied PC and resulting cathode potential were examined on an oscilloscope. A digital coulometer was used to record the number of DC coulombs (based on the average current) passed during the experiment. After a desired number of coulombs was passed, the run was terminated. The cathode was then removed from the cell, washed, dried, and weighed to determine the weight of copper deposit. The deposit area was also noted. All the experiments were performed at a constant temperature of 25 $\pm$ 1 ^{o}C.

Results and Discussion

With the present cell geometry, the active area on the cathode where the deposition took place varied with experimental conditions. Thus, unless otherwise noted, the current density values reported in this paper will be all based on the anode area. In this study, the pulse plating was performed with rectangular current pulses over a range of PC density from 0.05 to 10 A/cm^2 at the pulse period (on-time plus off-time) of 0.001-1 s, and the duty cycle (percent on-time) of 1-100%. The average current density varied from 0.05 to 0.5 A/cm^2. Two anode-cathode gap spaces were examined; they were: h/d = 0.5 and 1.0, where d is the anode diameter, and h is the anode-cathode distance. The plating was terminated after 30 coulombs of charges passed the cell. Within the range of PC investigated, no appreciable changes were noted on the cathode current efficiency which was around 90-100% as calculated from the weight of copper deposits.

Figure 2 is a set of photographs of copper deposits obtained at h/d = 0.5, average plating current density of 0.1 A/cm^2, and pulse period of 10 ms. Figure 2b and 2c shows the copper deposits with the duty cycles of 10% and 1%, respectively. For comparison, the copper deposit obtained with DC plating at the same average current density and anode-cathode spacing is shown as Figure 2a. The black dot in each photograph represents the actual anode size. The area of copper desposit is seen to decrease drastically with decreasing duty cycle. This indicates that PC made the current distribution less uniform at the cathode. For a given average plating current, the deposit became more localized with increasing magnitude of current pulses and with decreasing duty cycles.

The extent of localization in selective plating can be expressed in term of a ratio of copper deposit area to anode area. The best selectivity (or localization) is achieved when the ratio is equal to one; the deposit becomes less localized when the ratio increases. Figure 3 shows the area ratio as a function of peak pulse current density for two anode-cathode gap spaces at the pulse period of 10 ms. In this figure, the average current density was fixed at 0.1 A/cm^2. Thus, the data points at 0.1 A/cm^2 represent the the results of DC plating. The results indicate that PC improves the selectivity of copper deposition by decreasing the area ratio. The effect of PC on the area ratio was greater at small anode-cathode spacings. At h/d = 0.5, for instance, the area ratio was reduced from 10.5

with DC to 4.6 at the PC density of 10 A/cm^2.

The effect of average current density on the selectivity of copper deposition is shown in Figure 4, where the ratio of cathode deposit area to anode area is plotted against the average current density for h/d = 0.5, pulse period of 10 ms, and duty cycle of 5%. The results of DC plating at h/d = 0.5 and 1.0 are also given in the figure for comparison. It is interesting to note that for both DC and pulse platings, the area ratio decreased with increasing average current density. However, the ratios with PC were smaller than those with DC, implying that the deposit was more localized with PC than with DC. The average deposit thickness as calculated from the weight gain data for the runs in Figure 4 are shown in Figure 5. Since the deposits were more localized with PC, the thickness of copper deposit in pulse plating was greater than that of DC plating. At the average current density of 0.5 A/cm^2, the thickness of copper deposit was about one order of magnitude greater than that of DC plating.

In the potential theory, an important quantity which characterizes the uniformity of current distribution is the value of a dimensionless group called the Wagner number:

$$Wa = k(d\eta_{DC}/di_{DC})/L \qquad (1)$$

where k is the conductivity of the electrolyte, $d\eta_{DC}/di_{DC}$ is the slope of DC polarization curve of the cathodic deposition reaction, and L is a characteristic length of the plating system. For the present geometry, the diameter of the anode may be chosen as the characteristic length. The Wagner number represents the ratio of the activation or charge-transfer resistance to the ohmic resistance of the electrolyte. The current distribution is generally more uniform at large Wagner numbers. In other words, the deposit at the cathode is more localized when the Wagner number is small.

In order to interpret the present results with the potential theory, a set of experiments was conducted to determine the polarization behavior of copper deposition reaction in the standard acid copper sulfate bath under the current pulse coditions. A copper rotating disk electrode having a surface area of 0.506 cm^2 was used for the experiments. The method of pulse current control was used to experimentally determine the relationship of average electrode potential vs average current of the copper rotating disk electrode. In this method, a constant PC of known pulse period and duty cycle was applied to the electrode, and the instrumentation was constructed to enable one to measure the average electrode potential with respect to a reference electrode as a function of the average current density of the pulse current. The details of experimental technique are discussed in Ref. (9)-(11).

Figure 6 shows a set of average potential vs. average current data obtained with the copper rotating disk electrode at 2500 rpm for a set of

PC with pulse period of 5 ms. The measured polarization curves are given for five duty cycles ranging from 20 to 100%. The curves with 100% duty cycle represents the results of DC plating; an anodic DC polarization curve is also shown in the figure for serving as a reference. The measured results agree with a theoretical calculation made earlier by Chin (11) for the acid copper sulfate bath that PC behaves as a depolarizer and reduces the average overpotential required for the plating process. The extent of the overpotential reduction increased with decreasing duty cycle of PC. In other words, PC reduced the slope of the polarization curves, $d\eta_{DC}/di_{DC}$, and shifted the polarization curves to a more horizontal position as seen in Figure 6. Thus, for a given average current density, the Wagner number with PC is smaller than that of DC plating:

$$[Wa]_{PC} < [Wa]_{DC} \qquad (2)$$

This implies that the current distribution in the pulse plating of copper from the acid copper sulfate bath is less uniform than in DC plating, and more localized copper deposit is obtained with PC. This notion is in qualitative agreement with the present experimental results of Figures 2-5. However, any quantitative comparison between the theory and experiments would require the simultaneous solution of the potential and electrokinetic equations. The type of the polarization curves shown in Figure 6 appears to be useful in the estimate of the secondary current distribution in pulse plating.

Conclusions

An experimental study has been made of the selective pulse plating of copper from an acid copper sulfate bath. The experiments were carried out by directing a small insoluble anode toward a large unmasked cathode, and by applying a pulse current of 0.1-10 A/cm^2. The use of PC was found to greatly improve the localization of copper deposition at the cathode. The extent of improvement increased with increasing pulse current density and with decreasing duty cycle of PC. The polarization characteristics of the copper plating bath under the pulse plating conditions were examined with a copper rotating disk electrode. Pulse current served as a depolarizer and reduced the average overpotential of the plating process. The Wagner number generated from the slope of the polarization curves was used to discuss the current distribution in pulse plating.

Acknowledgement

This project is supported by the American Electroplater's Society. The authors wish to thank James E. Voytko of AT&T Net Work Systems, Omaha, NE, for his discussion, interest and encouragment of this work.

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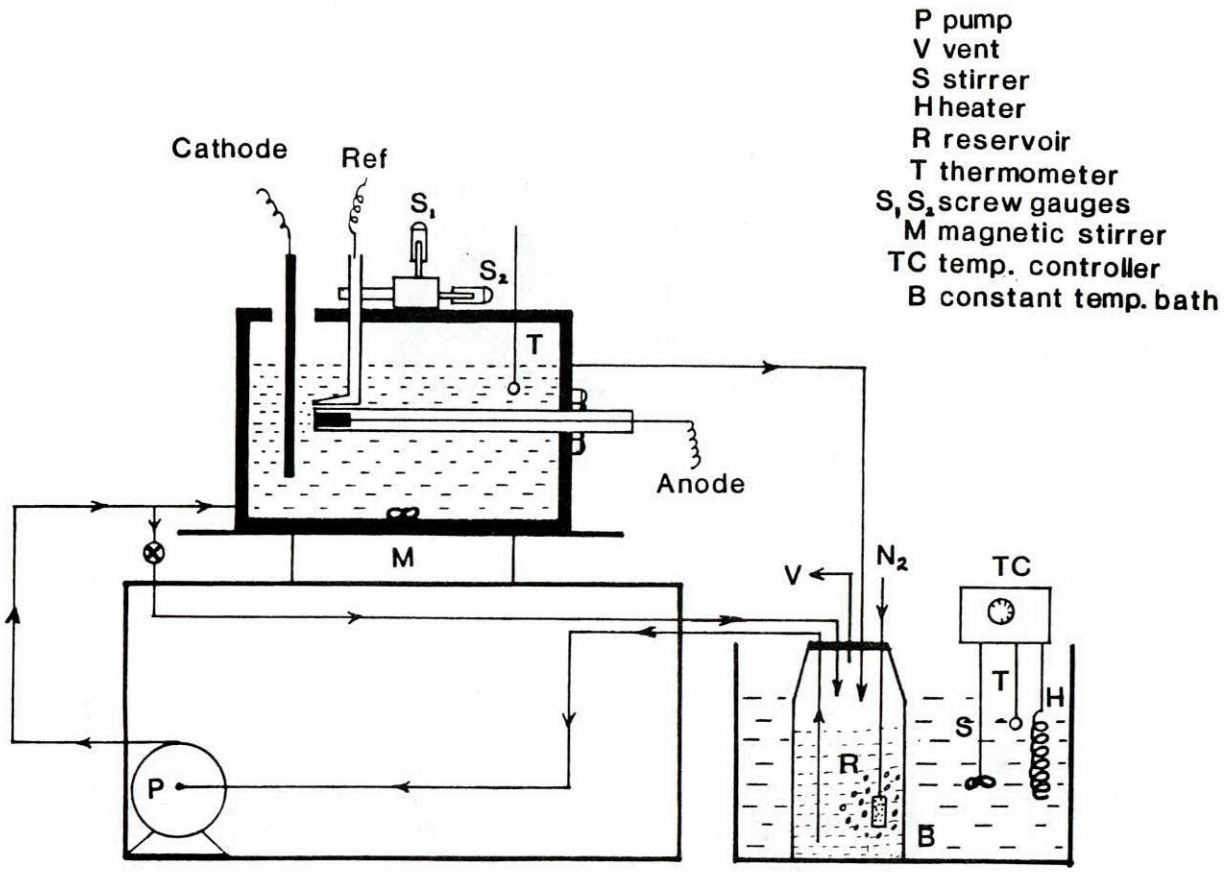

Figure 1. Schematics of experimental setup.

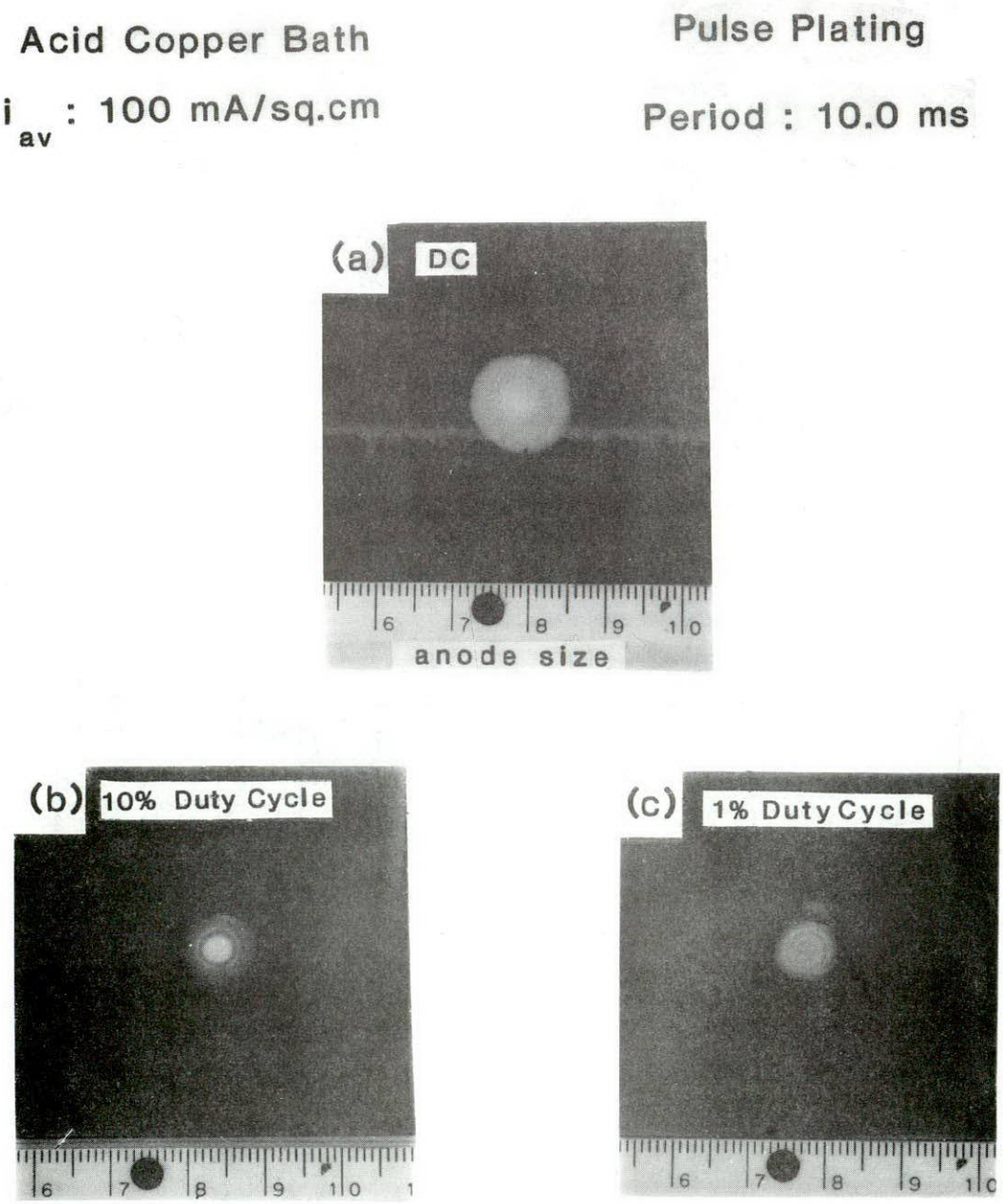

Figure 2. Photographs of copper deposits with DC plating (a), and pulse plating (b), and (c), at an average current density of 0.1 A/cm^2. The anode size is represented by the black dots in the photos.

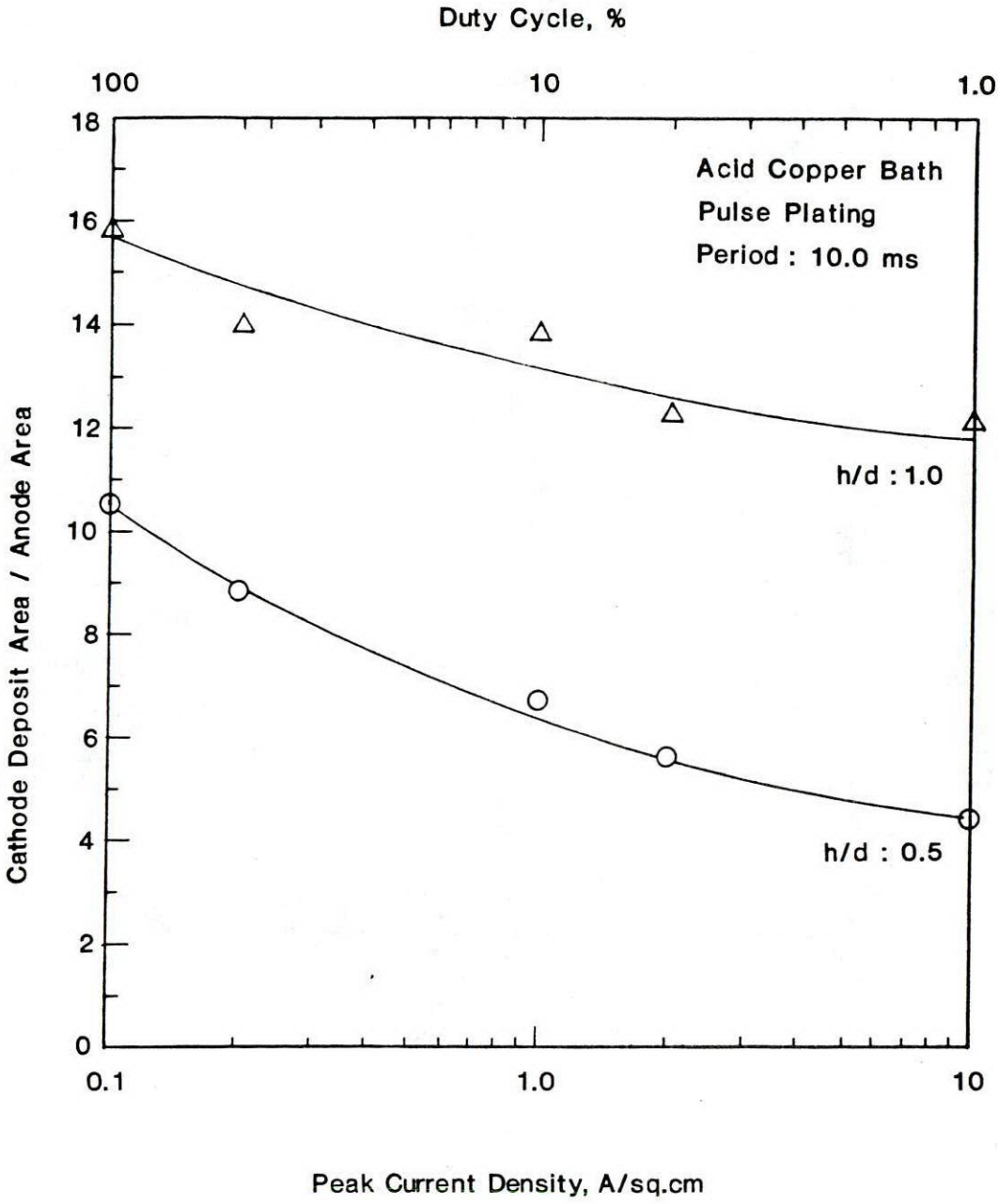

Figure 3. Effect of pulse current density on the localization of copper deposition expressed in the form of a ratio of copper deposit area to anode area. The average current density in these runs was kept at 0.1 A/cm^2; thus the data points at this current value represent the results of DC plating.

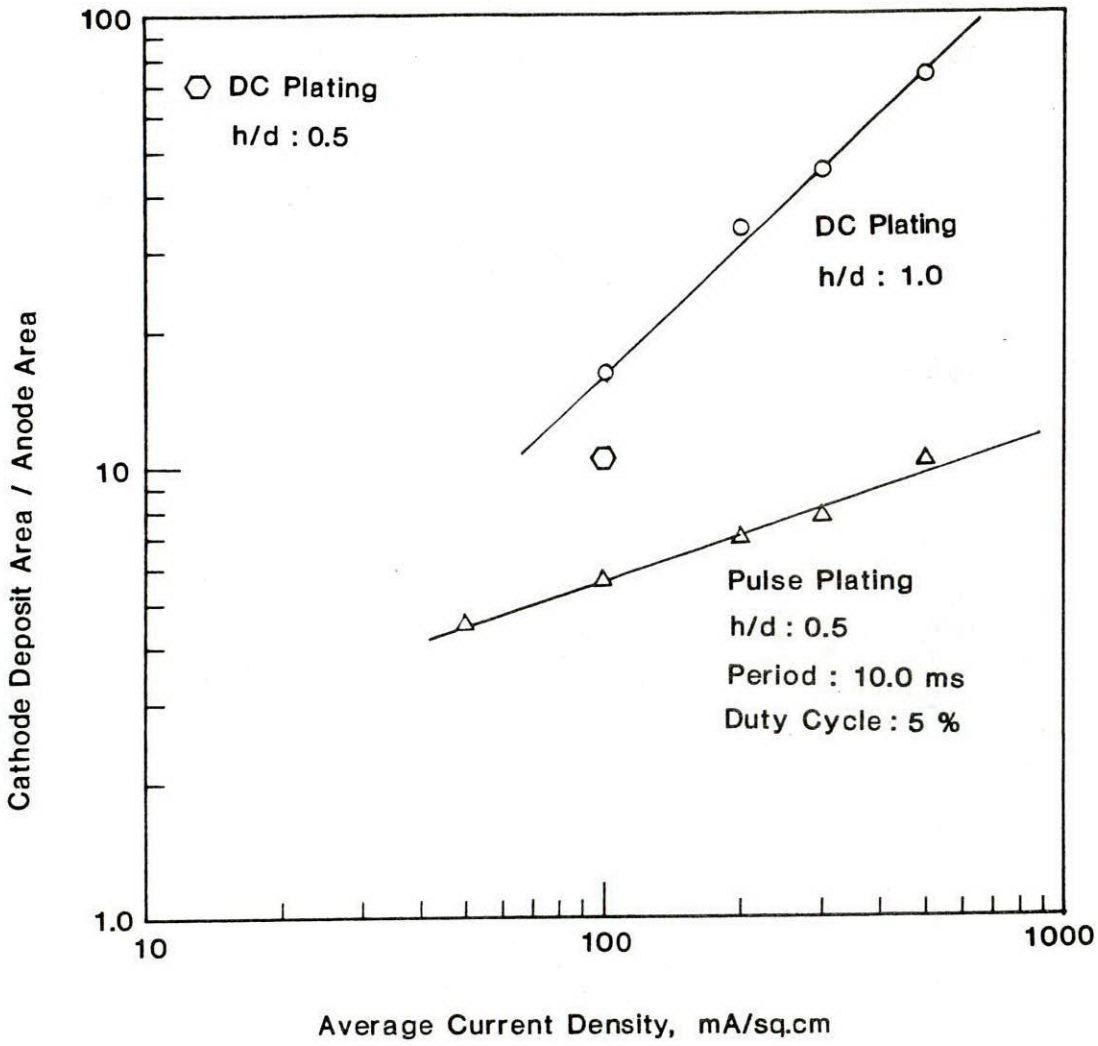

Figure 4. Effect of average current density on the localization of copper deposition expressed in the form of a ratio of copper deposit area to anode area. The results are given for a PC of 10 ms pulse period and 5% duty cycle. For comparison, the results with DC plating are also shown in the figure.

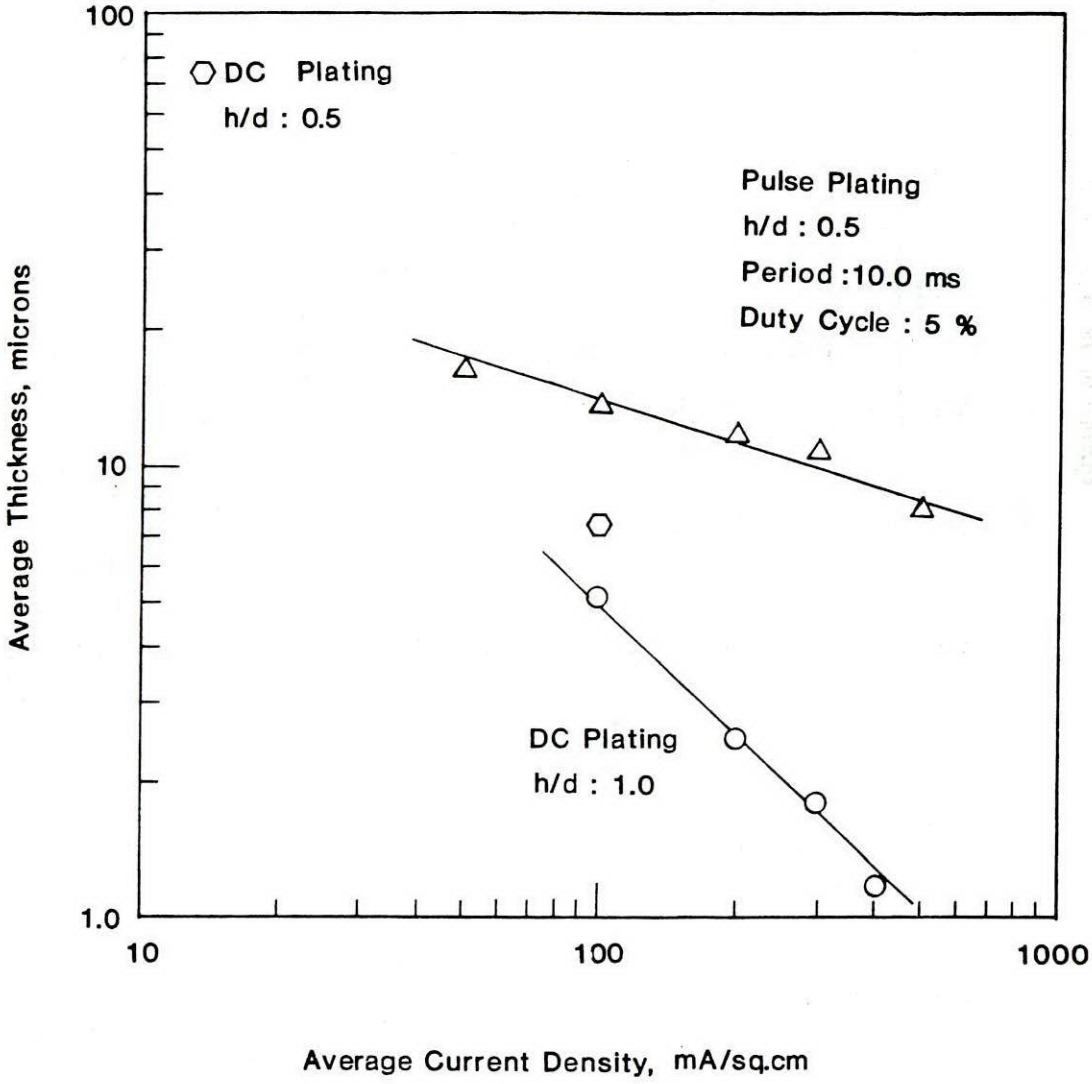

Figure 5. Thickness of copper deposits vs. average current density for the runs shown in Figure 4.

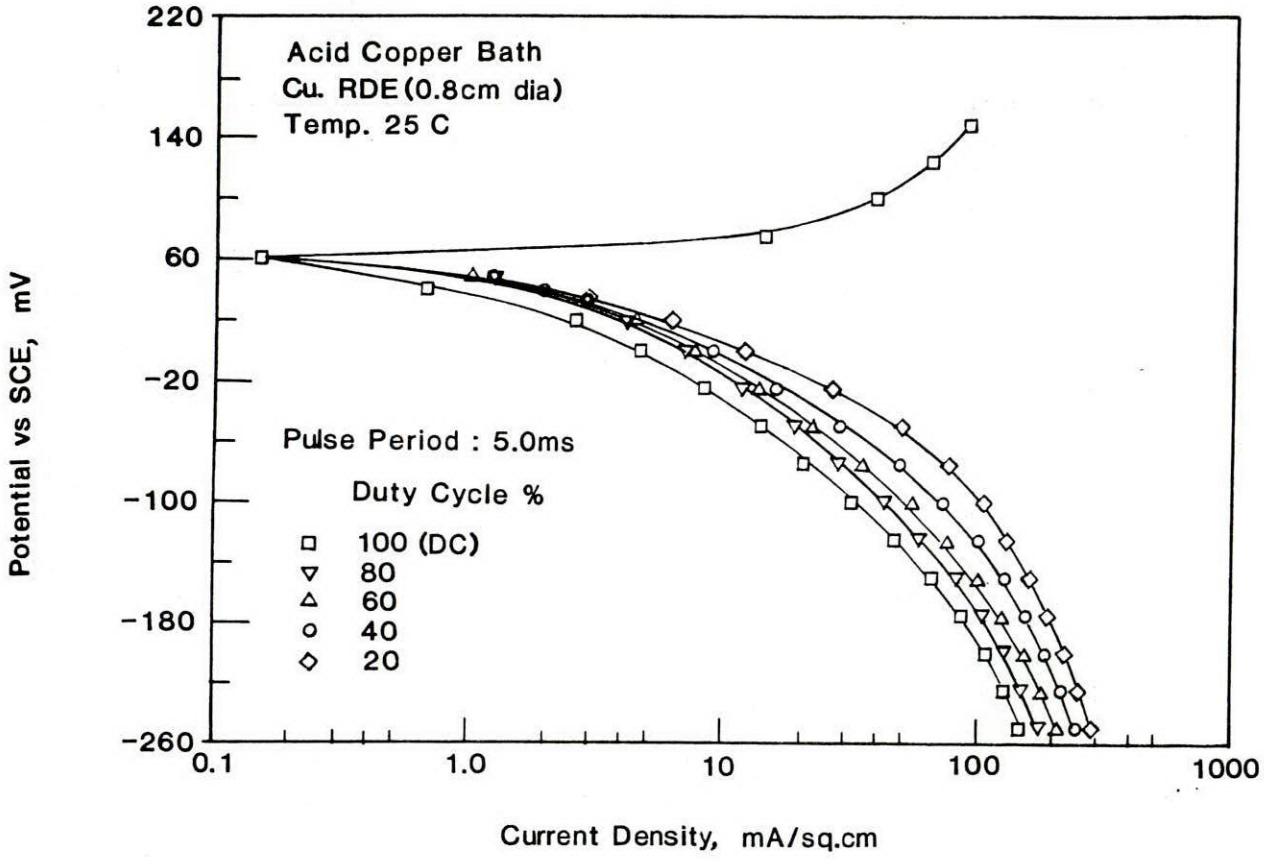

Figure 6. Effect of PC on the polarization curves of the copper deposition process with the standard acid copper sulfate bath. The data were obtained with a copper rotating disk electrode at 2500 rpm.

H-1

Analytical Methods Session H

A New Approach to On-Line Plating Analysis

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A NEW APPROACH TO ON-LINE PLATING ANALYSIS

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ABSTRACT

This paper describes the design and implementation of an on-line liquid analyzer for the plating industry. The instrument was designed with the following criteria.

1. Provide better control than existing pH/conductivity type analyzers by measuring specific constituents in the process stream.

2. Maintain simplicity of operation, hardware reliability and cost similar to pH type analyzers.

INTRODUCTION

Tighter specifications for plated products increase the costs associated with low product yield. Many times laboratory analyses of grab samples are too infrequent to detect problems in bath chemistries. Plating engineers are looking to on-line instruments to provide more frequent analysis to avoid problems due to chemical imbalances.

Previously, two types of on-line instruments were available to plating engineers:

1. Simple pH/conductivity analyzers measure a bulk property of the plating bath. These type of instruments do not measure directly the critical constituents in the process and only provide crude control. An example is the use of an ORP electrode to control Cu(1) in a cupric chloride etching solution. The potential of the ORP electrode is a function of the concentration of Cu(1), Cu(2) and hydrochloric acid. The electrode does not measure directly the Cu(1) concentration, the important constituent for correct bath operation.

2. Complex laboratory type analyzers are able to measure individual constituents with a precision of better than $\pm$0.5%. Laboratory hardware components must be used to achieve this level of precision. This type of components is

not designed to withstand the rigors of the industrial environment; 24 hr/day, 7 day/wk operation under difficult environmental conditions.

Tytronics has developed an instrument which is able to make compositional measurements with a precision of ±2%. This reduced precision specification permits the use of a less complex sampling system for lower instrument cost and the use of industrial grade components for reliability. In addition the instrument must have two other characteristics:

1. Reduced hardware and operational flexibility to simplify operation.

2. Affordable price so more applications in the plating facility have an attractive payback.

By making this compromise, plating engineers are able to specify an on-line compositional analyzer for better control without sacrificing simplicity of operation, hardware reliability and affordable price found in pH type instruments.

INSTRUMENT DESIGN

The instrument is an on line industrial titrator. The method of endpoint detection is an electrode. The instrument is able to use a variety of electrodes.

1. pH electrode: Acid base titrations.

2. Ion selective electrodes: An example is the analysis for chloride in acid copper by silver nitrate titration.

3. ORP electrode: An example is the analysis for permanganate by titration with ferrous sulphate.

Figure 1 is a diagram of the instrument showing location of all hardware components.

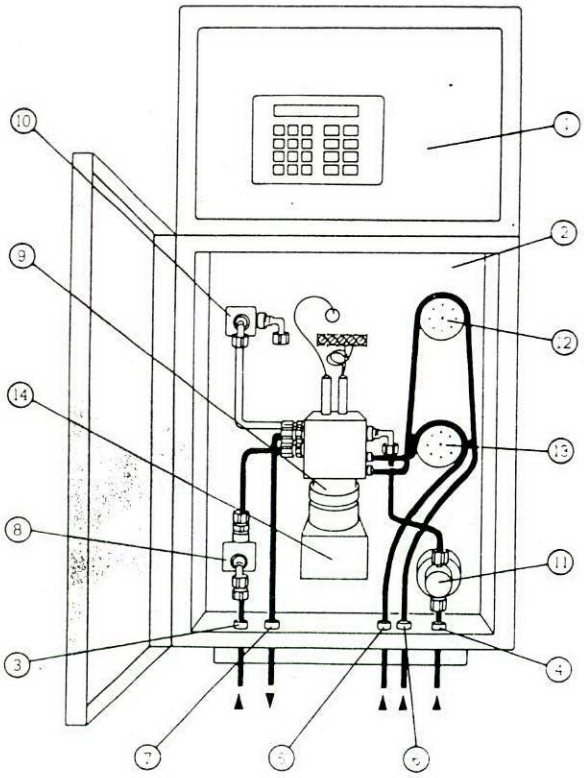


FIGURE 1

Sampling System

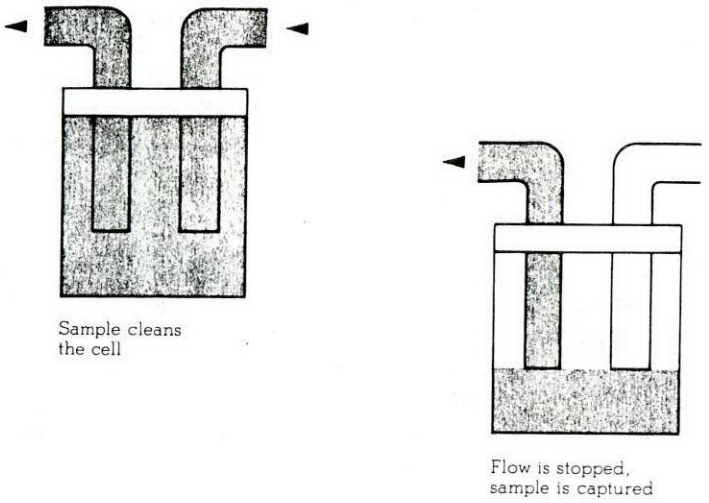


FIGURE 2

The instrument does not use a precision pump or complex sample capturing valve to introduce a sample in the titration vessel. A flow thru reaction cell is used both to volumetrically capture a sample and perform the analysis. The benefit of the reaction cell is that it reduces system complexity and instrument cost. Figure 2 shows a simplified cut away of the flow thru reaction cell. The section below describes how the reaction cell works.

The pressurized sample enters through a two way shut off valve (8). The sample flows through the reaction cell (9) and exists through a drain tube to waste (7). The sample is used to clean the cell between analyses. Sample flow is stopped and the pressurized reaction cell is vented to atmosphere by use of a valve (10). The sample is captured volumetrically in the cell by the use of a siphon. Reagent and titrant are added directly to the cell to perform the analysis. Stirring is accomplished using a Teflon stir bar and a magnetic stirrer assembly (14) located below the cell.

The volumetric reproducibility of sample capturing is $\pm$1%. Two different sample volumes can be selected; 18 or 8 ml. All surfaces in contact with the sample can be supplied in Teflon for chemical compatibility. Sample inlet and outlet tubing are 1/4" OD and 1/8" ID to minimize clogging and sample handling problems. Calibration is automatically performed at programmed intervals to adjust for cell volume changes due to solids collecting or coating of cell walls.

Hardware Components

The hardware components were selected to maintain system repeatability to ±2% while withstanding the rigors of the industrial environment. A modular design for fluidic and electronic components was selected for ease of maintenance and to reduce down time. System wiring for AC, alarm relays and analog outputs are accessible for ease of installation.

1. Instrument cabinet

The electronic compartment (1) is a Nema 12 construction and is sealed fron the environment and the fluidic section. A positive pressure purge is used to protect the electronics from corrosive vapors. The lower section or fluidic compartment (2) is Nema 3 construction. Liquid connections sample (3), titrant (4), standard (5), reagent (6) and waste (7) are located at the base of the fluidic compartment.

2. Titrant pump

A positive displacement piston pump is used to volumetrically add titrant. The piston pump is simple in construction and requires minimal maintenance. The pump has no internal check valves and all wetted surfaces are rulon and ceramic which have excellent corrosion resistant characteristics. The only maintenance is replacement of the rulon seals every 6 months.

3. Shut off valves

The valves have an internal diaphragm to isolate fluids from the plunger, resulting in a valve resistant to abrasion and corrosion. The wetted parts can be supplied in Teflon and Kal-rez for chemical compatibility considerations.

4. Peristaltic pumps

Peristaltic pumps are a cost effective way of dispensing standards and reagents where volumetric reproducibility is not required. Standards and reagents are very clean solutions containing no solid or particulates to degrade pump tubing. Pump tubing life is greater than 1000 hours continuous use thus requiring replacement every 3 to 6 months. Tubing installation requires about 2 minutes of an operator's time.

APPLICATIONS

The instrument has been tested on a number of applications within the plating industry. The data demonstrates the instrument is an excellent sensor to monitor critical constituents in plating and etching solutions. The next step in our study will be to use the data supplied by the instrument to control feed pumps and valves and quantify improvements in product quality, reduction in chemical consumption and elimination of laboratory grab sampling.

Electroless Copper

The instrument was set up to analyze first copper and then hydroxide in an active and working electroless copper bath. The method for copper analysis is an EDTA titration using a cupric electrode to detect the endpoint. The reagent was ammonium buffer and the titrant was 0.05 M EDTA. The method for hydroxide analysis is an acid base titration using a pH electrode to detect the endpoint. The titrant was 1.0 N hydrochloric acid.

Figures 3 and 4 are plots of data collected on active baths over a five hour period. In region 1 in each figure, the bath has been cooled and deactivated. The upper and lower lines are a 2% window around the mean of the data and is used to illustrate the instruments repeatibility. In region 2 in each figure, the bath is active and plating is occuring. Rapid concentration changes in copper and hydroxide are detected by the analyzer. These changes reduce plating efficiency and affect product quality.

An instrument set up for hydroxide could also analyze for formaldehyde by adding sodium sulfite after the first titration and re-titrating with hydrochloric acid.

Copper in Waste Stream

The waste streams from plating and etching areas must be treated prior to sending the final effluent to the city sewer. The streams are treated with sodium hydrosulfite to reduce the copper. By monitoring the copper concentration, control of hydrosulfite addition can be achieved resulting in cost savings from reduced chemical consumption and elimination of odor problems related to excess hydrosulfite in the waste stream.

Copper was analyzed by an oxidation/reduction titration using a platinum electrode to detect the endpoint. The reagent was potassium iodide in sulfuric acid and the titrant was 0.01 M sodium thiosulfate. The data supplied by the instrument was compared to analysis of grab samples by Inductively Coupled Plasma (ICP). Figure 5 is a plot of the data. The data shows the instrument's results were offset from the ICP analyses. The copper concentration changes detected by the instrument were reliable relative to the ICP analysis and the instrument could be used to control hydrosulfite addition.

Other applications

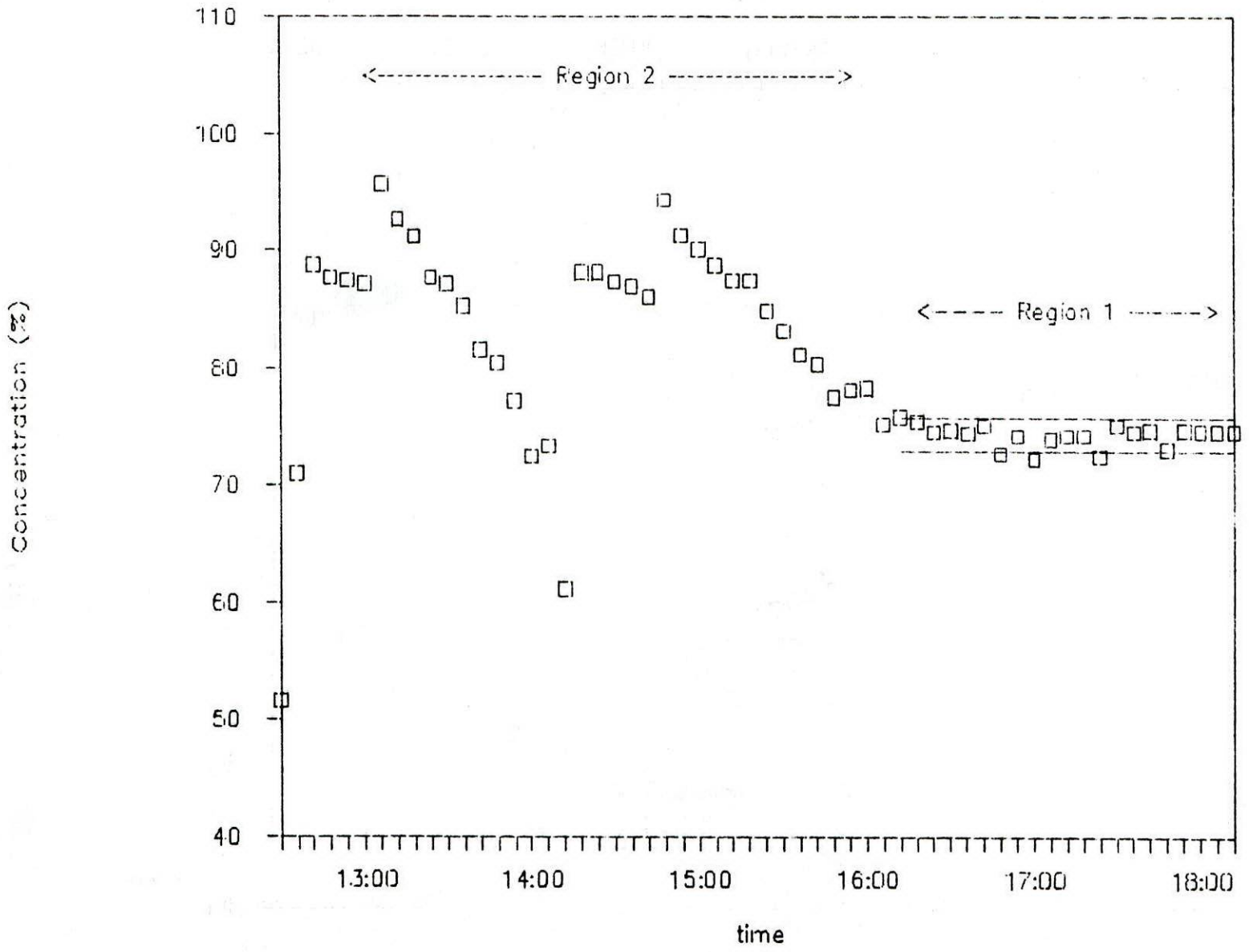
1. Figure 6 is the data from analysis of sodium hydroxide and sodium carbonate in a potassium permanganate etch solution. The analysis is a dual endpoint pH endpoint titration. The instrument is able to detect both endpoints and output results for both sodium hydroxide and sodium carbonate in concentration units. The system reproducibility for both analysis is better than $\pm$2%.

2. Figure 7 is the data from analysis of chromate in a chrome plating solution. The analysis method is an oxidation/reduction titration using a platinum electrode to detect the endpoint. The reagent is sulfuric acid and the titrant is 0.5 N ferrous ammonium sulfate.

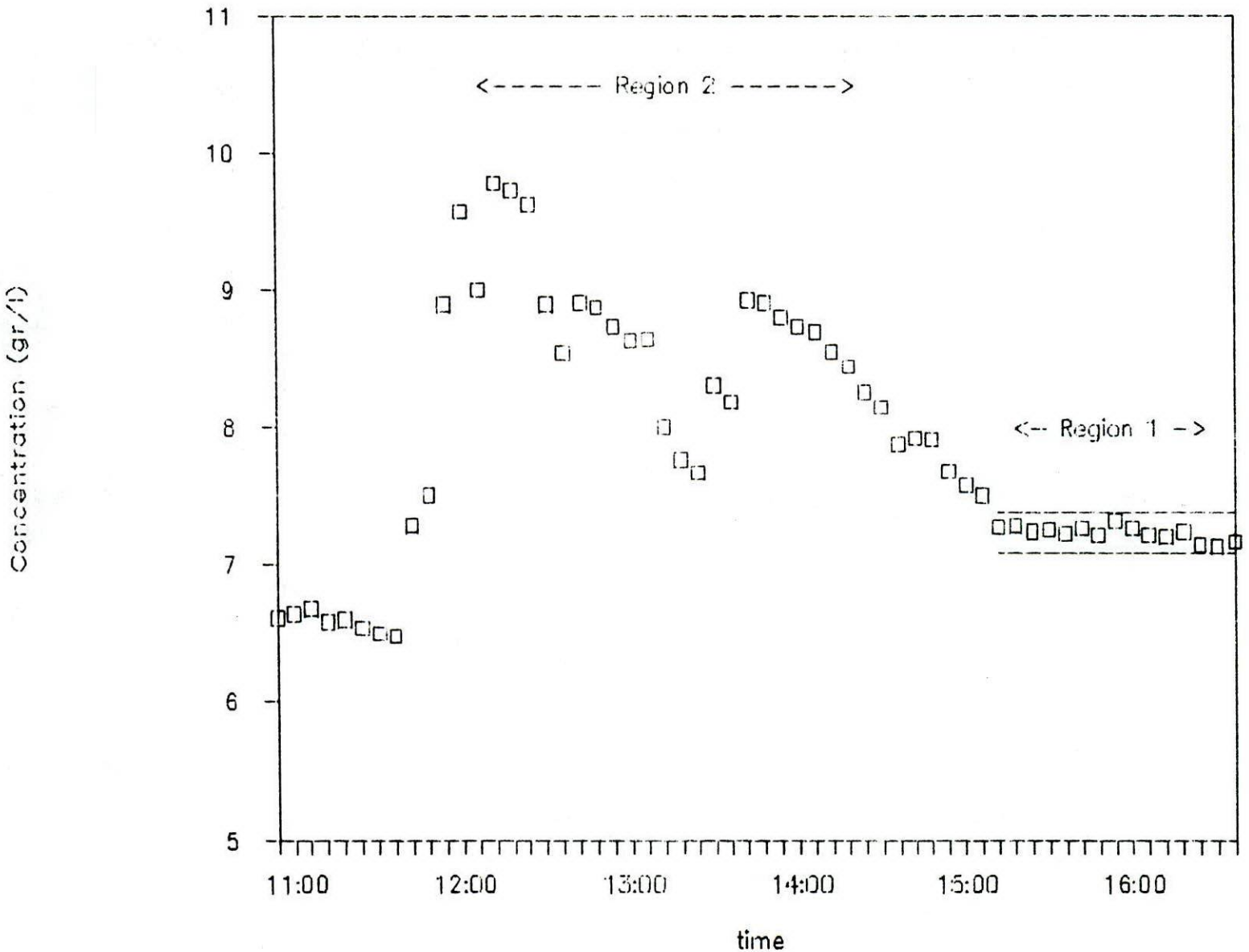
CONCLUSIONS

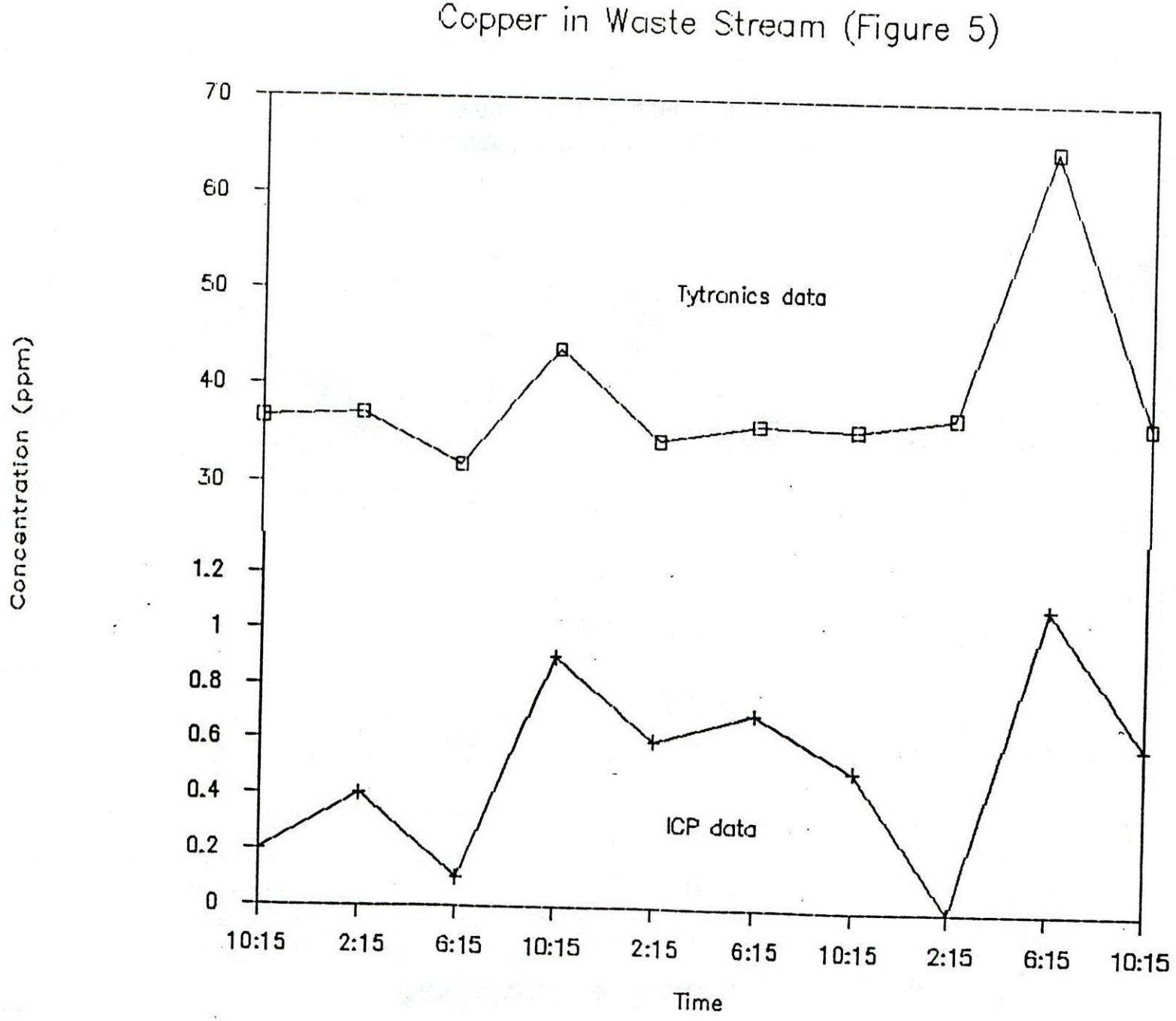
Tytronics has developed an on-line industrial titrator with simplicity of operation, hardware reliability and affordable price found in pH type instruments. This allows plating engineers the ability to specify an on-line analyzer to provide more frequent analysis to avoid problems caused by imbalances in bath chemistries. The next step is to use the data supplied by the instrument to control feed pumps and valves and to quantify improvements in product quality, reduction in chemical consumption and elimination of laboratory grab samples.

Copper in Electroless Copper (Figure 3)

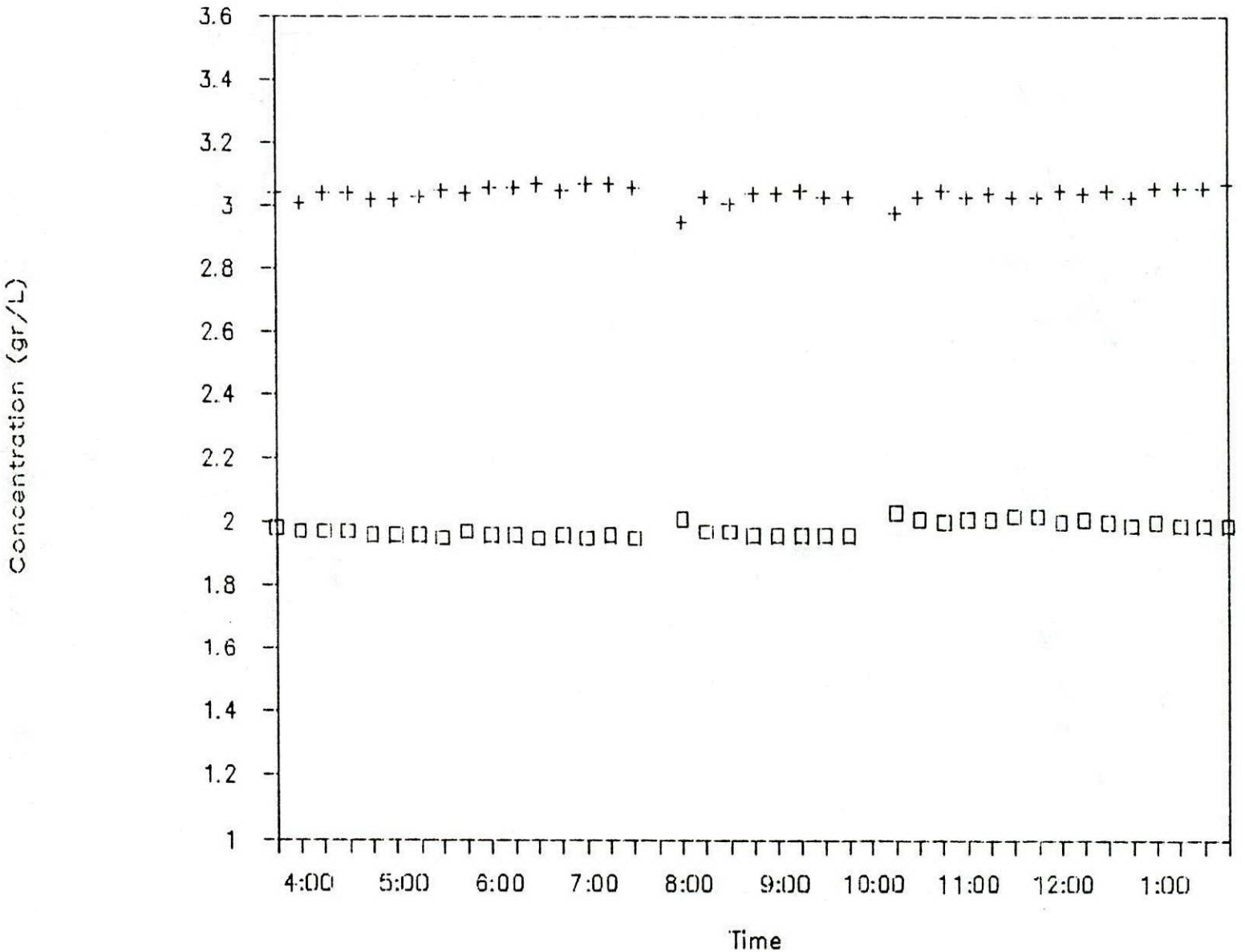


Hydroxide in Electroless Copper (Fig.4)

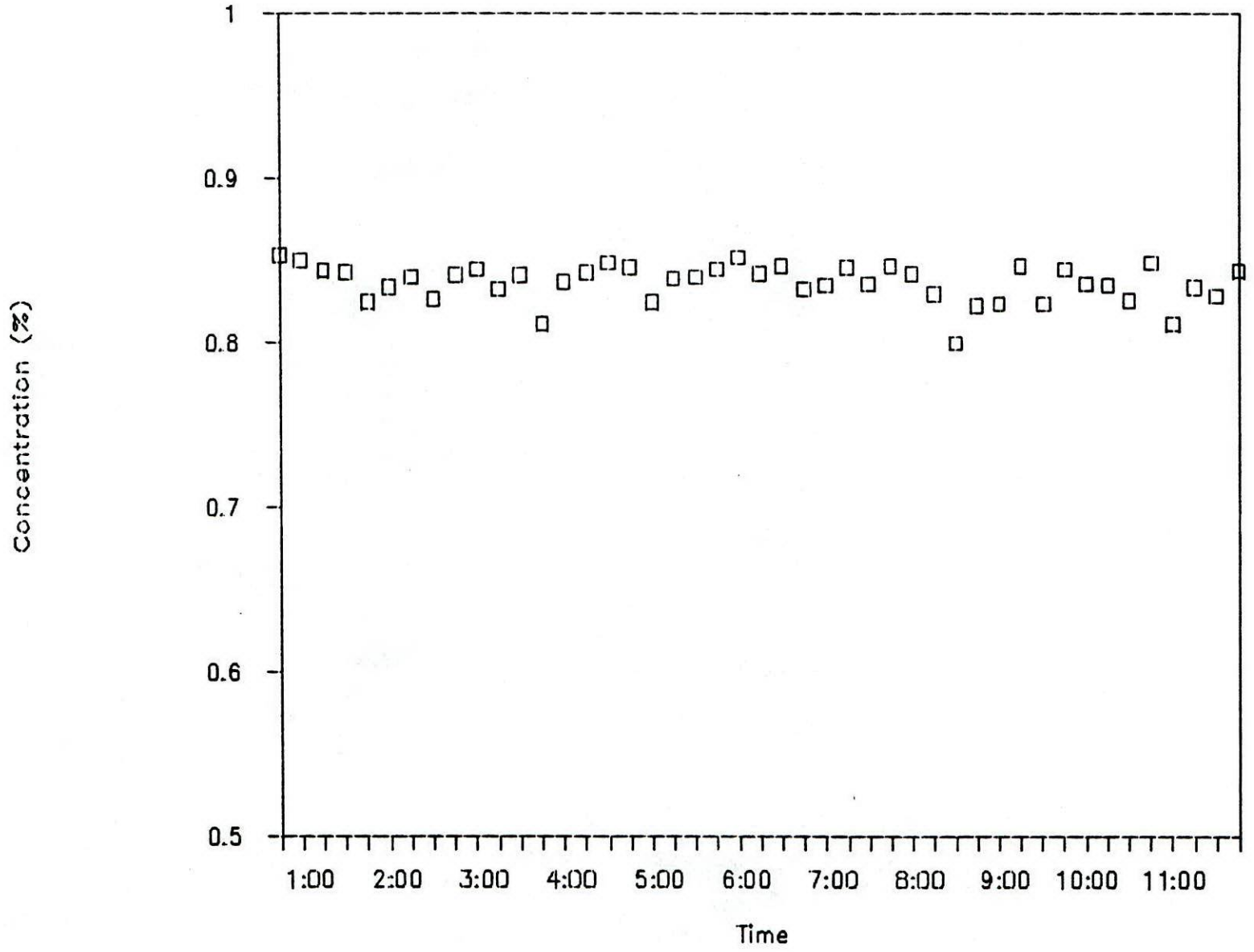



Copper in Waste Stream (Figure 5)
Concentration (ppm)
70
60
50
40
30
1.2
1
0.8
0.6
0.4
0.2
0
Tytronics data
ICP data
10:15
2:15
6:15
10:15
2:15
6:15
10:15
2:15
6:15
10:15
Time

NaOH and Na2CO3 in Etch (Figure 6)



Chromium Plating Solution (Figure 7)



H-2

Analytical Methods Session H

State of Implementation Of Cyclic Voltammetric Stripping Analysis in the Plating Industry

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STATE OF IMPLEMENTATION OF CYCLIC VOLTAMMETRIC STRIPPING ANALYSIS IN THE PLATING INDUSTRY

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Abstract

Cyclic Voltammetric Stripping (CVS) analysis has emerged as one of the more useful techniques in plating bath analysis. It has been widely applied to the analysis of organic additives and their components in copper, tin, nickel, zinc and solder plating solutions, as well as for monitoring of oxidizable contaminants and some major bath components. The state of implementation of the technique within the printed circuit industry is presented and illustrated by a few typical examples, pointing out some obvious accomplishments of CVS analysis in improving quality and yields of PC boards.

Introduction

With rapid developments in the electronics and metal finishing industries, the lack of reliable, simple and sensitive analytical techniques is becoming quite obvious. The search for new analytical techniques is on, as can be seen from the number of papers in the journals serving the plating community.

Among the techniques recently introduced, Cyclic Voltammetric Stripping technique (CVS) [1] is rapidly emerging as one of the most promising analytical tools presently employed for plating bath control.

The CVS technique has been successfully used for analysis of brightening agents in copper pyrophosphate solutions [2,3] and acid copper sulfate solutions [4-7], with initial work reported on experiments with tin sulfate [8], Watts nickel [9,10] and solder plating solutions.

This paper will concentrate on reviewing practical experience with CVS during the past few years, touching on such topics as additive control, contamination control and chloride analysis.

Theory

Cyclic Voltammetric Stripping analysis takes advantage of the polarization effects that most of the plating additives exert on the metal being plated. CVS measurements are performed by cycling the potential on an inert rotating disc electrode (e.g. Pt) so that a small amount of metal is alternately deposited on the electrode surface and stripped off by anodic dissolution. During the cycle, the charge required to dissolve the metal back to the solution, A_R, is measured (see Figure 1). Since the sweep rate is constant, the area under the stripping peak (charge), A_R, is proportional to the amount of metal plated. It is this quantity that is affected by additives and can, therefore, be used to determine their active concentration. To accomplish that, one can construct a calibration curve of A_R vs the concentration of additive. The calibration curve or one of the recently developed standard addition techniques are then used to measure active concentration of the additive or its components. One such calibration curve is shown in Figure 2. Details of the various CVS approaches to measurement of additives and their components can be found in original literature [1,4,5,7,9,11,12] and recent reviews [13,14]. In addition to the analysis for additives, CVS instrumentation* has been successfully used for monitoring of oxidizable contaminants and chloride in some acid copper sulfate plating solutions. Figure 1 shows a voltammogram indicating the various regions where additives, contaminants and chloride are measured.

Production Feedback

Most of the facilities performing CVS analysis at the present time are concentrating on the monitoring of the organic additives in copper pyrophosphate and acid copper sulfate plating baths. The analysis of the activity of the additives is performed using a calibration curve or one of the modified analytical procedures [13,14]. In all cases, the effect of additive on the metal plating is the basic principle for additive analysis.

In copper pyrophosphate solutions, the additive is dimercaptothiodiazole (DMTD) or a commercially available additive based on this compound. A calibration curve for DMTD is shown in Figure 3. Tench et. al. have described CVS analysis and performance with pyrophosphate solutions employing low levels [15] as well as high levels [16] of additive. The actual production implementations of CVS have

* An instrument, designed specifically for CVS analysis of plating solutions, is manufactured and distributed by UPA Technology, Inc., Syosset, NY, under the trade name of QUALIDERM™, Q-1000.

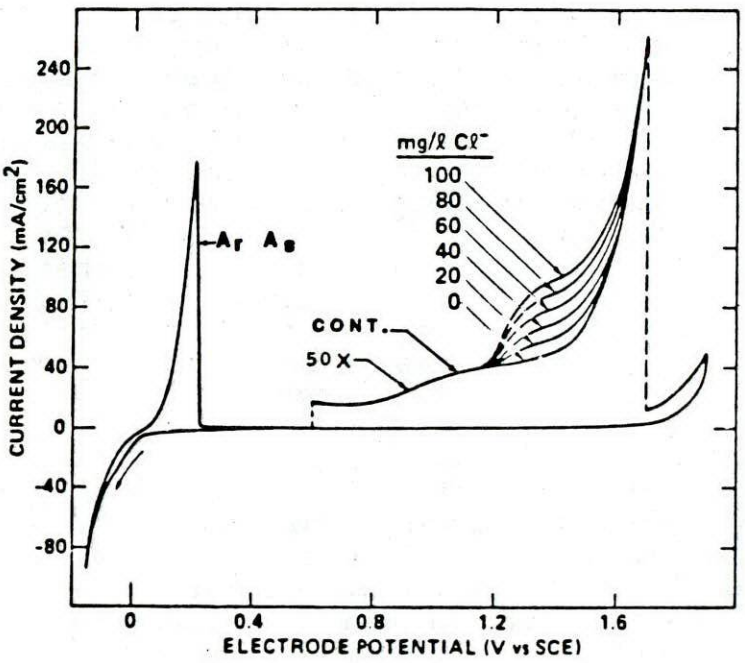

Fig. 1 Cyclic Voltammogram for Acid Copper Sulfate Solution

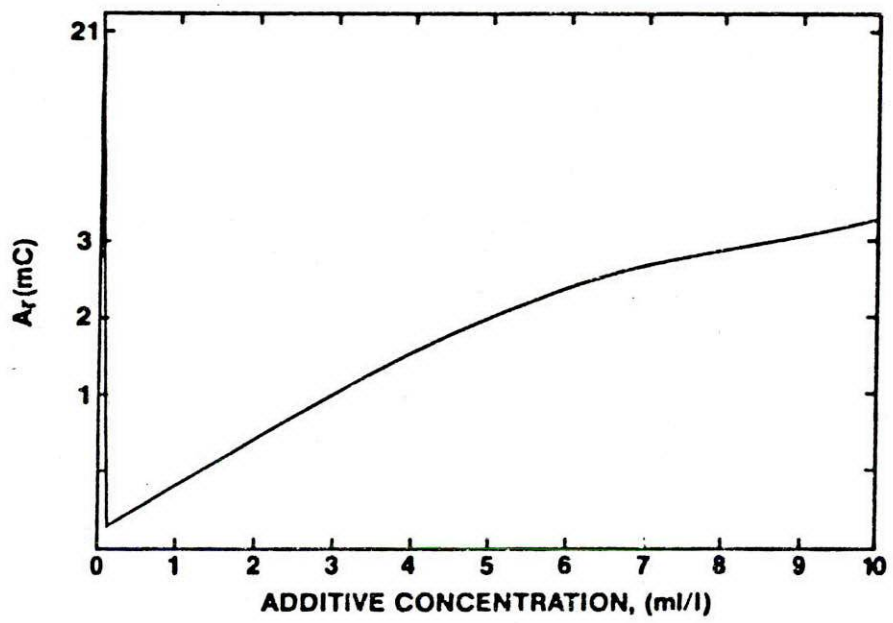

Fig. 2 Typical CVS calibration curve for SAS-type additives in acid copper plating bath (scan rate = 100mV/S, rotation rate = 500RPM, scan limits = -0.2 to 1.6V).

been described by Lowry et. al. [2] and Puippe [3]. All of these papers indicate that CVS is a convenient and appropriate technique for monitoring DMTD activity. Since the facilities operate on various load schedules, some pyro plating baths are used on a non-stop basis (24 hours a day, 7 days a week), while others are used only sporadically, and since DMTD undergoes a long-term activation process, it is often not possible without CVS analysis to pin-point the effective or "active" concentration of DMTD. Experience in production facilities, however, indicates that it is far more practical to establish the "window" of A_R/A_S values that give acceptable plating, rather than trying to find absolute concentrations of additives. Thus, for example, Puippe [3] recommends an A_R/A_S value around 1.35 for the additive and conditions used at his facility, while Lowry et. al [2] report an A_R/A_S window between 0.95-1.15 at Rockwell-Collins Printed Circuits Products facility. A note of caution, however, is appropriate here. The actual additive activity necessary for the best plating will vary from one facility to the next, depending on such variables as the type of boards plated, current density, agitation, chemistry of the bath, temperature, contamination, etc. It is therefore necessary to establish this window at each facility independently, using results from other facilities as guidelines only.

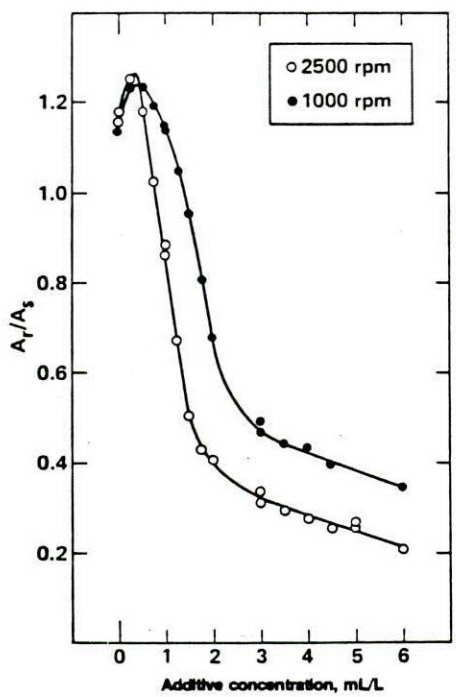

Fig. 3 Typical Calibration Curve for dimercaptothiodiazole-based additive in copper pyrophosphate solution (scan rate = 50m V/s, scan limits = -0.7 to 1.0V)

Similar success stories have been reported from a variety of facilities using various acid copper sulfate additives. One such story was reported by Bacchetta [6] at an EAS Analytical Methods Symposium in Chicago. Her facility has been using CVS for over 2 years. They have experienced severe plating problems leading to high reject rates. Using CVS, they have linked the problems to excessive concentrations of the additive. Since they had been following the manufacturer's specifications, her facility started working with the additive manufacturer to decrease the addition rate. As can be seen from Figure 4, they decreased the addition rate from 1.00 ml/gal Ahr to 0.25 ml/gal Ahr, a four-to-one decrease. Their additive concentration in the plating bath has decreased from over 200 ml/gal to the recommended level of about 35 ml/gal. As a consequence, their reject rate decreased from an average of 3% to an average of 0.5% in the first year (see Figure 5), and to about 0.25% in the second year (see Figure 6). Similar results have been reported to us by a few other facilities using CVS and cooperating with the same additive manufacturer.

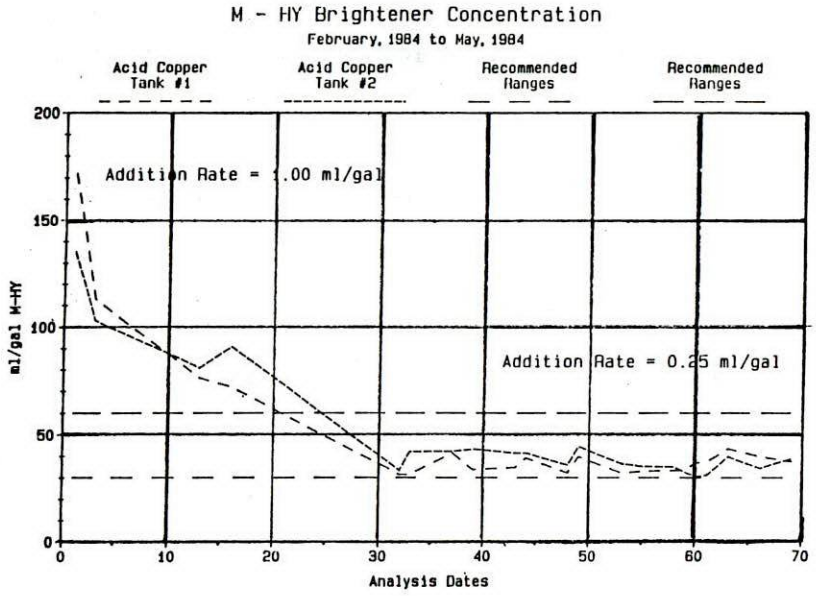

Fig. 4 Decrease in Additive Level with Addition Rate Decrease, Courtesy of M. Bacchetta, HP Rockaway, NJ.

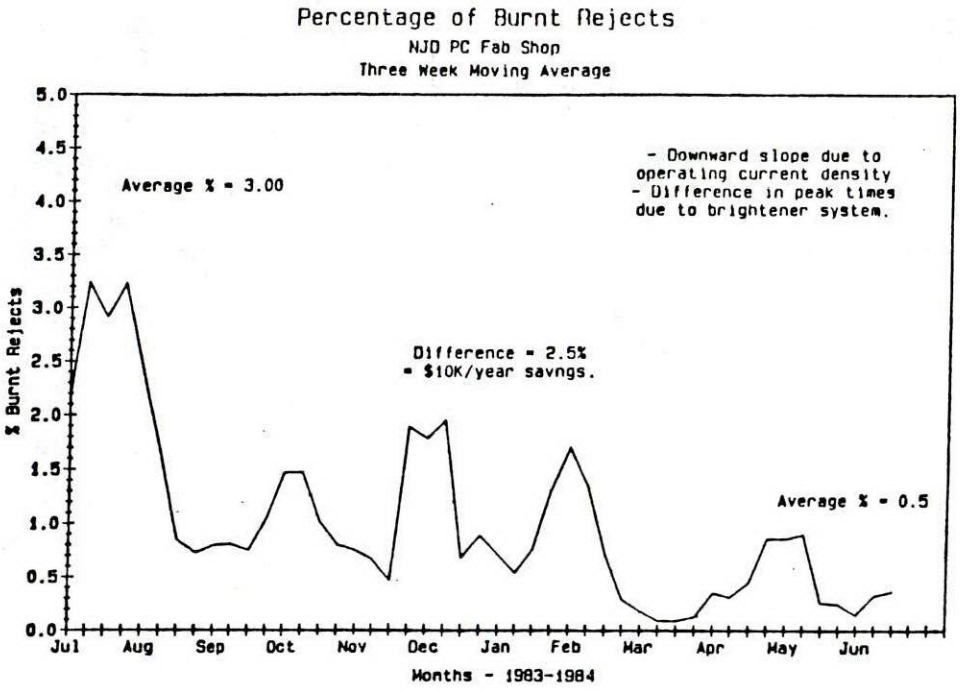

Fig. 5 Reject Rate in First Year of Evaluation, Courtesy of M. Bacchetta, HP Rockaway, NJ.

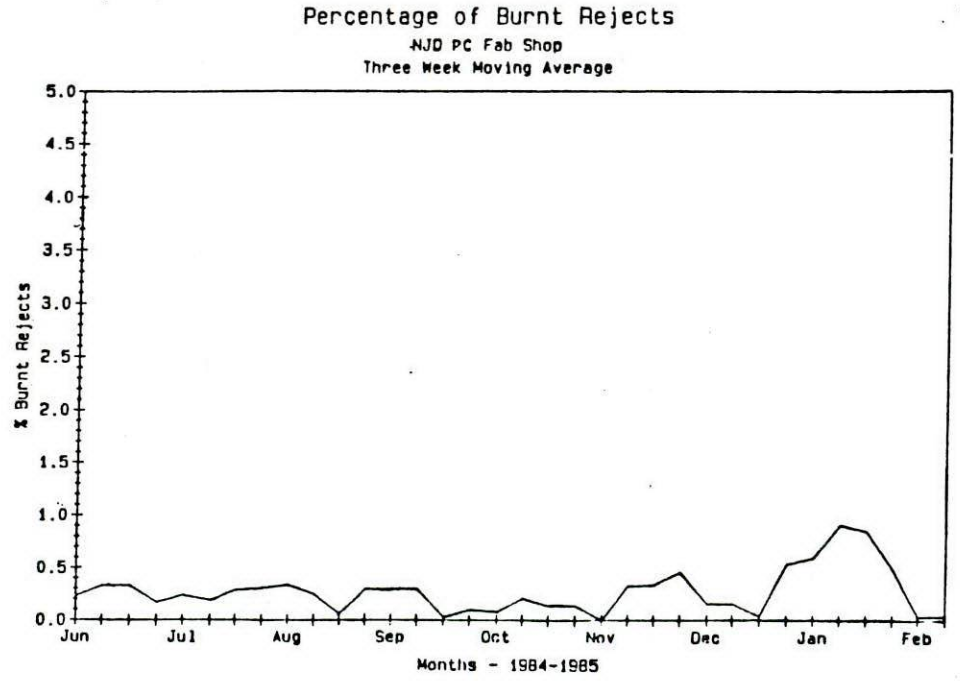

Fig. 6 Reject Rate in Second Year of Evaluation, Courtesy of M. Bacchetta, HP Rockaway, NJ.

A similar story of improved quality and decreased additive usage has been reported by Dr. Magdi Hanna of Graphic Research Corp. in Los Angeles [13,17]. In their facility, they linked plating problems to high additive levels caused by increased contamination, despite regular and frequent carbon treatments. Experimenting with CVS, they evaluated a number of carbons and techniques which led to a more efficient carbon treatment procedure [17]. This improved carbon treatment led to more effective usage of additive, allowing them to decrease addition rates to 1/3 of their previous values, which had been necessary to overcome the contaminant interference in their solutions. Since lower additive levels lead to lower breakdown rates of the additive systems resulting in less contaminants, they report [13] that they could run up to 3 years with simple periodic carbon filtration without addition of H_2O_2 or $KMnO_4$, and with significantly improved product yields. Similar results have been reported by Hughes [13] and KAM Circuits in the UK and some other facilities.

In addition to additive control leading to improved product yields, decreased waste of additives and decreased down-time, CVS has been extensively used to monitor additive quality and consistency by bath manufacturers and users. Most of the major manufacturers of copper plating additives presently own and use CVS equipment. One manufacturer even reported to us using CVS to improve production yields of their brightener.

Other improvements and uses of CVS include improvements in carbon treatment procedures by allowing evaluation of completeness of the treatment, screening and selection of proper carbon, filters, as well as the process itself. CVS has also been credited with finding some contaminated anodes [2,18] and finding better techniques for adding the additive (a lot of small additions are perferred over one large addition, i.e., at the beginning or end of the shift).

In addition to monitoring additive and contamination levels, CVS has been used to monitor the balance between the components of the additive. Even if the brightener level is within the recommended "window", lack of balance between the components can cause plating problems. Techniques have been developed for independent measurement of brighteners and "suppressors" in the baths [7,13,14]. Periodic evaluation of the balance can be very useful in adjusting the additive to the most appropriate ratio for the given facility or application.

Despite these success stories, CVS technique is just at the beginning of its fruitful future. Extensive improvements have been made over the past 3 years in CVS instrumentation and techniques, which include a new step approach to CVS

[12], expansion of CVS to monitor additives in bright tin sulfate, Watts Ni and tin-lead plating solutions, as well as monitoring some major constituents of the baths and contaminants. So extensive has been progress in CVS, that work has started at some facilities to include CVS in closed-loop, "hands-off" systems.

Summarizing, some typical results have been presented indicating successful implementation of the CVS technique in PC board production facilities. Some benefits derived include increased yields, decreased down-time and decreased usage of additive; increased quality of the boards, a record of the bath history leading to faster trouble-shooting and thus shorter down-time; and in general, satisfied and more confident chemists and production managers - all leading to considerable monetary savings.

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18. Private Communications.

H-3

Analytical Methods Session H

Advances in Color Control Technology for Metal Finishing

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ADVANCES IN COLOR CONTROL TECHNOLOGY FOR METAL FINISHING

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Advances made in spectrophotometric instrumentation tied to the computer age have dramatically increased the capabilities for measuring and controlling color in the metal finishing industry. New systems that incorporated the latest in spectrophotometer and computer know-how are offering unprecedented accuracy and speed while performing an expanding number of tasks in the field.

Among the jobs that off-line and on-line instrumentation and systems are now doing are color matching, initial formulations and batch correction, quality control, batch ticketing, inventory control and on-line monitoring and correction in continuous production operations.

They are meeting needs spurred by the increased use of color in the design and styling of products and by materials from different production points in a final color-matched product. New systems are not only providing a consistency and interpretation of color that is unmatched by the human eye but significantly reducing the time needed to accomplish many of these tasks, thereby lowering costs.

Today I would like to discuss some of the key developments that have brought color control technology to this point and describe several of the latest innovations that promise even greater utility for the metal finishing industry in the near future.

Color Difference Instruments

Many of you are familiar with the colorimeter and more advanced spectrophotometer. They have been employed for some time in quality control and production applications to evaluate the magnitude and direction of color differences for a given product by providing numerical data for comparison with predetermined tolerances. The colorist uses this information either to accept a product or make color adjustments.

The colorimeter uses optical filters that determine the tristimulus values of the sample. Although these values adequately describe color, the instrument is limited to measurements under one illuminant and hence cannot detect metamerism (the condition in which color appearance changes under different illuminants). Its accuracy also depends on the precise control of the spectral characteristics of the light source, filters and photo-detector.

The spectrophotometer, in comparison, describes color by measuring reflectance at a number of wavelengths and provides more accurate and reproducible measurements including the detection of metamerism. Products that operate in either colorimetry or spectrophotometry modes depending upon choice of software are now common in the industry.

Color Formulation Systems

Computerized color formulation and correction systems incorporate spectrophotometer and computer capabilities to provide fast, accurate matches with cost and metamerism control, rapid-fire corrections, and match programs that automatically evaluate new colorants. Basic components of such systems generally consist of a spectrophotometer, microprocessor, terminal with video display, printer, and a variety of hardware and software options. The Sherwin-Williams Company, for one, is equipping its commercial stores throughout the country with these color formulation capabilities to meet the paint and coating needs of its industrial customers.

The company provides each store with a multi-component system that consists of an optical sensor connected to a computer console and a high-speed printer. The system allows operators to achieve accurate and consistent color matches in a fraction of the time formerly required to perform the job. In the case of Sherwin-Williams, the color formulation and batch correction capabilities are provided via a central computer installation. Stand-alone systems that contain their own computer capabilities are also common in the field.

The optical sensor in these systems evaluates color samples by measuring reflectance at a number of wavelengths and transmitting the results to the computer console consisting of a microprocessor, video display and keyboard for giving program commands. The system computes and displays the magnitude and direction of color difference for a given set of samples, and the printer can record the measurement data on paper for future reference or documentation.

Color control has become especially critical for industrial customers of the Sherwin-Williams stores as the marketplace has become sophisticated in its use of color and more exacting in its requirements. Business machine manufacturers, for example, assemble multi-component products with individual parts supplied by different vendors at different locations. It is vitally important that the paints for each part match because variations will be obvious in the finished products.

New System Developments

Recent developments in both hardware and software have advanced

the capabilities of such systems for the metal finishing industry to a new level. One of the latest is a computerized color matching system designed specifically for the paint and coatings field. The unit can match a sample shade to a standard color in the desired paint system or calculate a new matching recipe in less than 90 seconds.

The new system has been introduced both as an integrated system linked to an automatic dispenser and also as a stand-alone unit for those seeking the color matching capability to complement existing dispensing methods.

In a typical application, the user first selects or supplies a sample of the color to be matched, measures it using the optical sensor and specifies the paint system desired. The computer then provides the appropriate formula in the desired finish or paint base. The computerized color matching process finds an acceptable match in a matter of seconds. It will perform a full combinatorial match using existing pigments and bases; find the existing standard match if present; or correct the closest existing formula.

When the system is employed with the automatic dispensing unit, the formula is electronically transferred to the dispenser. The dispenser checks to determine that a container is in place, measures its size, and automatically dispenses the correct colorant volume.

Other New Systems

The new automatic system is one of a family of color formulation systems recently developed to provide users with the level of capability they actually need.

The most basic models are designed for those whose primary need is quality control capabilities but who may wish to add other system functions in the future. The QC units incorporate a choice of color difference equations and illuminants to insure that both user and customer can talk the same color language and agree on tolerances for acceptability.

Advanced models contain the features of the basic quality control unit but are specifically designed for production areas where QC and batch corrections are critical. With these systems, the colorist can check production batches for acceptability and calculate any necessary corrections, either as an addition to a batch or as a new formula.

Full-capability units incorporate all the features of the other models and are also a versatile color matching system. Among their software features are manual or automatic selection of colorants, groups of colorants by end-use or specific

properties, output of formula sorted by metamerism or price or both, and output of formula in full or abbreviated form.

On-Line Systems

On-line color measurement systems are now being employed for continuous finishing operations such as coil coating to identify and correct color variations before they exceed specifications. These systems continuously make non-contact spectrophotometric measurements with optical sensors and process the color data by computer to provide complete color variance information that enables operators to adjust formulas or metering rates without disrupting the production process.

In a representative coil coating operation, the optical sensor is located just before the shear at the exit end of the line. The unit is mounted on a motorized assembly to allow its positioning at a predetermined measurement location or offstrip for calibration.

The strip is engineered to run over a roll which may be raised or lowered to provide the proper focal length. When fully lowered, the roll does not touch the strip which prevents unnecessary wear when running material for which color is no concern.

The operator programs the intervals between individual color measurements along with the desired time between groups of averaged measurements. Color tolerances are selected and entered, and a series of alarms indicate when tolerances are exceeded.

The on-line system is being employed to monitor color on a wide variety of coil-coated surfaces including wood grain finishes. Among the advantages cited by users are increased color accuracy and consistency, throughput and quality control. It has also reduced color startup and change time, recycling and/or scrap costs and sampling costs.

On-Line Innovations

A number of recent developments in the controls and software designed for on-line color control systems are enhancing the application of this technology. One is the design of smaller and lighter weight optical sensors. Their reduced size not only simplifies installation on existing production equipment but also facilitates use in areas where space is very limited.

A good deal of attention is now being directed to presenting color data obtained by the system in simpler and more meaningful formats that will help operators identify and track variations more easily. One such format displays data on

a video monitor in a series of graphs that indicate the color difference from the standard of the three color coordinates (light-dark, red-green, yellow-blue) in any of the standard color formulas.

The monitor not only provides continuously updated trend information in graphic formats but also signals tolerance variations by changes in the color of the graph bars--blue for values within the acceptable tolerance range, yellow for warning of a drift away from specs within a pre-determined range, and red for deviations beyond the acceptable limits. Display of the color measurements data in graph rather than numeric form simplifies operator monitoring of the on-line process.

Programs that enable the system to store colorimetric data and provide various types of management reports and statistical analyses are also being devised. Among the areas for which they will provide information are:

- Location of out-of-tolerance material within a reel either by footage or time.
- Sorting of groups of reels or sets by color so they can be processed together in converting operations such as multiple ply sheeters.
- Statistical analysis that provides color standard deviation, high, low and mean for a reel or order.
- Storage of permanent production records on computer disks for evaluation of quality and process improvements.

The most recent development is a system employing a pulsed-xenon spectrophotometer that measures the color of samples at distances of up to 15 feet with the accuracy comparable to a typical industrial spectrophotometer. The measurement is not affected by ambient light due to the intense xenon illumination that has a peak power of 100,000 watts. The distance from the sample to the sensor is insensitive to variations as might occur in many applications that have uneven surfaces or unstable positions.

What's Ahead

What's ahead? On-line color measurement technology lends itself to closed-loop control in which the system not only measures the color but also automatically makes the adjustments that maintain the desired standard. Such installations already exist in the paper, textile and plastics industries. They reduce the quantity of off-shade products produced before

adjustments are made, speed color changes and cut colorant consumption.

Now in development are networking systems that will enable an on-line installation to communicate and exchange information with other types of color control equipment such as color formulation, batch correction and quality control units. Networking systems could connect units not only within a facility but also at different locations of an organization to simplify and speed color-related tasks.

Continuing progress in these and other areas makes it evident that the versatility and efficiencies offered by on-line systems will extend far beyond the capabilities available to the finishing industry today.

I-1

Electronics I
Session I

Conveyorized Impingement-Agitated Copper Plating Of Circuit Boards, A Case History

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CONVEYORIZED IMPINGEMENT-AGITATED COPPER PLATING OF CIRCUIT BOARDS, A CASE HISTORY

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In the summer of 1981 Hewlett-Packard Inc. began circuit board manufacturing operations in a new facility at its Boise, Idaho, site. One of the core processes at this facility was a conveyorized impingement-agitated, plating system. This choice has proven, in the retrospect of five years of routine production operation, a success. Implementation of this technology has proven to be challenging, and accompanied with some controversy. During this period much was learned about the operational practicalities for this system. Further, a great deal has been learned about the process determinants for the copper plating on this type of equipment. Our current status is that of routinely satisfying the present production demand on the Boise shop and of having aquired some knowledge of the capabilities and the limitations of this technology.

Summary of the Conveyorized System Operations

The conveyorized processing system for circuit-board outer-layer processing at the Boise shop is represented schematically by Figure 1. The processes are segregated into (1) the develop and plate line, and (2) the strip and etch line. The plating processes are bright acid copper, Watts nickel, and bright acid tin. Etching is a conventional proprietary alkaline process. The significant stages of the combined process are:

----> from outer layer imaging process
1. Load panels for develop and plate
2. Photoresist develop and associated rinses
3. Inspection access
4. Microetch and associated rinses
5. Copper electroplate and associated rinses
6. Inspection access
7. Microetch and associated rinses
8. Nickel electroplate and associated rinses
9. Inspection access
10. Tin electroplate and associated rinses
11. Dry
12. Unload and inspect
13. Load panels for strip and etch
14. Photoresist strip and associated rinses
15. Inspection access
16. Etch and associated rinses
17. Dry
18. Unload and inspect

<----- to dry-film solder mask processes

Figures 2 through 10 highlight some aspects of the operation. The Boise shop shop is based on a single panel size, 18 x 24-inch; the panels are racked for plating, strip and etch with the long dimension horizontal. This orientation is a constraint imposed by the dry-film resist technology used in the Boise shop. Future developments may enable hanging the long panel-dimension vertically, with a 25% increase in the capacity of the system.

All of the plating operations on this system are conventional in the sense that the panels are submerged in the plating electrolyte. The platings are somewhat nonconventional in the following respects;

1. The anode to cathode spacing is close (~5.5 inches).
2. The panels are carried through the plating cell in one continuous forward motion by the conveyor (the anodes are stationary). Copper plating is accomplished in a 26-foot length of plating cell.
3. The copper plating is done at a nominal 70 amps per square foot (at least twice the usual for copper plating on printed circuit boards).
4. The significant agitation is accomplished by hydraulic injection. Agitation accomplished by the panel motion through the electrolyte or by entrained air bubbles is insignificant.
5. The panels are carried into the plating cell(s) at one end through a vertical roller seal and out of the cell at the other end through an identical roller seal. These seals are the means by which panels can move into and out of the plating cell continuously, while at the same time the liquid depth is maintained.

With the exception of the plating processes, as just described, all other processes on the system are sprayed. Each of the process cells is fundamentally configured as depicted in Figure-11. When the process is operating the solution is pumped from the lower reservoir tank, through the sparging manifold, to be sprayed (or flowed) against the circuit-board panels, collected by the upper process tank and gravity drained back to the lower tank. When the process is shut down the working solution is held in standby status in the lower reservoir tank. Each of the upper process tanks is slotted at both ends (to allow the panels to move through). Solution containment is achieved by a combination of narrow slot width, and strategic placement of baffles and separation zones. There is unavoidably some "crosstalk" and dragover between adjacent process steps, this has been minimized by careful setup. Tests on our system have measured the dragover rate at about 1 ml/sq.ft.

Computerization

The computer resource for this system includes:

1. On/off control of mechanics (pumps, conveyor, etc.).
2. Process temperature control.
3. Function monitoring, and alarms, in event of malfunction. For example, in the event that a given process should provide an out-of-spec value for a temperature measurement an alarm will be actuated. In this particular case the general-alarm light for the plating system will be turned on and the CRT terminal will display the faulty temperature reading in inverse video mode.
4. Que management, for best-fit transitions from one lot to the next.
5. Rectifier control.
6. Automatic replenishment of additives.
7. Aquisition of rectifier and rack performance data, from which maintenance decisions are possible.
8. Aquisition of plating-current data associated with a selected group of panels, enabling both the verification of proper rectifier-control operation and the the aquisition of current and voltage data important for troubleshooting of plating inconsistencies.

The philosophy for application of computer resources to these processes has been, from the beginning, to magnify the capabilities of the operating crew, rather than wholesale automation. The objective has been to provide the tools for the operating crew to function as craftsmen.

Other Support Resources

An off-line complex of tanks, pumps, filters, etc. supports the conveyorized processing system, providing for mixing of process chemistries, carbon treatment, filtration and holding of standby solutions. This complex is located remote from the production system, in the basement of our building, and is "hard plumbed" to it. This resorce enables the maintenance of a complete standby solution for each of the plating processes, as a hedge against unforeseen chemical problems which could shut down production. Full off-line carbon treat and filtration capability is provided for the copper electrolyte and for the nickel electrolyte. The two micro-etches on the system employ a proprietary hydrogen peroxide/sulfuric acid chemistry; these are regenerable and are supported by a crystallizer/replenishment system which is part of the off-line complex.

The rectifiers for the plating processes (copper, 16 rectifiers; nickel, 6 rectifiers; tin, 2 rectifiers) are located remotely in

the basement. Air-knive blowers, process ventilation air, and all associated waste treatment equipment is also located in the basement. We credit this arrangement for a low noise-level and a process work-center environment approaching that of an office area. It is felt that this shop configuration has returned benefits in the way of a higher level of operational efficiency, of product quality, and of operator safety and health.

The Boise shop includes an analytical lab, but the responsibility for routine analysis, interpretation and replenishment associated with the production processes is conferred on the production operators. The plating processes are supported with automatic brightner addition systems which are normally under computer control; the production operators are, however, responsible for routinely verifying that the automatic replenishment systems are operating properly.

The Copper Plating Equipment

The copper-plating section is comprized of four(4) lower reservoir tanks, which are plumbed together to allow equilibration of the liquid levels, and a single, 32-ft. long, upper tank (through which the circuit board panels are passed). Each of the reservoir tanks contains a working volume of 250 gallons of plating solution, giving a total working volume of 1000 gallons. Each of the copper reservoir tanks is outfitted with a 10-hp sparging pump which provides a 25% section of the upper process tank with electrolyte-injection agitation. The upper process tank is comprised actually of two tanks, one nested inside of the other. The inner tank is 15 inches wide and 26 feet long, its ends are formed by the roller seals which provide containment of the electrolyte and enable the panels to enter and leave. The sides of the inner tank anchor to channels fixed along the bottom of the outer tank such that the bottom is, in fact, common to both the inner and the outer tanks. The outer tank is 30 inches wide and 32-feet long. The normal operating mode is for the pumped solution to completely fill the inner tank and overflow to the outer tank, where it is caught and drained back into the lower reservoir tanks. The actual solution sparging is accomplished by an array of sparger pipes placed in two rows parallel to the cathode plane of the cell (the path followed by the circuit-board panels), one row on either side of the cathode plane, each row respectively 2.5-inches from the cathode plane. The sparger pipes are set vertically, at regular (6-inch) intervals, and each extends the full depth of the inner tank. These pipes are manifolded along the bottom of the inner tank such that each of the four sparger pumps supplies 25% of the pipes along each side of the process tank. Figure-12 describes the major detail of the upper plating-process cell. A representative view of the copper cell interior is shown in Figure-13, when the solution is circulating the inner cell will be filled to the anode tops. We have

determined empirically that the sparging works best when the nozzles are oriented at an angle of about 40-degrees (from parallel to the cathode plane), angled "with" the conveyor direction for one side of the cell and "opposing" the conveyor direction for the other side of the cell.

The copper plating process utilizes phosporized (.03-.06% P) copper bar anodes, 1 x 4 x 17-inches. These are placed on 6-inch centers along each side of the inner process tank, about 5.5-inches from the cathode plane. The anode bars are hung in groups of six (6), each group associated with a different rectifier. The anodes are clamped to their respective bus bars to assure good contact. The copper plating is served by sixteen (16) independent 1000-amp rectifiers, arranged as eight symmetrical pairs along the length of the cell. The plating cell is operated in the constant current mode. The rectifiers are ramped by computer to make it possible to accommodate the frequent adjustments imposed by the small-lot-size strategy of the Boise shop.

Operation and Control of the Copper Plating Process

Extensive testing has been conducted to characterize the copper plating capabilities of this system, to assess the capabilities of "improved" versions of this equipment style, and to compare with the capabilities of typical conventional programmed-hoist installations. A typical "difficult" production part number was selected as the standard for this testing (see Figure-14). This part number is now used extensively for a variety of testing in the Boise shop and has been given the name "BOGUS" to prevent its confusion with regular production orders. Figure-14 also shows the locations from which standardized cross sections are taken. These locations were selected because they sampled the worst case conditions for the panel, the through-hole plate from a low current density area and the trace plating from a high current-density area. The "BOGUS" panel has become the standard for routine test runs to verify the performance of the plating process(es). It has become useful as the standard for assessing the effects of modifications to the copper plating process chemistry and for testing of proprietary alternates to the original copper process. Copper thickness and distribution has been characterized (see Figure-15) in terms of:

1. average hole-wall plating thickness (H)

$$H = (A+B+C+D+E+F)/6$$

2. average minimum hole-wall plating thickness (W)

$$W = (E+F)/2$$

3. average surface plating thickness, adjacent pad (S)

$$S = (G+H)/2$$

4. average plating thickness at corners of hole (SH)

$$SH = (A+B+C+D)/4$$

5. plating thickness on a high current-density trace (I)

6. The ratio I:W

7. The ratio S:H

8. The ratio SH:W

Table-1 summarizes some results of our testing of equipment/process alternatives. The Table-1 item marked with the * is the equipment/process configuration operating in our shop now. One result of this testing has been the choice of a nominal copper plating current of 70-ASF and a conveyor speed of 2.5-fpm. These conditions are a concession to the competing requirements for adequate copper thickness (.0007-inch minimum in the holes) and to the maximum allowed trace height of .0035-inch (imposed by the dry-film solder mask process used at the Boise shop).

It has been useful to study the capabilities of the plating process in terms of units that combine the dwell time (in the copper-plate process) and the current density. Units of "ampere-minutes/square-foot" were choosen for this. Using the copper-cell length, the nominal current density, and the conveyor speed reported herein, the process is seen to be operating nominally at the 730 amp-minute/ft^2 level. The design of our rectifier control system enables a custom configuration of the plating current for each part-number entered into the system. Most part-numbers will actually be plated at a.m/ft^2 values a bit higher or lower than 730 a.m/ft^2 (the best value is determined experimentally by the production operators).

The plating-distribution results reported in Table-1 for each of the equipment/process combinations include the associated amp.minute/square-foot value. Our observation has been that the distribution ratios I:W and SH:W behave approximately as constants as the a.m/ft^2 of the system is varied. On the other hand we see W, H and I vary linearly with changes in a.m/ft^2. Figure-16 shows how W varies as a function of current density as the a.m/ft^2 is held constant at two typical levels. The decline in W with increasing current density seems consistent with a model for deposition in the plated-through holes that sees ion diffusion (under the influence of a potential gradient) and hydraulic factors as rate determining, ref. [3], [4], [5],

[6], [7]. Double passes of some part numbers through the copper plate process have doubled the W and H values while the I:W and SH:W values remained about the same. Our testing has found the impingement-agitated copper plating system performance to be most significantly influenced by (1) the proprietary chemistry, (2) the plating current-density, (3) the plating-cell design. An overview of the hydraulic and chemical factors that determine the rate and quality of the plating in a plated-through hole is presented in [3] and [4]. The more rigorous theoretical discussion of the physical/chemical system for electrodeposition in plated-through holes to be found in the literature is represented in references [5] through [8].

Our copper plating thickness and distribution is monitored by routine runs of the "BOGUS" test panels. Cross sections are taken from the aforementioned locations, the measurements are entered into computer data base, enabling routine control charting of each of the plate distribution parameters. Figures 17, 19 and 21 show typical copper distributions that were obtained from our system in the past. A variety of operational and design improvements have improved the system to give the performance shown by Figures 20, 21 and 22.

Another property of the copper electrodeposit that is routinely watched is its ductility (ie., its %-elongation). The ductility is useful in a cross-check scheme for trouble shooting. Ductility is routinely measured on copper foils that are deposited at the same time the "BOGUS" test boards are normally run. Measurement of %-elongation is performed with a bulge tester (Figure-23). The design and method of use for our bulge tester draws heavily from information published in [1]. Ductility values obtained with the bulge-tester have been compared with those from a conventional linear gage pull method to qualify the use of the former. This testing has shown the bulge method to give comparable absolute results and significantly better reproducability. The method is quickly and easily performed by a production operator.

We periodically audit the through-hole plating for resistance to thermal shock. The PTH specimens are subjected to multiple solder floats (1x, 2x, 3x and 4x), 500F, 15 seconds, allowing cooling to ambient between floats on the 2x, 3x and 4x specimens. The thermal shock specimens are cut from the routine test run panels (BOGUS). Cross sections of these specimens have shown us no evidence of barrel cracking or corner cracking. A more rigorous study [2] of the susceptability of the Boise-shop plated-through holes to thermal shock failure has been completed. The thermal cycle for this study was: 45-sec at -65C, 45-sec at ambient, 45-sec at 180C, 45-sec at ambient, repeated a minimum of 500x. This study concluded that (1) the plated-through holes will provide reliable performance throughout the thermal excursions expected in a typical product

lifetime (2) no failures could be expected at 6 thermal cycles. A follow on to this study [9] determined that it was 90% probable that the Boise system plating would see no more than 40 ppm failure when subjected to this kind of thermal cycling.

Our testing has so far shown that modifications of a given plating bath chemistry offer minor opportunities for improved plating characteristics (eg., distribution). We have seen, on the other hand, that a change in the proprietary chemistry can result in major improvement in the copper distribution. A comparison of the distribution parameters for conditions 1 and 6 in Table-1 illustrates this. Modifications of the impingement angle for the injection spargers has made little difference in the copper-plate distribution; on the other hand we have seen that increased tendency for plating degradation (burning) can occur if the spargers are angled improperly.

Our experience indicates that there are seven primary factors involved in the routine, consistent, quality operation of this process (and of the complete conveyorized system).

1. Integrity of process chemistry.
2. Integrity of rectifier system.
3. Proper plating-current settings for individual part numbers.
4. Integrity of plating cell maintenance.
5. Integrity of plating rack maintenance.
6. Integrity of pumping and sparging system maintenance.
7. Procedural discipline in operation of the system.

We credit progress in each of these areas for the improved performance represented between Figures 17, 19, 21 and Figures 18, 20, 22. Although it is beyond the scope of this report to to comment exhaustively on each of these factors, we will touch on some important highlights. Our shop experience has demonstrated that the first key to practical success with this system is maintenance: of the plating cell, of the rectification system, of the anodes, of the process chemistry, of the racks, etc. The second key is the "ownership" of the process by trained operators. Bringing this system from start-up status to a status of routine successful operation required establishment of the "maintenance" and the "ownership". As we tightened up on operational factors it became progressively easier to identify and correct design weaknesses in the system.

Our experience with the rectifier-control system exemplifies this. During the period represented by Figures 17, 19 and 21 we experienced chronic inconsistencies in the plating results for different runs, at different times, for any given part number. Our operational and maintenance improvements were not correcting the problem of thin plating one time and thick plating another. To address this we set up data aquisition to report the plating current measured for each of the panels in a production lot as

it presented itself serially to each of the copper rectifiers. The data, presented in histograph format (Figure-24), showed the rectifier control to be very erratic. Electronic-hardware and control-program improvements were worked out, bringing us to the more accurate rectifier control represented by Figure-25 (typical data from one of our routine test lots). Now when a routine test run gives a histograph which is degraded in the direction of Figure-24 this invariably results in the discovery of a maintenance problem (eg., rectifier control malfunction, or inferior rack maintenance).

Panel loss in the plating cells was a serious problem until improvements in the panel-guidance rail system were made. Improvements in the synchronization of the roller-seal speed to the conveyor speed also helped solve this problem. Rack maintenance is a continuing challenge; inconsistent plating from one panel to the next is usually a symptom of poor rack maintenance. Measures to deal with this issue have included: an in-line rack performance monitoring system, a rigorous cleaning and parts replacement program, a rack reconstruction and maintenance area. "Burned" plating was a chronic problem from time to time. This has been largely solved by: anode clamping, improved sparger system maintenance, improved maintenance of the plating chemistry, improved rack maintenance. By and large scratching of the panels (and plating resist) has not been a big problem, when it occurs it is usually readily traced and corrected.

The principle opportunity for improvement of the copper plating quality is to increase the plating thickness in the hole. The options for accomplishing this include some combination of (1) improvements in the performance of the proprietary chemistry, (2) retrofitting for improved design of the inner plating cell, (3) extention of the copper plating cell. Testing and characterization of this processing method is continuing. Challenges for the future include:

1. Improved copper distribution in high aspect ratio holes.
2. Improved copper distribution in small diameter holes (eg., .0018-inch and less).
3. Improved leveling of the copper plate in the holes.
4. Thorough characterization of the performance with finer lines and spaces (.008-inch and smaller).

The original expectations for this system have largely been realized: lower costs of operation, a 40% advantage in the capacity:floor space ratio over the conventional programmable hoist type of system, significant benefits for process monitoring and control offered by processing the panels serially on the conveyor, and panel to panel uniformity, to name a few. The Boise shop has recently completed a rigorous analysis of

capabilities, costs and benefits of plating system types for its next phase of growth. This analysis demonstrated that this technology should be considered seriously competitive with the conventional alternatives.

The system described herein is the result of many skilled and dedicated people in the Hewlett-Packard, Boise Div., Printed Circuit Shop, taking a part in the "ownership" of the system and resolving to make it work. Special recognition must go to Jim Jensen, Jim Luginbill, Eileen Winterrowd, Tom Browning and Lee Glover for their key roles in helping to bring it all together.

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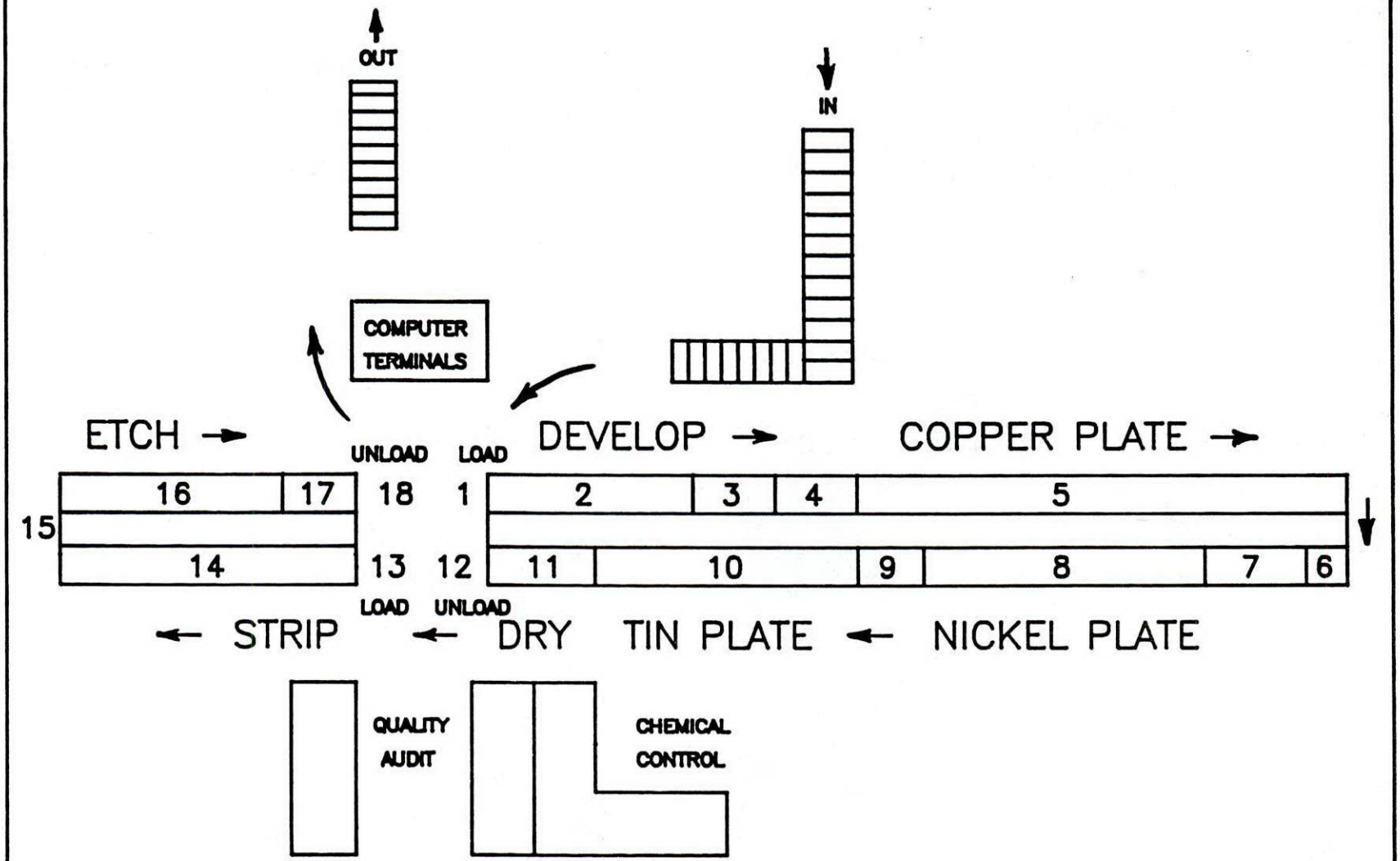
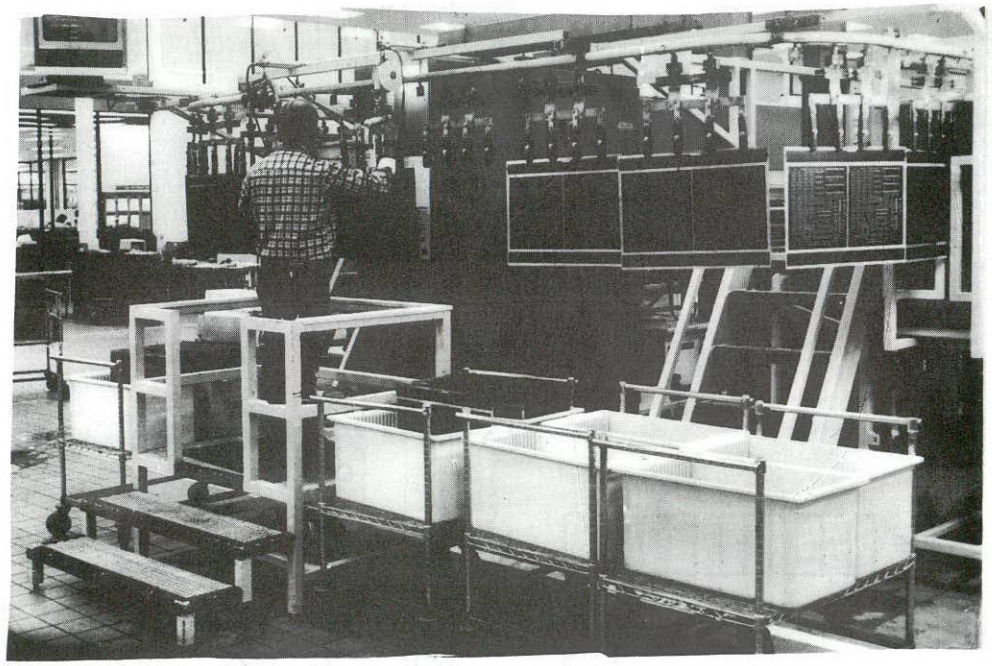
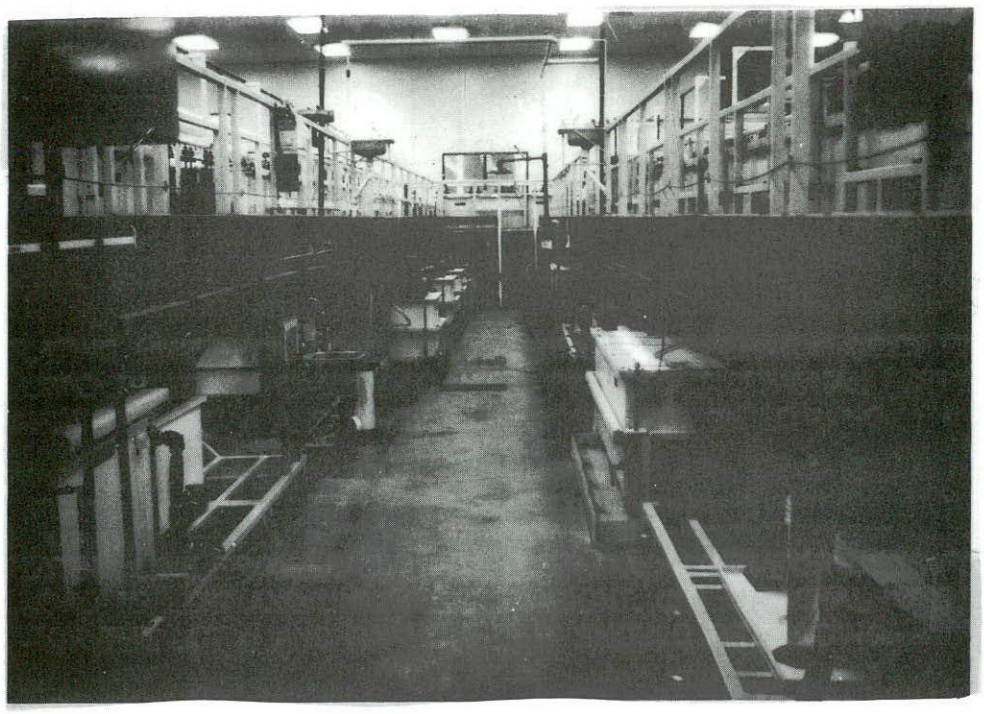
FIGURE–1: PLATE/STRIP/ETCH WORK CENTER



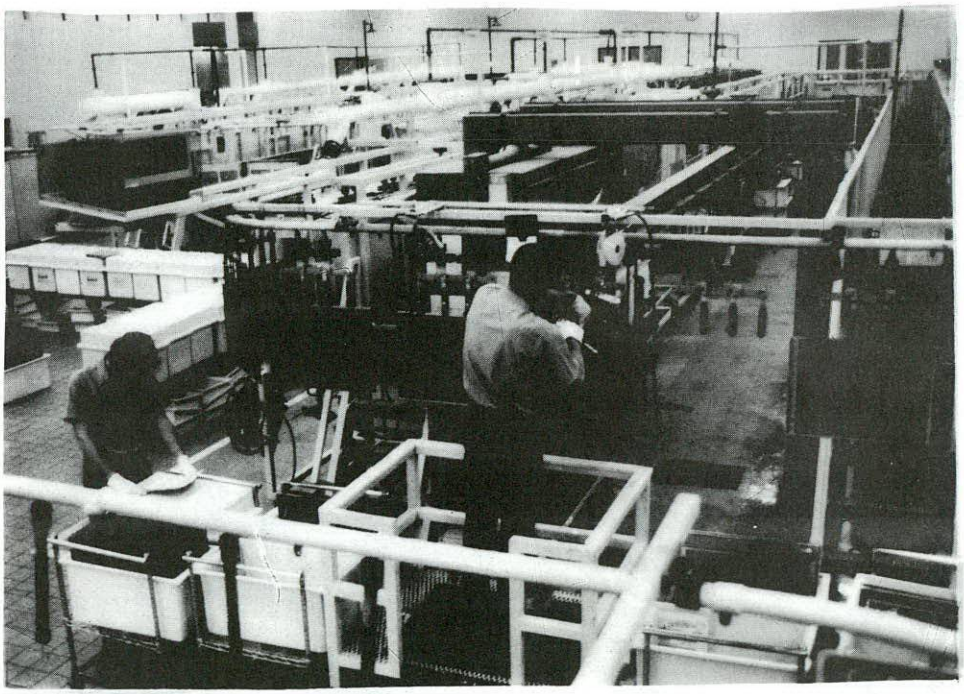
FIGURE–2: PLATING LINE FROM LOAD/UNLOAD STATION. OPERATOR USES PNEUMATIC WRENCH TO LOAD TO LEFT AND UNLOAD FROM RIGHT. CRT TERMINAL (UPPER RIGHT) TELLS OPERATOR THE LOT # AND PANEL # THAT SHOULD BE LOADING.



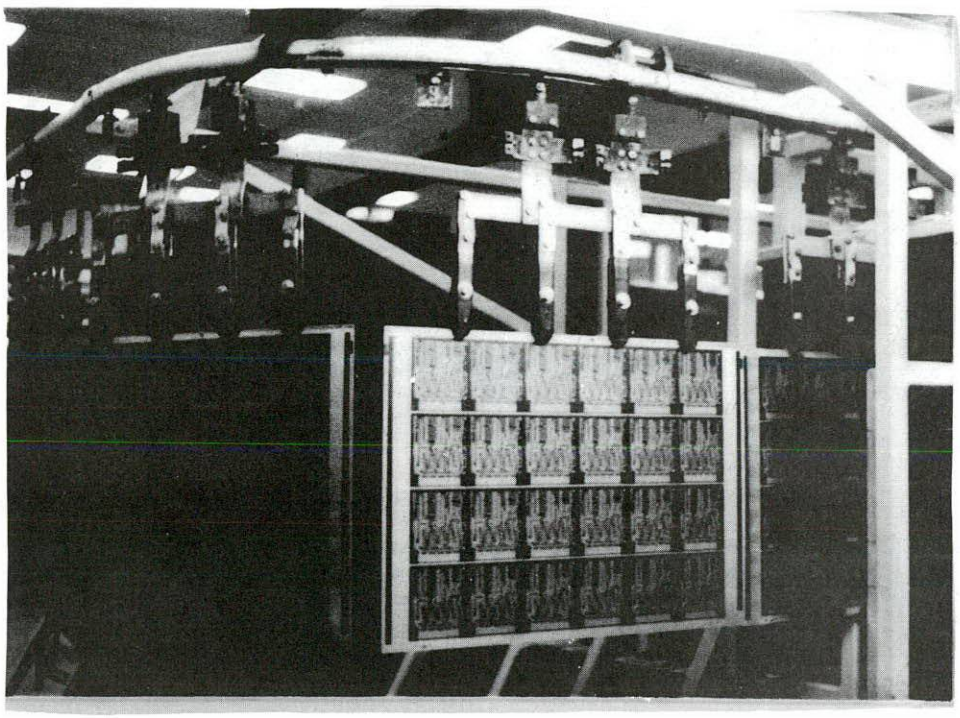
FIGURE–3: PLATING–LINE VIEW DOWN CENTER AISLE. CATWALK GIVES TOP ACCESS TO UPPER (PROCESS) TANKS AND CONVEYOR.



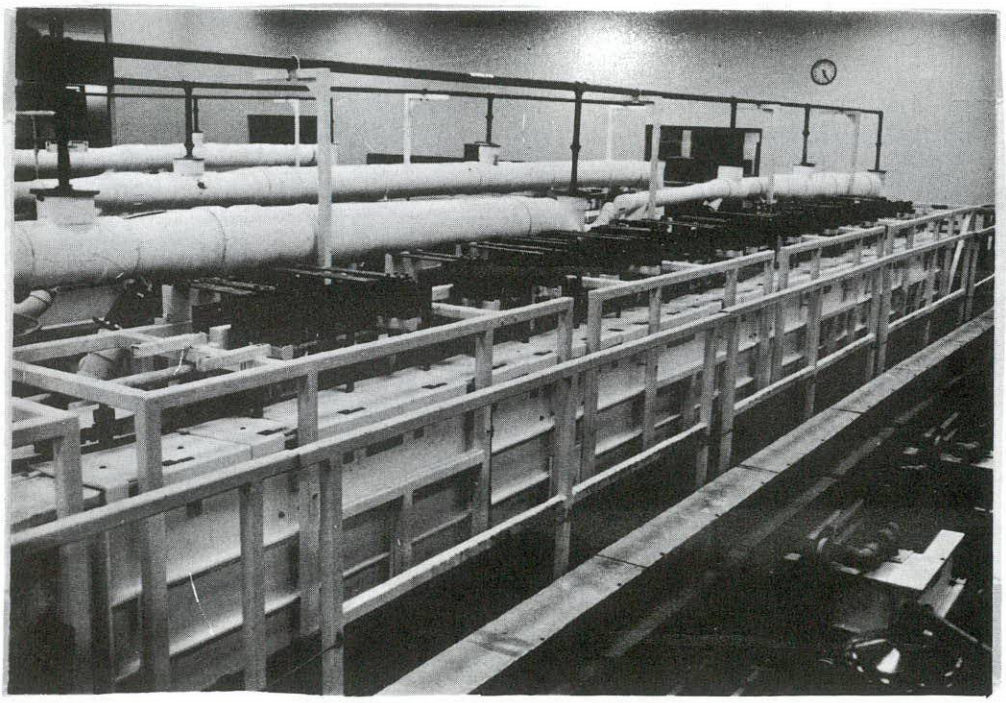
FIGURE–4: PLATING LINE, VIEW FROM CATWALK OF STRIP/ETCH LINE. INFRARED SENSORS AT OPENING OF FIRST TANK COUNTS RACKS AND PANELS TO SYNC CONVEYOR WITH RECTIFIERS.



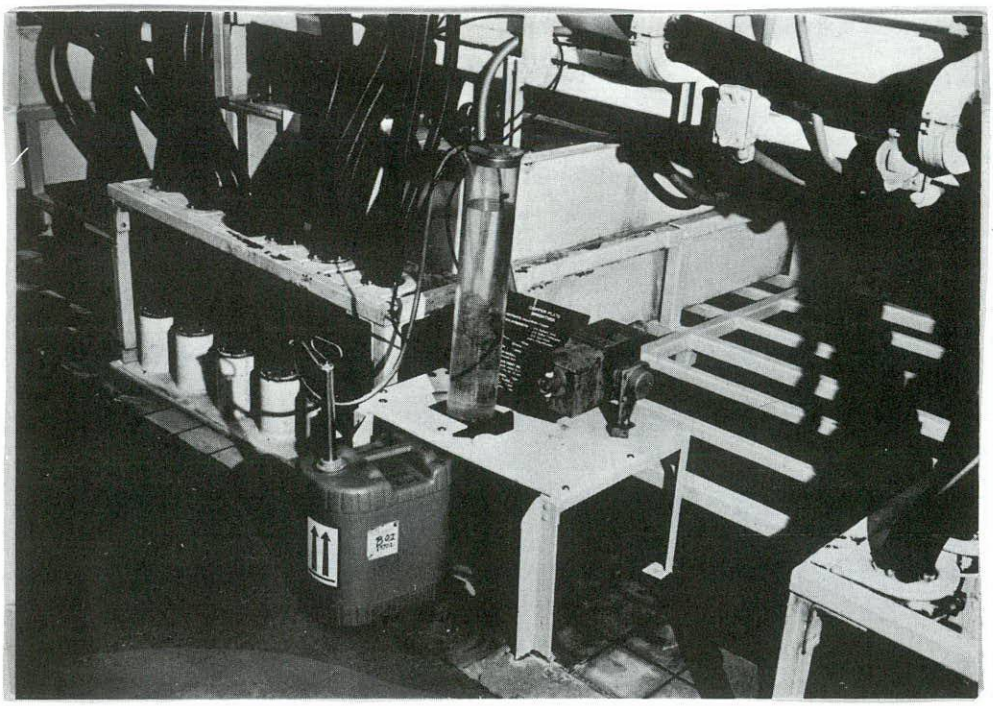
FIGURE–5: PANELS EMERGE FROM DRIER WITH COPPER, NICKEL AND TIN PLATE. NOTE RACK DESIGN.



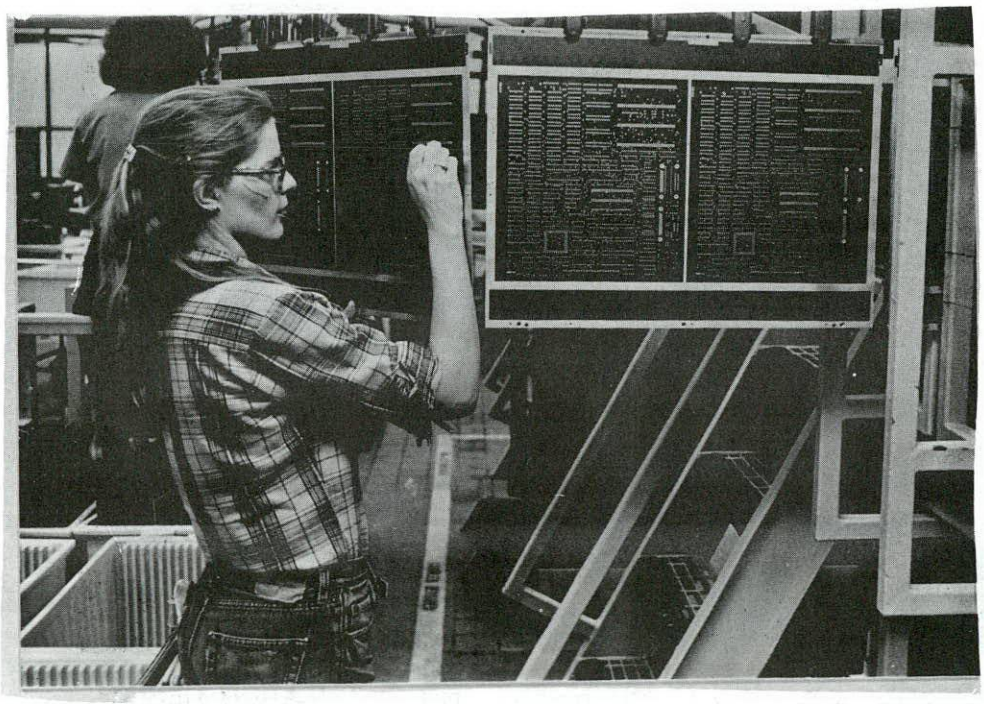
FIGURE–6: COPPER PLATING SECTION IS 32 FEET LONG, PROVIDES 26–FOOT LONG PLATING CELL. ANODE BUSSING IS SEEN (SHORT SECTIONS ALONG TOP OF EQUIPMENT). THE CATHODE BUSS RUNS BENEATH THE CONVEYOR.



FIGURE–7: BRIGHTNER ADDITIONS ARE MADE AUTOMATICALLY, A FUNCTION OF THE COMPUTER PROGRAM THAT PROVIDES REAL–TIME CONTROL OF THE RECTIFIERS.



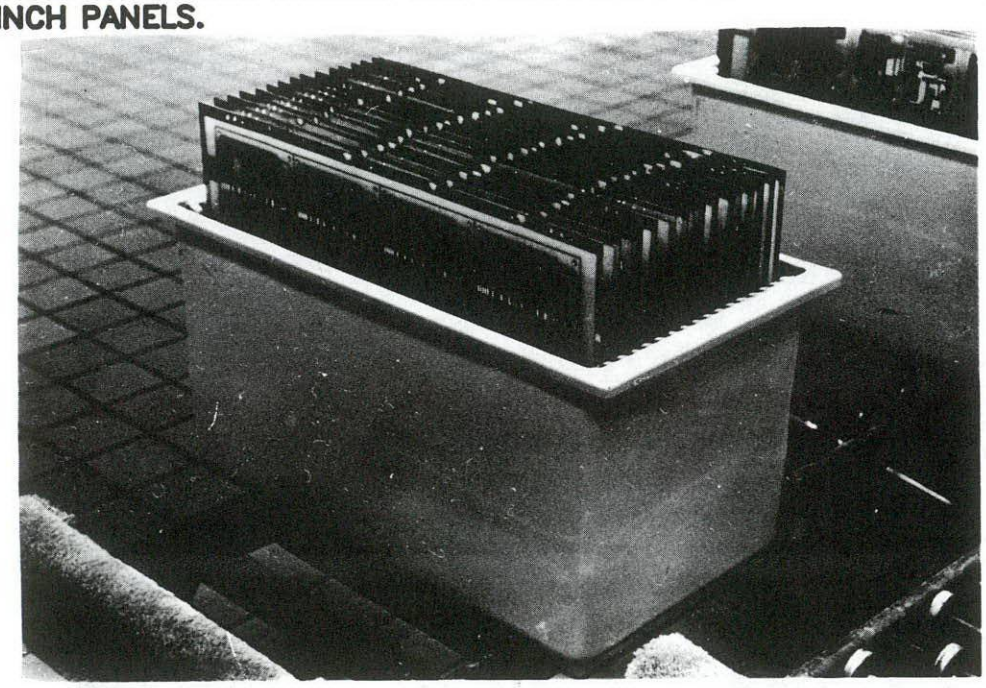
FIGURE–8: THE PLATING QUALITY IS ROUTINELY AUDITED FOR FINISHED HOLE SIZE, PLATING THICKNESS, TRACE HEIGHT, IMAGE–EDGE QUALITY, SCRATCHES, ETC.



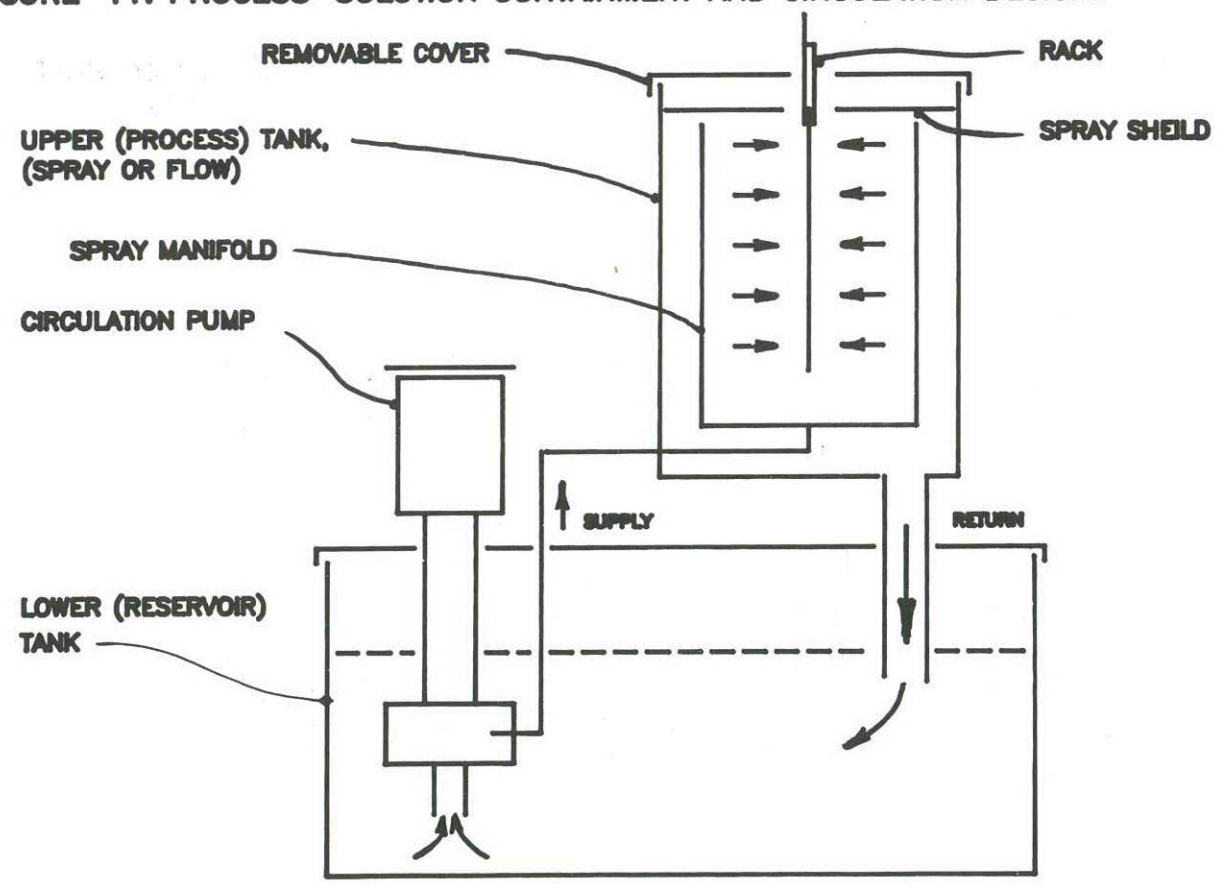
FIGURE–9: METALLURGICAL CROSS–SECTIONS TO MONITOR QUALITY OF THROUGH–HOLE PLATING IS ROUTINE. PLATING THICKNESS IS MEASURED AND CONTROL CHARTED.



FIGURE–10: WORK LOTS MOVE TO AND FROM THE PLATE/STRIP/ETCH AREA IN MOLDED PLASTIC TOTES. EACH TOTE CARRIES ONE PRODUCTION ORDER OF SIXTEEN (16) 18 X 24–INCH PANELS.



FIGURE–11: PROCESS–SOLUTION CONTAINMENT AND CIRCULATION DESIGN.



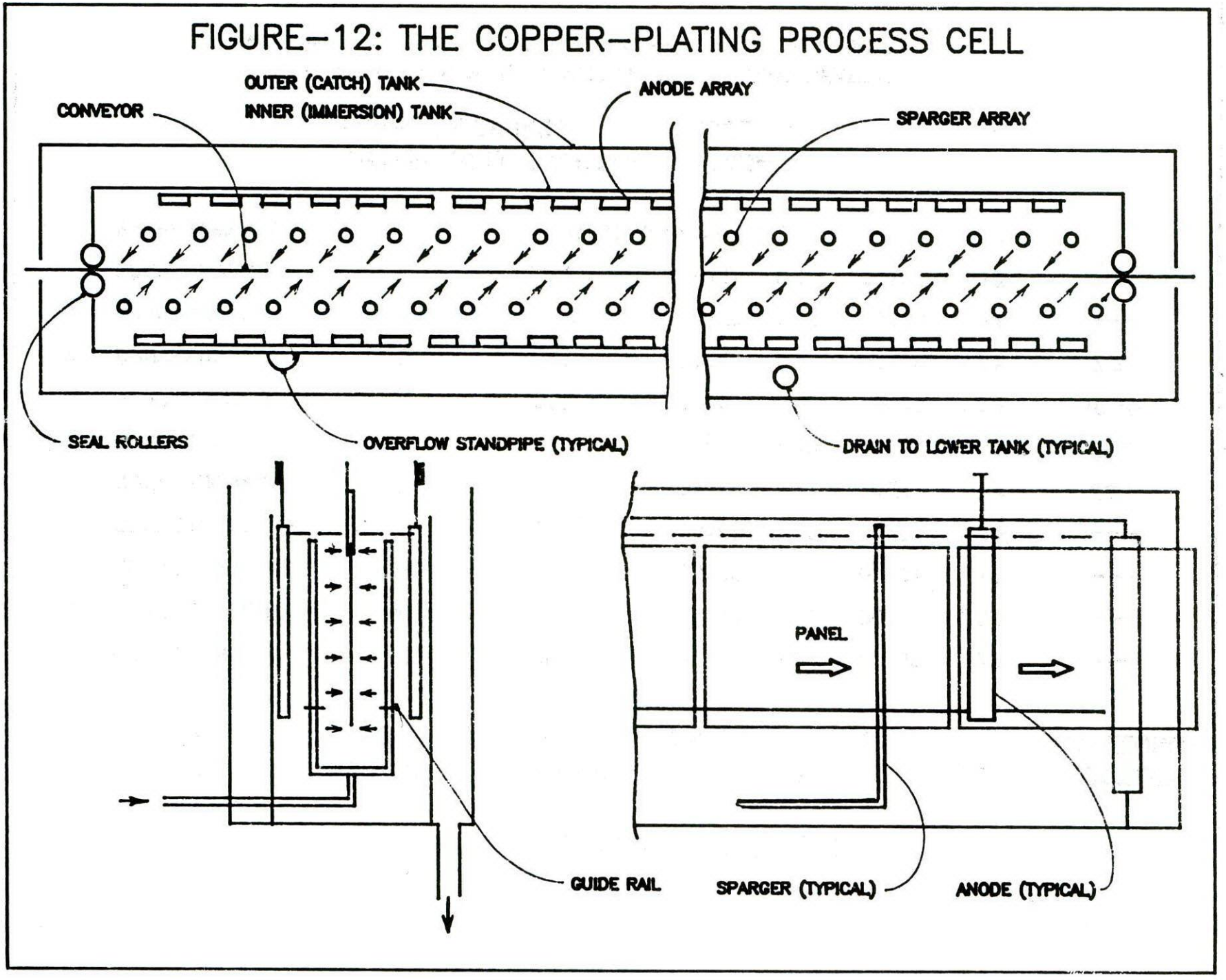
TABLE–1: PLATING CHARACTERISTICS DATA FROM SEVERAL EQUIPMENT/CHEMISTRY SYSTEMS

SYS	EQUIPMENT TYPE	CHEMISTRY TYPE	AMP*MIN / SQ–FT	W (INCH)	I:W	H (INCH)	SH:W	DUCTILITY (%–ELONG)
1	IMPINGEMENT, A	A	684	.00087	5.30	.00158	2.23	---
2	IMPINGEMENT, B	A	715	.00094	2.86	.00127	1.56	---
3	CONVENTIONAL, C	B	1715	.00120	1.77	.00135	1.19	---
4	CONVENTIONAL, C	B	2360	.00168	2.48	.00204	1.32	---
5	CONVENTIONAL, D	C	1280	.00226	1.77	.00249	1.17	5.82
* 6	IMPINGEMENT, A	D	730	.00084	2.46	.00112	1.52	7.28
7	IMPINGEMENT, B	D	900	.00127	2.14	.00142	1.18	10.19
8	CONVENTIONAL, C	E	1750	.00168	1.71	.00179	1.11	7.25
9	IMPINGEMENT, E	E	1350	.00158	2.40	.00185	1.24	---
10	CONVENTIONAL, F	F	1105	.00115	2.80	.00126	1.15	---
** 11	IMPINGEMENT, A	E	(TESTING IN PROGRESS)					

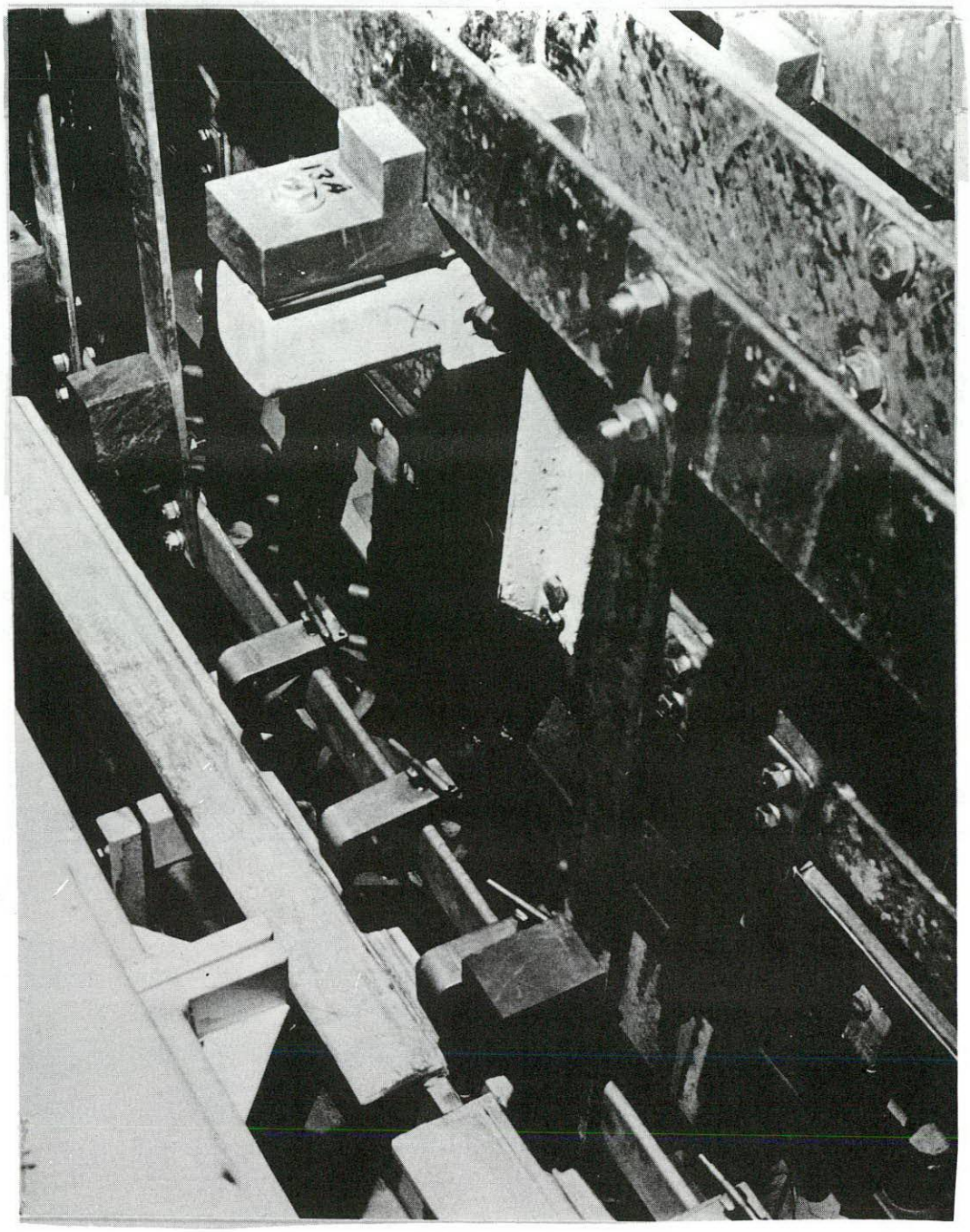
DRILLED HOLE DIAMETER .043–IN
BOARD THICKNESS .062–IN

* BOISE SHOP PRESENT EQUIPMENT/PROCESS CONFIGURATION
** BOISE SHOP CANDIDATE EQUIPMENT/PROCESS CONFIGURATION

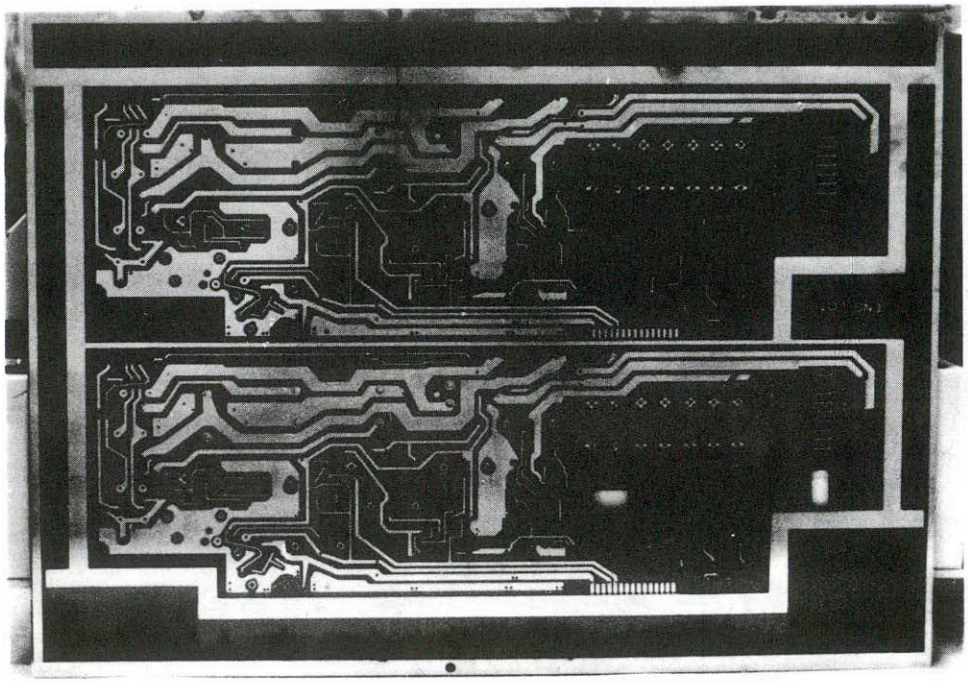
FIGURE–12: THE COPPER–PLATING PROCESS CELL



FIGURE–13: COPPER CELL SPARGERS AND ANODES AS SEEN LOOKING INTO THE TOP OF THE PLATING CELL.



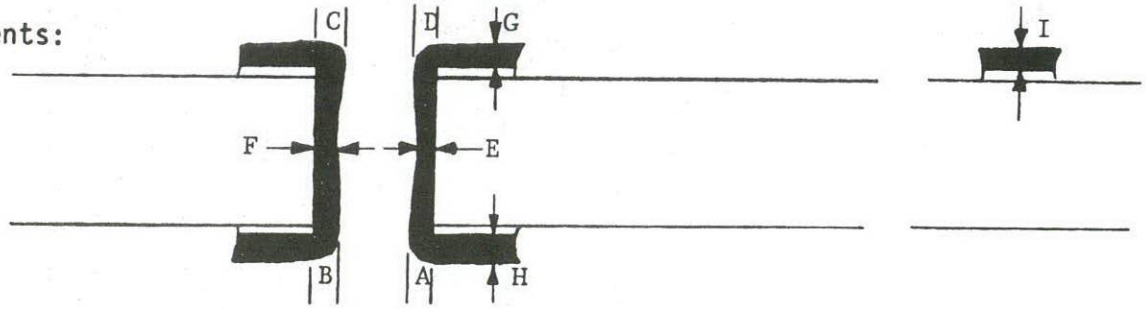
FIGURE–14: TEST IMAGE FOR CHARACTERIZING THE PLATING DISTRIBUTION



FIGURE–15: PLATING DISTRIBUTION MEASUREMENTS

Board Parameters: Board Thickness = .062"
Drilled Hole Diameter = .043"

Measurements:



Board Cross-section

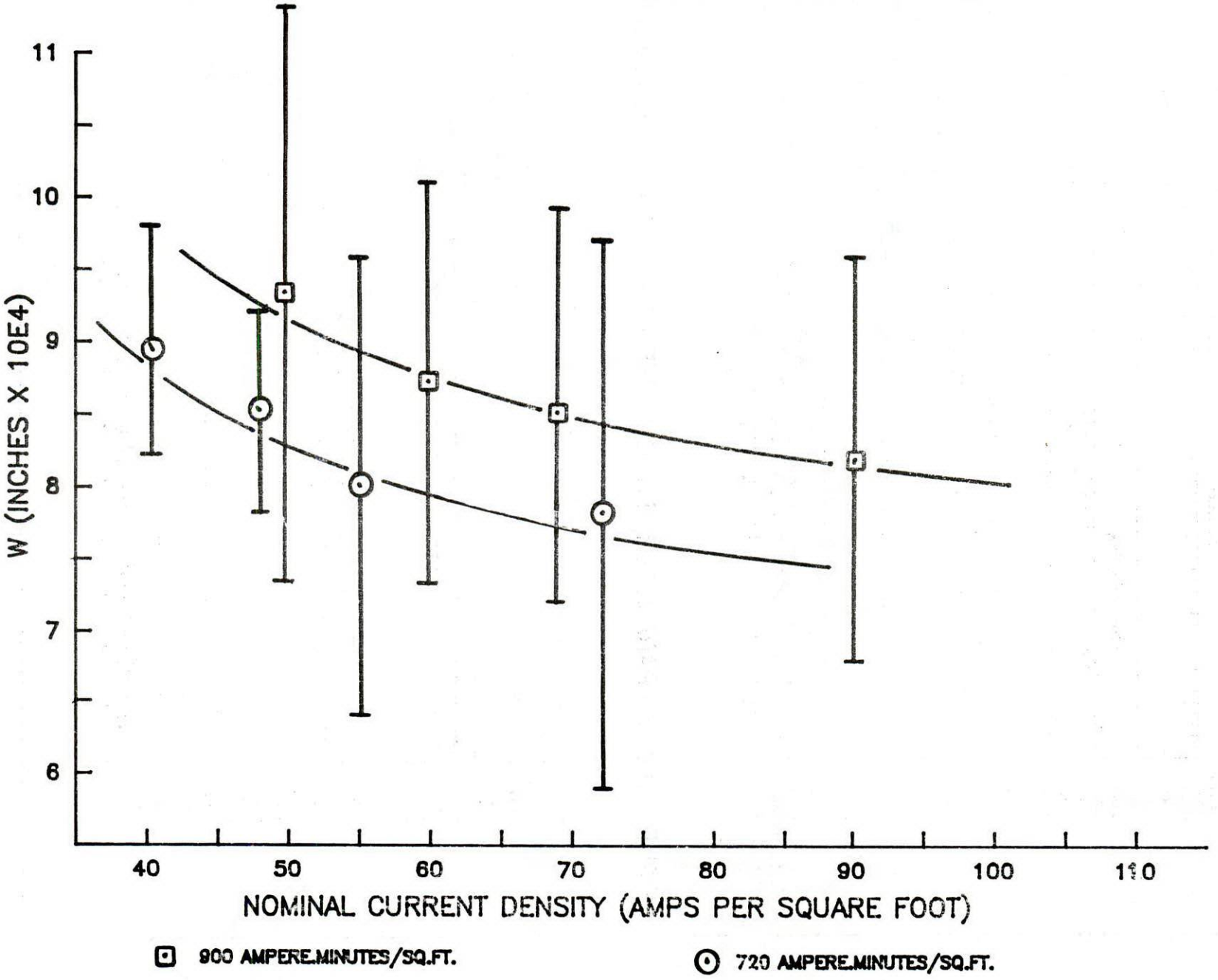
$$\frac{A + B + C + D}{4} = \overline{sh}$$

$$\frac{A + B + C + D + E + F}{6} = \overline{h}$$

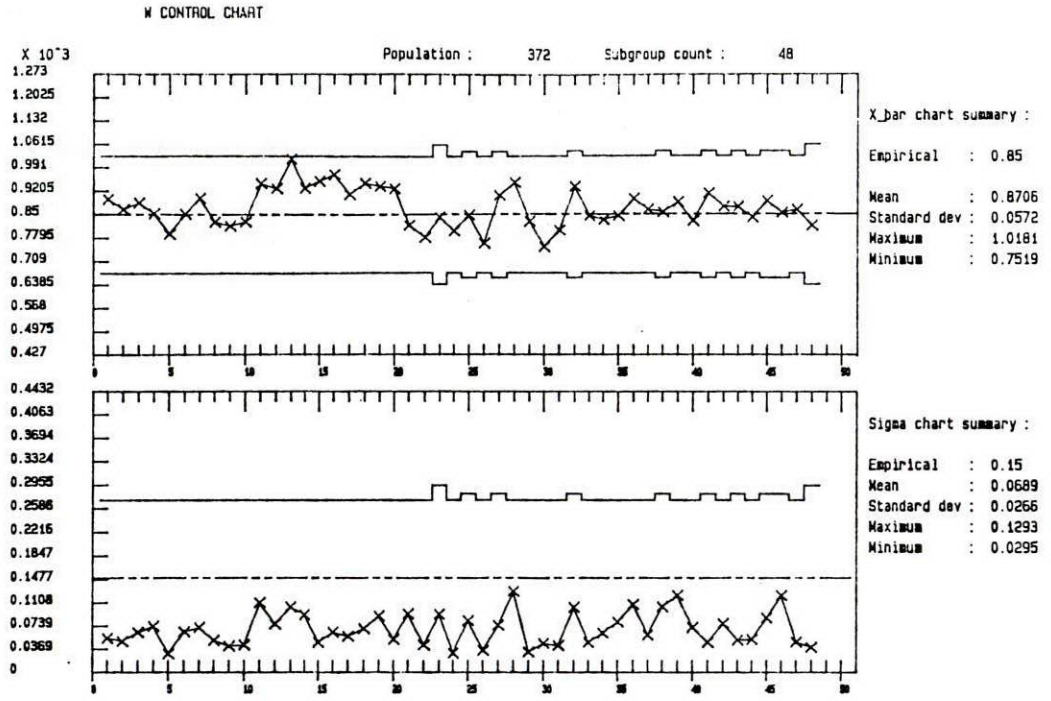
$$\frac{E + F}{2} = \overline{w}$$

$$\frac{G + H}{2} = \overline{h}$$

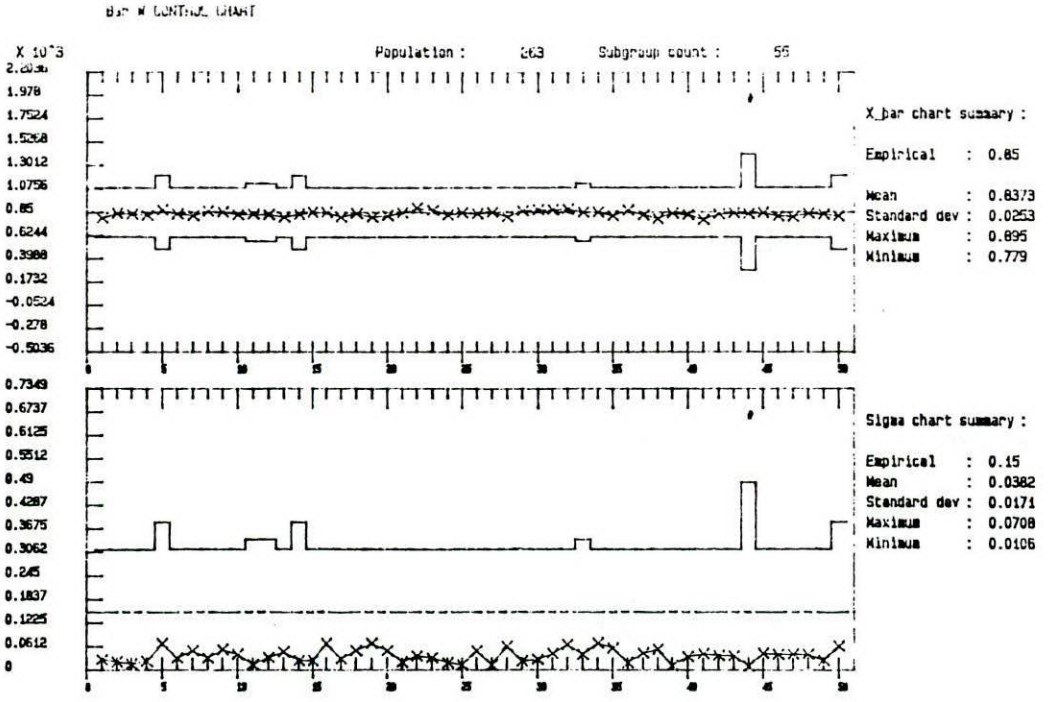
FIGURE–16: W AS A FUNCTION OF PLATING CURRENT



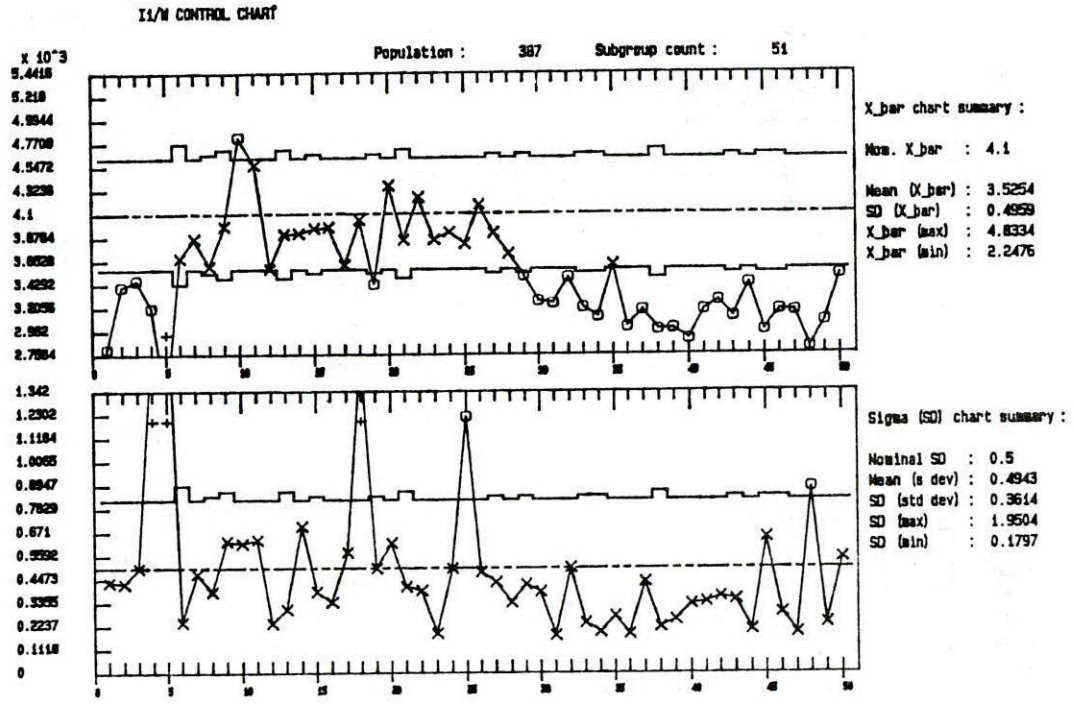
FIGURE–17: W–PARAMETER, TYPICAL RESULTS BEFORE IMPROVEMENTS



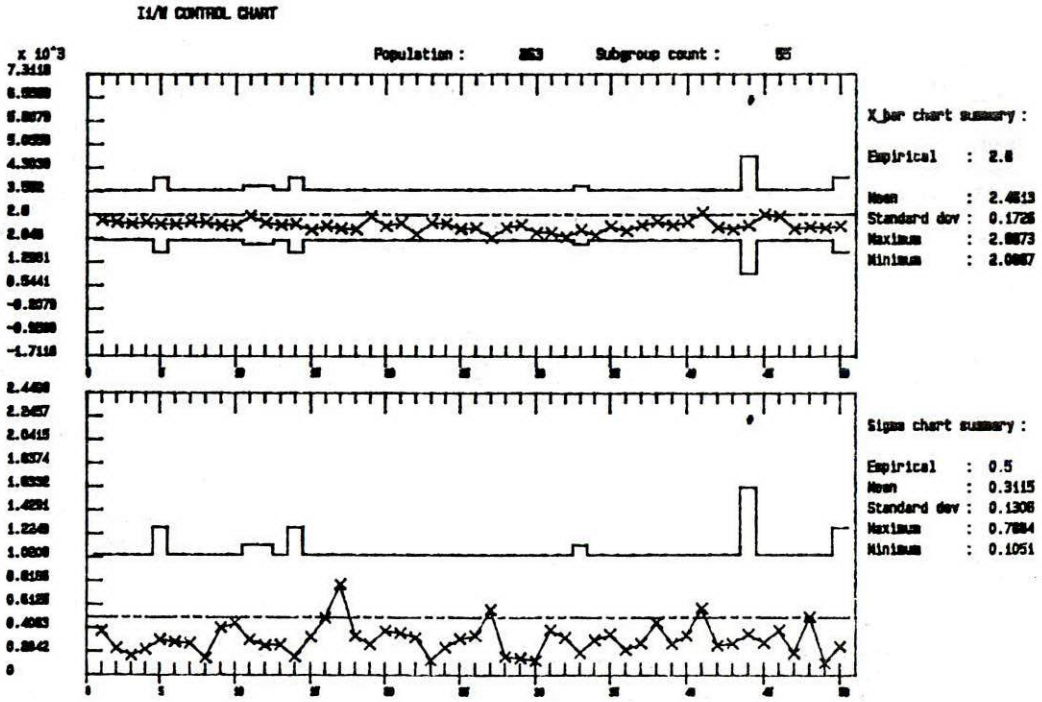
FIGURE–18: W–PARAMETER, TYPICAL RESULTS AFTER IMPROVEMENTS



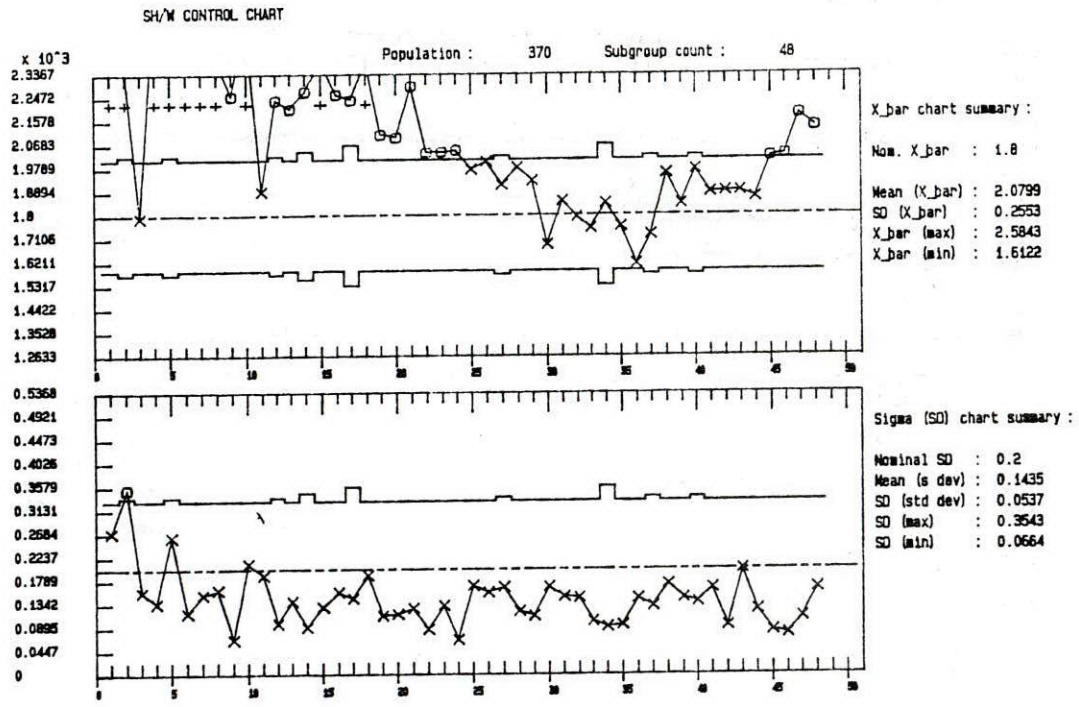
FIGURE–19: I:W RATIO, TYPICAL RESULTS BEFORE IMPROVEMENTS



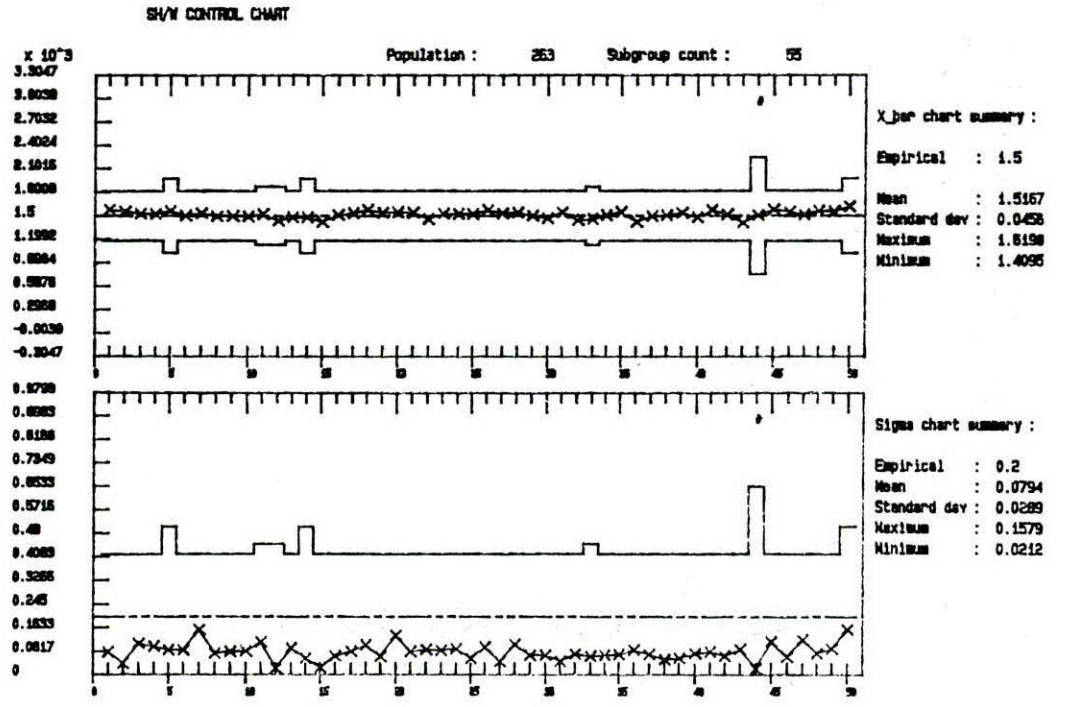
FIGURE–20: I:W RATIO, TYPICAL RESULTS AFTER IMPROVEMENTS



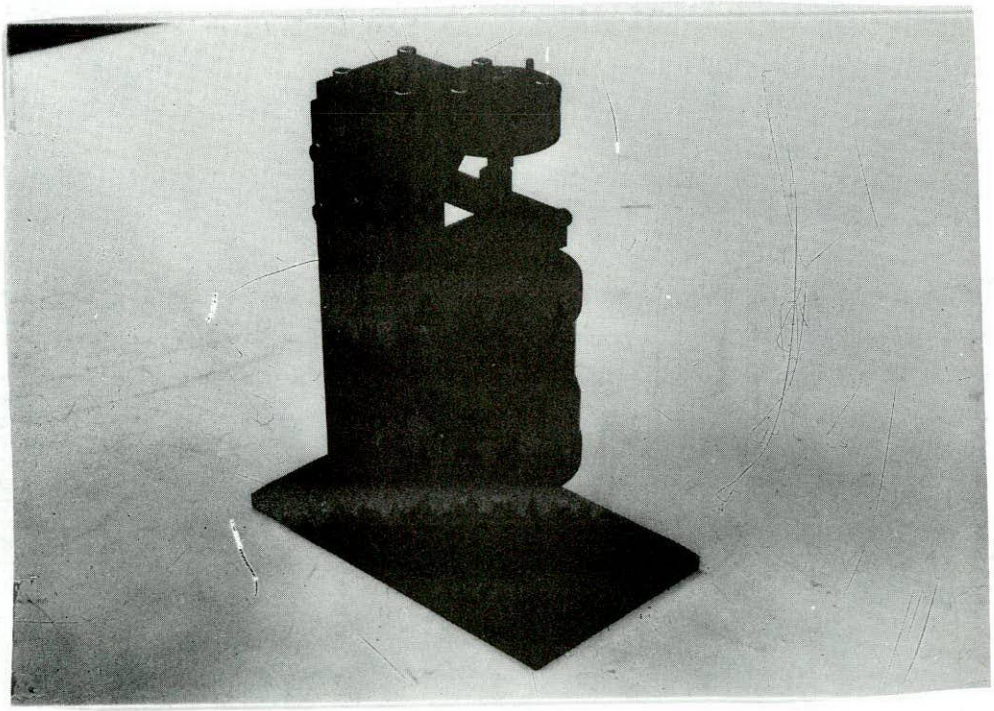
FIGURE–21: SH:W RATIO, TYPICAL RESULTS BEFORE IMPROVEMENTS



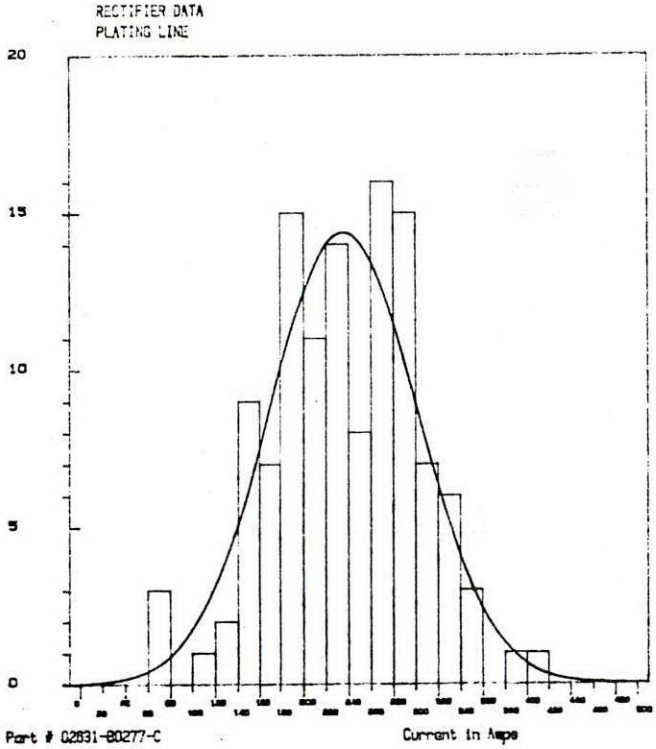
FIGURE–22: SH:W RATIO, TYPICAL RESULTS AFTER IMPROVEMENTS



FIGURE–23: THE BULGE TESTER IS USED ROUTINELY TO AUDIT DUCTILILTY OF THE COPPER PLATING.



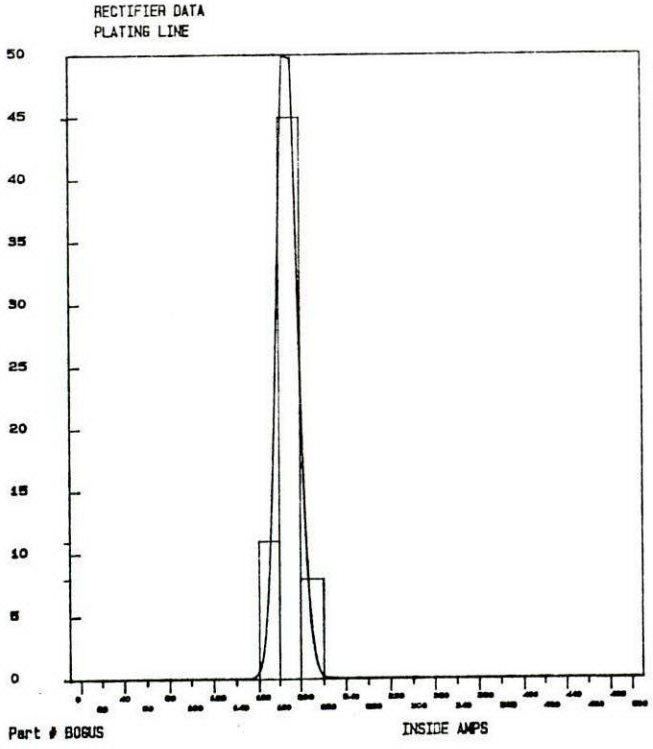
FIGURE–24: RECTIFIER PERFORMANCE, BEFORE IMPROVEMENTS



N	: 119	Mean	: 235.807
In scale	: 119	Std Dev	: 88.0575
Out scale	: 0	Cells	: 25
		Width	: 20

#	Mid_point	Count	Rel Freq	Cum Freq
1	10	0	0	0
2	30	0	0	0
3	50	0	0	0
4	70	3	0.0252	0.0252
5	90	0	0	0.0252
6	110	1	0.0084	0.0336
7	130	2	0.0168	0.0504
8	150	9	0.0756	0.1261
9	170	7	0.0588	0.1849
10	190	15	0.1261	0.3109
11	210	11	0.0924	0.4034
12	230	14	0.1176	0.521
13	250	8	0.0672	0.5882
14	270	16	0.1345	0.7227
15	290	15	0.1261	0.8487
16	310	7	0.0588	0.9076
17	330	6	0.0504	0.958
18	350	3	0.0252	0.9832
19	370	0	0	0.9832
20	390	1	0.0084	0.9916
21	410	1	0.0084	1
22	430	0	0	1
23	450	0	0	1
24	470	0	0	1
25	490	0	0	1

FIGURE–25: RECTIFIER PERFORMANCE, AFTER IMPROVEMENTS



N	: 64	Mean	: 188.5609
In scale	: 64	Std Dev	: 9.461
Out scale	: 0	Cells	: 25
		Width	: 20

#	Mid_point	Count	Rel Freq	Cum Freq
1	10	0	0	0
2	30	0	0	0
3	50	0	0	0
4	70	0	0	0
5	90	0	0	0
6	110	0	0	0
7	130	0	0	0
8	150	0	0	0
9	170	11	0.1719	0.1719
10	190	45	0.7031	0.875
11	210	8	0.125	1
12	230	0	0	1
13	250	0	0	1
14	270	0	0	1
15	290	0	0	1
16	310	0	0	1
17	330	0	0	1
18	350	0	0	1
19	370	0	0	1
20	390	0	0	1
21	410	0	0	1
22	430	0	0	1
23	450	0	0	1
24	470	0	0	1
25	490	0	0	1

I-2

Electronics I
Session I

A Fully Automated Resource Recovery Approach to Chemical Waste Management in the Printed Circuit Board and Metal Finishing Industries

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Bruce Cardoza and George Schore,
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44 Fasken Drive
Rexdale, Ontario, Canada

A Fully Automated Resource Recovery Approach to Chemical Waste Management in the Printed Circuit Board and Metal Finishing Industries

Dr.Bernard Fleet, Dr. Colin Small, Bruce Cardoza and George Schore,
SCADA Systems Inc. 44 Fasken Drive, Rexdale, Ontario, Canada

Introduction

Increasing environmental pressures, along with the decreasing availability of chemical landfills and the ever-escalating cost of disposal, is causing many printed circuit board manufacturers and metal finishers to seriously re-evaluate their waste disposal options. At one time resource recovery technology was an expensive alternative to conventional chemical treatment but the above pressures coupled with increasing liability insurance costs and the potential threat of litigation from landfill pollution incidents is making it ever more necessary.

The situation in the U.S is even more critical than in most other countries due to the heavy reliance on ground waters for most urban water supplies. Asso, the increasing number of environmental nightmares have fuelled local community pressures for more rigorous environmental legislation and especially more serious enforcement. There is also a growing awareness at all levels of industry of their social image and corporate responsibility. On a practical level, with a generally healthy economy there is no longer the possibility of delaying waste management investments on anti-inflationary grounds.

All of these factors contribute to the current environmental regulatory climate in the U.S , which is unequivocal in its view that a zero-discharge resource recover approach provides the most realistic solution to industry's hazardous waste management needs. The present paper aims to support this contention by describing the design and performance of an existing automated, zero-discharge printed circuit board waste treatment facility along with an evaluation of the relative technical, economic and less tangible "social" costs of the two approaches. It should perhaps be pointed out that that a large proportion of manufacturing industries, particularly the chemical process industry already apply zero-discharge closed loop treatment processes to handle a substantial part of their waste management problems. The printed circuit board and metal finishing industries also apply the concept, for example in precious metal recovery; the only significant change is for these industries to adopt this approach to treat their total chemical waste management problems.

Recovery Technologies

A wide variety of resource recovery technologies have found use in the printed circuit and metal finishing industries, including evaporative recovery, various membrane technologies,electrodialysis, electrophoresis, ultrafiltration, reverse osmosis etc, adsorption techniques using beds of carbon, zeolites or diatomaceous earth, etc, ion-exchange technologies and a range of electrolytic recovery techniques.

The solution of industrial chemical waste management problems in general requires a broad spectrum of technologies to be incorporated into the final turnkey package including both the chemical process and the contol technology. The requirements of the metal finishing and particularly the printed circuit board industries are, however, usually fairly well defined, and in the authors' experience can usually be solved by a combination of ion-exchange and electrolytic recovery processes.

A key feature of modern waste reduction technologies is their requirement for effective process control. The new microprocessor based distributed control systems of the SCADA * type now makes these requirements economically feasible.

The SCADA Solution

For the plant manager faced with the need to upgrade an existing waste treatment system to meet increasing demands or to design a system for a new plant, the following areas need to be addressed.

1. A plant assessment study should first be carried out to identify and quantify all of the sources of toxic wastes. From this study some genral process changes may be recommended to monimise the levels of treatable waste. These might for example include the use of flow and conductivity controls on running rinses,

2. Process modification or substitution could be considered to adopt the use of less toxic or more easily treated process chemicals. These could include the use of sulphuric-peroxide etch to replace ferric chloride or cupric chloride etches, the substitution of chelated with non-chelated/complexed materials, etc.

3. The selection of the overall waste management approach, either a zero-discharge, resource recovery route or a conventional chemical "sludge" process. Clearly these two approaches represent extremes and in some instances a compromise may be appropriate.

The goals for the design of the SCADA System design were firstly to eliminate the generation of disposable regulated waste, to recover all of the metals for sale, reuse, or safe disposal, to regenerate some process chemicals and especially to allow for recycling of more than 95% of process water.

* Supervisory Control and Data Acquisition

The SCADA Solution

The basic approach to the design of the waste treatment system for a printed circuit plant (Figure 1), is based on segregation of waste streams into acid copper, chelated copper, tin/lead and nickel. Ion-exchange is used for primary metal capture from process rinses using a cationic resin for acid copper, tin/lead, and nickelstreams, and an anionic resin for chelated or complexed metal bearing streams. An electrochemical recovery process is used to treat the ion-exchange eluates, and all other high level sources including the continuous treatment of etchant baths. A mixed-bed ion exchange process is also used for final demineralization.

The overall system is monitored and controlled by the SCADANET waste management controller. This system is a distributed control concept where a seies of microprocessor based remote stations handle the various segments of the treatment process. These include pH On/Off and PID control, conductivity, flow and level control, as well as a programmable logic controller which handles valve, pump and alarm actuation. Additional units include an amp-hour controller for chemical feed control and will eventually incorporate metal monitoring sytems for checking performance of treatment units and measurinf final effluent levels. Each of these units is connected via a simple network to the SCADANET supervisory controller which provides a simple menu-driven approach to overall control of the process.

SCADA has also developed a plating line hoist control system with a demand driven scheduler providing for operation of up to 30 separate schedules. This system can also provide for control of other process variables such as plating current density via rectifier control, chemical bath make-up control, temperature, rinse and level controls. The above SCADA systems will eventually provide a factory wide management tool for control ofpurchase orders, inventory, work-in-progress and waste management systems.

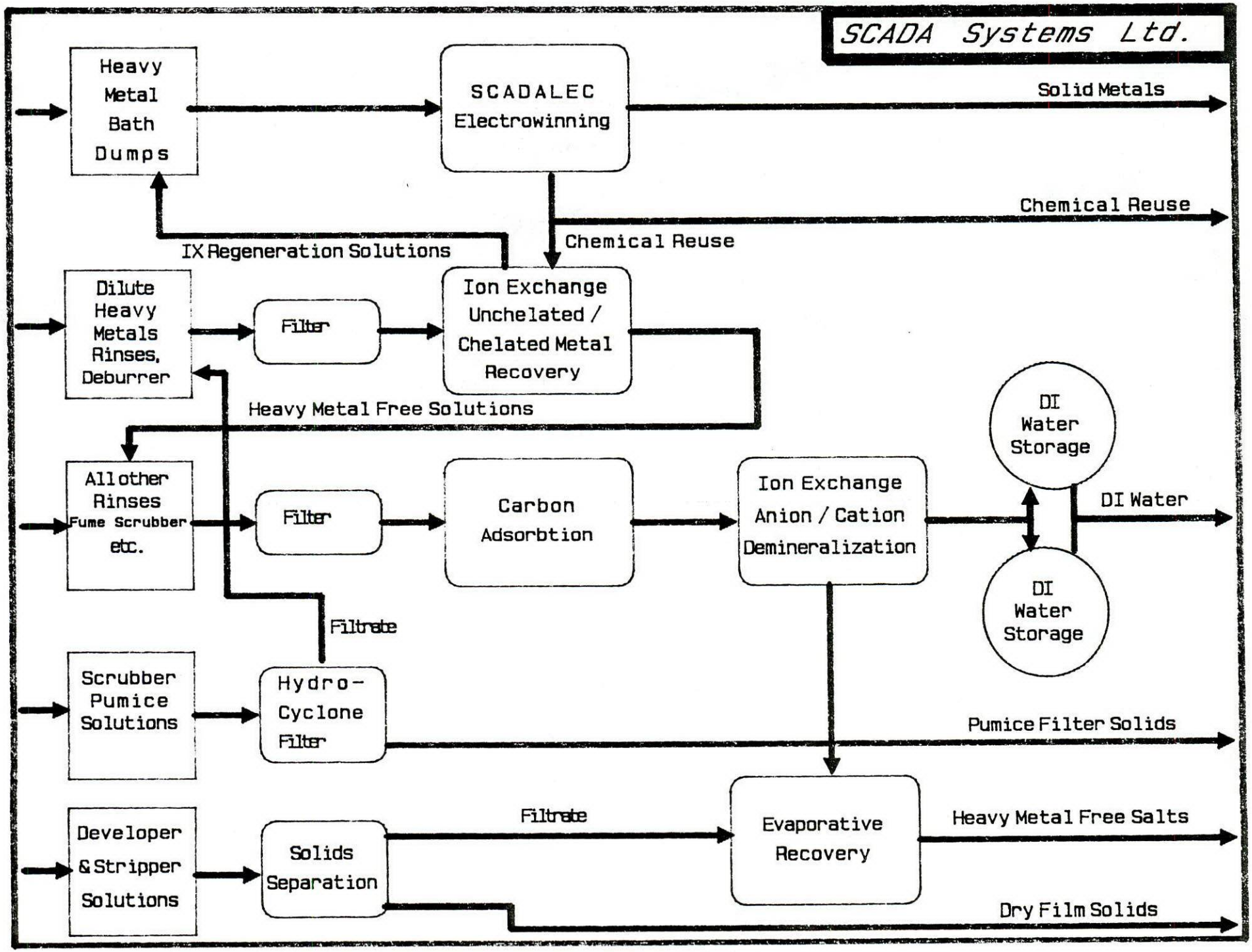
System Performance

The above system has now been operating for a little over six months and as performance and comparative cost data are still being collected; these will be presented in more detail at the meeting. Based on the design, installation and initial operating phases,however some general comparisons can be made between the zero-discharge and conventional chemical "sludge" routes. These are summarised in Table 1 below.

Zero-Discharge Resource Recovery	Conventional "Sludge" Treatment
Initial high capital cost (2 to 4 X Conventional)	Relatively low capital cost
No waste or sludge disposal	Ongoing, escalating cost of waste disposal, with decreasing landfill availability
Minimal treatment chemicals	Chemical treatment costs
High degreee of automation/ process control minimises labour costs	
Eliminates requirement to meet discharge regulations, submit manifests, etc.	Inability to treat all types of waste, especially chelated metals; susceptible to increasingly severe regulations
Reduced insurance costs, freedom from all risks associated with off-site disposal of wastes	Environmental impairment liability. Corporate liability for future landfill-related pollution incidents
Corporate image as an environmentally responsible company	Negative social impact of any pollution related publicity

Conclusions

While a detailed performance evaluation of the above system is still being carried out it is evident that on both environmental and technical grounds it represents a significant leap forward over conventional technology. Environmental pressures, based on groundwater quality concerns in most States will eventually eliminate landfill dumping as a disposal option. From a technical standpoint the adoption of zero-discharge closed loop technology in addition to its obvious environmental and insurance-related advantages, also provides full control over water quality in the plant, which should contribute positively to improved product quality and reliabilty.


SCADA Systems Ltd.
Heavy Metal Bath Dumps
SCADALEC Electrowinning
Solid Metals
Chemical Reuse
IX Regeneration Solutions
Chemical Reuse
Dilute Heavy Metals Rinses, Deburrer
Filter
Ion Exchange Unchelated / Chelated Metal Recovery
Heavy Metal Free Solutions
DI Water Storage
All other Rinses Fume Scrubber etc.
Filter
Carbon Adsorbtion
Ion Exchange Anion / Cation Demineralization
DI Water
DI Water Storage
Filtrate
Scrubber Pumice Solutions
Hydro-Cyclone Filter
Pumice Filter Solids
Developer & Stripper Solutions
Solids Separation
Filtrate
Evaporative Recovery
Heavy Metal Free Salts
Dry Film Solids

I-3

Electronics I
Session I

Uses of PVDF as a Cost Efficient Material For Fabrication Of Equipment Operating in Strongly Corrosive Environments Encountered In the Surface Treatment Industry

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USES OF PVDF* AS A COST EFFICIENT MATERIAL FOR FABRICATION OF EQUIPMENT OPERATING IN STRONGLY CORROSIVE ENVIRONMENTS ENCOUNTERED IN THE SURFACE TREATMENT INDUSTRY

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ABSTRACT

Polyvinylidene Fluoride, PVDF, is a thermoplastic material which has a range of very useful and interesting characteristics such as:

- resistance to corrosion, abrasion and aging
- good mechanical properties over a range of operating temperatures from -40 to 150°C (-40 to 302°F)
- excellent processability allowing easy fabrication of a wide variety of items

Because of these properties, PVDF is being used more frequently in the construction of chemical equipment such as: piping systems, pumps, heat exchangers, etching tanks and other items used in chemical processes like surface treatment.

* All references to physical properties, chemical resistance and performance of PVDF in this paper are for Solef® PVDF which is a product of Solvay & Cie, S.A. (Brussels, Belgium) Solef is a registered trademark of Solvay & Cie.

INTRODUCTION

For many years, thermoplastic materials such as PVC, CPVC and PP have been used in surface treatment equipment for piping systems, pumps, linings of etching or treatment tanks or solid constructions to handle corrosive chemicals. In the recent past, surface treatment processes, in order to improve both quality and efficiency have shown a trend to move to higher temperatures and to modify chemical compositions of the treatment baths. Often with these new conditions, those polymers formerly used reach their limits.

They lose their ability to perform satisfactorily due either to poor chemical resistance or to a lack of mechanical strength with chemical environments at elevated temperature. Therefore, PVDF due to its valuable combination of properties is being used more and more to improve and maintain the performance of materials used in such environments.

PROPERTIES OF PVDF

General Characteristics

PVDF has the general formula $(-CH_2-CF_2-)_n$. Compared with other traditional fluorinated polymers, it has exceptional rigidity and resistance to creep over the temperature range -40 to +150°C (-40 to +302°F). (Table 1 and Figure 1).

Since the polymer also has exceptional resistance to aging, these mechanical properties are demonstrated extremely well in experiments that show the burst resistance of pipes. In these tests, extruded tubes of PVDF have now been tested for up to 120,000 hours (February 86) continuously at 120°C (248°F) and under hoop stress of 9.5 MPa (1,378 psi) showing no trace of loss of burst resistance. Many polymers show a rapid deterioration of this property when exposed to the same conditions. (Figures 2 and 3).

The abrasion resistance of PVDF is far superior to that of PTFE, FEP or PFA, and is at a level comparable with that of the high performance polymers used in high abrasion applications - polyamide (PA) and ultra high molecular weight polyethylene (UHMW PE). (Table 2).

Also its chemical resistance (Tables 3 and 4) though lower than that of PTFE, FEP or PFA is such that it can be used over a wider range of highly corrosive applications when compared to other thermoplastics, metals and alloys conventionally used for the construction of corrosion-resistant equipment.

In addition to these properties, PVDF has a number of other characteristics:

- a high level of purity (the product contains no fillers, stabilizers or similar additives)
- a very low surface tension which makes the product very resistant

In addition to these properties, PVDF has a number of other characteristics:

- a high level of purity (the product contains no fillers, stabilizers or similar additives)
- a very low surface tension which makes the product very resistant to furring and scale deposits
- extremely easy to fabricate and weld
- good flame resistance (the product belongs to the M_1 group and is classed as a V_0 product according to UL 94/1975)
- non-toxicity: PVDF is FDA-approved

Because of these properties PVDF is suitable for applications requiring a material resistant to all types of corrosion phenomena and especially in those particular to the surface treatment industry.

Within its range of service temperatures, PVDF dual-laminate construction based on Fiber Reinforced Polyester (FRP) structure can compete advantageously with sophisticated alloys and metal such as stainless steel 316, HV 9, HV 904, alloys. Hastelloy C, Incoloy, Monel, Silver, Nickel, Titanium, Tantalum,...in applications where the medium concerned involves not only a risk of chemical attack and erosion by abrasion but also stringent requirements as regards the freedom from contamination of the product (Table 4).

From a strictly commercial point of view PVDF is an economic alternative of growing interest considering the price per unit of volume of the material which is used. This aspect is of particular importance these days in view of the constant rising prices of rare metals and engineering plastics, and their high specific gravities (Tables 5 and 6).

CHEMICAL RESISTANCE OF PVDF VERSUS CORROSIVE CHEMICALS INVOLVED IN SURFACE TREATMENT PROCESSES

PVDF has outstanding resistance even at high temperature to most organic and inorganic acids, oxidizing media, mixtures of both acids and oxidizing agents, aliphatic and aromatic hydrocarbons, alcohols and halogenated solvents. It is also resistant to halogens, (except fluorine) particularly bromine. It is degraded by fuming sulphuric acid, strongly basic amines, hot concentrated alkalis, and alkali metals.

It reveals poor resistance to stress cracking in caustic environment whether inorganic (weak and strong bases) or organic (basic amines).

It swells in strongly polar solvents such as acetone and ethyl acetate and is slightly soluble in aprotic solvents such as dimethylformamide, dimethylacetamide or dimethylsulphoxide.

In solid constructions where the PVDF wall is rather thick > 2 mm (0.078"), PVDF is perfectly suitable to handle the most frequently used chemicals in degreasing (Table 7), pickling, etching, and electroplating processing (Tables 8 and 9).

USES OF PVDF CONSTRUCTIONS IN SURFACE TREATMENT EQUIPMENT

Combining these chemical resistance characteristics with its intrinsic mechanical properties at high temperature service, it is no wonder that now PVDF is more and more commonly used in piping systems, valves, pumps, solid fabricated constructions, lined steel vessels, dual laminate FRP vessels, composite structures of PVDF/polyolefins extruded in multi layers tanks, extracting ducts, demisters, anti-evaporating balls, or heat exchangers where PVDF has proved to be equally satisfactory with regard to performance (Figure 4), and reliable and efficient with respect to cost price ratio (Figures 5, 6 and 7) as a material for the construction of such equipment used in surface treatment.

This could be emphasized by a significant list of references of the many uses of PVDF in the surface treatment industry (Table 10) of which two significant cases will now be described. The first example involves a whole chromium plating line where all the equipment in contact with corrosive chemicals either solutions or vapors, are made of PVDF.

The other one involves the largest steel tank lined with PVDF sheets that has been built and put into use to date. It is used for the surface treatment of parts of aircraft wings.

USE OF PVDF IN CHROMIUM PLATING LINE EQUIPMENT PRODUCING SHOCK ABSORBERS FOR AUTO INDUSTRY

In 1975, Solvay Central Laboratory was asked to perform chemical resistance trials of PVDF in contact with chromium plating solutions at 60°C (140°F) in order to determine if PVDF could be used to replace PVC piping systems which failed regularly after a short period of time in chromic acid environment.

When all the chemical resistance trials had been successfully passed, the company requesting the trials - a world famous American shock-absorber manufacturer with a plant in Belgium - decided to use a piping system made of SOLEF PVDF with a full guarantee of ten years. From 1975, PVDF parts were installed to replace PVC parts when the PVC parts failed. Many PVDF parts have been in service from that time and this has since extended to choosing PVDF to replace PVC, PTFE, FEP for numerous items also. In 1983, the management of the company decided to build a complete new line for chromium plating of shock absorbers. With an improved efficiency based on an extensive use of PVDF. Once again Solvay Central Laboratory got involved in chemical resistance trials of PVDF in corrosive etching solutions and also chemically modified chromium plating solutions at high temperature in order to increase resistance to aging. Chemical resistance trials combining mechanical properties evaluations and burst resistance of pipes subjected to internal pressure for over 3000 hours led to the conclusion that PVDF was a suitable material to recommend for the described service conditions. The chromium plating line built in 1984 involves:

- PVDF dual laminate based on FRP special constructions:
  4 etching tanks: 2300 x 2500 x 1500 mm (2.51 x 2.73 x 1.64 yds)
  4 chromium plating tanks: 2300 x 2300 x 1500 mm (2.51 x 2.51 x 1.64 yds)
  1 mixing tank: 3000 x 2300 x 1500 mm (3.28 x 2.51 x 1.64 yds)

Including circulation parts and solid equipment using about 250 m^2 (2690 sqft) of PVDF polyester fabric backed sheets.

- Solid PVDF fabricated constructions:
  -1 air filtering equipment
  -1 air washer equipment
  -extraction ducts from 315 mm (12.5") to 900 mm (36") in diameter using 200 m^2 (2150 sqft) of solid PVDF sheets.

- Solid PVDF piping system for process:
  -400 m (440 yds) of pipes from 63 mm (2.5") to 220 mm (8.5") diameter
  -86 valves of different sizes, either diaphragm valves or ball valves
  -15 solid PVDF centrifugal pumps
  -4 solid PVDF "bayonet" heat-exchangers units, having a total heat exchange surface of 75 m^2 (81 sqyd) allowing 30,000 (7,950 US gal) of corrosive chemicals to be heated to 60-65°C (140-150°F) within 6 hours.

The total cost of solid PVDF equipment was about 20 million BF (420,000 US$) while the same installation would have cost about half with PVC. But as Mr.

Linsen, maintenance chief engineer said: "With PVC pieces life time is about 2.5 to maximum 4 years, sometimes even less, all of them requiring constant maintenance operations with many break-downs and also shut-downs for repairs. Furthermore PVC couldn't be used anymore with the new chemical composition of the baths at the service temperature.

PTFE lined steel piping system gives problems of leakage and is not flexible enough for modifications of the lines. It is also less resistant towards abrasion, and after all is more expensive than solid PVDF systems.

FEP heat exchangers are limited by the maximum allowed temperature and pressure of the small diameter pipes and when submitted to the service conditions (hot-cold temperature cycles) they gave many problems of leakage resulting in frequent shut-downs of the process line. They are also more expensive (600,000 BF or 12.000 US$) than PVDF heat exchangers operating at the same conditions with better efficiency. With PVDF heat exchangers it takes 6 hours to heat up the treatment baths when it generally took 10 hours with FEP heat exchangers to start the line. PVDF gave not a single problem of maintenance operations since start up".

This new shock-absorber chromium plating line made of solid PVDF for the equipment in contact with the most corrosive chemicals has been operating successfully from the beginning of 1985, while the old line with many PVDF replacement parts is still in service with the oldest PVDF parts operating continuously from 1975. A new line is being planned to replace the old one this year and will be built according to the same construction choices: "made of solid PVDF".

USE OF PVDF SHEETS AS AN INSIDE LINER OF ETCHING TANK IN SERVICE IN THE AIRCRAFT INDUSTRY

In 1984, an etching tank 17,900 x 1,900 x 4,000 mm (19.57 x 2.07 x 4.37 yds) handling solutions of:

H_2SO_4 66° Be 275 g/l + H_2O
H_2CrO_3 50 g/l + H_2O

at 60-65°C (140-150°F) has been lined with solid PVDF sheets which are 3 mm (0.118") thick and backed with a stretchable polyester fabric. In all about 200 m^2 (2,150 sqft) of sheets were used.

This PVDF lined tank is mainly used for surface treatment of aircraft wings parts. It was put into service in 1984 and during yearly control operations performed in 1985 required no modifications.

CONCLUSIONS

Compared with the thermoplastics that are generally used in the surface treatment industry. PVDF considerably extends the chemical resistance limits as well as the temperature service conditions, increasing the life time of the equipment. In addition, PVDF parts require much less maintenance operations, and give a cost efficient solution whenever corrosion problems involved in surface treatment industry are concerned.

February 3, 1986

TABLE I - PROPERTIES OF MAIN FLUORINATED POLYMERS

	Type	PVDF	PTFE	FEP	PFA	ETFE	ECTFE	PCTFE
Specific weight	$g.cm^{-3}$	1.78	2.17	2.15	2.15	1.74	1.7	2.16
Melting point	°C	178	327	270	305	275	240	210
	°F	352	621	518	581	527	464	410
Tensile properties tensile strength	MPa	54	30	20	31.5	48	48	42
	psi	7830	4350	2900	4570	6960	6960	6090
yield stress	MPa	46	10	12	15.5	24	31	40
	psi	6670	1450	1740	2250	3480	4500	5800
elongation at break	%	20 to 150	200 to 500	250 to 350	300	200 to 500	200 to 300	80 to 250
elastic modulus	MPa	2400	600	500	700	1500	1650	1500
	$psi.10^3$	348	87	72.5	101.5	217.5	240	218
Shore D hardness		79	60	57	62	75	75	90
Impact strength Izod	jm^{-1}	100 to 200	160					
	$ft.lbs.in^{-1}$	2to4	3.2					
HDT at 0.46 MPa	°C	148	121	70		104	115	120
	°F	300	250	158		219	240	248
Thermal linear expansion coefficient	$10^{-5}K^{-1}$	12	13	13	13	12	12	12
Thermal conductivity	$W.m^{-1}K^{-1}$	0.19	0.23	0.20	0.22	0.23	0.15	0.19
	$BTU.ft^{-2}.h^{-1}.F^{-1}.in^{-1}$	1.3	1.6	1.4	1.5	1.6	1.0	1.3

TABLE 2 - ABRASION RESISTANCE

Taber abrasion tester, abrasion ring CS-10, load 1 kg

	Loss of weight mg/1000 cycles
PVDF	5 - 10
Polyamide 6 - 10	5
UHMW PE	5
PVC (rigid)	12 - 20
PP (homopolymer)	15 - 20
CPVC	20
CTFE	13
PS	40 - 50
Stainless steel 304	50
ABS	60 - 80
PTFE	500 - 1000

TABLE 3 - CHEMICAL RESISTANCE OF THERMOPLASTICS AS A FUNCTION OF THE TEMPERATURE

Medium		PVC oC (oF)			CPVC oC (oF)			PP oC (oF)			PVDF oC (oF)			FEP oC (oF)			FRP oC (oF)		
		20 (68)	60 (140)	90 (194)	20 (68)	60 (140)	90 (194)	20 (68)	60 (140)	90 (194)	20 (68)	60 (140)	90 (194)	20 (68)	60 (140)	90 (194)	20 (68)	60 (140)	90 (194)
H_2SO_4	96%	+	o	-	+	+	-	o	o	-	+	+	o	+	+	+	-	-	-
HCl Conc.		+	+	o	+	+	+	+	o	-	+	+	+	+	+	+	+	o	-
HNO_3	50%	+	o	-	+	+	-	-	-	-	+	+	+	+	+	+	-	-	-
HF	40%	+	o	-	+	o		+	+		+	+	+	+	+	+	-	-	-
NaOH	50%	+	+		+	+	+	+	+	+	o	o	o	+	+	+	+	+	
NaOCl	15 % Cl_2	+	+		+	+		o	-		o	o	o	+	+	+	+	o	
CL_2 wet gas		o	o		+	+	+	-	-	-	+	+	+	+	+	+	o	o	o
Ketones, esters		-	-	-	-	-	-	+	-	-	o	-	-	+	+	+	-	-	-
Aromatics		-	-	-	-	-	-	o	-	-	+	+	o	+	+	+	-	-	-
Chlorinated Solvents		-	-	-	-	-	-	-	-	-	+	+	o	+	+	o	-	-	-

+ no significant change in properties
o some changes but can be used under certain conditions
- attack

TABLE 4 - CHEMICAL RESISTANCE OF DIFFERENT MATERIALS AT 50°C (122°F)

	H_2SO_4 conc.	H_2SO_4 dil.	HCl conc.	HCl dil.	HF 50%
Tantalum	+	+	+	+	-
Hastelloy B	+	o	+	o	o
Hastelloy C	+	o	o	+	+
Stainless Steel 316	o	o	-	-	o
Titanium	+	+	+	+	+
Monel	+	+	+	+	-
Incoloy	+	+	+	+	+
Zirconium	+	+	+	+	+
PE	+	+	+	+	+
PP	+	+	+	+	-
PVC	+	+	+	+	+
FRP	-	+	+	+	-
PVDF	+	+	+	+	+
PTFE	+	+	+	+	+

TABLE 5 - PRICES OF ANTI-CORROSION MATERIALS
(BASE JUNE 1985)

MATERIALS	SHEET SIZES	SURFACE PRICE US $ / FT^2	SPECIFIC WEIGHT g/cm^3
Inox 304 L	48" x 120" x 0.078"	5.89	7.9
Inox 316 L	48" x 120" x 0.078"	7.57	7.9
Inox 317 L	48" x 120" x 0.078"	12.62	7.9
Nickel 200	48" x 120" x 0.078"	38.09	8.9
Monel 400	48" x 120" x 0.078"	30.20	8.83
Incoloy 825	48" x 120" x 0.125"	41.03	8.14
Incoloy 800	48" x 120" x 0.062"	15.03	8.0
Inconel 600	48" x 120" x 0.078"	32.05	8.5
Hastelloy B2	48" x 144" x 0.078"	85.09	9.28
Hastelloy C 276	48" x 144" x 0.078"	69.13	8.94
Hastelloy C 4	48" x 144" x 0.078"	74.94	8.64
SOLEF PVDF	39.4" x 78.8" x 0.078" 39.4" x 78.8" x 0.118" 39.4" x 78.8" x 0.157" 39.4" x 78.8" x 0.197"	12.01 17.99 24.03 30.00	1.78

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TABLE 6 - PRICES OF SHEETS MADE OF FLUOROPOLYMERS USED AS A LINING IN DUAL LAMINATE CONSTRUCTIONS BASED ON FRP (BASE JUNE 1985)

MATERIALS	SHEET SIZES	SPECIFIC WEIGHT g/cm^3	SURFACE PRICE US$ ft^2
FEP w/fiberglass fabric backing	50' x 39.37" x 0.060"	2.15 *	50.24
	35' x 39.37" x 0.090"		72.97
PFA w/fiberglass fabric backing	50' x 39.37" x 0.060"	2.15 *	63.63
	35' x 39.37" x 0.090"		92.84
PVDF with polyester fabric backing	78.8" x 39.4" x 0.060"	1.78 *	11.02
	78.8" x 39.4" x 0.078"		14.36
	78.8" x 39.4" x 0.118"		20.75

* specific weight without considering backing

TABLE 8 - CHEMICAL RESISTANCE OF SOLID PVDF TO STRONG ACIDS

MEDIUM		CONCENTRATION IN WATER %WT	TEMPERATURE 25 77	50 122	75 167	100 212	125 257	°C °F
HCl		UP TO 100	+	+	+	+	+	
HSO_3Cl		100	o	-				
$HClO_4$		up to 70	+	+	+	+		
HF		up to 50	+	+	+	+		
		up to 70	+	+				
HBF_4		up to 100	+	+	+	+		
H_2SiF_6		50	+	+	+	+		
HNO_3		up to 85	+	+	+	+		
H_3PO_4		up to 85	+	+	+	+	+	
NH_2SO_3H		45	+	+	+	+		
CO_3-H_2SO_4-H_2O	50-15-35	up to 90	+	+	+	o		
H_2SO_4		up to 60	+	+	+	+	+	
		60 up to 80	+	+	+	+		
		90	+	+	+	o	-	
		93	+	+	+	-		
		97	+	+	o	-		
H_2SO_4-HNO_3-H_2O	65-20-95	100	+	+	+	+		
H_2SO_4-HNO_3	50-50	100	+	+				
CH_3COOH	acetic	100	+	+	-			
$ClCH_2COOH$	chloro acetic	50	+	+	+	+		
		75	+					
		100			-	-		
$Cl_2CHCOOH$	dichloro acetic	50	+	+	o			
Cl_3-CCOOOH	trichloro acetic	50	+	+	o			
		100	+	+	o			

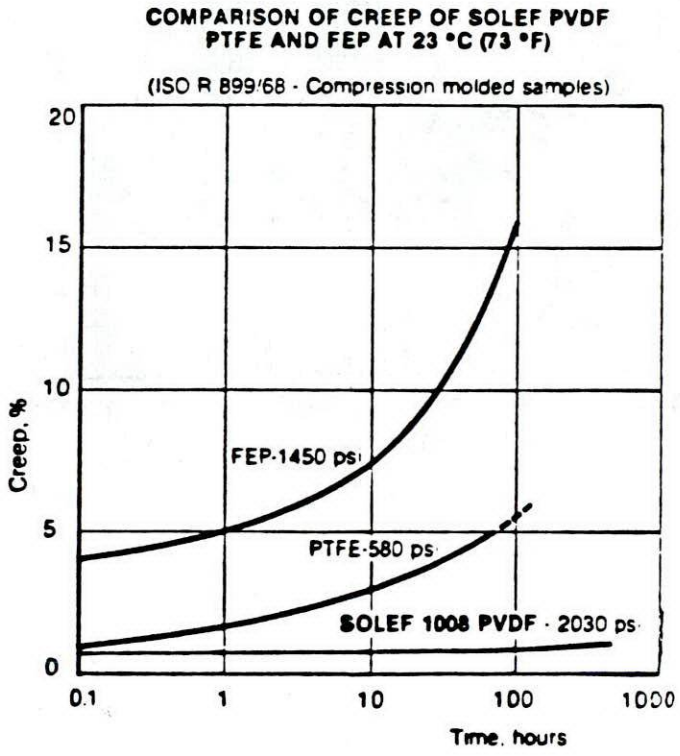
F_3CCOOH	trifluoro acetic		50	+	+	+	+
			100	+	+	o	
$C_6H_5SO_3H$	benzene sulfonic		sat	+	+	+	+
$ClC_6H_4SO_3$	4(2 chlorobenzene sulfonic)		80	+	+	+	+
$HOC(CH_2COOH)_2COOH$	Citric		50	+	+	+	+
HCOOH	Formic	up to	99	+	+	+	+
HOOCCOOH	Oxalic		50	+	+	+	+
			sat	+	+		
$C_6H_2OH(NO_2)_3$	Picric	up to	50	+	+	+	+

TABLE 9 - CHEMICAL RESISTANCE OF SOLID PVDF TO SOME SURFACE TREATMENT BATHS VERSUS TEMPERATURE

METALS TO BE TREATED	BATH COMPOSITION	% WT	RESISTANCE AT 25 °C / 77 °F	50 °C / 122 °F	75 °C / 167 °F	100 °C / 212 °F
Aluminum and Al Alloys	H_2SO_4	24				
	$Na_2Cr_2O_7$	7	+	+	+	+
	H_2O	69				
Aluminum and Al Alloys	H_3PO_4	22				
	Cr_2O_3	11	+	+	+	+
	H_2O	67				
Chromium and Chromium plating	HCl	18.5				
	H_2O	81.5	+	+	+	+
Stainless steel	HCl	30				
	H_3PO_4	10				
	HF	2.4	+	+	+	+
	H_2O	52.6				
Stainless steel	Hexamethylene tetramine	18				
	HCl	2.6				
	H_2O_2	1.1	+	+	+	+
	H_2O	78.3				
Magnesium and Mg Alloy	CH_3COOH	43.5				
	Cr_2O_3	6.6				
	$NaNO_3$	8.2	+	+	+	+
	H_2O	41.7				
Copper and C_4 alloys	$Fe_2(SO_4)_3$	10				
	H_2SO_4	8	+	+	+	+
	H_2O	82				
Titanium and Ti alloys	HNO_3	15.2				
	HF	30.6	+	+	+	
	H_2O	54				

Titanium and Ti alloys	H_2SO_4	16				
	NaF	3	+	+	+	+
	CrO_3	1.5				
	H_2O	79.5				
Tungsten & W. alloys	HNO_3	19.8				
	HF	3				
	H_2SO_4	30.9	+	+	+	+
	H_2O	46.3				
Zinc and Zn alloys	HCl	3.7				
	CH_3COOH	10	+	+	+	+
	H_2O	86.3				

FIGURE 1 - COMPARISON OF CREEP OF SOLEF PVDF, PTFE AND FEP AT 23°C (73°F)



Since the polymer also has exceptional resistance to aging, these mechanical properties are demonstrated extremely well in experiments to show the bursting resistance of pipes. In these tests, extruded tubes of Solef PVDF have now been tested for up to 120,000 hours (14 years) continuously at 120°C (248°F) and under hoop stress of 9.5 MPa (1,378 psi) without showing any trace of loss of bursting resistance while many polymers show a rapid deterioration of bursting pressure under the same conditions (Figures 2 and 3).

Figure 2

HOOP STRESS CURVES OF PVDF PIPES

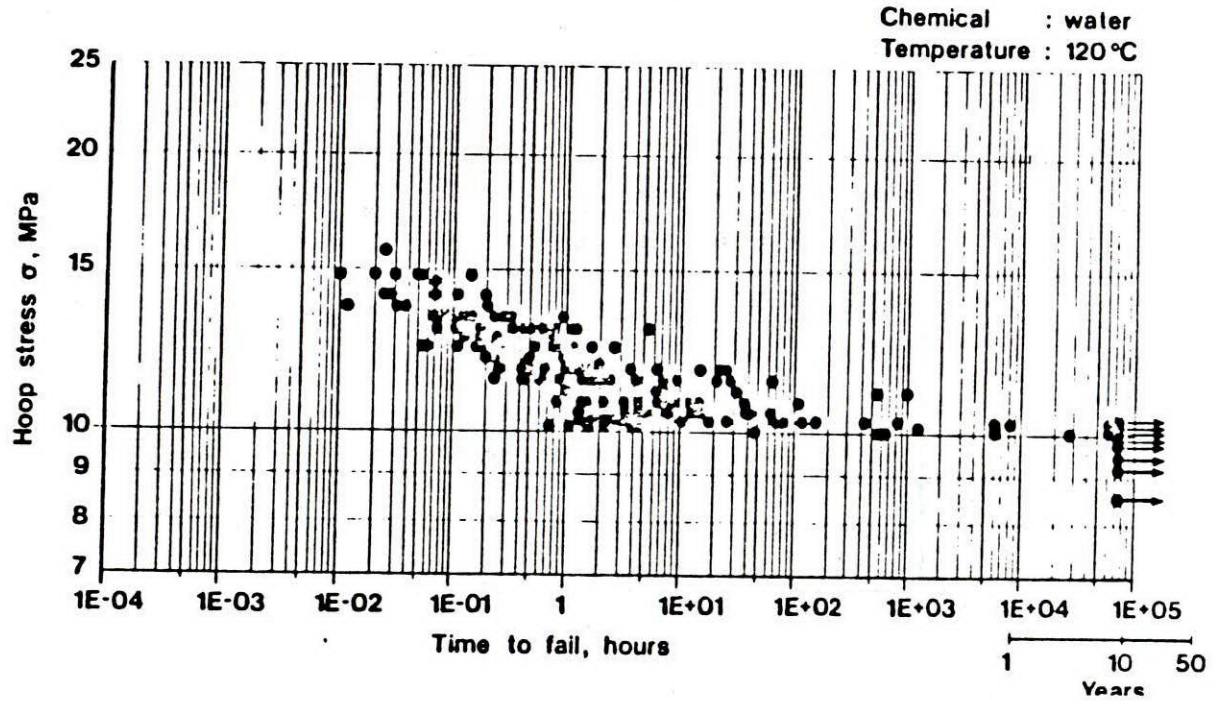


FIGURE 3 - STRESS RUPTURE DATA PLOTTED AGAINST TIME
FOR DIFFERENT POLYMERS AT 100°C (212°F)

Figure 3

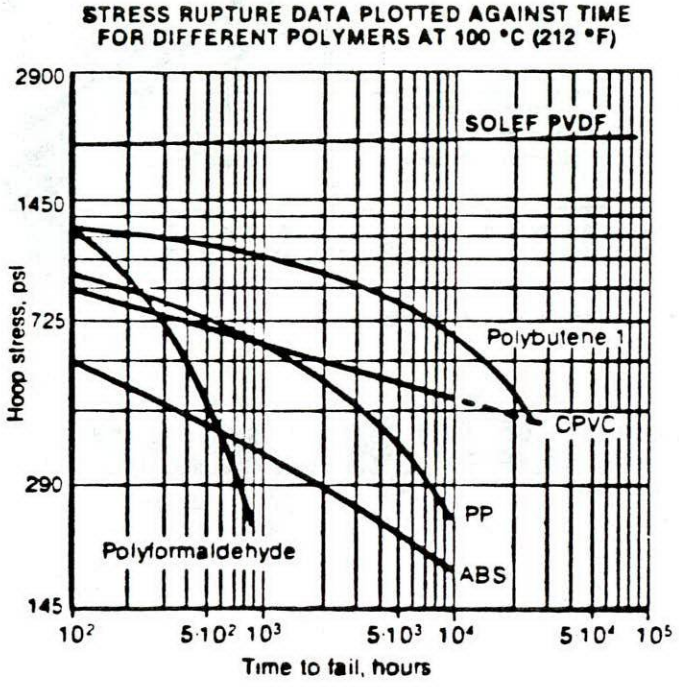
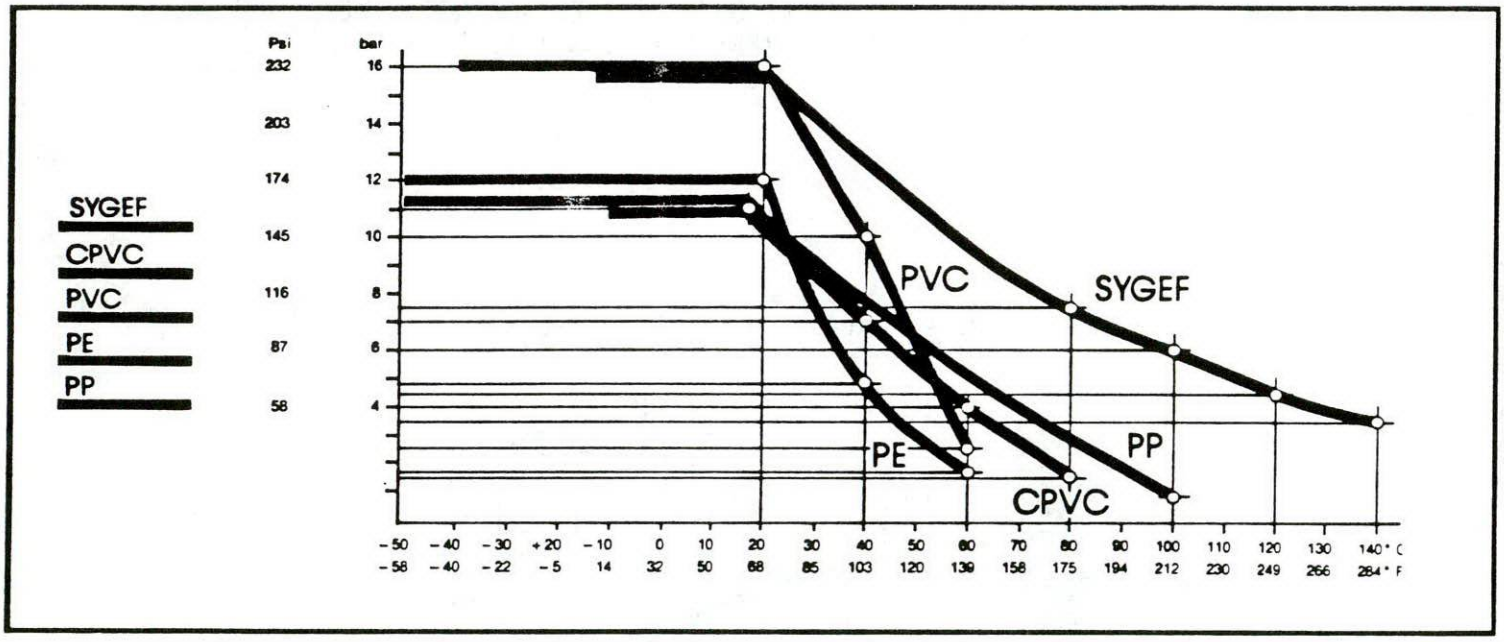


FIGURE 4 - PRESSURE - TEMPERATURE CAPABILITIES OF PVDF PIPING SYSTEMS VERSUS PVC, CPVC, PE, PP PIPING SYSTEMS



SYGEF in the trade name of PVDF piping systems made by GF (Switz) and Symalit AG (Switz) from SOLEF PVDF, these systems are sold in USA and Canada by GF-PSI Tustin California.

FIGURE 5 - COSTS COMPARISONS OF SEVERAL INSTALLED PIPING SYSTEMS VERSUS PVDF ONES

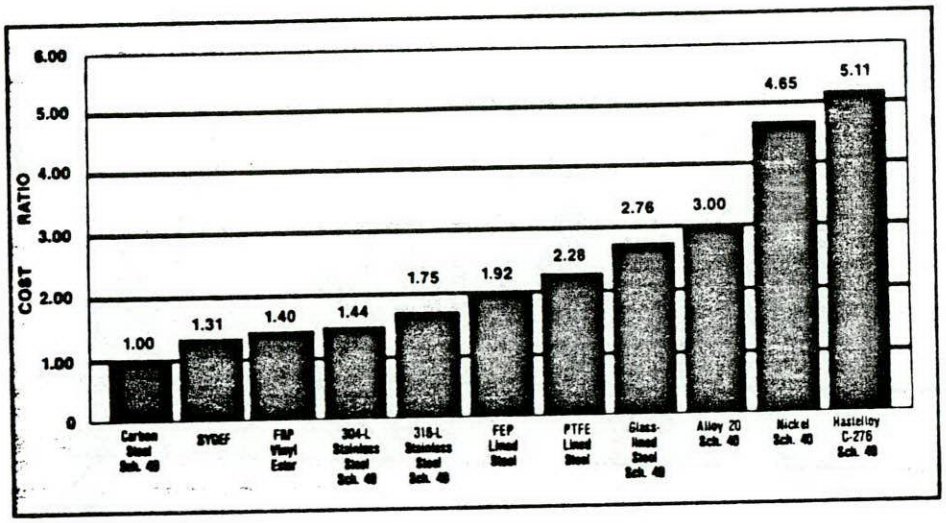


FIGURE 6 - INDEX OF PRICES OF STEEL LININGS (BASE JUNE 85)

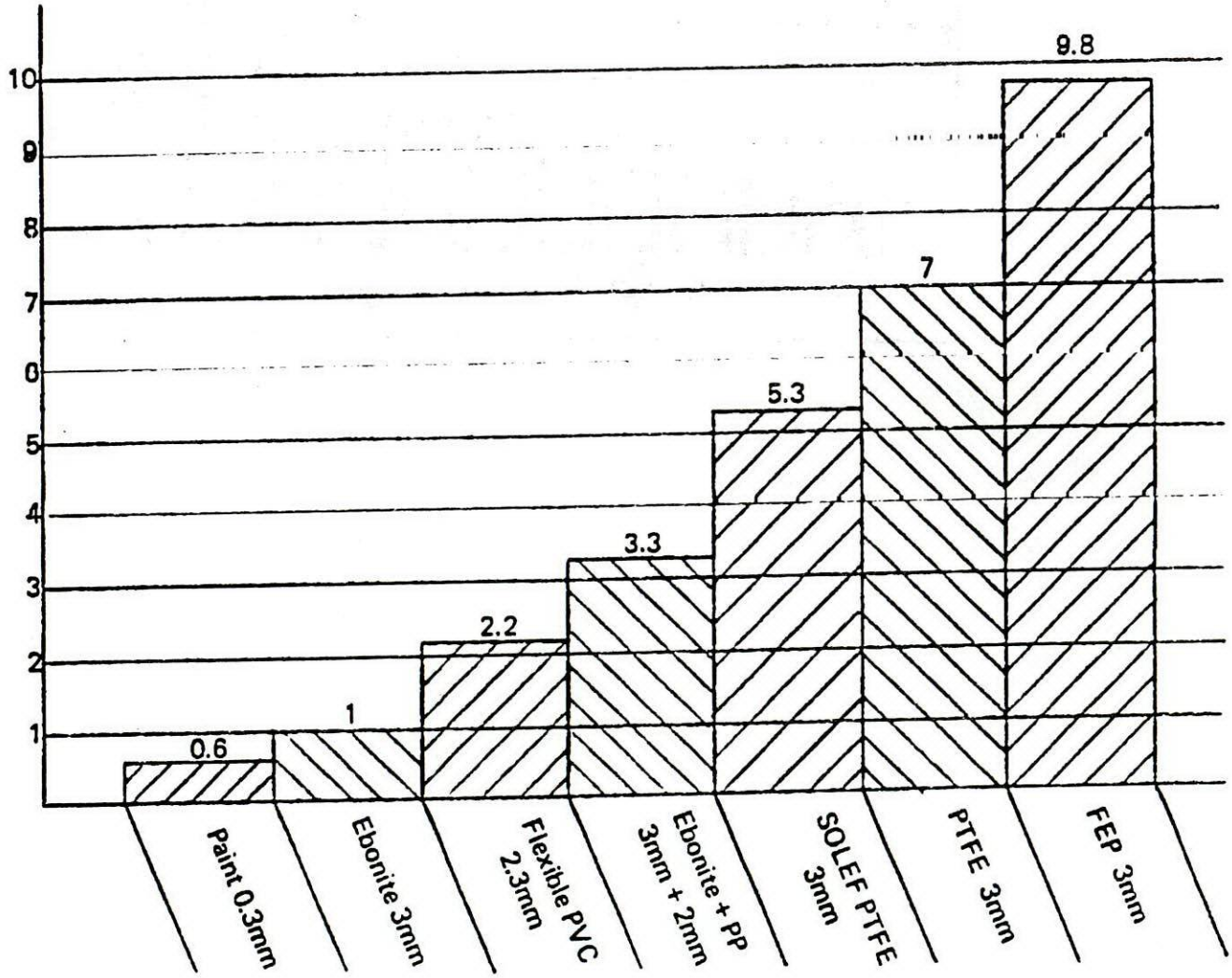


FIGURE 7 - INDEX OF PRICES OF DUAL LAMINATES CONSTRUCTIONS
BASED ON FRP (BASE JUNE 1985)

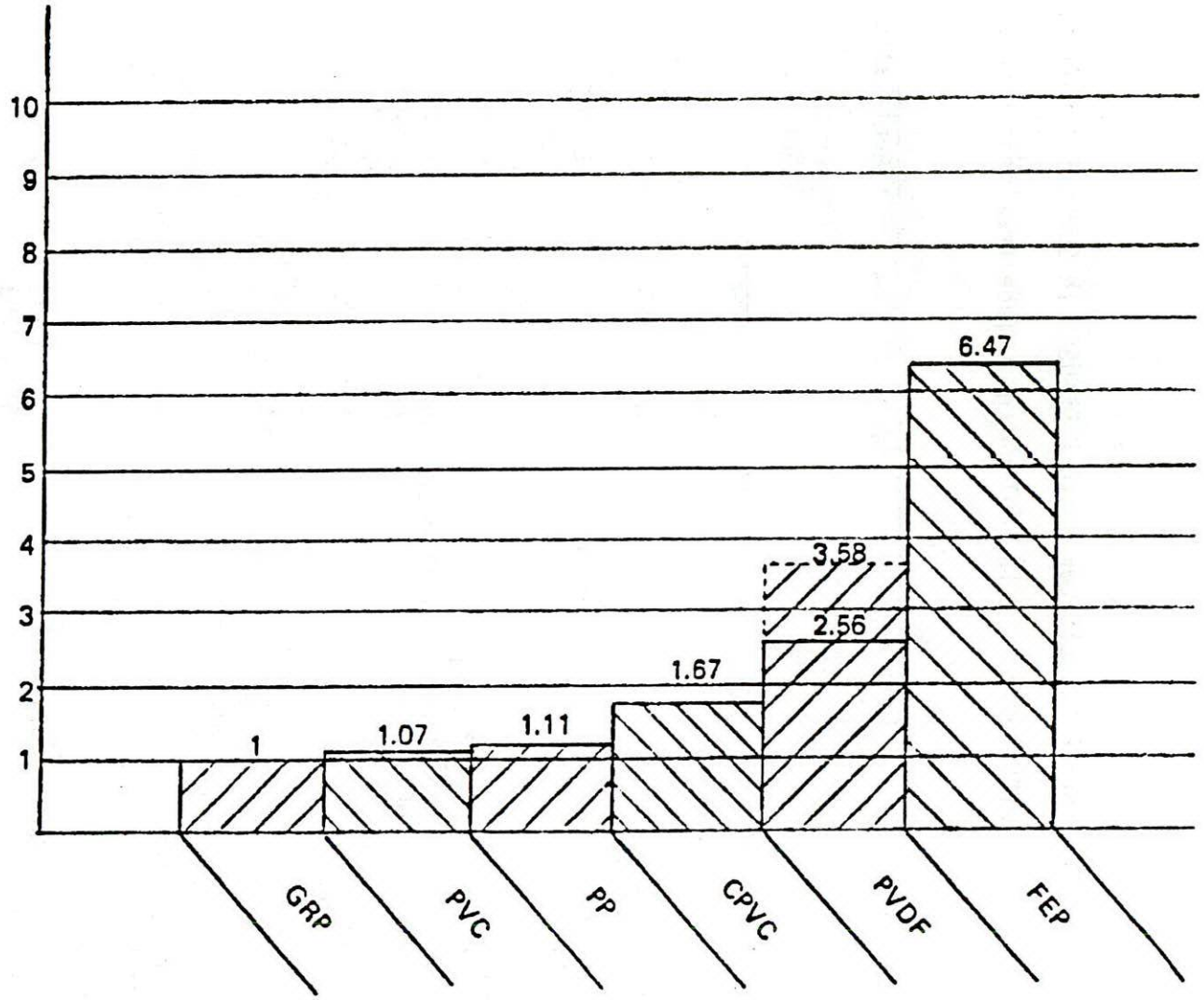


TABLE 10 - REFERENCE LIST OF SOLID PVDF USES IN SURFACE TREATMENT INDUSTRY

Among many cases of use of PVDF in the CPI the following surface treatment process applications should be noted.

Still In Service From (year)	Service Conditions (medium) Nature	Temp. °C	Temp. °F	Pressure bar	Pressure psi	Application Types
1973	Methylene chloride	60	140			piping system & solid construction
	Hydrochloric Acid	80	176	3		
	Dichloroethane Chloroform, carbon tetrachloride	45	113	1, 5		piping system
	Methylene chloride					
1974	Chloromethane	60	140	2, 5		piping system
	Perchloroethylene & CCl_4	60	140	1, 8		" "
	Dichloroethane & Perchloroethylene	60	140	1, 8		" "
	Chloroform & HCl	60	140	1, 8		" "
	HCl (conc.)	50	122	1, 2		" "
	HF (70%)	50	122	1, 2		" "
	H_2SO_4 (93%)	50	122	1, 2		" "
	CCl_4 + HF	50	122	1, 2		" "
	HCl (30%)	30	86			pump output $45M^3/H$
	Isobutanol, methylene chloride & dicalite	30	86			" " "
	Trichloromethane, H_2SO_4 + dicalite	30	86			" " "
	Trichloromethane, HCl, H_2SO_4 + dicalite	30	86			" " "
	H_2SO_4 (95%)	20	68			" " "
1975	Dichloroethane + CCl_4 + ...	50	122	2		piping system
	HCl (32%)	95	203			" "

	Methylene Chloride	60	140	1, 5		" "
	$H_3PO_4 + Cr_2O_3$	80	176			" "
	$CrO_3 + H_2SO_4 + H_2O$	66	150	1		" "
1976	Cl_2 + HCl + Chloromethanes	60	140	2		piping system
	HF (70%)	40	104	1, 2		" "
	H_2SO_4 (90%)	40	104	1, 2		" "
	H_3PO_4 (85%)	40	104	1, 2		" "
	HCl (32%)	40	104	1, 2		" "
	Methylene chloride + HCl	73	163	1		" "
	1, 1, 1 trichloroethylene + HCl	60	140	1		" "
	Trichloroethylene & Perchloroethylene	60	140	1		" "
	H_2SO_4 (66 BE), CrO_3	65	150	1		" "
	$CrO_3 + H_2SO_4 + H_2O$	65	150	1		pump
1977	HF (30%)	30	158	atmos		piping systems & solid construction
	H_2SO_4(12%) + $NaNO_3$ (0.7%) + NH_2SO_3H (0.35%)	70-75	158-167	atmos		piping systems & pumps lined steel tanks & solid construction
	$CrO_3 + H_2SO_4 + H_2O$	66	150	atmos		piping systems & pumps
	HNO_3 + HF + H_2SO_4 + H_2O	90	194	atmos		piping systems & dual laminate PVDF/FRP tank
	Nickel Electroless Baths	90	194	atmos		piping systems
	$CrO_3 + H_2SO_4$	58	136	atmos		" "
	$H_3PO_4 + H_2SO_4 + CrO_3$	80	176	atmos		" "
1978	$CrO_3 + H_2SO_4$	68	158	atmos		" "
	H_2SO_4 (conc.)	85	185		50	" "
	HCl (conc.)	66	150		30	" "
	HF	50	120		70	" "
	HCl	88	190		25	" "
	HCl (30%) + H_2SO_4 (10%)	100	212		1	" "
	HCl + MCB	44	110		10	" "
	HCl (50%)	ambient			35	" "
	HNO_3	"			30	" "
	H_2SO_4 (96%)	"			60	" "

	HCl + phenol (1.2%)	100	212			pumps
	H_2SO_4 + Monochlorobenzene (20%)	80	176			"
	HCl, H_3PO_4, HC, CrO_3	60	140			"
	HNO_3, HF (>70%)	60	140			"
	HCl + H_3PO_4	35	95			"
	HNO_3 (34%) + HF (9%)	40	104			"
	H_2SO_4 (62%)	40	104			"
	HCl (33%)	40	104			"
	HCl	103	217	1, 5		piping system & solid
	CrO_3 + H_2SO_4	50	122	atmos		laminate PVDF/FRP
	H_2SO_4 (96%)	80	176			" " "
	HCl (33%)	60	140			" " "
	CrO_3 + H_2O	60	140			" " "
1979	H_2SO_4 (90%)	94	200		50	piping systems
	H_2SO_4 (75%)	38	100	atmos		" "
	HCl (30%), Chloral (34%), $FeCl_3$	38	100	"		" "
	HCl (30%)	ambient			20	" "
	H_2SO_4 + HCl	122	250			" "
	H_2SO_4 + HCl	110	230		35	" "
	HF + HNO_3	125	257			" "
	Nickel Electroless Baths	90	194	atmos		piping systems & pumps and lined steel tanks
	CrO_3 + H_2SO_4 + H_2O	66	150	"		" " "
	H_3PO_4 + H_2SO_4 + CrO_3	80	176	"		" " "
	CrO_3 + H_2SO_4	40	104	"		" " "
	ATP (alloy tin plate)	90	194	"		" " "
	CrO_3 + H_2SO_4	60-70	140-158	"		" " "
	Methylene Chloride & Trichloroethylene Trichloroethane & Perchloroethylene	75	167	"		degreasing treatment units made of solid construction & piping systems & pumps & dual laminate PVDF/FRP

HEAT EXCHANGERS MADE OF PVDF HISTORIC CASES

Still in service from year	Service conditions (Medium) Nature	Temperature °C	°F	Heating Fluid Temp °C	Pressure
1982	Fluoronitric baths HNO_3 - HF	55	131	water vapor 155	
1980	H_2SO_4 10-15%	10	50	ethylene glycol water	
1984	CrO_3 + H_2SO_4 + H_2SiF_6	55	131	water 90	
1985	H_2SO_4 10-15%	60	140	water vapor 135 and as cooling system water and glycol	
1985	Nickelling bath $NiCl_2$ + CL + ...	60	140		
1984	HF + HNO_3	55	131	water vapor 135	
1983	H_2SO_4 15%	55	131		
1983	H_2SO_4 55-60	55	131	water vapor 135	
1985	H_2SO_4 + HF + CrO_3	35	95	water	

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Electronics I
Session I

Alternative Tin Strip Solutions For Copper - Tin Plated Circuit Boards

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Alternative Tin Strip Solutions for Copper - Tin Plated Circuit Boards

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Introduction

Many circuit board manufacturers plate thin layers of tin (about 50 microinches) over copper as an etch resist, and then remove the tin before soldermask application. This tin strip process must selectively remove the tin, and leave the copper circuit pattern intact. Generally, these solutions need to have high tin strip rates and low copper etch rates leaving smooth, shiny copper circuit patterns. These requirements become increasingly important for controlled impedance and fine line circuitry.

Most of the tin strip solutions used in the United States are fluoride based and many contain ammonia. A 27 wt % Ammonia Bifluoride solution with 10-14 vol % hydrogen peroxide gives good tin strip results in terms of circuit board quality and throughput, but the Ammonia and fluorides cause problems for a waste treatment facility. Treating the tin strip effluent with calcium hydroxide (lime) leads the calcium fluoride precipitation, but the residence time for complete reaction ranges from 14 to 24 hours depending on local waste effluent regulations, treatment procedures, effluent volumetric flow, and constituent concentrations. In addition, raising the pH of the effluent streams to 9 or 10 is a common way to remove metals in solution (see Figure 1), but the ammonia present in the tin strip effluent acts as a metal chelator* holding copper, tin and other metals in solution.

Moreover, the base chemical cost of Ammonia Bifluoride solutions is about $2.00 to $2.50 per liter of mixed solution. With a chemical consumption rate in a spray processor of 260 liters per 4,000 panels, the cost starts becoming substantial. As more circuit board designs require soldermask over bare copper, the cost and capacity requirements increase for this process.

As a result, these waste treatment and cost considerations led to a search for an alternative tin strip solution. The goal was to find an alternative that had no ammonia, no fluorides, and a low make-up cost, while maintaining process throughput and quality. After a library search of patents, articles, and books, the following alternatives were chosen:

1) Fluoroboric Acid, Hydrogen Peroxide, and peroxide stabilizer
   300 - 500 m/l Fluroboric Acid
   30 - 50 m/l 50% Hydrogen Peroxide
   30 - 50 m/l Peroxide Stabilizer
   (Reference 2)

* Chelator: A donor molecule called a ligand that attaches to a positively charged metal ion through coordination of its unshared pair of electrons. They form cyclic chelate[1] compounds with the ligands encircling the metal ion. Nitrogenous molecules like ammonia and amines are good chelators.

2) Cupric Chloride, Stannous Chloride, Hydrogen Peroxide, and Hydrochloric acid

4 - 20 g/l Cupric Chloride
12 - 40 g/l Stannous Chloride
13 - 18 g/l HCl
0.5 - 7 ml/l H_2O_2
(Reference 3)

3) Ferric Chloride, Copper Sulfate, and 56% Acetic Acid

10 - 14 oz/gal Ferric Chloride
18 - 21 oz/gal Copper Sulfate
40 - 60 fl oz/gal 56% Acetic Acid
(Reference 2)

The fluoroboric mixture did not eliminate fluoride waste treatment, but it did eliminate a source of Ammonia chelator, and represented a 20% reduction in base chemical cost. The second alternative is used mainly in the chemical milling industry with little or no use in the circuit board industry, and although it does not contain ammonia and fluorides, it introduces some metal removal problems for a waste treatment facility. The third alternative is the best in terms of waste treatment, and base chemical cost, but it is difficult to control in order to maintain process quality and throughput.

Some alternatives were not considered for known safety or process control considerations. Organic hallides like allyl bromide, benzl chloride, and chloromethyl methyl ether are known to react with tin metal leading to toxic diorganotin dihalides*, but this would cause obvious safety problems and increased organic chemical content in the waste effluent (high COD**). Some concentrated acids like hydrochloric are known to remove tin from copper surfaces, but they don't selectively strip tin, and the process effluent would require a very significant pH adjustment to acceptable levels. These concentrated acids also require immersion processing for tin removal, because spraying leads to dangerous gas or vapor generation.

As a result, this report represents an initial investigation into alternative tin strip solutions. Initially it compares the tin strip rates, copper etch rates, and surface finish after immersion tests with each mixture. Then it goes on to describe the relative cost of each mixture with an additional description of the cost of mixing chemicals on-site. Finally, it describes the results of the first line test with the second alternative, the cupric chloride/stannous chloride mixture. The immersion tests and the line test gave indications of necessary process control requirements for the cupric chloride/stannous chloride solution as well.

* Diorganotin dihalides are usually used as heat stabilizers in PVC plastic.

** COD is Chemical Oxygen Demand. It is used to measure the organic chemical content of waste streams in terms of the oxygen required to break down the organics.

Experimental

Instrumentation

1) The immersion tests were done in 1 liter beakers with air agitation and magnetic stirrers. The tin strip rate and copper etch rates were determined by weight loss measurements.
2) The in-line test was completed in a Schmid CE-00-891/1 Tin Stripper unit.

Evaluation of Alternatives

An Ammonia Bifluoride solution with hydrogen peroxide* strips tin through the oxidation of the tin with hydrogen peroxide in the presence of fluoride ions. A stannous fluorate "complex" holds the tin in solution, and the ammonia chelates any copper etched from the surface to give a shiny, smooth copper surface.

A fluoroboric acid mixture with hydrogen peroxide reacts like the Ammonia Bifluoride mixture, but it does not have ammonia in the solution to chelate the copper. This is good in terms of waste treatment, but it leads to higher copper etch rates as shown in Table 1. Higher fluoroboric acid concentrations increase the tin strip rates and reduce the copper etch rate, but the copper etch rate is still many times higher than the Ammonia Bifluoride mixture etch rate. Without ammonia chelate present Copper (I) ions are oxidized to Copper (II) ions by hydrogen peroxide, and the presence of Copper (II) ions leads to increased copper etch rates.

Oxidation - Reduction Half Reactions

$$2Cu^{+1} \rightarrow 2e^{-} + 2Cu^{+2}$$
$$H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$$

Copper (I) to Copper (II) Oxidation

$$Cu^{0} \rightarrow 1e^{-} + Cu^{+1}$$
$$Cu^{+2} + e^{-} \rightarrow Cu^{+1}$$

Copper Etching

Cupric Chloride and hydrogen peroxide solutions are widely used as copper etch solutions in the circuit board industry.

The second alternative tin strip solution contends with these same half reactions. It contains Cupric, hydrogen peroxide, stannous chloride, and hydrochloric acid. However, in this mixture the hydrogen peroxide is kept at a low concentration just to start the oxidation reactions, and air agitation is used to reoxidize Copper (I) to Copper (II) as the process proceeds. Keeping the hydrogen peroxide at low levels minimizes the copper etch rates to immeasurable levels, but still maintains significant tin strip rates as shown in Table 2.

* The Ammonia Bifluoride mixture used for these tests was a proprietary mixture. It may contain additives like polyacrylamide or amino acids with carboxylic acid groups to reduce copper etch rates.

Tin is oxidized by the cupric ions in solution as shown in the following oxidation/reduction reactions.

$$Sn^0 \rightarrow Sn^{+2} + 2e^-$$
$$2Cu^{+2} + 2e^- \rightarrow 2Cu^{+1}$$

Tin Stripping

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
$$2Cu^{+1} \rightarrow 2e^- + 2Cu^{+2}$$
$$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2$$

Reoxidation of Copper

During these immersion tests, a tin oxide layer did form on the tin surface, but it was easily washed away from the smooth panel surface after immersion.

The third alternative containing Ferric Chloride, Copper Sulfate and 56% Acetic Acid uses the ferric chloride to oxidize tin from the surface. The copper concentration is maintained at near saturation levels to minimize copper etch, and acetic acid is added to maintain sufficient acidity to prevent the metals from falling out of solution as shown in Figure 1. Table 1 shows the tin strip and copper etch rates which are very comparable to the Ammonium Bifluoride solution, but the surface finishes were very poor. It gave a matted surface, with tin oxide and iron oxide smut after the tin strip test, and it left a dark green copper surface after the copper etch test. With these results, no further tests were tried on this alternative.

Cost Analysis

The cost of Ammonia Bifluoride Tin Strip solutions are $8.50 to $9.50 per gallon or $2.20 to $2.50 per liter of mixed solution from various chemical vendors. The cost of alternative tin strip mixtures can be broken down into base chemical cost and automatic mixing tank material costs. The following section is an example of a real price breakdown per liter of mixed solution.

Alternative 1 - Chemistry

48% Fluoroboric Acid	
300 ml/l	$0.93/l
500 ml/l	$1.56/l
50% Hydrogen Peroxide	
30 ml/l	$0.03/l
40 ml/l	$0.04/l
50 ml/l	$0.05/l
Hydrogen Peroxide Stabilizer	
30 ml/l	$0.12/l
40 ml/l	$0.16/l
50 ml/l	$0.20/l
TOTAL:	$1.18/l - $1.81/l

Alternative 2

The make-up for this alternative involves mixing cupric chloride, hydrochloric acid, hydrogen peroxide, and water. The tin concentration can be obtained by adding stannous chloride or placing a tin anode in the spray processor[3].

Cupric Chloride at $1.50/lbm	
12 g/l	$0.04/l
16 g/l	$0.05/l
18 g/l	$0.06/l
Hydrochloric Acid at $0.15/lbm (concentrated HCl is 1.35 g/ml)	
13 vol % conc. HCl	$0.06/l
18 vol % conc. HCl	$0.08/l
50% Hydrogen Peroxide	
5 ml/l	$0.005/l
TOTAL:	$0.10/l - $0.14/l

Alternative 3

Ferric Chloride at $2.70/gal 40 wt. %	
75 g/l, 10 oz/gal.	$0.08/l
105 g/l, 14 oz/gal.	$0.11/l
Copper Sulfate at $0.58/16m	
135 g/l, 18 oz/gal	0.17/l
158 g/l, 21 oz/gal	$0.20/l
56% Acetic Acid-Electrochemical Grade Acetic Acid $4.20/l	
40 fl oz/gal, 310 ml/l	$1.31/l
60 fl oz/gal, 470 ml/l	$1.97/l
TOTAL:	$1.56/l - $2.28/l

Summary Table

Ammonia Bifluoride	$2.20/l - $2.50/l
Alternative 1	$1.18/l - $1.81/l
Alternative 2	$0.10/l - $0.14/l
Alternative 3	$1.56/l - $2.28/l

Obviously Alternative 2 would be substantially more cost-effective in terms of base chemical cost. Waste treatment would involve pH adjustment and metal filtration, which would be less costly than the calcium fluoride precipitation, pH adjustment, and metal filtration for Ammonia Bifluoride mixtures. The additional cost of mixing would be about $20,000* for the mix tanks, plumbing, and microprocessor flow control. Dosing rate also affects cost.

* This is only the cost of parts and materials for a day tank and mix tank arrangement. It does not include the installation labor cost

Cupric Chloride/Stannous Chloride Extended Evaluation

This alternative gave the best results in terms of cost, copper etch rate, waste treatment, and final surface finish after washing. However, the tin strip rate was more variable than the Ammonia Bifluoride solution, making it more difficult to control. Figure 2 shows how the tin strip rate varies with copper concentration and percent hydrochloric acid in solution, but the copper etch rate also varies with the hydrogen peroxide concentration as shown in Table 2. As a result, the process requires pH control, copper concentration control, and controlled hydrogen peroxide concentrations in a highly aerated bath. It will probably need hydrogen peroxide stabilizers.

Figure 3 shows how the tin strip rates vary with tin and copper concentration, and Table 3 shows the actual values. Basically, the tin strip rate does not significantly change for tin concentrations between 16 g/l and 30 g/l. A metal recovery cell or bath bail-out may maintain the tin concentration in this range.[3] The patent suggests that the 9 g/l to 40 g/l concentration range is acceptable.

The patent also contends that copper concentrations between 2.5 g/l and 6 g/l are best for good bath performance.[3] It states that above 6 g/l of copper bath aeration cannot reoxidize copper (II) at a sufficient rate. Competitive tin strip rates did not occur in the immersion tests, until the copper concentration reached 12 to 16 g/l as shown in Table 1 and Figure 2. Consequently, dosing hydrogen peroxide in small quantities to maintain sufficient reoxidation of Copper (II) may be necessary, but the bath concentration of peroxide must remain below 5 ml/l to keep copper etch rates low (Table 2).

The patent suggests that tin and copper concentrations can be controlled by colorimetric or redox potentials, and dosing small quantities of hydrogen peroxide will effect this control. For colorimetric control there was a major change in the solution color from a clear and slightly yellow color to a dark lime green color at 16 - 18 g/l copper with 13 vol % HCl and 0.5 ml/l peroxide. An immersion test with 18 g/l copper, 13 vol % HCl, and 0.5 peroxide showed that this lime green mixture also discolored and stained the copper surface, while a solution with 16 g/l copper and 0.5 ml/l peroxide was still clear and did not etch or stain the copper surface at all. This color transition point could serve as the upper control limit for the copper concentration. The next step would be to identify optimum redox potentials and dosing rates to maintain 12 - 16 g/l copper and below 5 ml/l hydrogen peroxide. The overall control of the system may include a combination of colorimetric, redox potential, and pH control, but more work is necessary.

An in-line test with 20 Wt % HCl, 12 g/l Copper (II) and 20 g/l tin without any of the before mentioned process control devices gave poor results. Processing a number of panel plated copper-tin flats. The tin strip across the surface was uneven, and some black tin oxide remained on the rough spots formed by the uneven tin strip. In addition, parts of the surface had shiny copper exposed. Modifying the spray processor may reduce tin oxide build-up and lead to more even tin stripping across the surface.

The hydrogen peroxide concentration was not measured, but it may have been unusually high (over 5 ml/l) after spray processing. Moreover, the final process solution had a slight lime green color, meaning that either the copper concentration had risen above 16 g/l or the pH of the solution had risen during processing*. In the lab tests, addition of concentrated HCl changed the solution color from green to a clear and slightly yellow color. Therefore, any colorimetric control will probably be pH dependent.

Conclusions

More lab tests are necessary before further in-line testing is warranted. Cupric chloride copper etchers run at over 100 g/l copper (usually 150 - 170 g/l) and this solution would only have 12 - 16 g/l copper, but minimized copper etch rates are essential. Furthermore, overall process control is critical, and additional experiments will be oriented towards this. This would include taking spectrophotometric readings and redox potential readings for various concentrations of copper, tin and hydrogen peroxide with varying pH levels. Cost reduction is the motivating influence for more investigation.

The Ammonia Bifluoride tin strip mixture is much easier to control. The stannous fluorate "complex" holds tin in solution to prevent tin oxide deposition, and the ammonia chelates any copper in solution. The final surface finish is excellent, tin strip rates are relatively fast, and the copper etch rates are minimal.

References

1 Othmer, D.F., Encyclopedia of Chemical Technology, 3rd Ed., Wiley - Interscience Publication, 1979, p. 339.

2 Langdon, P.H., et. al., Metal Finishing Guidebook and Directory Issue, 51st Ed., Metals and Plastics Publications, Inc., 1983, pp. 496-497.

3 U.S. Patent 4,424,097, E. Lipka and E. Lendle of Federal Republich of Germany, Jan. 3, 1984.

4 U.S. Patent 4,297,257, Elias, et.al., Youngstown, Ohio, October 27, 1981.

5 U.S. Patent 4,306,933, Da Fonte Jr., Carson City, Nevada, December 22, 1981.

* Hydrogen ions are consumed in the breakdown of hydrogen peroxide.

TABLE 1

ALTERNATIVE TIN STRIP RATES VS. COPPER ETCH RATES

			TIN STRIP RATE $\left(\frac{g}{Min.\ cm^2}\right) \times 10^{-3}$	COPPER ETCH RATE $\left(\frac{g}{Min.\ cm^2}\right) \times 10^{-3}$
AMMONIA BIFLUORIDE / H_2O_2 (Proprietary Mixture)			5.5	0.43
FLUOROBORIC (ml/l)	H_2O_2 (ml/l)	H_2O_2 STABILIZER (ml/l)		
500 ml/l	50 ml/l	50 ml/l	9.1	2.1
500 ml/l	40 ml/l	40 ml/l	6.2	1.7
500 ml/l	30 ml/l	30 ml/l	5.0	1.1
300 ml/l	50 ml/l	50 ml/l	4.3	3.4
FERRIC CHLORIDE	12 oz/gal.		6.6	0.73
COPPER SULFATE	18 oz/gal.			
56% ACETIC ACID	50 fld. oz/gal.			
CUPRIC CHLORIDE	12 g/l Copper		4.7	IMMEASURABLE
STANNOUS CHLORIDE	12 g/l Tin			

TABLE 2

COPPER ETCH RATE VS. HYDROGEN PEROXIDE CONCENTRATION

H_2O_2 Concentration (ml/l)	Copper Etch Rate $\left(\frac{g}{Min.\ cm^2}\right) \times 10^{-3}$	
	4 g/l	6 g/l Cu
0.5	0	0
3.0	0	0
5.0	0.31	0.16
7.0	2.6	2.8

NOTE: This was run with 13 Vol % HCl and 28 g/l Tin.

TABLE 3

Copper Concentration (g/l)	Tin Concentration (g/l)	Tin Strip Rate $\left(\frac{g}{Min.\ cm^2}\right) \times 10^{-3}$
4	12	1.4
	16	1.7
	20	1.7
	28	1.2
8	12	2.2
	16	3.1
	20	2.9
	24	3.1
	30	3.1
	40	2.9
12	12	3.4
	16	4.1
	20	3.6
	28	4.1
	30	4.8

DATA FOR FIGURE 2

TABLE 4

13 Vol % HCl

Copper Concentrate	Tin Strip Rate $\left(\frac{g}{Min.\ Cm^2}\right) \times 10^{-3}$
4 g/l	1.4
6 g/l	1.9
8 g/l	2.2
12 g/l	3.4
16 g/l	3.3
18 g/l	8.6
20 g/l	12.1

18 Vol % HCl

Copper Concentrate	Tin Strip Rate $\left(\frac{g}{Min.\ Cm^2}\right) \times 10^{-3}$
6 g/l	1.9
12 g/l	4.7
18 g/l	9.3

DATA FOR FIGURE 3

TABLE 5

Tin Strip Rate Vs. Tin and Copper Concentrations

Tin Strip Rate $\left(\frac{g}{Min.\ cm^2}\right) \times 10^{-3}$

Tin Concentration g/l	4 g/l Cu	8 g/l Cu	12 g/l Cu
12	1.4	2.2	3.3
16	1.7	3.1	4.1
20	1.7	2.9	3.6
24	--	3.1	--
28	1.2	--	4.1
30	--	3.1	4.8

FIGURE 1

SOLUBLE METAL VS. pH

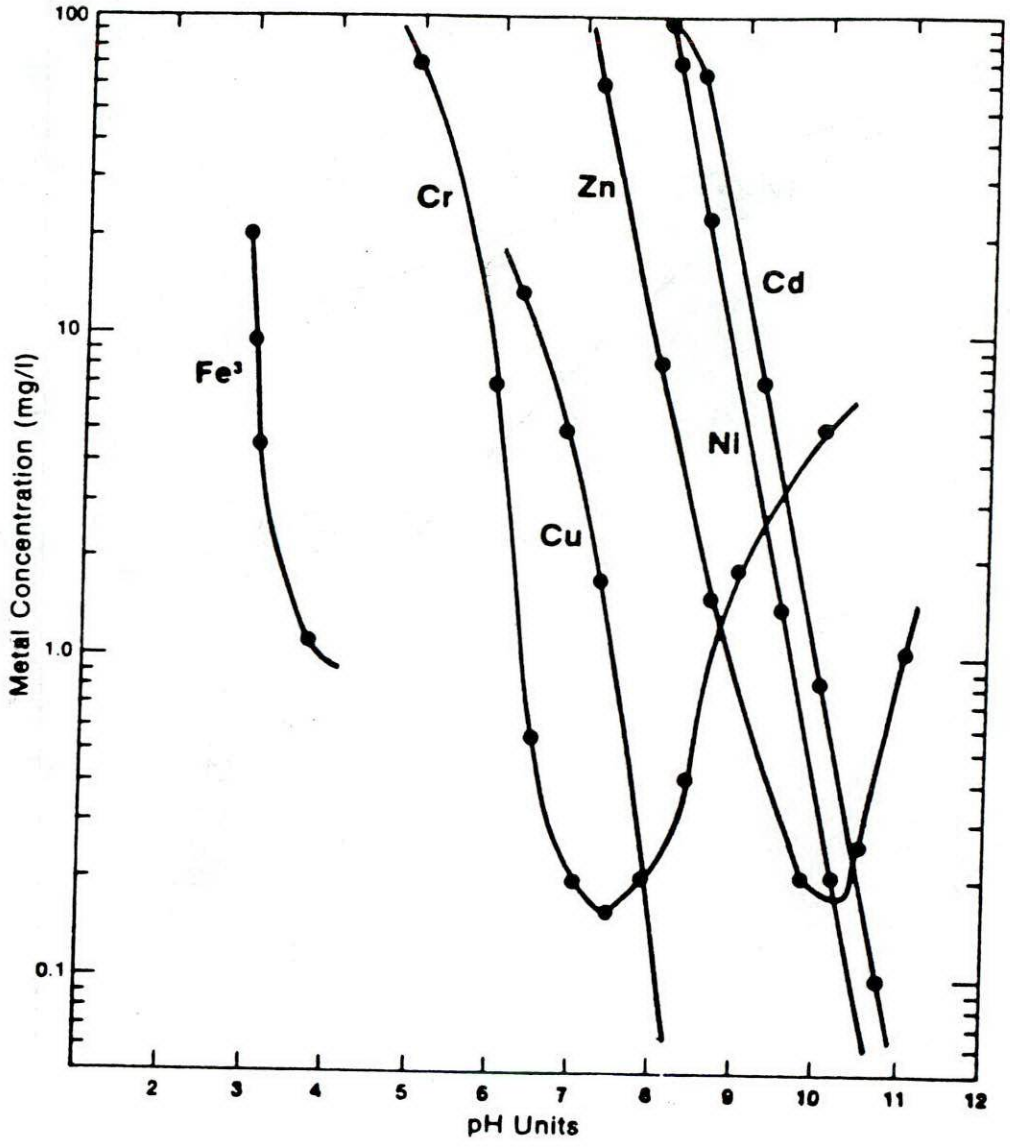
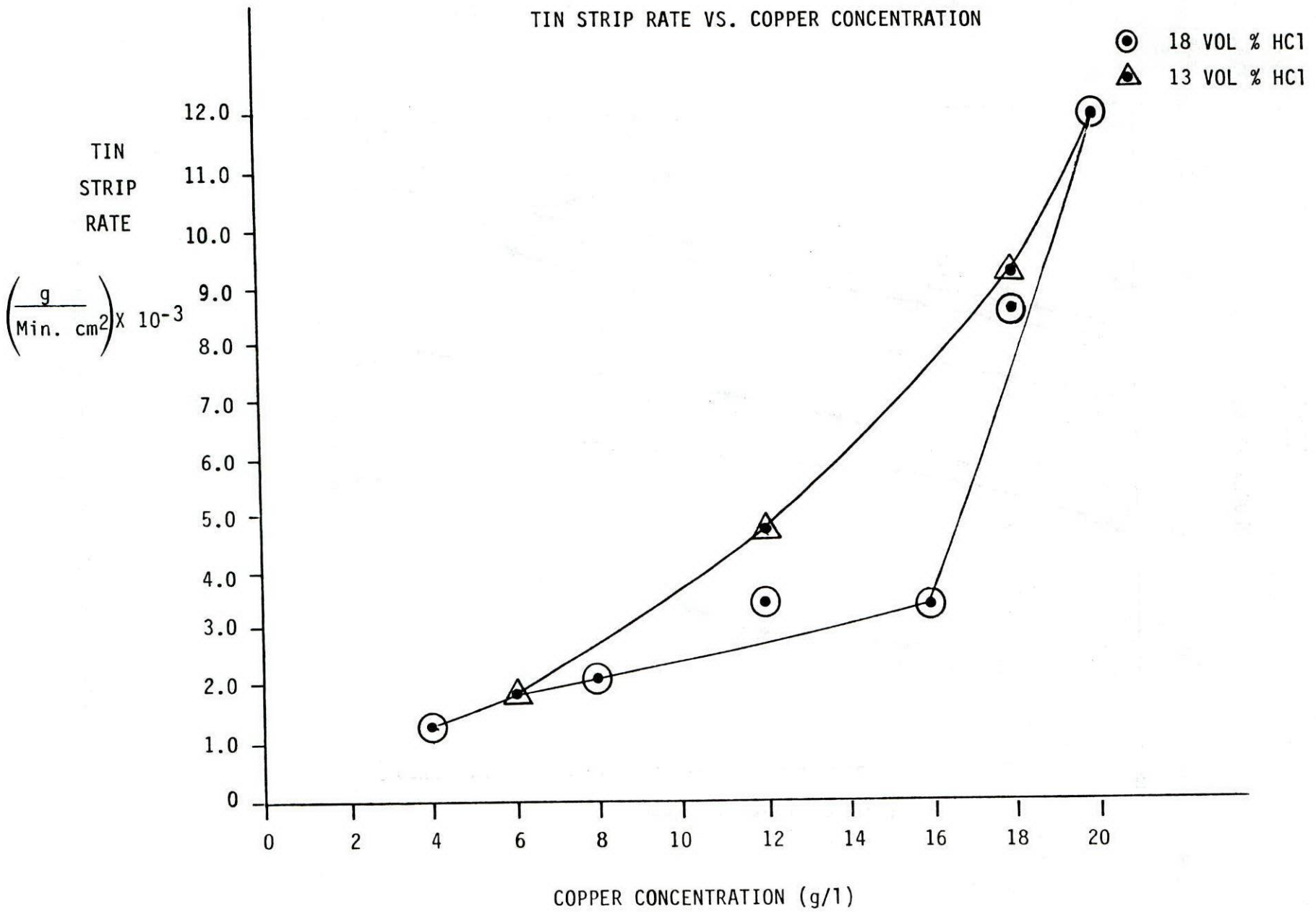


Figure 1
Precipitation of Metal Salts versus pH. from Weiner.
(Reference Unknown)

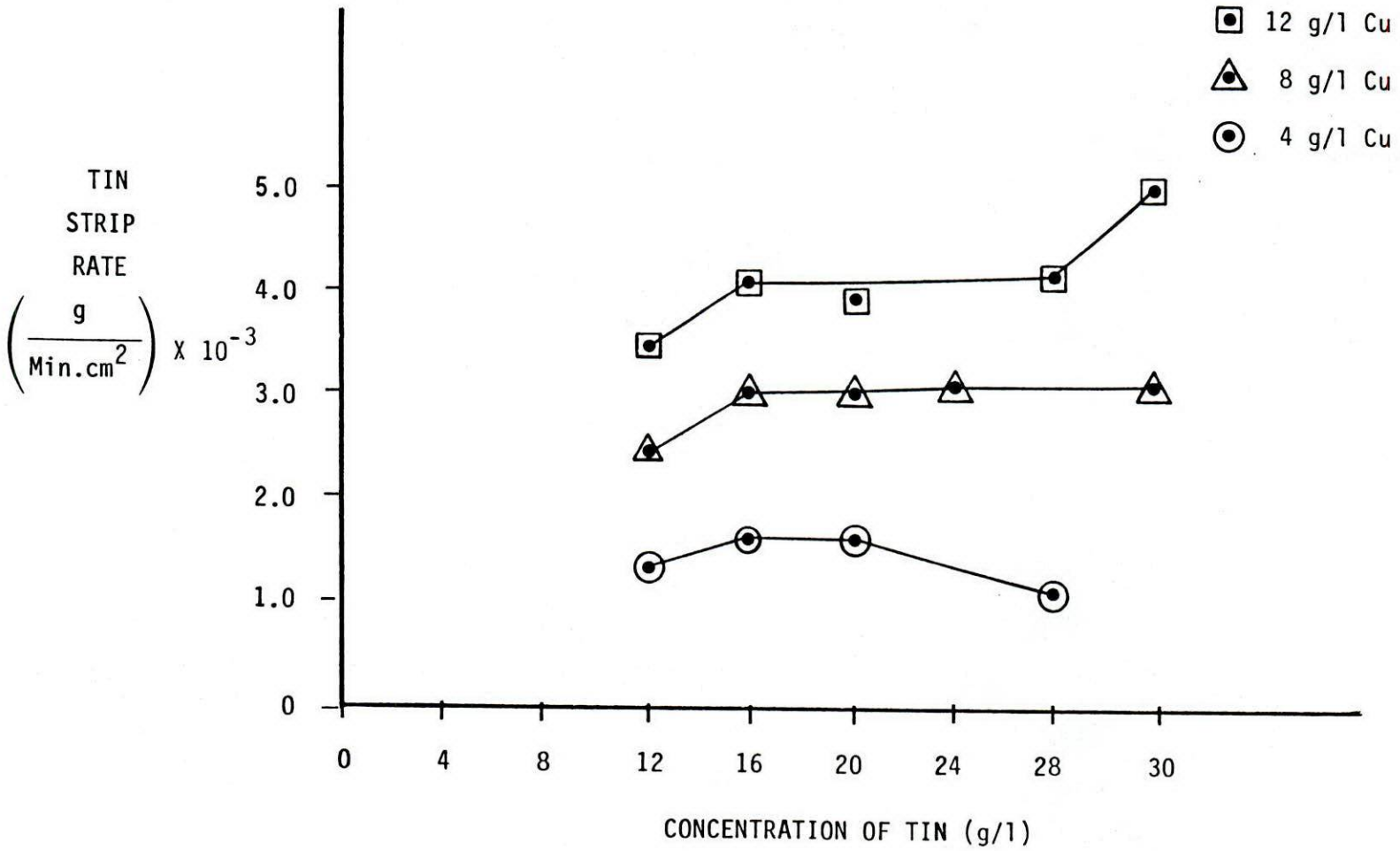
FIGURE 2



NOTE: See Table 4 for data

FIGURE 3

TIN STRIP RATE VS. TIN CONCENTRATION



NOTE: These tests were run with 14 Vol % HCl and 58 cm^2 plated panels. See Table 5 for the data.

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Session I

Mass Balance Control of Process Chemicals for Printed Wiring Board Production

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MASS BALANCE CONTROL OF PROCESS CHEMICALS FOR PRINTED WIRING BOARD PRODUCTION

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Mass Balance Control defines a technology recently adapted for chemical processing in the Printed Wiring Board industry. By using Mass Balance Control to monitor organic levels, many cause and effect relationships in the plating process can be elucidated. Since the Law of Conservation of Mass states that mass can be neither created nor destroyed, a general equation describing the concentration of a component in a system can be written as follows:

INPUT + GENERATION - OUTPUT - CONSUMPTION = ACCUMULATION

In this application, the component of interest is carbon, therefore the generation and consumption terms become zero and the equation reduces to:

INPUT - OUTPUT = ACCUMULATION

The Mass Balance Control approach provides a comprehensive picture, described as organic content, of the accumulation in the process baths. As the specifications for printed wiring boards continue to become more stringent, the need for tighter control and better understanding of process baths becomes increasingly more important. Through the use of Mass Balance Control, a method is now available for monitoring the overall organic characteristics of chemical process baths.

The Mass Balance Control method can be used to indicate cross contamination of cleaners, rinses, conditioners, etches, plating baths and other wet processing steps. The organic levels in plating baths can be monitored throughout the bath's lifetime, providing a reliable and predictable method of determining when carbon treatment is necessary. During the carbon treatment process organic levels can be observed to determine the effectiveness of the procedure used and to optimize that procedure. The organic levels of the pre-plate line can also be analyzed, monitoring the drag-in and drag-out of the sequential chemical processes.

Acid copper electroplating baths have organic additives added to them in low concentrations to control and mediate the deposition process. Proper concentration of these additives is important to assure superior physical properties which will permit the copper to withstand thermal shock. The additives will, if properly controlled, provide for uniform deposition of the copper in the plated through hole. Since techniques are now available for the quantitative analysis of additive components in plating baths, this information can be integrated with the Mass Balance Control data to provide a comprehensive understanding of organics in the plating bath. Using the

mass balance theory on a plating bath one can now begin to understand many of the previously "unknown" variable components of the bath and their effects on performance. The input term of the mass balance equation is made up of two elements, the acid copper additive and the drag-in from the other process baths. The additive breaks down during plating, requiring its continuous addition to the bath. As a result, the organic level in the bath rises at a constant rate. The output term is made up of the components which are dragged out of the plating bath. Both the drag-in and drag-out terms should be small in relation to the additive term, therefore, the organics will build up in the bath at a fairly constant rate with time.

Graph 1 shows how Mass Balance Control can be used to evaluate and troubleshoot the plating process. Line A is the steady state accumulation of the plating bath additive and its breakdown products with time. Line B shows the steady state accumulation of the additive plus drag-in from the pre-plate process baths. The slope of this line is slightly greater than that of Line A since drag-in is occurring. Line C shows what happens if a deviation occurs in the process. Some explanations for this change would be:

1) the additive is being added at a higher rate than previously,
2) The rinses after the acid soak cleaner are contaminated with surfactant and are not rinsing effectively,
3) the acid soak cleaner was made up at a higher concentration than normal, increasing the amount of rinsing required to remove the surfactants

Mass Balance Control can be used to predict carbon treatment cycles. By analyzing the baths on a weekly amp-hour basis and plotting these as shown in Graph 2, the build up of organic material can be monitored. Once this information has been correlated to bath performance, such as plated through hole uniformity and physical properties, the timeframe for the next carbon treatment can be extrapolated. The carbon treatment procedure can also be optimized by using the Mass Balance Control system.

Graph 3 illustrates how mass balance was used to determine the effectiveness of removing organics by passing the solution through a carbon packed column. The packed column removed 67 percent of the organics in approximately 15 minutes. The rate of removal drops quickly and after one hour the carbon packed column was replaced. The second packed column reduced the organic level by only 7 percent of the original concentration. This pattern of diminishing returns for each carbon packed column replacement continues. Information such as this can be used to determine how frequently and how many times the carbon packed column should be replaced for the most complete carbon treatment to occur. It is obvious from this data that recirculating the solution for more than a half hour did not increase the effectiveness of the carbon treatment. This Mass Balance Control approach could also be used to evaluate the effectiveness of different types of carbons or batch treatment versus in-tank packed column filtration.

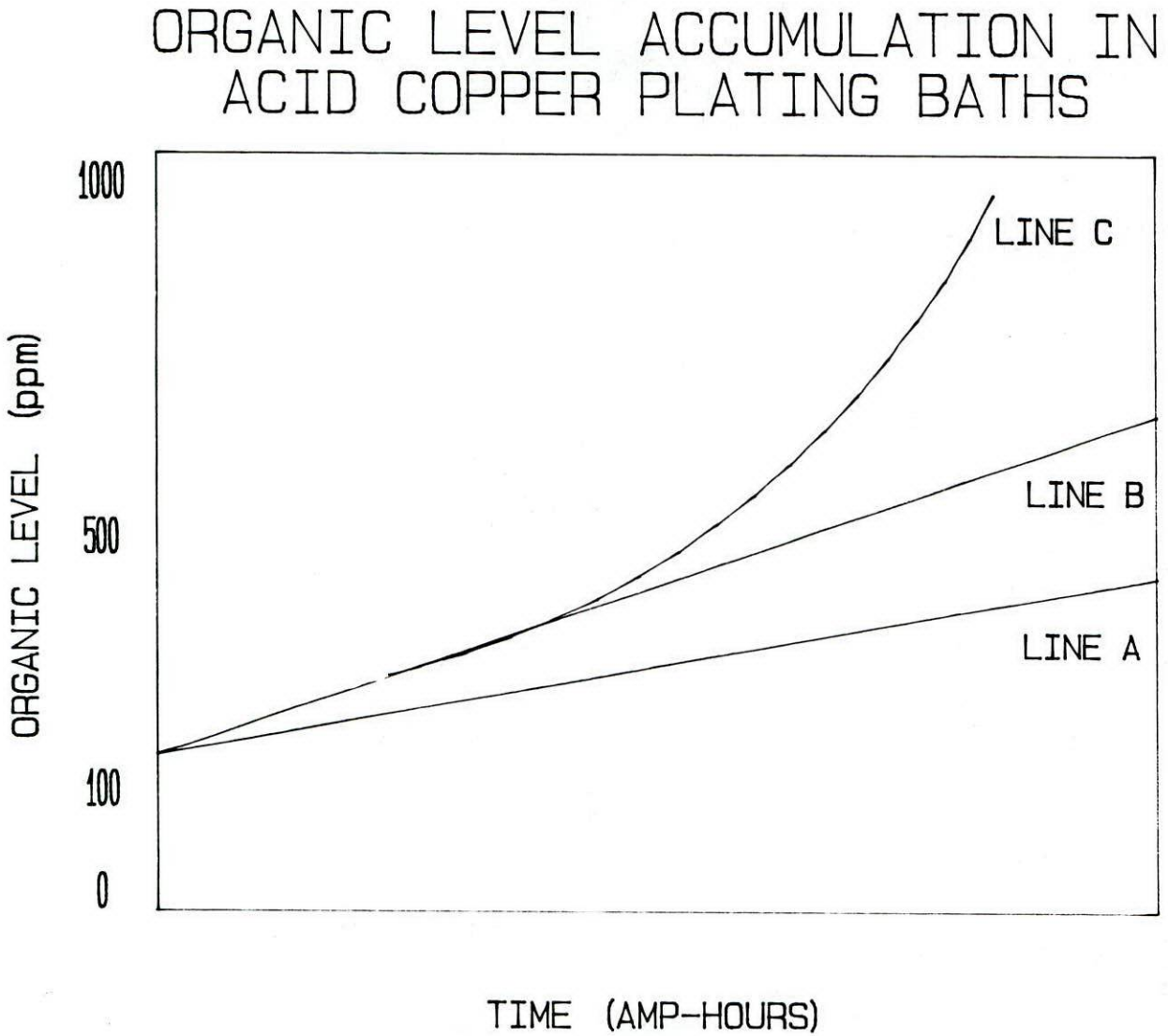
The mass balance approach is also very useful in monitoring pre-plate process baths. A typical pre-plate line for copper consists of an acid soak cleaner,

a micro-etch, a sulfuric acid pre-dip and the rinses. Acid soak cleaners and micro-etches typically contain surfactants which cling to the surface of the board. If these are not carefully rinsed from the boards, they will be dragged from one process bath to the next, finally ending up in the plating bath. Being surface active, they can have a potentially detrimental effect on the plating of the board.

To evaluate the rinsibility of an acid cleaner, the following simple experiment was performed. Two small still rinses were set up and boards were dipped into an acid cleaner. The boards were allowed to drip for 15 seconds and then dipped into the D.I. water rinse for 15 seconds. They were then dipped into the second D.I. water rinse for 15 seconds. Graph 4 shows the change in organic level versus the number of boards rinsed. In the first rinse the organic level rises linearly with the number of boards rinsed, while the change in organic level in the second bath is barely detectable. This indicates that the acid cleaner rinses readily from the boards and only very small quantities are being dragged into the next tank. At some point the concentration of acid cleaner in the first rinse will become significant and the organic level in the second bath will begin to rise more rapidly. This kind of data permits the optimization of rinse tanks, whether they be counterflow or single stage, reducing the amount of water used while still assuring quality rinsing.

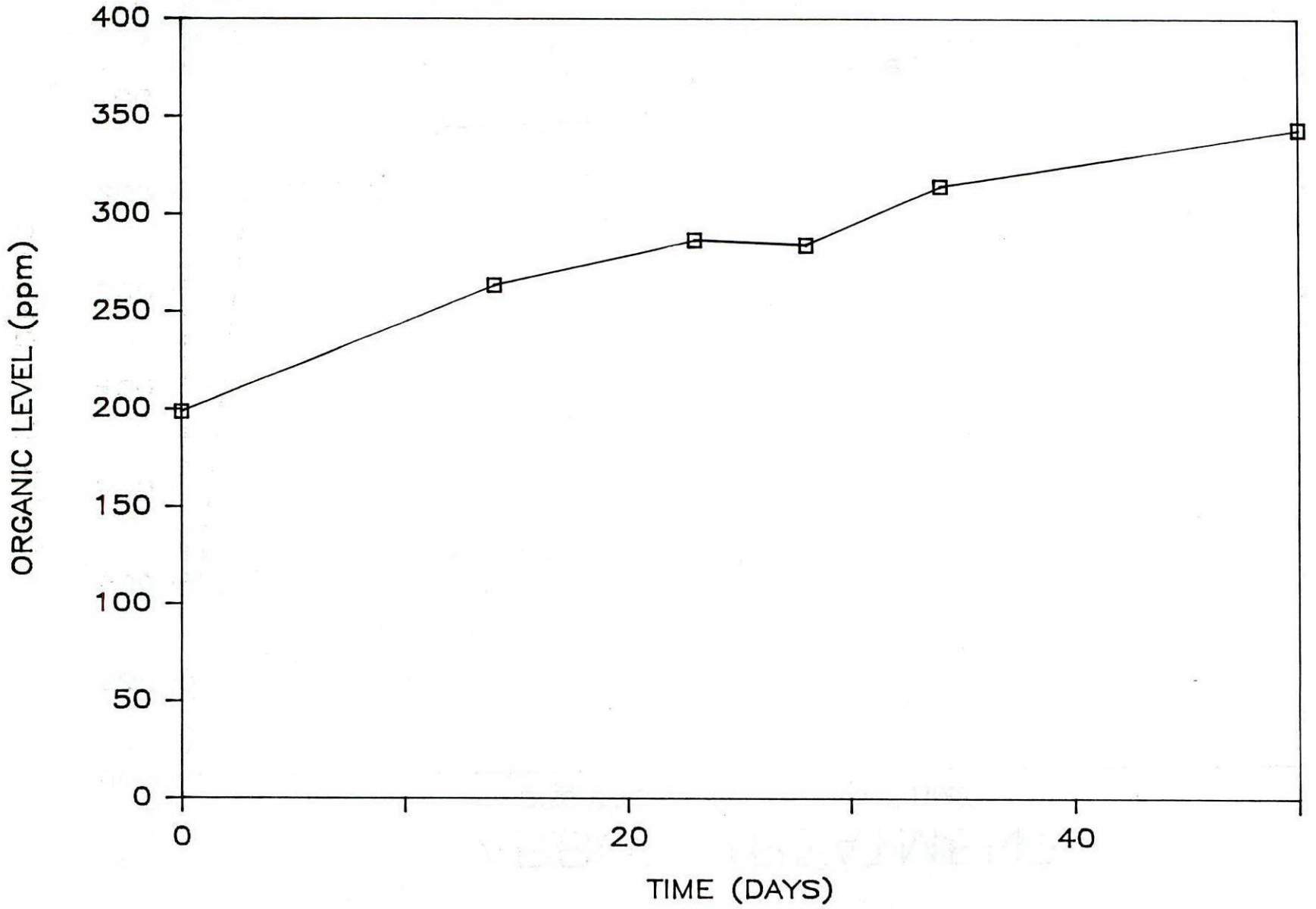
In recent years the industry has become aware of the important role that organics play in the plating process. Within the last couple of years, methods have been developed allowing the organic additives in the acid copper plating bath to be quantitatively analyzed. While this has provided more information than was previously available, Mass Balance Control takes this ability to understand the plating process one step further. Not only can the plating additives be monitored but the total amount of organics in the plating process and its accumulation with time can be investigated. Tolerance for organic contaminants can be documented and process control methods then implemented. Decisions regarding choice of acid soak cleaner, amount of rinse water required and frequency of carbon treatment can now be based on data gathered from Mass Balance Control experiments rather than relying on past history and experience.

GRAPH 1

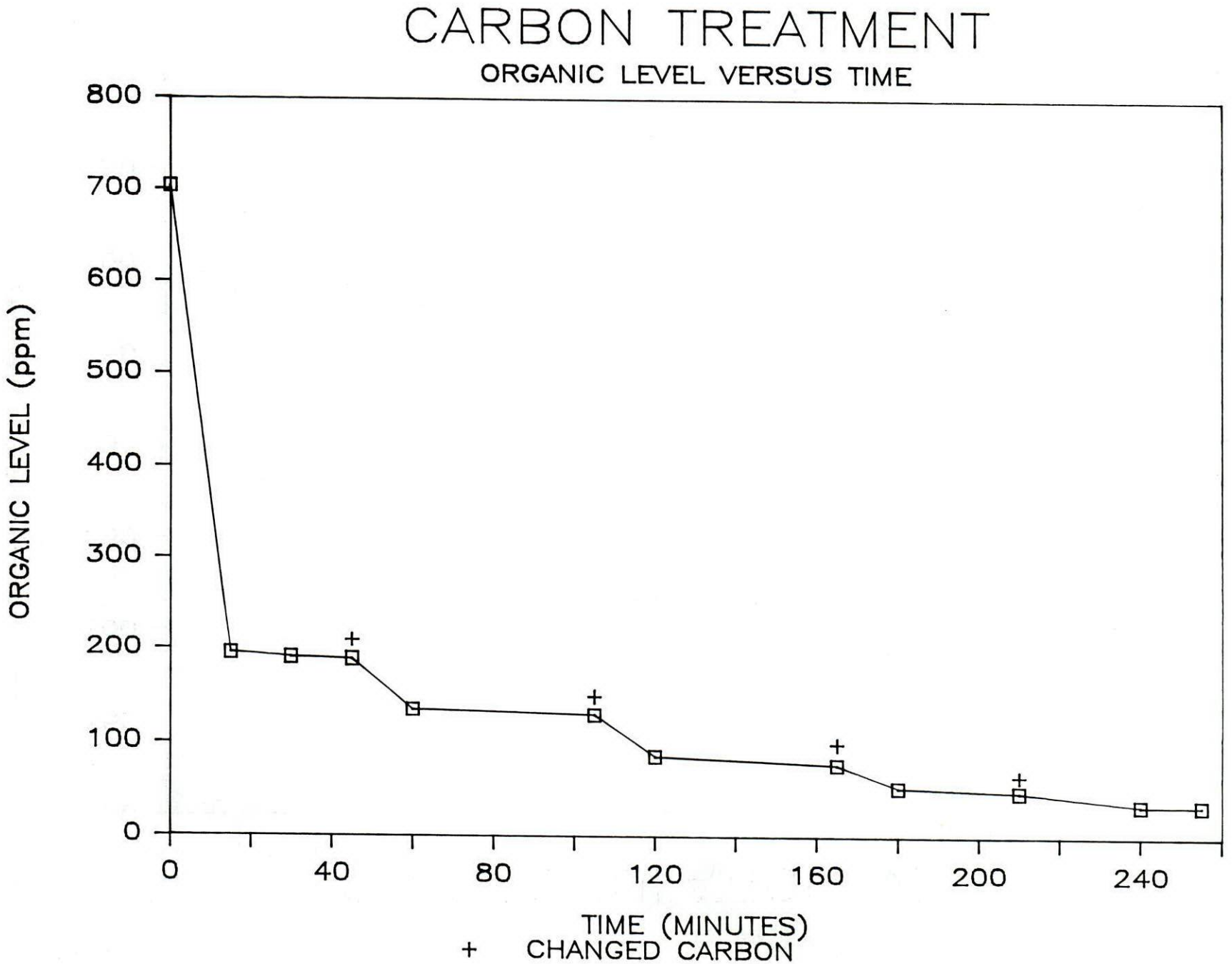

ORGANIC LEVEL ACCUMULATION IN ACID COPPER PLATING BATHS
1000
500
100
0
ORGANIC LEVEL (ppm)
LINE C
LINE B
LINE A
TIME (AMP-HOURS)

GRAPH 2

ORGANIC ACCUMULATION VERSUS TIME

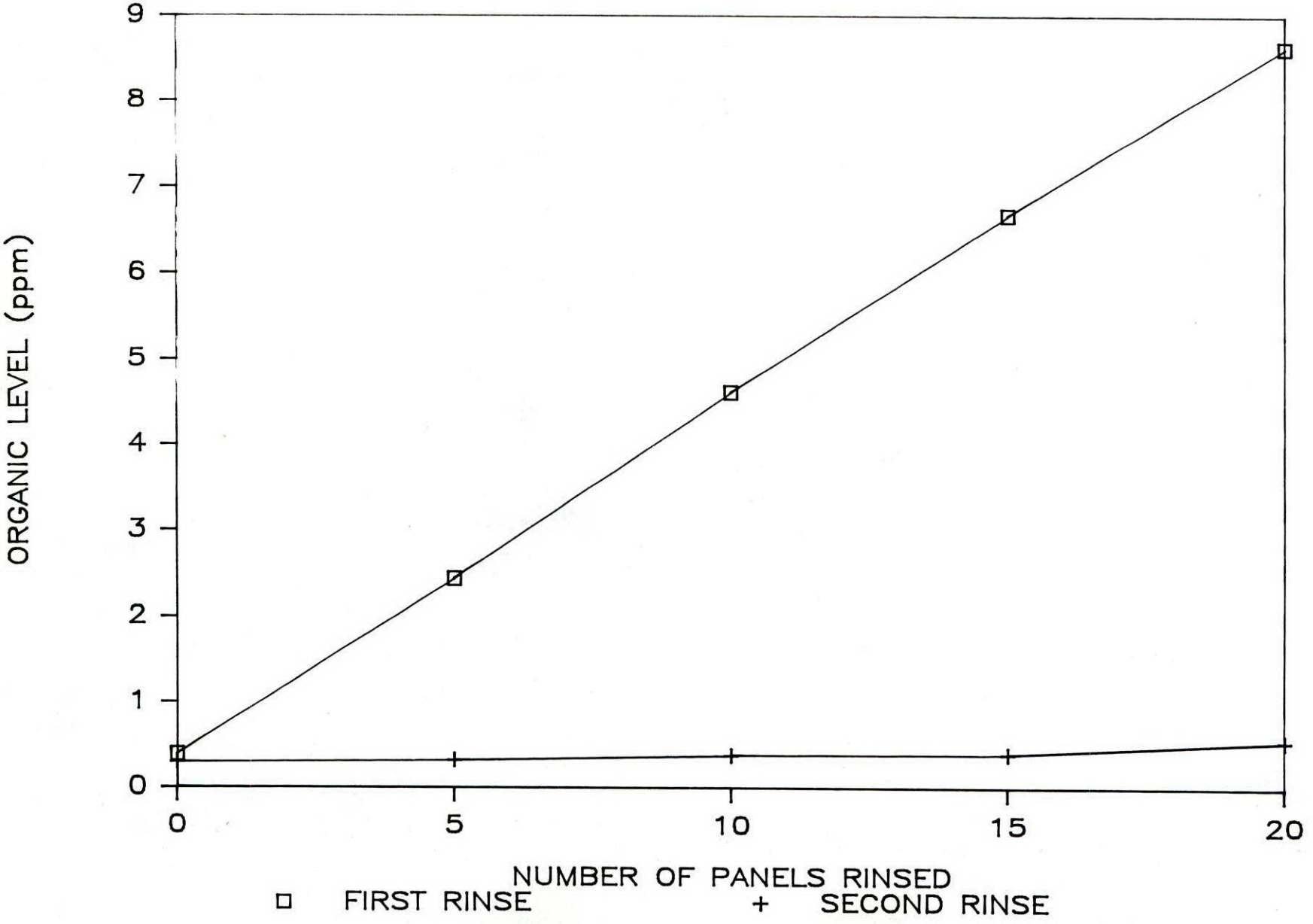


GRAPH 3


CARBON TREATMENT
ORGANIC LEVEL VERSUS TIME
ORGANIC LEVEL (ppm)
800
700
600
500
400
300
200
100
0
0
40
80
120
160
200
240
TIME (MINUTES)
+ CHANGED CARBON

GRAPH 4

ORGANIC LEVEL VS NUMBER OF PANELS



I-6

Electronics I
Session I

Direct Recycling of Copper From Etching to Plating

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Direct Recycling of Copper from Etching to Plating

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1. Introduction

In the manufacturing of rigid printed circuit boards (PCB), an additive and subtractive process is commonly used. The two key steps of the process are copper electroplating and etching. The starting laminate boards come with a thin copper film. Then copper is plated onto the masked boards to form the circuit pattern in a copper sulfate/sulfuric acid bath using copper anodes. To remove the initial thin film from the areas that are not part of the circuit, that copper is etched. Thus, copper anodes are consumed, and spent copper etchant is generated. A process to replace the copper anodes with copper from the spent etchant would be environmentally and economically desirable.

A method to reuse copper using insoluble anodes has been proposed by C. G. Smith.[1] The copper plating baths were to be replenished with powdered CuO precipitated from the spent etchant. A hopper-mixer, slurry-filtration system was developed. With this process, the etchant can not be recycled, and the ammoniacal solution left from the precipitation step has to be disposed properly. Handling of fine powders on a large scale could be difficult. A different approach may be more attractive and a simpler process could be developed if the copper could remain in solution as cupric ions during the transfer.

The use of liquid ion-exchange agents in the recovery of copper from the etchant[2] indicates that direct recycling of copper from ammonia etching solutions to acid plating solutions may be feasible. The recovery process is based on the ability of certain chelating agents to form organic copper complexes from ammonia solutions and then to reverse the process at low pH:

$$\begin{aligned} \text{pH} \geq 8, \quad & Cu^{2+}_{aq} + 2\,RH_{org} \rightarrow R_2Cu_{org} + 2\,H^{+}_{aq} \\ \text{pH} \leq 4, \quad & 2\,H^{+}_{aq} + R_2Cu_{org} \rightarrow 2\,RH_{org} + Cu^{2+}_{aq} \end{aligned}$$

Thus, the organic phase, containing the chelating agent and its copper complex, acts as an ion-exchange resin system. By using an organic phase as a means to transfer cupric ions from

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ABSTRACT

In the manufacture of printed circuit boards (PCB), an additive and subtractive process is commonly used. The two principal steps of the process are (1) copper electroplating to form the circuit pattern and (2) chemical etching to define the conductor paths. Thus, copper anodes are consumed and the spent copper etchant is generated.

A process of transferring the copper as cupric ions from the etchant to the plating bath has been investigated using organic liquid ion-exchange agents. With this process incorporated into the manufacture of printed circuit boards, the net operation is:

$$\text{Cu (etched)} \rightarrow \text{Cu (plated)}.$$

The extraction and stripping studies demonstrated the process feasibility. The etch quality of the etchant was found not to be affected by the presence of organic liquid ion-exchange agents. We were able to plate good quality deposit from the stripping solution with a current efficiency of 100%.

alkaline solutions to acidic media, the precipitation of copper oxide is avoided.

Phenyl alkyl β-diketone, commercially available*, was found to be effective in complexing copper from ammoniacal etchants without extracting either ammonia, ammonium copper complexes or chloride. This high selectivity of the diketone should make it possible to recycle the etchant and to minimize the waste disposal problem. Figure 1 shows the process scheme. The transfer of cupric ions to the plating bath can be easily achieved by conventional liquid/liquid extraction equipment. This direct transfer of copper from etchant to plating bath could result in the recycling of etchant and eliminate the need for copper anodes.

In PCB manufacturing plants where the amounts amount of copper in spent etchant is more than the amount of anodes consumed, the incorporation of this copper transfer process would mean that the thin copper layer on the laminate boards would provide all the copper needed. This can be illustrated simply by the following reactions:

(1) Etching: $Cu(etched) + 4NH_4OH + 1/2O_2 \rightarrow Cu(NH_3)_4^{2+} + 2OH^- + 3H_2O$

(2) Org.Extraction: $Cu(NH_3)_4^{2+} + 2RH + 2H_2O + 2OH^- \rightarrow R_2Cu + 4NH_4OH$

(3) Org.Stripping: $R_2Cu + 2H^+ \rightarrow Cu^{2+} + 2RH$

(4) Plating: $H_2O + Cu^{2+} \rightarrow 2H^+ + 1/2O_2 + Cu(plated)$

The net reaction is:

$$Cu(etched) \rightarrow Cu(plated).$$

If the amount of copper etched is more than that plated, the excess can either be recovered as copper sulfate or be plated out as copper metal.

The objective of the present work is to investigate the feasibility of using phenyl alkyl β-diketone to transfer copper from the ammoniacal etchant to the acid plating solution without affecting the performance of the etchant or the plating bath. The etch quality of PCBs using etchant containing a trace amount of the diketone was examined. The selectivity of the

* LIX-54, Henkel Corp., Tucson, AZ.

diketone in not transporting chloride ions from the etchant to the plating bath and the influence of the diketone on the copper deposit were also studied.

2. Experimental

The phenyl alkyl β-diketone used is commercially available. As received, the liquid ion-exchange reagent(LIR) is a 40 vol % solution of diketone in kerosene. It is non-toxic and is no more of an irritant than kerosene. LIR has a light amber color and when it is loaded with copper, the color becomes dark green. The etchant used in the present work is the spent proprietary** etchant except in the etch quality experiments, where the high speed proprietary** etchant also from P. Hunt Chemical Co. was used. The plating bath used was a proprietary bath***.

The concentration of the copper-diketone complex was determined spectrophotometrically. The concentration of copper in aqueous solution was analyzed by titration with 0.2 N disodium ethylene diamine tetraacetate(EDTA). The sample solution was added to 500 ml of 4.0% ammonium hydroxide solution (pH=12) in such an amount that the mixture had a copper concentration of about 0.1 g/l. The indicator was PAN (1-(2-pyridylazo)-2-naphthol). 0.01 gm/liter of isopropanol. The chloride concentration was determined with the standard mercuric nitrate titration.

For evaluating the etch quality, printed circuit boards were etched in a Kepro bench top spray etcher (Model BTE 202). Four gallons of the etchant was kept at 120° F and were sprayed onto both sides of the PCB. An etch time of about 0.5 minute was just enough to have both over-etched and under-etched areas. To simulate LIR contamination, 50 ml of LIR solution was added to the etchant.

** ENDURA, P. Hunt Chemical Co., Palisades Park, NJ.

*** CUBATH M, Sel-Rex, Oxy Metal Industries Corp., Nutley, NJ.

3. Results and Discussion

Although LIR has been reported[2] to be effective in extracting Cu from ammoniacal solution and in being stripped of Cu by acids, it was necessary to show that similar performance can be achieved using the ammoniacal etchant and the sulfuric acid plating bath commonly employed in the manufacture of PCB. The extraction and stripping processes are discussed first. Then the effect of the copper transfer process on the etching and plating steps is presented.

3.1 Extraction

The extraction isotherm of LIR and the spent etchant, depicted in Fig. 2, is a plot of equilibrium Cu concentrations in organic and etchant phases obtained when different volume ratios of the spent etchant (142 g/l of Cu) and the pure LIR solution were mixed. The isotherm can be explained in terms of mass balance and equilibrium considerations (Appendix I). The line in Fig. 2 is the predicted behavior for an equilibrium constant of 15. The fit is good for the organic Cu concentration up to 35 g/l. It is not surprising to have the disagreement at higher concentrations because the saturation concentration is about 45 g/l.

The ability to predict the isotherm makes it possible to calculate the relationships between various operating parameters. For example, the ratio of the volumetric flow rate of etchant and LIR solution into a continuous mixer is important in operating the extraction process. Figures 3 and 4 show the ratio's influence on the Cu concentration of both the etchant and the LIR solution. These relationships are useful for process optimization.

3.2 Stripping

Similar equilibrium data were obtained for stripping of copper from the loaded LIR solution by the plating solution. Because of the high acid concentration of the plating solution, there is no difficulty in stripping the copper. The Cu concentration was set by the solubility limit of copper sulfate in sulfuric acid, about 60 g/l. In runs with the volume ratio of organic/plating solution larger than 2.5, copper sulfate was crystallized out, and the concentration data in Table 1 represent the copper concentration of the plating solution in the presence of the crystals.

This suggests that the plating solution was super-saturated. Note that the copper-diketone complex in the organic phase was stripped to less than 2 g/l of Cu.

3.3 Plating

The copper plating solution used in this study is described in experimental section. For the brighteners to work properly, the chloride concentration has to be maintained at less than 100 ppm. Chloride contamination by the organic could make the process unworkable. In a copper recovery process using other liquid ion-exchange agents, a step for washing the organic solution was included.[5] Since the chloride in the etchant is very concentrated (180 g/l), it is necessary to determine whether any chloride is carried over by the organic solution. Our stripping experiments show that the equilibrium chloride concentration of the plating solution contacting the LIR solution is about 40 ppm, which is within the acceptable level.

Since trace amounts of LIR are unavoidably present in plating bath, the influence of LIR on the copper deposit has to be determined. To evaluate this effect, copper was plated in a Hull Cell, where the effect can be easily observed over a wide range of current densities. Three plating conditions were studied: (1) the standard containing only the plating bath; (2) the plating bath exposed to LIR; and (3) the same as (2) but the anolyte and catholyte were separated by a cationic membrane****. The results are shown in Figure 5. The effect of the membrane is to prevent the organic from diffusing to the anode where it can be oxidized.

The use of a cationic membrane in plating is also required to prevent the decomposition of the plating bath brighteners by insoluble anodes.[1] For process implementation, it is more convenient to have an anode membrane bag than an anodic membrane chamber. A technique for bonding the membrane and thus providing a simple method for making the bag was developed.[6] In experiments using such a bag, the cathodic current efficiency has been determined to be 100%. Thus, copper plating with insoluble anodes in the presence of trace

**** NAFION, E. I. du Pont de Nemours, Wilmington , Delaware.

amounts of LIR is feasible.

3.4 Etching

Because the etch rate of ammoniacal etchants is high, the PCB is often etched in a sprayer etcher in which the cuprous ions formed are oxidized immediately by oxygen to cupric ions(equation (2)). Since LIR is selective, the spent etchant after mixing with the LIR solution would be the same as a copper rich replenishing solution. One obvious problem that could prevent the etchant from being recycled is the change of the etch quality of the etchant by trace amounts of LIR. The etching performance of the etchant with and without the presence of LIR was evaluated, and the etch time was selected such that both over-etch and under-etch areas existed. No significant difference was observed between the samples etched with the etchants containing or not containing LIR. Thus recycling the spent etchant is possible and deserves further investigation. Such a study, however, requires many etchant bath turnovers, and it could best be performed in pilot-plant studies.

4. Summary

The feasibility of recycling directly copper from etching to plating has been demonstrated. The extraction of copper from the etchant by the LIR solution and the stripping of the copper from the loaded LIR solution to the plating bath were performed without difficulty.

The extraction isotherm shows that LIR solution can be loaded to 40 g/l of Cu. We explained the extraction isotherm using mass balance and equilibrium calculations. Thus, various operating parameters were also calculated. For example, the influence of the ratio of the volumetric flow rate of etchant and organic in a continuous process was predicted. In the stripping process, there is no difficulty in removing copper. The copper concentration of the acid(plating bath) is set by the solubility of copper sulfate, about 60 g/l of copper.

Although the etchant has a concentration of 180 g/l chloride ions, the stripping solution has less than 50 ppm of chloride. Thus, the brighteners of the plating bath work properly. Trace

amounts of LIR were found to be easily oxidized anodically and the by products influenced the plating. Hull Cell panels illustrated clearly this effect. This problem was eliminated when an anode bag made of cationic membrane was used. Then we were able to plate good copper deposit from the stripping solution with a current efficiency close to 100%.

Although we did not attempt to regenerate the etchant, no major problem is expected. The etch quality of the etchant was found not to be affected by the presence of LIR. The regeneration of etchant should be investigated in pilot plant studies.

Acknowledgments

We are grateful for the assistance of the Chemical and Etching Process Engineering Dept. at AT&T Technologies, Richmond Works. Thanks are also due to Mr. P. C. Milner and Mr. C. Merigold for many helpful discussions.

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6. S. G. Seger, private communication.

Appendix I: Calculation of Extraction Isotherm

The extraction reaction can be expressed as:

$$Cu(NH_3)_4^{2+} + 2RH + 2H_2O + 2OH^- \rightarrow R_2Cu + 4NH_4OH \qquad (A\text{-}1)$$

The hydrolysis of ammonia also occurs:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (A\text{-}2)$$

From the mass balance, we have three more equations:

$$[RH] = [RH]_o - 2([CuR_2] - [CuR_2]_o)$$
$$[Cu(NH_3)_4^{2+}] = [Cu(NH_3)_4^{2+}]_o - V_o/V_a([CuR_2] - [CuR_2]_o)$$
$$[NH_4^+] + [NH_3] = [NH_4^+]_o + [NH_3]_o + 4V_o/V_a([CuR_2] - [CuR_2]_o)$$

where V_o and V_a are the volumes of organic and aqueous phase and the subscript o designates the initial concentration. Along with two equations relating the equilibrium constant to the concentration, we have five unknown concentrations and five equations. Through algebraic manipulations, a fifth order polynominal of one concentration was obtained. Solving for the positive real root numerically, the concentrations of all five species are calculated for a given equilibrium constant and a set of initial concentrations. The solid line in Fig. 2 was based on these conditions:

For (A−1), $K = 15$
For (A−2), $K_b = 1.79 \times 10^{-5}$
pH (etchant) = 8.4
$[Cu(NH_3)_4^{2+}]_o = 2.2$ M
$[NH_3]_o + [NH_4^+]_o = 5$ M
$[RH]_o = 2.5$ M
$[CuR_2]_o = 0$ M

Table 1. STRIPPING EQUILIBRIUM DATA

Vol Ratio org/acid	Cu(org) g/l	Cu(acid) g/l
2.5	1.74	69
3.0	2.78	64.9
5.5	27.2	63
6.5	25.3	57
7.5	25.5	58

FIGURE CAPTIONS

Figure 1. Process Scheme.

Figure 2. Extraction isotherm with the spent etchant containing 142 g/l of Cu: the solid line represents the calculated values (Appendix I).

Figure 3. Calculated dependence of the concentration of copper in the etchant on the volumetric flow rate ratio.

Figure 4. Calculated dependence of the concentration of copper in the LIR solution on the volumetric flow rate ratio.

Figure 5. Influence of LIR on the appearance of the deposit as a function of the plating current density.

DIRECT RECYCLING OF COPPER

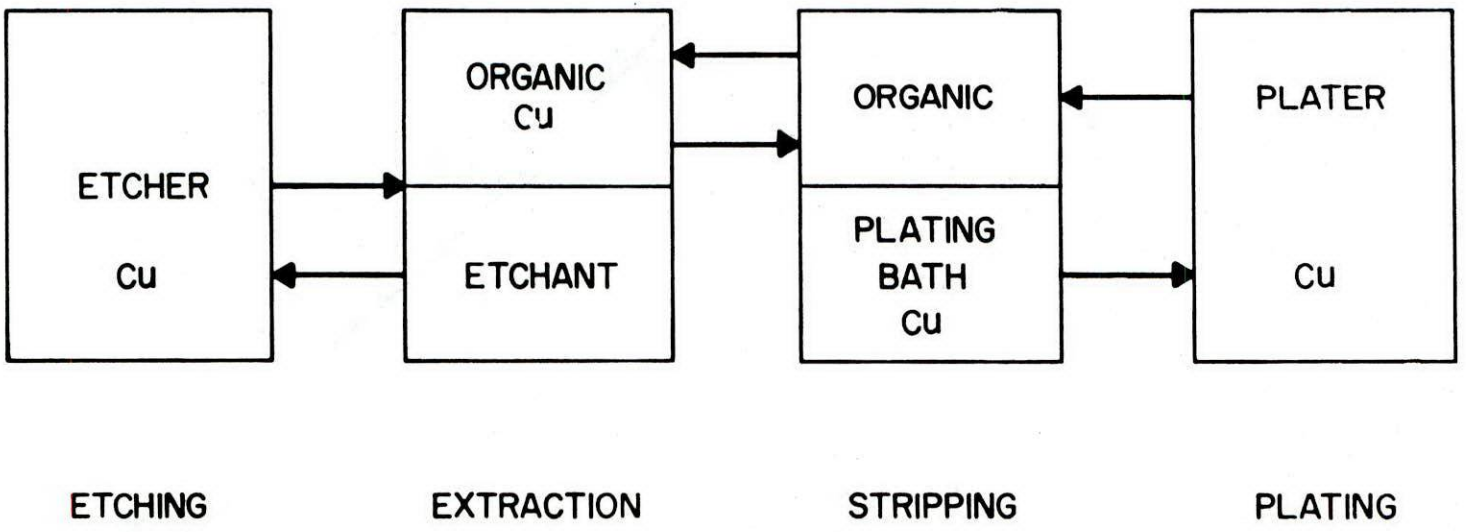

FIGURE 1

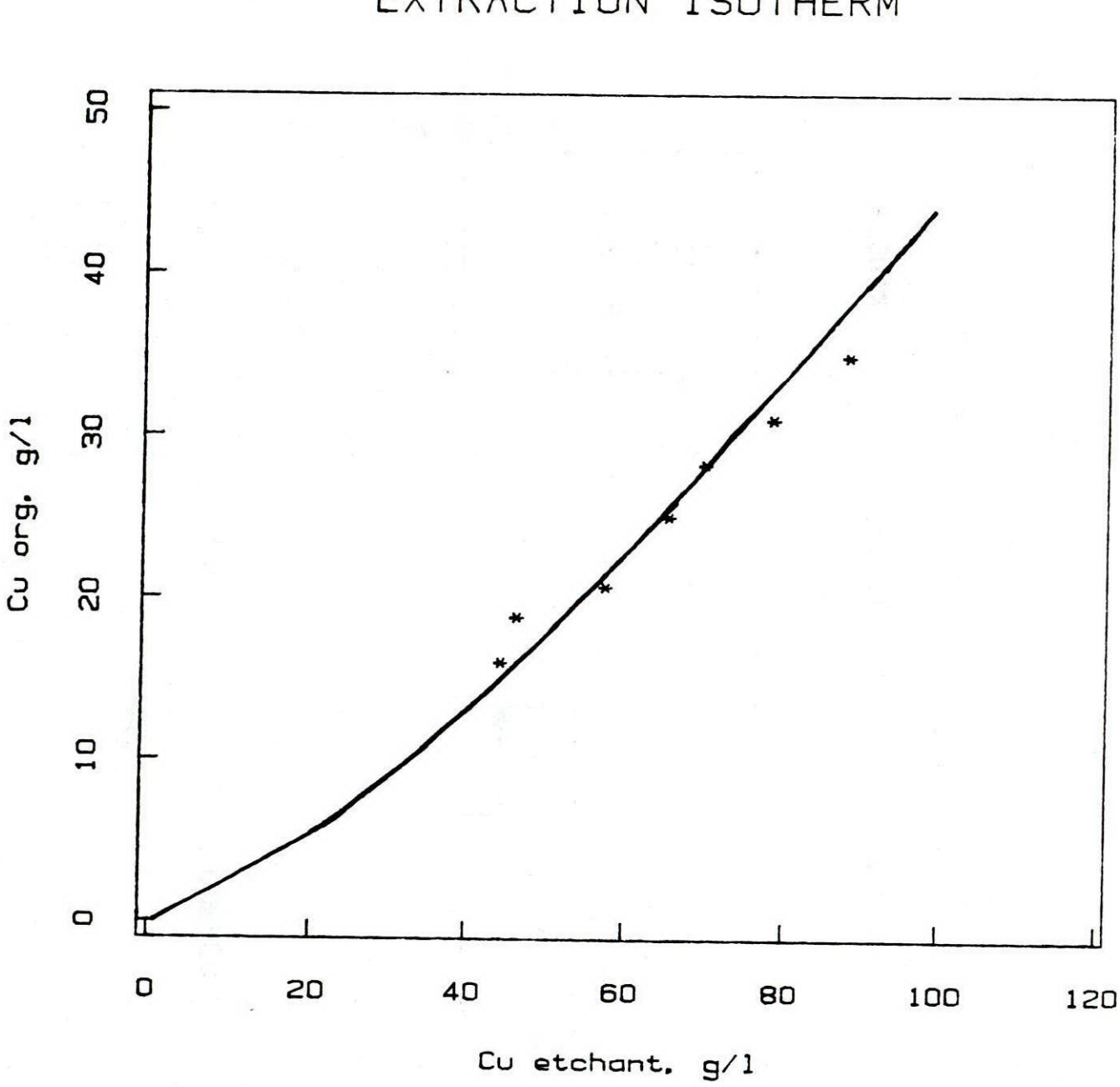
EXTRACTION ISOTHERM
Cu org. g/l
0
10
20
30
40
50
0
20
40
60
80
100
120
Cu etchant. g/l

FIGURE 2

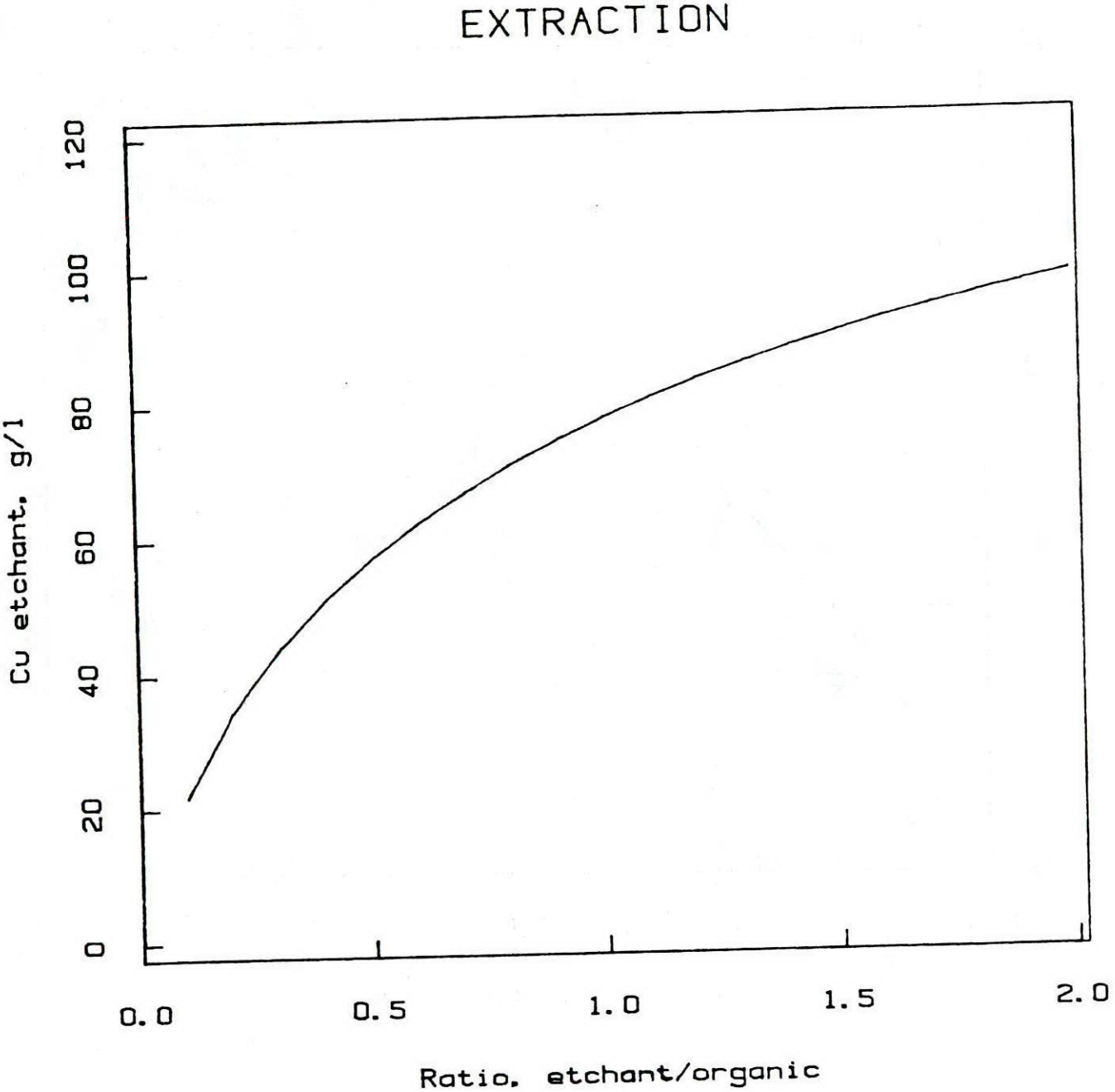
EXTRACTION
Cu etchant. g/l
0
20
40
60
80
100
120
0.0
0.5
1.0
1.5
2.0
Ratio. etchant/organic

Figure 3

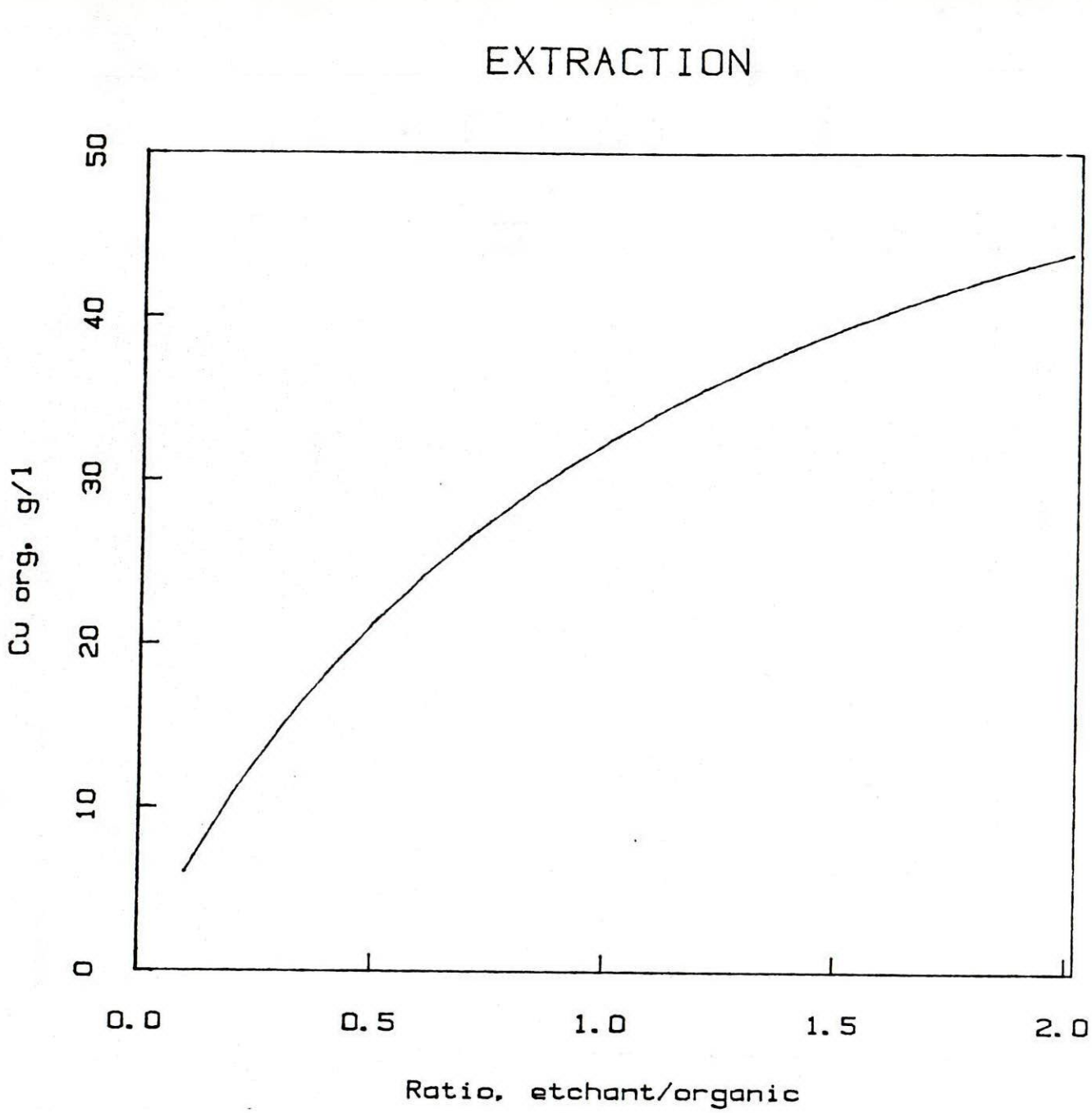
EXTRACTION
Cu org. g/l
0
10
20
30
40
50
0.0
0.5
1.0
1.5
2.0
Ratio, etchant/organic

Figure 4

HULL CELL PANELS

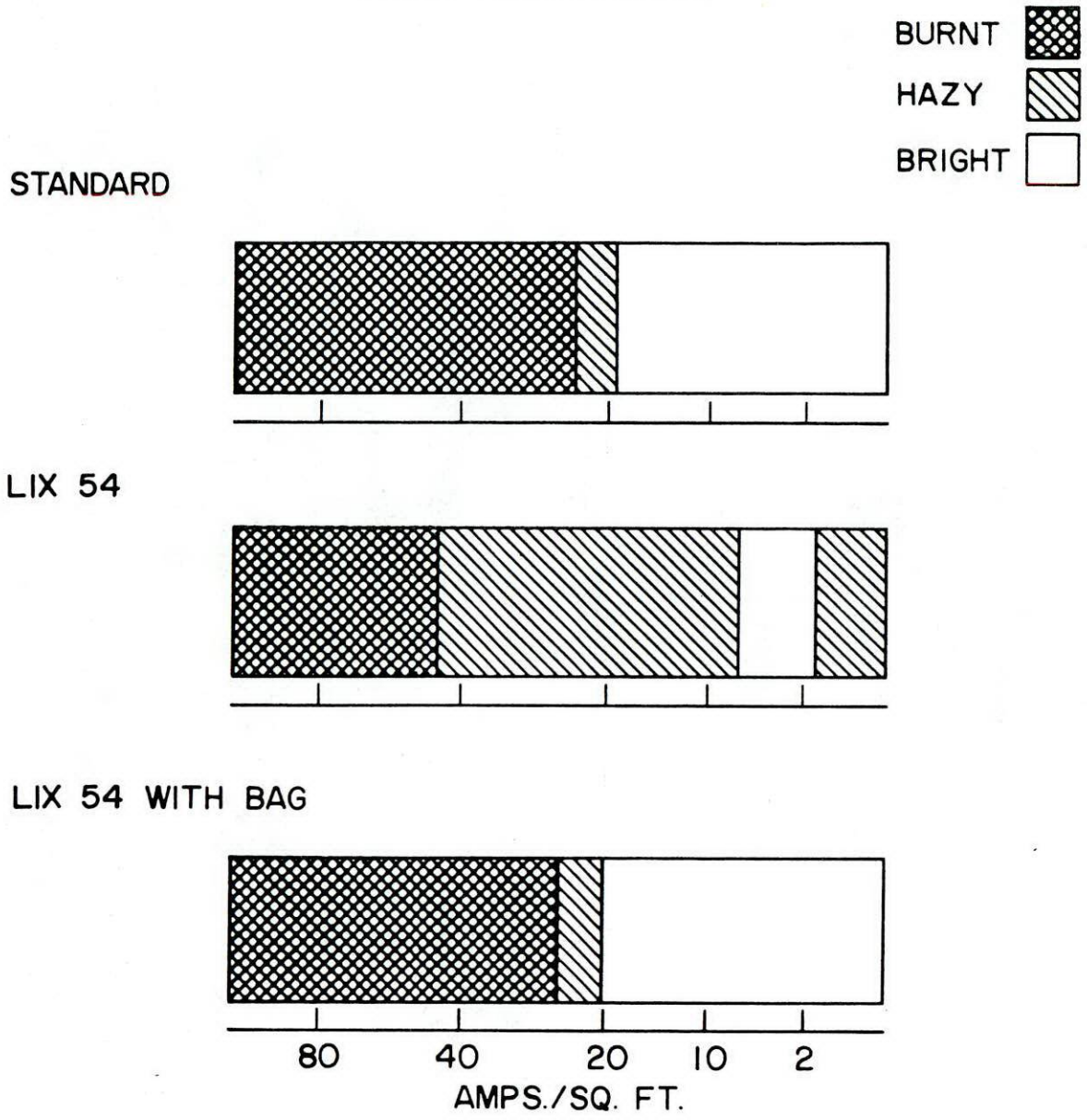

Figure 5

J-1

Electronics II
Session J

Sensor Systems in Automatic Electroplating

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Sensor Systems in Automatic Electroplating

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There is a growing trend toward automatic manufacturing and the electroplating industry is adopting many of the techniques[1-3]. Automatic electroplating can have many levels of automation depending on how automatic one wants to make it. A reel to reel strip plater having only a motor drive that pulls the strip through the processing cells can be considered an automatic machine. Similarly, a barrel plater which moves a barrel of parts through all the tanks with a programmed timer is also automatic. In both examples only the transport of parts is automated and the machine operator must monitor and maintain all the chemical processes, watch the movement of parts through the machine and check all the electrical components such as power supplies to make certain they are functioning properly. To get the maximum production from a plating machine with high quality plating, machines must run faster and meet tighter end point plating requirements. This can make life very difficult for even the best operators.

To free the operator from machine watching and fine tuning critical process variables, an integrated system of sensors tied to an electronic controller is required. Sensor technology has developed rapidly in recent years and we now have a vast array of commercial sensors available and many are useful for plating machine applications. In fact the number of sensors available for some applications is so large that one must study the features of each sensor and make a choice. For example, a recent survey showed there were 144 manufacturers of level sensors making over 20 different types[4]. Table I lists 40 different sensor devices and phenomena useful for automatic electroplating. Those with an asterisk are commonly used in automatic plating machines built today. Many of the others will be utilized when the specific need arises and commercial devices are offered which are attractive to the machine designer.

There are several things to consider when choosing a sensor to monitor plating variables. The important items are: accuracy, reliability, sensor life, cost, signal conditioning and maintenance. Accuracy required depends on the process or machine part function. Solution temperatures controlled to $\pm 1^{o}C$ are usually adequate. Cumulative variables such as plating current, plating efficiency and line speed need to be controlled so the overall accuracy is within acceptable limits. For example, if each of the three parameters are allowed to vary as much as +1%, then the plating thickness can vary +3%.

Plating machine sensors usually must live in a hostile environment with corrosive fumes and electrical noise in abundance. For high reliability the design and choice of construction materials must be considered carefully. The sensor should hold its calibration for at least a day and most do for long periods. The only assurance that a sensor is working properly is either to check it frequently or build in a self checking system utilizing sensors within the sensor together with special electronics. These are referred to as smart sensors although sometimes there are other features included such as having the sensor system provide the control signal or be programmed by a remote computer.

Sensor life not only depends on how well made it is or the wear out mechanism but also on how it is used and maintained. A glass pH electrode, for example, once put to use must be kept wet for reliable operation. If removed from plating solution, it should be stored in water or buffer solution until returned to the bath. A float solution level sensor can become inoperative if plating salts crystallize out on the float causing it to stick. The problem is avoided if water added to maintain the level is put in at the float. This removes any tendency for salts to form on the float.

How much one should pay for a sensor depends on the value of the variable being sensed. Temperature sensors are used in many places in a plating machine and they are relatively cheap. On-line plating thickness monitors involve expensive equipment but if gold is plated one can afford to spend $20,000 for the sensor system if it means a $100,000 a year saving in gold by avoiding excessive overplating or producing scrap due to underplating.

Sensor signal conditioning involves converting the electrical signal from the sensor into a form that can be displayed in engineering units such as grams per liter metal ion concentration and/or fed into a programmable logic controller (PLC) or computer. Signal conditioning can be electronic hardware or computer software or a combination of the two. If only a few sensor systems are involved, hardware is the most cost effective interface. If hundreds are used, then software becomes practical. Computer software can be developed to instruct the computer on how to convert the raw sensor signal to a form useful for process control. Linear relationships between signal and process variable are easy to handle electronically. Non linear relationships involve more electronics but operational amplifiers, converters, counters, timers, etc. can be put together to linearize most any sensor output relative to the process variable.

Maintenance of sensors for reliable performance should be considered. Zero or little maintenance is most desirable because that is what most instruments get in a typical production facility. Usually if the maintenance schedule recommended by the sensor manufacturer is followed few if any problems will occur and the sensor will have a long useful life.

An automatic electroplating facility's dependence on sensors is illustrated in Fig. 1. Without sensors the electronic PLC or computer controller is ignorant of what is going on in the plating process. It responds only to information it is given. There are three sensor types: on-off, analog and digital. The on-off sensor is a simple yet very useful in many parts of the plating process. It does not require a signal conditioning interface except when power switching is involved and then a relay interface is necessary. Sensors that provide analog information can display their information on meters which is useful to operators who want to monitor the status of certain variables even though control of that parameter is automatic. Automatic control often requires that the analog signal be converted to a digital form for PLC or computer processing. Some sensors provide a digital signal directly such as a photoelectric line speed sensor which generates pulses at a rate proportional to the line speed. Electronic processing then converts pulse rate into line speed which can be displayed on a digital voltmeter in feet per minute or whatever units are desired and/or the processed signal can be fed into an electronic motor speed controller to maintain constant line speed.

The PLC or computer is programmed to react to information it receives. It can provide electrical signals for display of the status of process variables, sound alarms to alert the operator of trouble, process and store information and control devices such as motors, valves and power supplies.

As sensor technology expands utilizing new ways to use established sensors and develop new concept sensors involving solid-state and optical phenomena, the electroplating industry will soon be able to process parts at very high rates, with precision and reproducible high quality Technology developed to make complicated semiconductor devices such as large scale silicon integrated circuits is being adopted to create new sensor devices which are small and also have the interface electronics on the same chip with the sensor[5].

Optical devices will allow us to analyze important process variables on-line. For example, spectrographic analysis of solutions can be done on-line utilizing optical fibers to conduct the light to and from the solutions allowing the spectrometer to be remote in a safe clean place. Continuous on-line optical inspection of parts before and after plating is also feasible.

There are many new sensitive gas sensors available for detection of low levels of noxious gases from plating solutions[6]. These can alert the operator to deficiencies in ventilation or some problem in the machine.

For critical process variable monitoring multiple sensors or an advanced sensor called a smart sensor will be used. Fig. 2 illustrates the concept in which the smart sensor system includes a small microprocessor which is programmed to do sophisticated control functions based on the sensor information. another important feature is a self checking ability employing sensors which monitor critical parts of the basic sensor. For example, if the sensor includes a light source, a photodetector can be used to sense if the light is emitted. The microprocessor can be programmed to recognize when a sensor signal is not in the range it should be and call for a calibration check. Information collected in the microprocessor can be transferred to a computer for storage and/or further data processing. The computer can also reprogram the microprocessor to change the compensation values of the sensor input, change high-low limits or modify the signal given to the control device.

Automatic load and unload of parts in plating machines is already done in barrel plating. This is more difficult with continuous reel to reel platers, but with the right sensors, electronic and mechanical equipment, it is technical feasible.

Another advantage of a highly automated plating facility with sensors monitoring all important plating variables is that plating conditions can be documented automatically correlating each section or group of parts with specific plating conditions. This documentation is essential toward maintaining high quality control of plating for critical applications requiring high reliability.

Summary

Technology already exists to design and build highly automated electroplating machines which can relieve the operator of machine watching and fine tuning to achieve high quality plating at high production rates. Sensors provide the information electronic controllers need to make on-line adjustments to the process. Commercial sensors are available to monitor most of the important plating variables. A suitable electronic interface is often needed to display the status of a process variable and/or communicate with the PLC or computer controller. New solid-state and optical devices are being developed that will allow on-line chemical analysis of solutions and increase the level of machine and plated part inspection to improve plating speeds and yields of high quality product.

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6. Third Internat. Conf. on Solid-State Sensors & Actuators, IEEE Cat. No. 85CH2127-9, W.H.Ko Gen. Chairman June 1985.

TABLE I

SENSOR TYPES USEFUL FOR AUTOMATIC ELECTROPLATING

1. Chemical *
2. Gas & vapor
3. Color
4. Displacement
5. Electrical properties
6. Fiber optics
7. Flow *
8. Force
9. Frequency
10. Friction
11. Hall effect sensors
12. Humidity & moisture
13. Integrated circuit sensors
14. Laser beam
15. Level *
16. Light
17. Load cells
18. Magnetic
19. Mass
20. Microwave
21. Motion *
22. Photoelectric *
23. Position
24. Pressure *
25. Proximity
26. Radiation
27. SAW devices
28. Smoke
29. Sound
30. Sonar
31. Strain
32. Tactile
33. Temperature *
34. Vacuum *
35. Velocity *
36. Vibration
37. Vision
38. Volume
39. Weight
40. Width

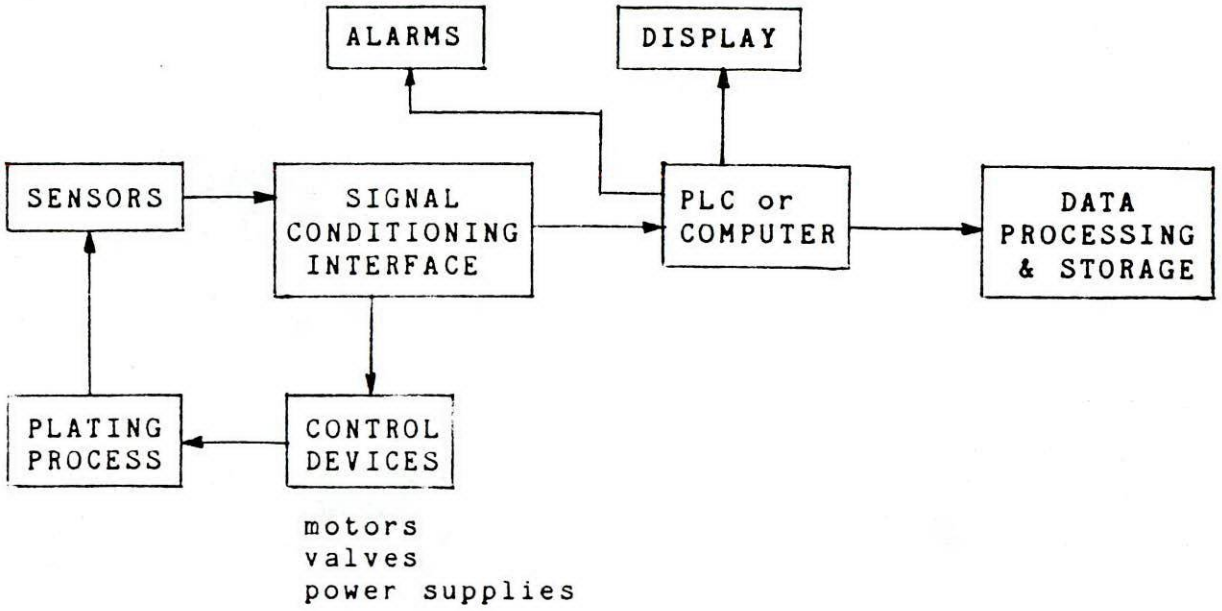

Fig. 1 SCHEMATIC OF AN AUTOMATED ELECTROPLATING PROCESS MONITORING AND CONTROL SYSTEM

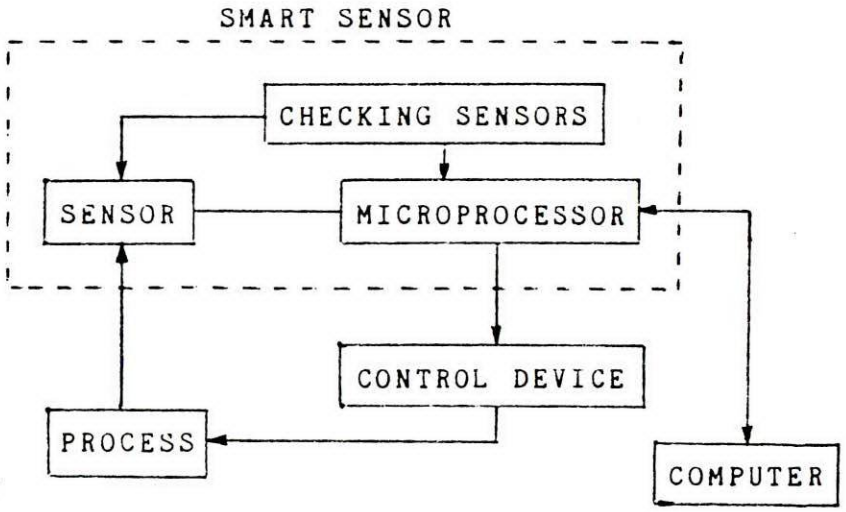

Fig. 2 SMART SENSOR CONCEPT FOR MONITORING CRITICAL PROCESS VARIABLES

J-2

Electronics II
Session J

Automation of the Dry Film Imaging Area

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AUTOMATION OF THE DRY FILM IMAGING AREA

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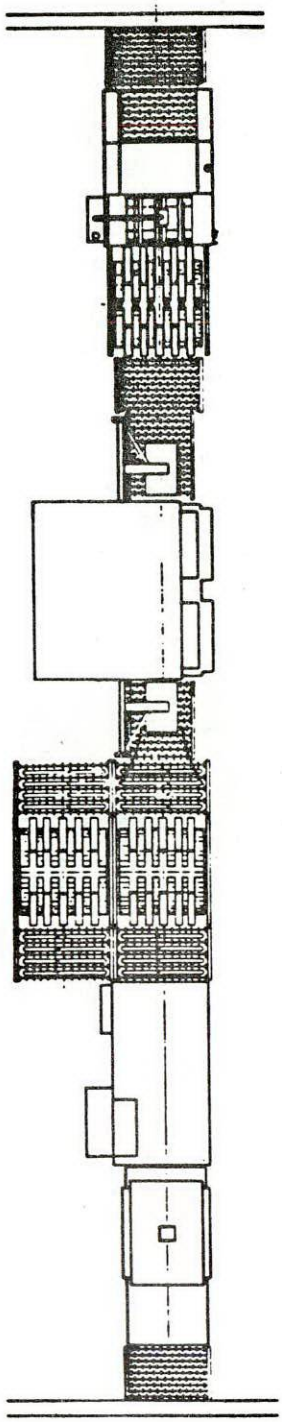
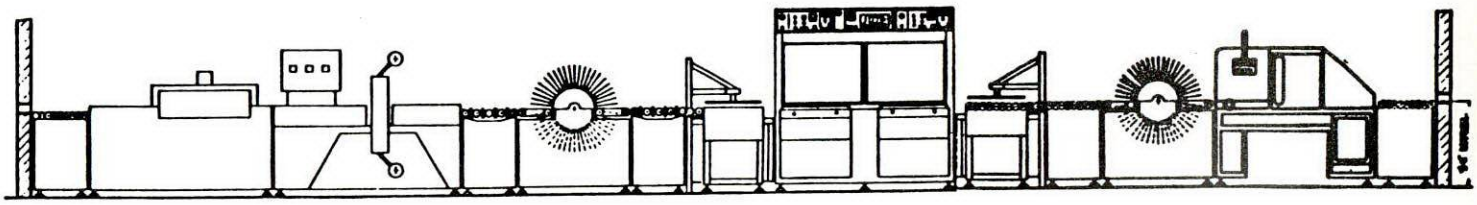


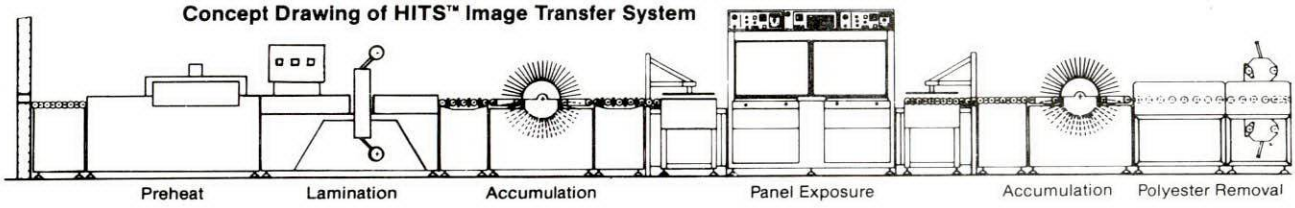


Automation of the imaging area has become an important topic for printed circuit manufacturers interested in reducing their costs and improving their quality (which, in effect, reduces costs) by changing a labor-intensive operation into one that is capital-intensive.

This paper focuses on the equipment that makes it technically possible to automate the financial impact, the factors requiring attention prior to commitment to automation, and the approaches to automation available to the printed circuit fabricator.

The dry film imaging area is defined as the fabrication steps between panel preclean and photoresist development, which includes dry film lamination, exposure, polyester removal, and material handling. In line, these steps would look similar to what is pictured here (Figure 1), but the alternative to the integrated system approach is modular automation, where each discrete step (laminates, exposure, etc.) in the fabrication process is automated independently.

Figure 1
Concept Drawing of HITS™ Image Transfer System



We will now focus on the modular approach and the modular components.

Most material handling equipment has been in use for many years and can be used throughout the facility. Most processes have the potential to use a material loader like the one pictured here (Figure 2).

Material loaders and stackers have been in use in many areas, including both wet- and dry-process. Devices like the one pictured in Figure 2 serve the function of loading or unloading panels from a particular process.

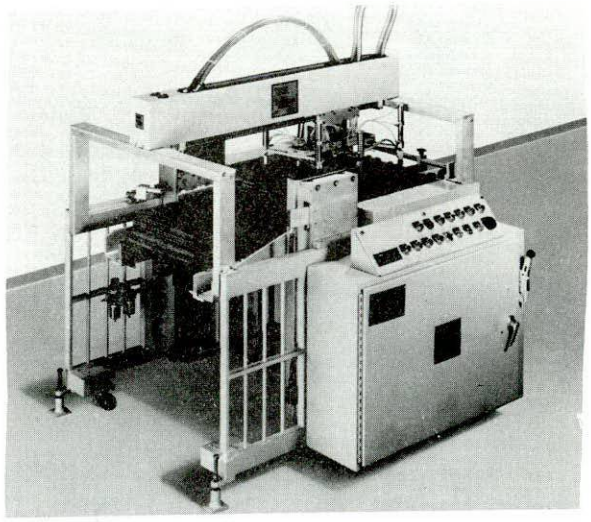


Figure 2

Other material handling equipment available to the user includes conveyors that move materials from one point to another, staging devices or accumulators that provide dry film cure times, and stackers that store materials for downstream processing (Figures 3, 4, and 5).

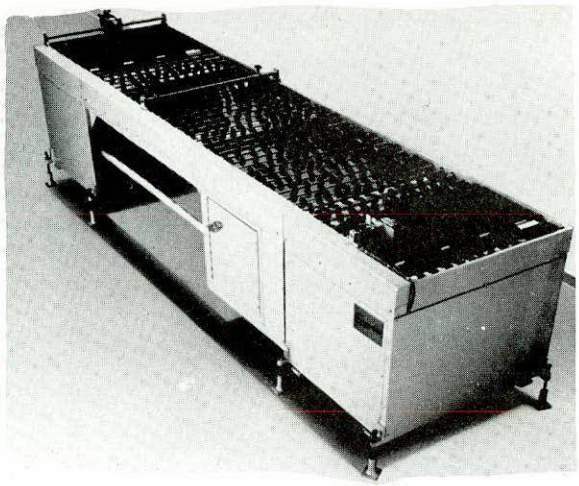


Figure 3

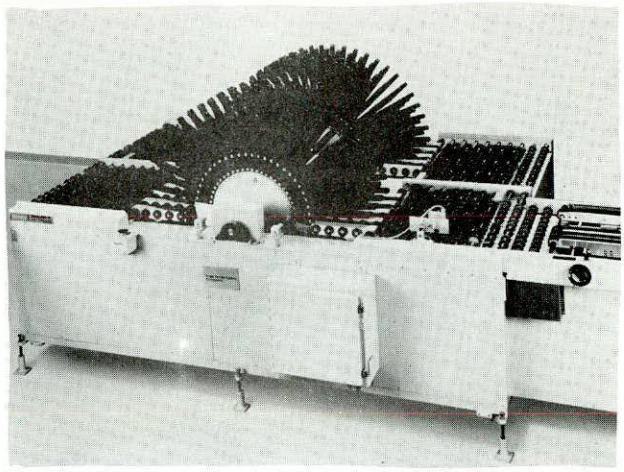


Figure 4

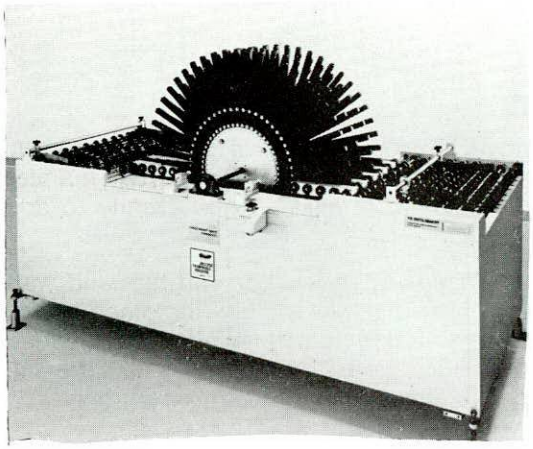


Figure 5

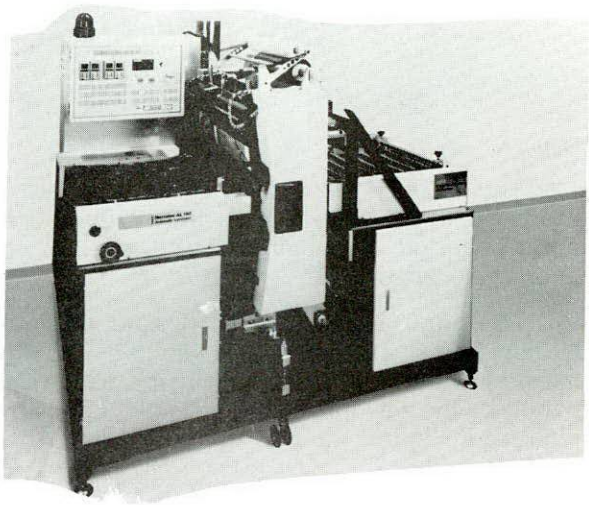


Figure 6

Automatic laminators (Figure 6) became available in 1983 and offer significant savings in dry film consumption and operating labor. These machines eliminate the waste associated with manual operations because dry film photoresist is laminated within panel borders (Figure 7). No trimming is required; thus, operating costs are reduced, panel handling is minimized, and the operation becomes safer because operators no longer need to trim the excess dry film from the panel.

In an effort to estimate the financial benefit of imaging automation, Hercules has set up the HITS™ financial model. Running the model, we input the following data pertinent to a particular facility:

- Processes two million square feet per year
- Resist price = $.30 per square foot
- Operated two shifts
- Labor rate with benefits is $12.35 per hour
- Manual labor requirements: two per shift
- Automatic labor requirements: one per shift

The results were labor savings of $49 thousand and dry film savings of $60 thousand, or $109 thousand over the conventional manual process.

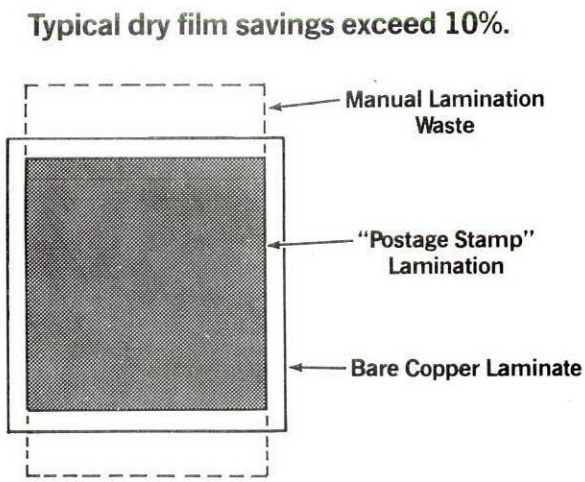
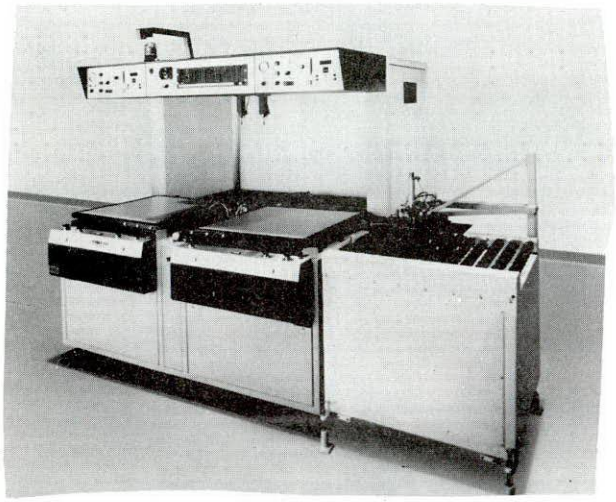


Figure 7

Automatic printers (Figure 8) first appeared in 1984 and offer significant savings in operating costs. This unit includes loader and stacker. Data were loaded into the HITS financial model for this unit.



- Processes 400 thousand panels annually
- Operated two shifts
- Produces 100 panels per hour
- Replaces three manual printers

	$, Thousand
Operating labor	99
Reduced artwork damage	10
Reduced maintenance	10
Total	119
Additional capacity	50
Total	169

Figure 8

The resulting savings are illustrated above. Because handling is reduced, a saving in artwork damage is assessed. In addition, records show that reduced downtime from three manual printers resulted in maintenance savings. Depending on the facility's operating productivity, there is also an opportunity to add additional capacity.

The printers and laminators function independently, can be used in tandem, or can be used with loaders and stackers. It is possible to operate them discretely and enjoy quick financial returns and link or integrate them at a future date. But the option exists to install a preintegrated system that will take precleaned panels all the way through to development with minimal operator participation. These systems, like the one pictured in Figures 1 and 10, can be designed for the user to the user's specifications, and can be supplied as a turnkey unit.

The system schematic is displayed in Figure 9. It includes a loader, a laminator, an accumulator to stage the panels for printing, an exposure unit, another staging unit, and a polyester cover sheet removal unit. As the panels leave the system, they are delivered to a developer.

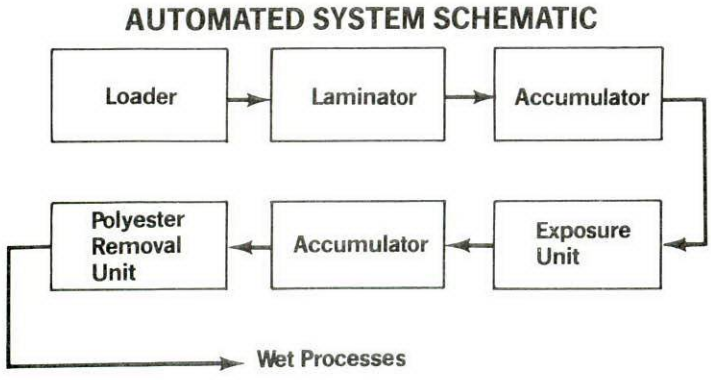


Figure 9

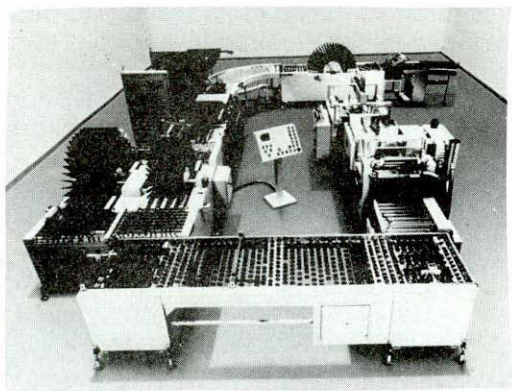


Figure 10

The system can operate with two operators, one to monitor the system and another to load the panels. The HITS financial model is equipped to provide financial impact analysis for the complete system.

The model has the built-in flexibility necessary to tailor it to a unique facility. In this case, the facility will begin the process with a preclean unit that accepts panels from a loader and delivers them to a developer. The profile for this facility is shown in Figure 11. Sales are $22.5 million. The facility operates two shifts and produces 333 thousand panels with an average size of 18 x 24 inches. Annual dry film consumption is 2 million square feet, and the facility's labor rate (with benefits) is $12.34 per hour. As shown in Figure 10, the imaging area to be automated is staffed with 13 operators.

Initial results from running the model are the annual savings resulting from the use of the automated system. Savings are summarized as follows:

	$, Thousand
Operating labor	535
Materials	60
Yield	80
Capacity	50
Miscellaneous	20
Total	745

Figure 11

Facility Profile
(Facility annual sales: $22.5 million)

Imaging Step	Requirements (Per Shift)
Preclean material handling	2
Lamination	2
Printing	3
Cover sheet removal	2
Material handling	2
Inspection/touchup	2
Total	13

Shifts operated	= 2
Labor rate, including benefits*	= $12.34/hr
Annual dry film consumption	= 2 MMSF
Average dry film cost	= $.30/SF
Average panel size	= 18 × 24
Annual panel volume imaged	= 333M

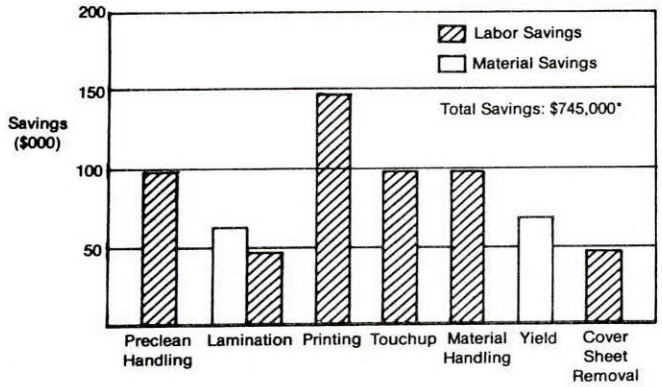
*Benefits include FICA, FUTA, and SUI taxes, hospitalization insurance, vacation and holiday pay, pension costs, and miscellaneous benefits.

The model calculates yield savings resulting from an assumed 1% finished product yield improvement, which, in turn, results from reduced handling. This conservative savings estimate results from the incremental gross profit (at a 35% rate) resulting from increased yields. The Miscellaneous category includes reduced artwork damage and maintenance.

By manufacturing step, the savings are broken down by type in Figure 12. The largest (and most easily identified) contribution is a result of labor reductions (Figure 13).

Figure 12

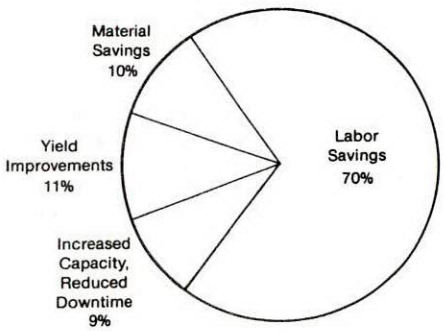
Annual Savings by Manufacturing Step



*Including: Capacity increase, reduced downtime.

Figure 13

Contribution to Savings



Total Annual Savings: $632,000

Annual savings typically need to be carried further to justify a major capital decision, so the model goes several steps further. Figure 14 shows that an incremental income statement is developed by the model, which accounts for depreciation (10-year book) and taxes (at the maximum 46% rate). The model assesses an annual $366 thousand profit after tax.

Figure 14

Incremental Income Statement

	Year 1	Year 2	Year 3	Year 4	Year 5
Projected Savings	$745	$745	$745	$745	$745
Depreciation (Book 10-yr. Life)	68	68	68	68	68
Gross Profit	677	677	677	677	677
Indirect Expense	0	0	0	0	0
Profit before Taxes	677	677	677	677	677
Taxes (Rate = 46.0%)	311	311	311	311	311
Profit after Taxes	$366	$366	$366	$366	$366

Figure 15

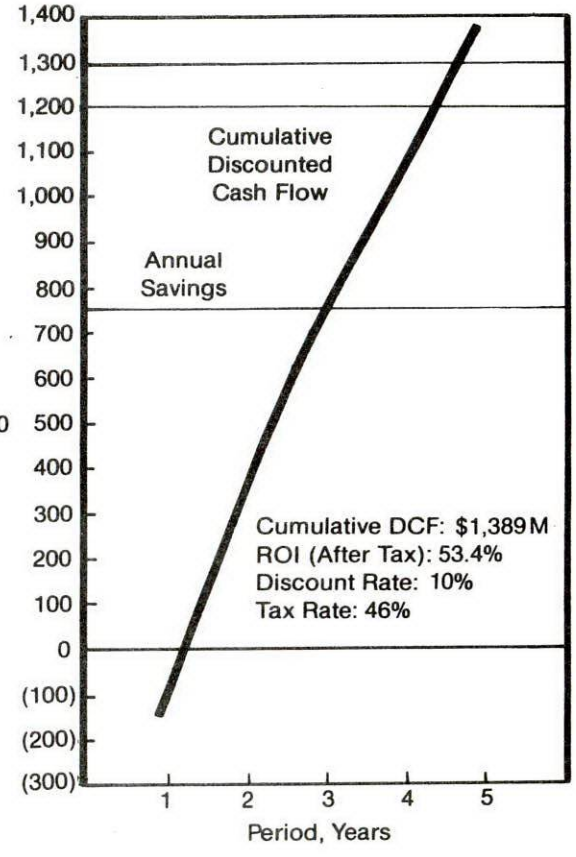
Cash Flow Statement

	Year 1	Year 2	Year 3	Year 4	Year 5
Profit after Taxes	$368	$368	$368	$368	$368
Depreciation (Tax Basis)	102	150	143	143	143
Investment Tax Credit	55	—	—	—	—
Total Cash Flow	(160)	516	509	509	509
Discounted Cash Flow	(154)	447	401	364	331
Cumulative DCF	(154)	293	693	1,058	1,389
ROI% (After Tax)	53.4	53.4	53.4	53.4	53.4

For the financially oriented decisionmakers, the model also performs a cash flow statement that assesses the five-year financial impact. The cumulative discontinued cash flow over five years is $1 million, and after tax return on the investment, 53.4% (Figure 15).

The data are summarized graphically in Figure 16. The investment breaks even in one year; annual savings are $775 thousand and the cumulative discounted cash flow (DCF) is over $1 million.

Figure 16
Annual Savings and Cumulative Discounted Cash Flow (DCF)



It is technically feasible to automate the imaging area, as suppliers have clearly moved to fit the needs of the industry. Financially, it pays off.

The other necessary component to automation is facility commitment. The facility must be committed to automation or the successful implementation of this strategy will be difficult to achieve. Automation planning and operational changes will likely be a part of the move.

Factors to consider include:

Panel types: Selection of equipment may depend on its ability to handle certain panel types such as flexible and/or rigid board.

Panel sizes: A facility running numerous part sizes may want to standardize around two or three panel sizes to reduce changeover time. The tradeoff is increased laminate scrap, but it is usually more than offset by productivity savings.

Photoresist: The types and thicknesses run will affect system productivity. It is important to assess the productivity relative to film exposure speeds.

Flexibility: To select the proper equipment, you must assess where you need flexibility. Areas of concern are part sizes, number of sizes, panel types, and productivity required.

Tooling: Standard tooling becomes a requirement. Machines operate off tooling holes or slots. One system should be selected and all parts should be adapted to it.

Once you have considered the factors, established your needs, and made the decision to automate, you must also decide whether to procure a system or to automate with modules.

Both approaches have their advantages. Modular automation allows great flexibility in machine placement and function. Should you need to automatically laminate all panels but automatically print a portion, in-line automation may be limiting. You can automate in a stepwise fashion or gradually and spread your capital expenditures over several budget periods. Since your operating labor requirements will change, you will have the opportunity to gradually redeploy your personnel.

System automation lets you quickly follow through and plan your move to automated manufacturing. It's possible to have a single supplier take responsibility for designing a system that leads to turnkey installation and support. All this adds up to reduced burden on the facility and a smooth transition from a labor-intensive to a capital-intensive operation.

Automation of the dry film imaging area is a reality today. Technically and financially, it makes sense. All you need is COMMITMENT.

J-3

Electronics II
Session J

The Effect of Organic Addition Agents and Cell Design on Selective Tin and Tin-Lead Deposition

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THE EFFECT OF ORGANIC ADDITION AGENTS AND CELL DESIGN ON SELECTIVE TIN AND TIN-LEAD DEPOSITION

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Selective deposition of bright tin and tin-lead alloy deposits on terminals joined to a continuous carrier strip presents challenges in cell design to maximize the plating rate, minimize overall plating station length and reduce electrolyte foaming. This paper presents a study of the effect of organic addition agents in bright tin and tin-lead alloy electrolytes on the limiting current density, plating efficiency and deposit solderability. The proportions and quantity of organic addition agents in these electrolytes and cell design can be optimized to increase production rates and reduce rejects.

Electrical components in the communications industry are protected by metallic finishes to increase their electrical conductivity, their corrosion resistance and solderability. In earlier years the great variety of selective deposition techniques we know today was not available and costly compromises were necessary. Terminals requiring gold coatings for low force mating and low contact resistance, yet possessing a solder tab or post were gold plated all over. Now such terminals are almost exclusively plated in the contact area with a noble metal and with tin or tin-lead coatings on the area to be soldered.

Bright tin and tin-lead layers are frequently preferred to matt finishes. These deposits exhibit the desirable features of good shelf life and excellent solderability, they are economical to use and they are esthetically pleasing in appearance. They provide the most widely used means of retaining solderability. The bright deposits have exceptional resistance to staining during handling and storage and they form less surface oxides than matt tin and tin-lead coatings. Therefore, they tend to retain their solderability better than the matt deposits. Under normal storage conditions the rates of oxide growth on the surface are low, and the resulting thin oxide films are readily soluble in rosin fluxes.

The ability of bright tin and tin-lead coatings to retain good solderability during storage and handling is influenced by the deposit thickness and by the amount of organic material derived from the addition agents used in the electrolyte selected for electrodeposition. Coatings less than about 5 μm in average thickness may be sufficiently porous to permit damaging corrosion of the basis metal to occur during storage. Coatings of these metals exceeding 5 μm in thickness do not suffer from this disadvantage and they usually retain good solderability for several years.[1]

In preparing baths for plating tin and tin-lead coatings, care must be taken to assure an acceptable balance of the leveling, brightener and bright-

ener solublizer constituents. Bright plating these metals involves the use of large organic molecules to span the irregularities during metal deposition to decrease the surface area and create a shiny appearance. Peptone, glue, resorcinol, beta-naphthol, catechol and gelatin are commonly employed as brighteners and grain refiners in the electrodeposition of tin and tin-lead coatings and are usually codeposited to a varying degree within the metal layers. As the organic content of the plating bath increases, the codeposited amount generally increases as well.[2] This can cause erratic solderability behavior since it leads to the evolution of volatile organics during fusing. Grain refiners are usually codeposited at levels from 0.05 to 1 percent.[3] Problems begin when the level exceeds 0.2 percent, resulting in the production of voids and crater-like defects in the fused solder surface.

Excessive entrapped organic brighteners cause a tendency to dewet when the deposit is soldered. They also reduce the effective cross section and therefore reduce the joint strength. The solder becomes less ductile due to the presence of organic materials which prevent ductile flow and also serve as nucleation sites from which fractures can readily propagate.[4] Brightener and solubilizer imbalance in the electrolyte can also effect the solderability of parts adversely as plated. For example, excessive brightener in the presence of insufficient carrier additive in an acid stannous sulfate bath allows insolubilized organic material to form a thin layer on the parts as they are withdrawn from the bath. This contamination is nearly impossible to remove with rinsing. It ultimately leads to severe dewetting problems.

Tin deposits are plated primarily from acid sulfate and fluoborate formulations. Tin-lead deposits can be plated from electrolytes including fluoborate, sulfamate, chloride, fluosilicate, pyrophosphate and organic sulfonic acid. The organic sulfonate baths are becoming more popular because they permit high current density values while maintaining the desired alloy composition and they simplify waste treatment problems.[5] The electrolytes selected for evaluation as reported in this paper include bright acid stannous sulfate, bright 60/40 tin-lead fluoborate and bright 60/40 tin-lead organic sulfonate.

Immersion Depth Cell Design

While optimizing electrolyte chemistry for a given plating cell design can yield increased deposition rates, the design of the electroplating cell also has a very significant influence on plating rates and the overall length required for a plating station utilized for immersion depth plating on a continuous reel to reel line.

The length of the immersion depth selective deposition cells described within the scope of this paper for bright tin and tin-lead plating is directly proportional to the plating efficiency. Table 1 shows the relationship between various cell lengths and the required overall plating station length on a reel to reel line for 100 microinch deposit thicknesses using an acid stannous sulfate electrolyte in cells having solution input at the bottom center and end solution overflow, current being applied to the connector strip just beyond the cell ends. Maximum cell amperage values reflect the current at which deposit burning began to occur or foam extended 0.5 cm

upward on the terminal strip above the solution level. The total tin plating station length indicated includes 15 cm. for each electrical contact to connector strip location between each cell and at the station ends. The data is based on the station length to deposit 100 microinches at 6.1 meters/minute. From Table 1 it is readily apparent that shorter cells are more advantageous. This is due to two basic phenonomen. First, electrical contact stations are usually limited to about 20 amperes on typical connector strips before problems of arcing and overheating develop. Second, in each cell most of the metal deposition takes place near to the current input stations, so excessive foam generation and deposit burning occur near the cell ends quite irrespective of cell length.

The most limiting factor observed while studying the variable of cell length was foam generation along the plated strip. Therefore, a cell length of 45 cm. was selected for evaluation that was equipped with various spargers and overflow techniques to transport foam away from the parts being plated. Two of these cells are illustrated in Figures 1-4. Figure 1 shows a cell with a bottom sparger and solution overflow at the cell ends where the terminal strip enters and exits the cell. An end view of this cell is shown in Figure 2. Figure 3 shows a cell with a side sparger and solution overflow at the cell ends and along a cell side. Figure 4 shows an end view of this cell. A bottom sparger similar to that shown in Figure 1 was also evaluated in the side overflow cell. Note the arrows in the sketches that illustrate solution flow patterns in the working cells.

The maximum practical flow rates for these strip plating cells is given in Table 2. The side sparger - side overflow cell was quite superior to the other cell and sparger combinations in removal of generated foam. This was the cell design selected for studying the performance of the bath formulations prepared.

Bright Acid Stannous Sulfate

The electrolyte compositions for plating from the bright acid stannous sulfate bath and the results obtained are listed in Table 3. The percent cathode plating efficiency is given for various current density values and bath formulations. The brightener levels were as follows: L (low) = 1.5% carrier, 0.3% additive and 0.2% maintenance brighteners; M (medium) = 2% carrier, 0.5% additive and 0.3% maintenance brighteners; H (high) = 3% carrier, 0.7% additive and 0.4% maintenance brighteners.

It is readily apparent for all tests run that the cathode efficiency is significantly reduced by increasing brightener levels. Also, higher cathode efficiencies were obtained by using 10% by volume sulfuric acid and greater tin concentrations in the electrolytes. It is noteworthy that usually increasing the amperage in the cell actually reduced the overall plating rate. Bath formulation E, however, yielded a 230% increase in the plating rate when the current was increased from 5 A/dm^2 and 17 A/dm^2 for the low brightener formulation. Figure 5 shows a graph of the data for bath composition E.

All tin plated terminals were bright except for the low brightener 5 A/dm^2 and 10 A/dm^2 samples from bath formulation A. These were slightly cloudy. Most of the 25 A/dm^2 samples showed some deposit burning at edges or at the terminal tips. Bright acid tin electrolytes operate more efficiently at lower temperatures. Although the plating trials for this study were conducted at 22°C., cooling of these baths is recommended. While higher temperatures increase the plating efficiency, they make overall brightness more difficult to obtain and accelerate brightener consumption. For example, about twice the volume of brightener is required at 30°C. as compared to 18°C.

Samples of the 100 microinch bright tin plated terminals of Table 3 after a two week period were cleaned in alcohol and immersion solder tested with 60/40 solder at 240 C ± 5.6C using a nonactivated rosin-alcohol flux and a 5 second immersion time. All of the samples exhibited good solderability with less than 3% dewetting. However, the smoothest solder coatings showed a preference for lower current density values and higher metal concentrations in the electrolyte. Other samples plated from electrolytes containing as much as 7% by volume carrier showed excellent solderability even at 15 A/dm^2.

Most bright tin plating baths with sulfuric acid in the electrolyte contain one additive as wetting agent to sufficiently achieve solubility and maximum performance of an additional additive that serves as a brightener. In continuous reel to reel plating of connector strip products, bath drag-out is often substantial and failure to adequately replenish the brightener solubilizing agent can readily lead to solder failures. The insolubilized brightener can cover the work with a thin organic film as parts exit from the plating bath. This contamination resists rinsing and frequently drys on the surface, causing serious dewetting problems when soldered. It is usually advisable in reel to reel plating to maintain the carrier or wetting agent at about twice the concentration recommended by the vendor to guarantee complete brightener solubility. Typically the carrier additive has considerably less effect than the brightener constituents on reducing the cathode plating efficiency.

Tin-Lead Fluoborate

The use of tin-lead electroplating has advanced at an accelerated pace during the past decade and has found numerous applications in the electronics industry. Typically the fluoborate electrolytes offer high limiting current density values that lend the baths amenable to continuous plating of wire and strip. These baths plate at nearly 100% cathode efficiency. They exhibit good throwing power, ease of bath make-up and ease of bath control.

Three major concerns need to be addressed when tin-lead plating from fluoborate baths. These are agitation of the electrolyte, build up of organic contaminants and the composition of the deposit.

Agitation is an important factor in tin-lead plating and must be considered during the initial stages of cell design. A still bath causes nonuniform deposits due to local exhaustion of the electrolyte at the cathode surface. On the other hand, too vigorous agitation accelerates the oxidation

of stannous tin to stannic tin. Air agitation is necessarily prohibited.

Another caution with tin-lead plating particularly from fluoborate electrolytes is the accumulation of organic breakdown products as brighteners decompose during electrolysis. Periodic activated carbon treatments are recommended to remove these decomposition products which will adversely affect the solderability of the coatings. High organic contamination levels in these baths can also result in skip plating.

When tin-lead alloy plating terminal strip reel to reel, due to the high current density values frequently utilized it is recommended that the plated deposits be analyzed for composition. It may be necessary to adjust the quantities of tin and lead in the electrolyte to attain the desired deposit composition at the current density used for deposition. The percent tin in the deposit can increase substantially with increasing current density values. One of the baths studied showed composition changes as given in Table 4. Studies done by DuRose and Hutchison showed that with insufficient organic additive, the tin in the deposit varied greatly as the current density increased.[6]

For tin-lead fluoborate baths, the total metal can be anywhere from 25 to 250 g/l. Concentrated baths permit higher current densities. The best concentration is rather difficult to determine. However, two essential conditions for good performance exist; addition agents must be used and the deposit must acquire the desired amount of tin.

Table 5 lists several of the tin-lead fluoborate electrolyte compositions evaluated in the side sparger-side overflow plating cell at a flow rate of approximately 15 liters per minute. The effects of metal and brightener concentrations observed in these baths was found to be similar in influence to the values realized when using the bright acid tin baths. However, the reduction in cathode plating efficiency caused by increasing the current density is considerably less with the fluoborate electrolyte. In all cases foam generation in the strip plating cell was quite excessive at 25 A/dm^2. All samples plated at this current density showed some deposit tip and edge burning.

It should be noted that these trials incorporated fresh plating solutions that were virtually free of organic breakdown products. Significant build up of such materials can reduce the cathode plating efficiency to less than half the values shown in Table 5.

The fluoborate tin-lead deposits showed excellent solderability after two weeks storage in the laboratory. The best solder coatings were evident on the lower current density applied coatings. Metal content in the electrolyte appeared to have little effect on the deposit solderability.

Tin-Lead Organic Sulfonate

The organic sulfonate tin-lead plating electrolytes are relatively new, but they are gaining rapid acceptance for high deposition speed applications. These processes as compared to fluoborate tin-lead formulations are sometimes

capable of producing acceptable deposits up to twice as fast with one-half the bath metal concentration. They offer the advantage of greatly reduced sludge problems due to superior resistance to air oxidation of divalent tin to quadrivalent tin, so pumping and cascading the electrolyte freely is permissible for extended periods. Also, insoluble anodes can be used in high speed cells for applications where dimentional changes due to anode dissolution are more critical.

Deposit composition from organic sulfonate tin-lead baths is quite manageable. While the tin content in the deposit increases with increasing current density values, changes occur in considerably smaller increments than is evident with most other tin-lead plating formulations. For example, a properly balanced organic sulfonate chemistry yields approximately 63% tin in the deposit at 10 A/dm^2 and 75% tin in the deposit at 50 A/dm^2.

For most plating requirements, total metal in the organic sulfonate baths is limited to about 100 g/l. Excessive metal concentrations can cause low current density dullness, reduced throwing power and deposit treeing along part edges. High quantities of brightener can also result in low current density hazed deposits.

The organic sulfonate formulations evaluated in the side sparger-side overflow plating cell at a flow rate of about 15 liters per minute are listed in Table 6. A rather dramatic drop in cathode plating efficiency is realized with increasing current density, but this reduction is lessened by employing higher metal concentrations and lower brightener concentrations in the plating baths. Most of these baths showed a decrease in deposition rate when the current density was increased from 3 A/dm^2 to 50 A/dm^2. Bath D with low brightener, however, showed a 6% increase in plating rate for this current density change. While greater electrolyte agitation would have yielded higher deposition rates, solution agitation is limited when immersion depth cell plating.

Foam generation in the plating cell was significant at 50 A/dm^2, but not prohibitive. The greatest amount of foaming was observed with the low metal and high brightener electrolytes. It should be noted that the above baths were unused prior to these studies and therefore produced foam that could be considered maximum in degree. As these baths age, foam generation tends to decrease.

The appearance of the 5 A/dm^2 samples at lower metal concentrations was fully bright. However, the high metal 5 A/dm^2 samples showed low current density dullness and evidence of varied deposit thickness in a skip or step plating manner with all brightener levels tested. For the 20 A/dm^2 tests, the low metal and low brightener bath gave the brightest deposit. The 50 A/dm^2 deposits were bright to semi-bright, the brightest samples being plated from the low metal and high brightener electrolyte. The 50 A/dm^2 parts plated in the high metal concentration baths all exhibited treeing. The low brightener formulation treed most extensively. Treed deposits were not observed with any of the other 50 A/dm^2 samples.

Samples of parts plated as listed in Table 6 were solder tested according to the method described for the bright acid tin plated parts. Generally the solderability was excellent. Again, lower current density applied coatings showed superior solderability. A solderability preference was also noted for samples plated from lower metal and low to medium brightener electrolytes.

Conclusion

These studies reveal the importance of thoroughly examining brightener and metal concentrations, plating cell geometries and solution flow characteristics to optimize the continuous strip plating of tin and tin-lead coatings. While the author makes no claim in this paper for presenting fully optimized cell designs and electrolyte formulations for continuous reel to reel immersion depth bright tin and tin-lead plating, the studies reported do emphasize the advantages for tailoring electrolyte chemistry and cell designs for similar applications on a case by case basis.

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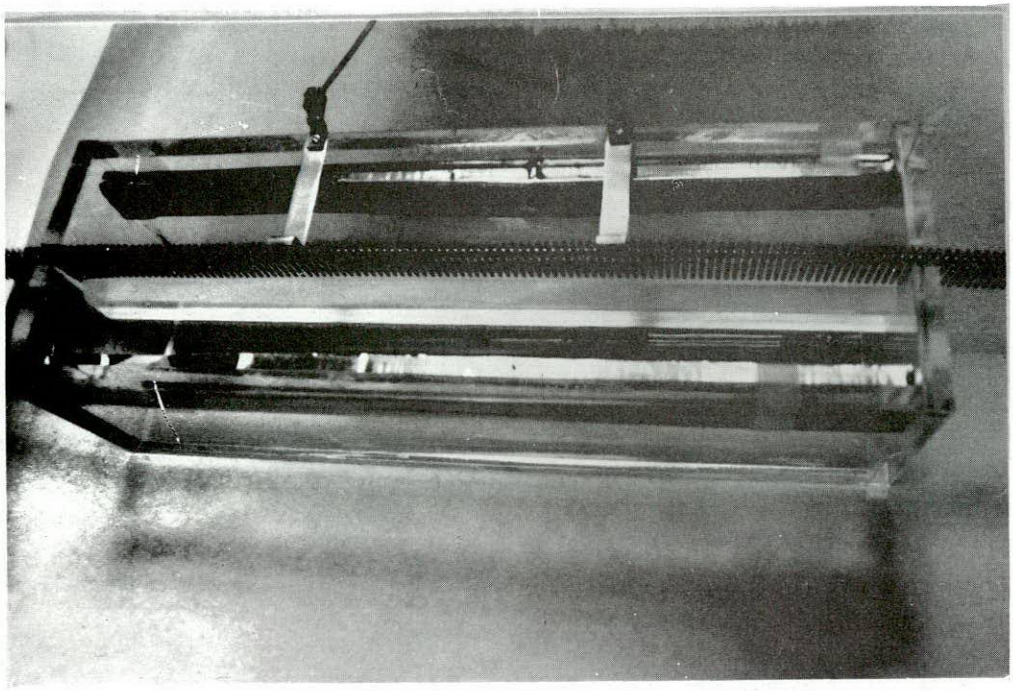

Fig. 1 — Bottom sparger-end overflow plating cell.

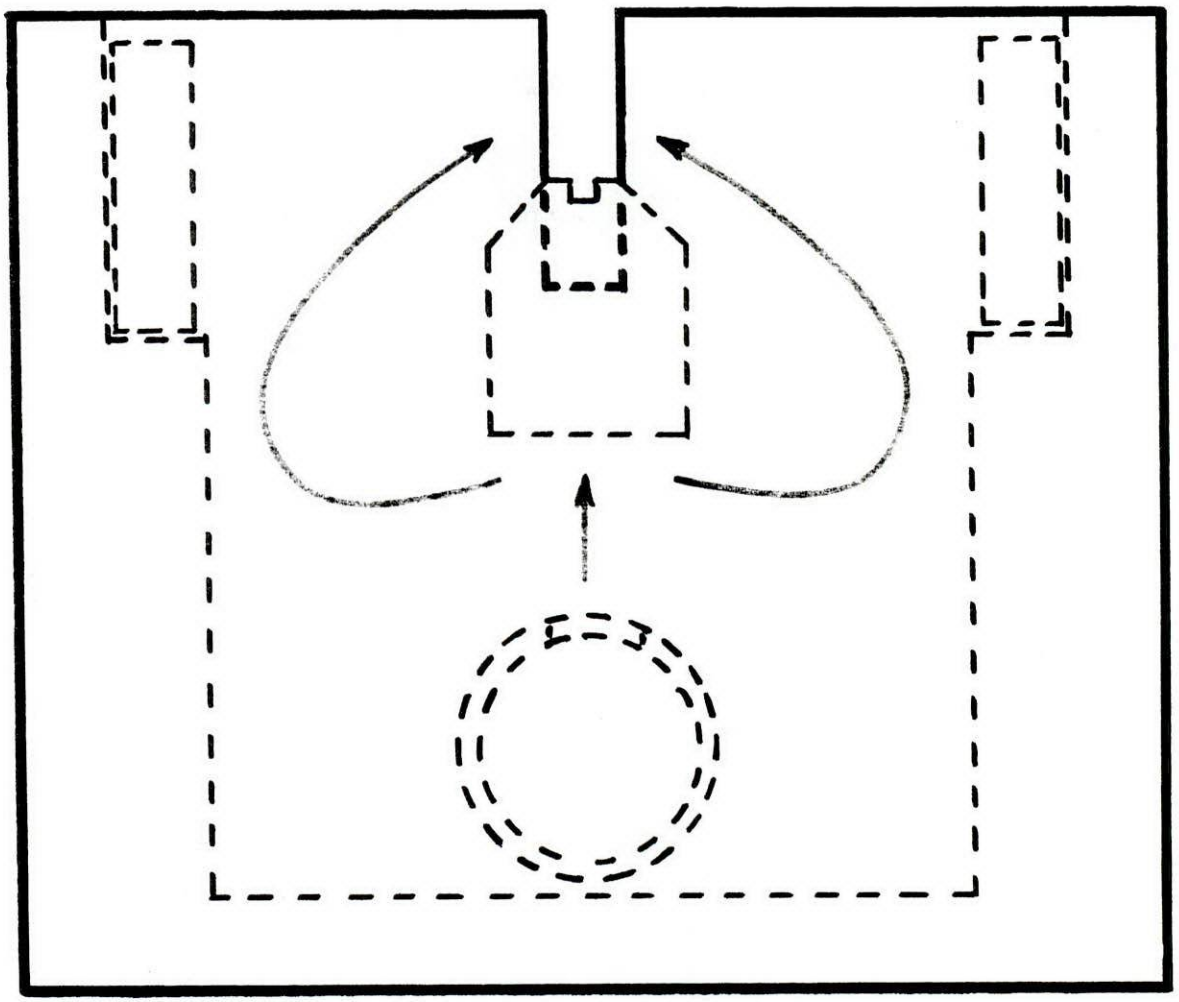

Fig. 2 — Bottom sparger-end overflow plating cell end view.

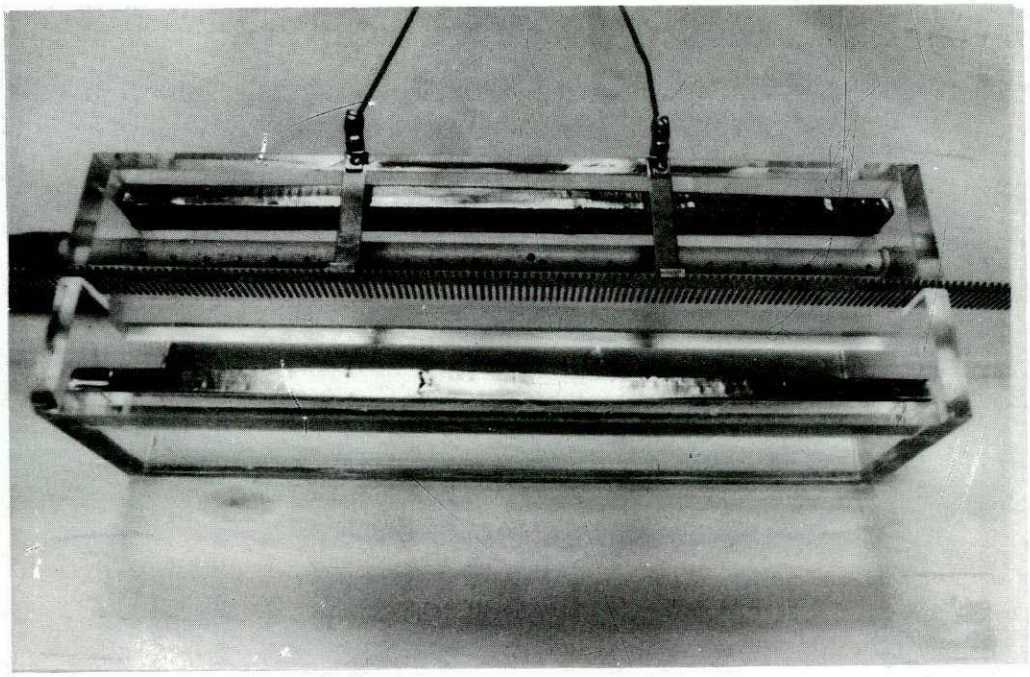

Fig.3 – Side sparger-side overflow plating cell.

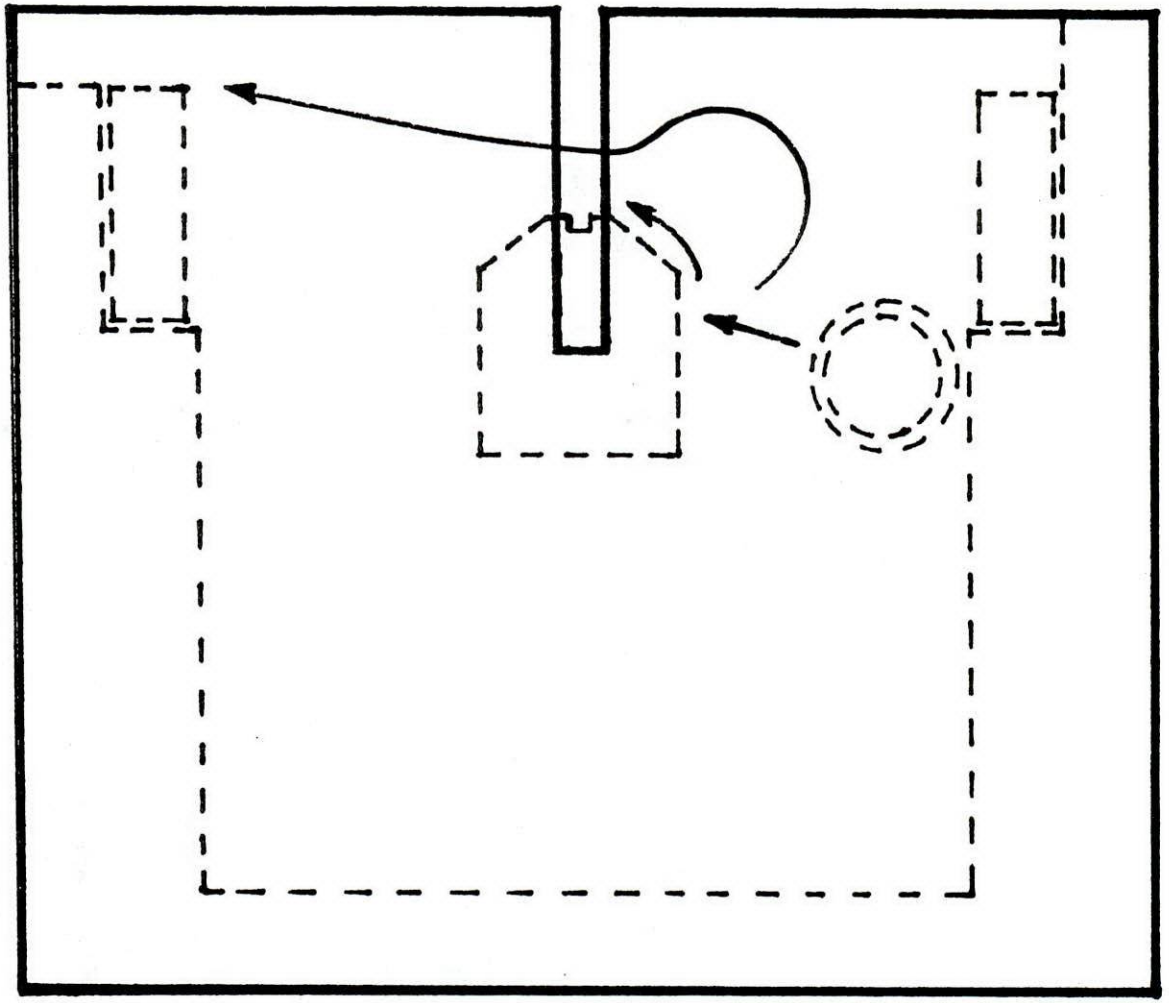

Fig.4 — Side sparger-side overflow plating cell end view.

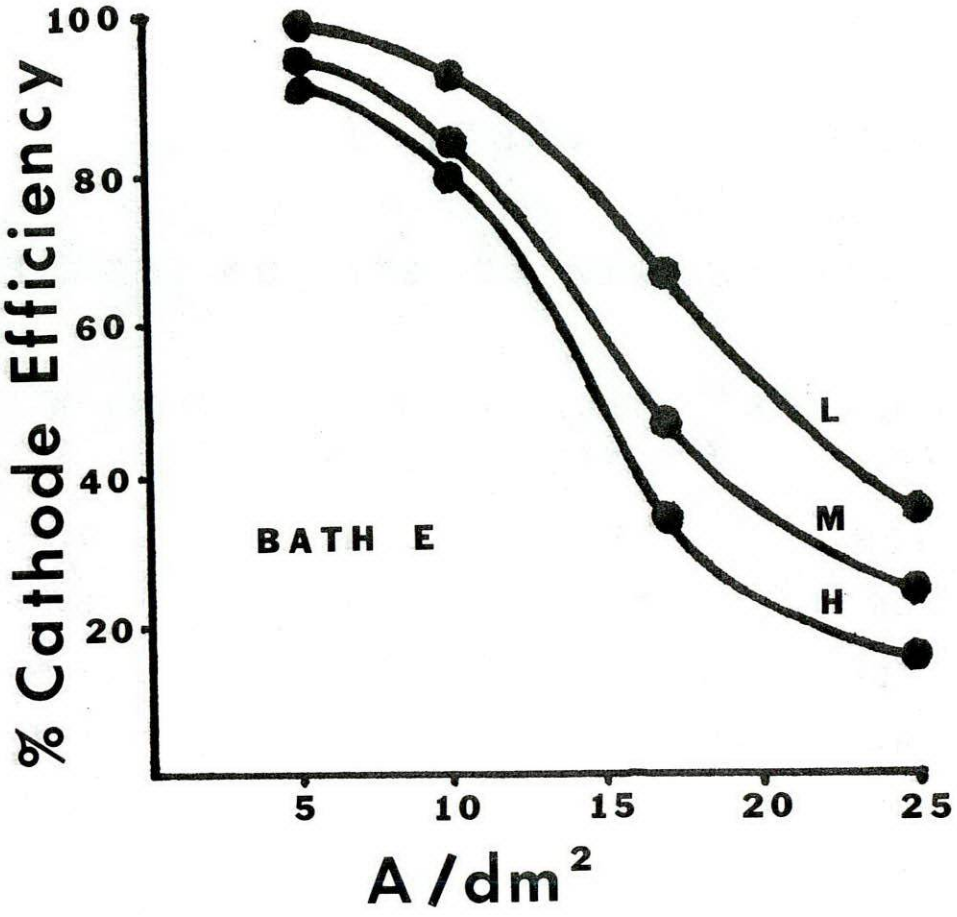

Fig.5 — Current density vs. % cathode efficiency.

TABLE 1

CELL LENGTH VS. STATION LENGTH

Cell Length cms	Max. Amperes	Max. A/dm^2	Station Length meters
105	33	5.0	7.2
90	33	5.8	6.6
75	32	6.7	5.6
60	31	8.1	4.7
45	28	9.8	4.3
30	20	10.5	4.5

TABLE 2

MAXIMUM CELL FLOW RATE

CELL	LITERS/MIN.
Bottom sparger-end overflow	7.9
Bottom sparger-side overflow	18.3
Side sparger-side overflow	15.1

TABLE 3

COMPOSITION			A/dm^2 vs. % Eff.			
mg/l $SnSO_4$	% by vol. H_2SO_4	Brightener	5	10	17	25
A. 30	5	L	83	48	21	20
		M	80	42	20	18
		H	77	44	19	14
B. 30	10	L	97	63	22	16
		M	85	55	15	13
		H	80	52	14	9
C. 30	15	L	89	52	22	17
		M	79	48	18	14
		H	76	46	15	11
D. 45	10	L	96	61	36	28
		M	89	45	35	23
		H	84	34	27	16
E. 60	10	L	98	91	66	34
		M	94	83	45	22
		H	93	80	34	14

TABLE 4

A/dm^2	%Sn	%Pb
10	64	36
15	72	28
20	81	19

TABLE 5

FLUOBORATE

BATH COMPOSITION				A/dm^2 vs. % Eff.		
g/l Tin	g/l Lead	% Carrier	% Brightener	10	17	25
A. 42	8	1	2	94	78	71
		2	4	91	74	68
		3.5	7	86	71	62
B. 84	16	1	2	98	83	76
		2	4	95	79	74
		3.5	7	93	77	71
C. 126	24	1	2	99	95	87
		2	4	96	91	81
		3.5	7	93	88	78

TABLE 6

ORGANIC SULFONATE

BATH COMPOSITION			A / dm^2 vs. % Eff.		
g/l Tin	g/l Lead	% Brightener	5	30	50
A. 25	12	2.5	93	36	19
		4	90	23	14
		6	84	17	13
B. 37.5	18	2.5	97	37	20
		4	94	29	17
		6	93	24	15
C. 50	25	2.5	98	39	23
		4	94	33	17
		6	93	27	16
D. 75	37.5	2.5	99	63	40
		4	98	53	34
		6	96	47	30
E. 100	50	2.5	100	79	42
		4	99	64	34
		6	99	57	31

J-4

Electronics II
Session J

Application of Statistical Process Control to Gold Plating

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APPLICATION OF STATISTICAL PROCESS CONTROL TO GOLD PLATING

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SUMMARY

A statistical process control (SPC) technique was developed for the gold plating processes. Gold concentration depletes as the bath is used; therefore, the process is not random. A team approach, involving production personnel (platers), statisticians, laboratory technicians, and manufacturing engineers, was employed. The team identified the data to be collected such as gold concentration, solution level, additions, temperatures and - most important - amp-minute readings. Then data was collected. After data had been collected for three months, the statistical analyses showed that the gold plating solution was under control within very close control limits. It became possible to detect and correct equipment malfunctions before failure. Additions of solution will be made on the basis of amp-minute readings rather than on results of chemical analyses. Eventually, correlation of the data with thickness and other coating quality data may reduce the frequency of required quality control testing.

OBJECTIVES

The primary objective of this project was to find a method to monitor and predict the quality of gold plating produced by Space and Communication Group's (S&CG's) plating shop. It was decided that the method should be able to:

* predict when a bath should be changed
* detect contamination of the solution
* monitor gold usage
* detect errors in taking or analyzing samples of plating solution
* detect changes in cathode efficiency
* provide documentation of how well the plating process actually performed
* satisfy and eventually reduce government testing requirements

* accommodate corporate policies on quality and incorporation of Deming's philosophy (5)

* detect equipment problems before producing faulty parts

BACKGROUND

S&CG's plating shop operates three gold plating baths plus a strike. The capacities of the baths range from 25 to 65 gallons. The plating process is controlled in accordance with S&CG's Manufacturing Engineering Instruction (MEI) 1.4.14 in order to meet the requirements of MIL-G-45204. Electronic parts (such as waveguides, chasis, housings, filters, resonators and Kovar carriers) are plated in these baths. Although comparatively small, these parts are quite complex and must be plated to meet high reliability standards. Because of intensive labor requirements, many of these parts are quite expensive to produce.

PROCEDURE

Preliminary Analysis

A decision was made to use statistical process control techniques to provide the desired control. However, the usual SPC control chart methods (1) could not be used because:

1. the solution constantly depletes and thus the analytical variations are not random

2. it is not possible to take average measurements of small samples of the solution continually throughout the production shift

3. samples of the solution are not taken and analyzed at constant intervals

Therefore, it was decided to develop control charts based upon variation of gold concentration with ampere-minutes. The resulting graphs should have a saw-tooth appearance. A similar approach is taken in control charts for tool wear (2).

Preliminary Investigation

At first the existing data (gold concentration from the laboratory combined with ampere-minute readings from the shop) was used. A regression analysis was attempted on an IBM PC. However, it became apparent that there was too much variation than was reasonable for this type of data. Consultation with in-house statisticians revealed that the existing data was not consistent enough to provide valid conclusions.

Final Investigation

A team approach was set up, including production personnel, statisticians, laboratory technicians, and manufacturing engineers. The team looked critically at how the process was carried out and found a number of discrepancies. These included:

* inadequate accounting for variations in solution level
* incorrect data for solution displacement due to filters and heaters
* inadequate accounting for variation in solution temperature
* lack of consistent, documented procedure for solution sample collection
* potential meter reading errors caused by the height of one of the analysts.

The combination of these deficiencies was enough to cause the observed problems.

After the problem areas were identified, the team decided that extensive data collection was needed. Logs were set up and the platers and technicians recorded gold concentration, solution level, additions of chemicals and water, temperatures, heating times, and gold hardness and thickness. This data was tied to the date, time and, most important, ampere-minute readings.

The data was adjusted for any increases in solution volume. Then it was adjusted for additions of chemicals. This resulted in a declining trend line. This data was analyzed using a simple linear regression approach (3), which enabled calculation of the process average, upper and lower control limits, plating efficiency, and quantity of gold used on each order. (A typical graph is shown in Figure 3.)

Finally, the process average, and upper and lower control limits were plotted on the usual trend chart for the solution. (A typical chart is shown in Figure 2.)

All calculations are done using Software from Statistical Analysis Systems (4) running on the Company IBM mainframe. Initially statisticians analyzed the data. Now, plating personnel input the data and generate reports.

RESULTS AND DISCUSSION

The statistical analyses show that the gold concentration is under control within very close limits. The project has provided production and their management with a better understanding of the gold plating process as well as the factors which affect its performance. Samples of the solution are now collected using a consistent procedure. Production monitors the process several times a week, using a program that generates three control charts and a table of gold usage for each tank. (See Table I, and Figures 1, 2 and 3 for examples.)

Any statistical deviation (more than 7 points to one side of the process average or points closely approaching the control limits) is cause for investigation. This enables production to detect equipment malfunction, solution contamination, analytical errors or a drop in cathode efficiency before these problems cause production of defective parts.

At present, solution corrections are made on the basis of chemical analysis. Chemical replenishment is made using 5 oz. bottles of solution. As soon as the present stock of 5 oz. bottles is used up and replaced with 1 oz. bottles, additions will be made based on amp-minute readings. This will result in a solution with even less variation in composition, allowing production of plating with even less variation in thickness.

Since hardness readings are only taken once a week, a long time was required to collect statistically meaningful data. It was not until late in the year when a potential hardness problem was detected. Figure 4 shows variations in hardness which are beyond those considered reasonable by the solution manufacturer. The chart also shows 7 points on the low side of the process average.

As soon as this trend was detected, production lowered the pH of the solution and added cobalt sulfate. (While the pH change had no effect, it is too early to tell if cobalt sulfate addition has been statistically effective.) Expanded data collection on preparation of the hardness samples has been instituted. Platers are now recording amp-minute readings, pH, current density, plating time, and solution each time they prepare samples. As soon as enough data is collected, statistical analysis will be performed.

CONCLUSIONS

This project provided the plating shop with a statistical tool that enables the platers to monitor the gold plating process and accurately charge for gold usage. This tool meets all of the objectives listed above and has been automated for ease of data entry by platers. Control charts are produced frequently and used by production personnel to provide early warnings of process problems.

PRODUCTIVITY AND COST SAVINGS

This project has enabled production to:

* reduce the weekly gold audits to monthly
* more accurately charge gold usage to each program
* detect problems well in advance and thus avoid line shut-down

Eventually, data from this project should justify a reduction of chemical and coating quality testing. It will now be easier for S&CG Quality to apply this technique to vendor processes.

Perhaps the most important benefit of this investigation has been to validate the plater's judgment and intuition. This provides the credibility that engineers and our customers require.

ACKNOWLEDGMENTS

The authors wish to acknowledge the valuable contributions of W.F. Rothschild of TSD, S.R. Roth of Systems Laboratories, and S.R. Wood of Product Assurance.

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TABLE I - TYPICAL GOLD USAGE TABLE

TANK	GALLONS	NEGATIVE SLOPE	USAGE RATE OZ./AMP-MIN	EFFICIENCY (1/USAGE RATE)
69	65.1	.000021833	.001421320	703.571
72	22.9	.000165369	.003786950	264.065
76	43.5	.000041873	.001821460	549.007

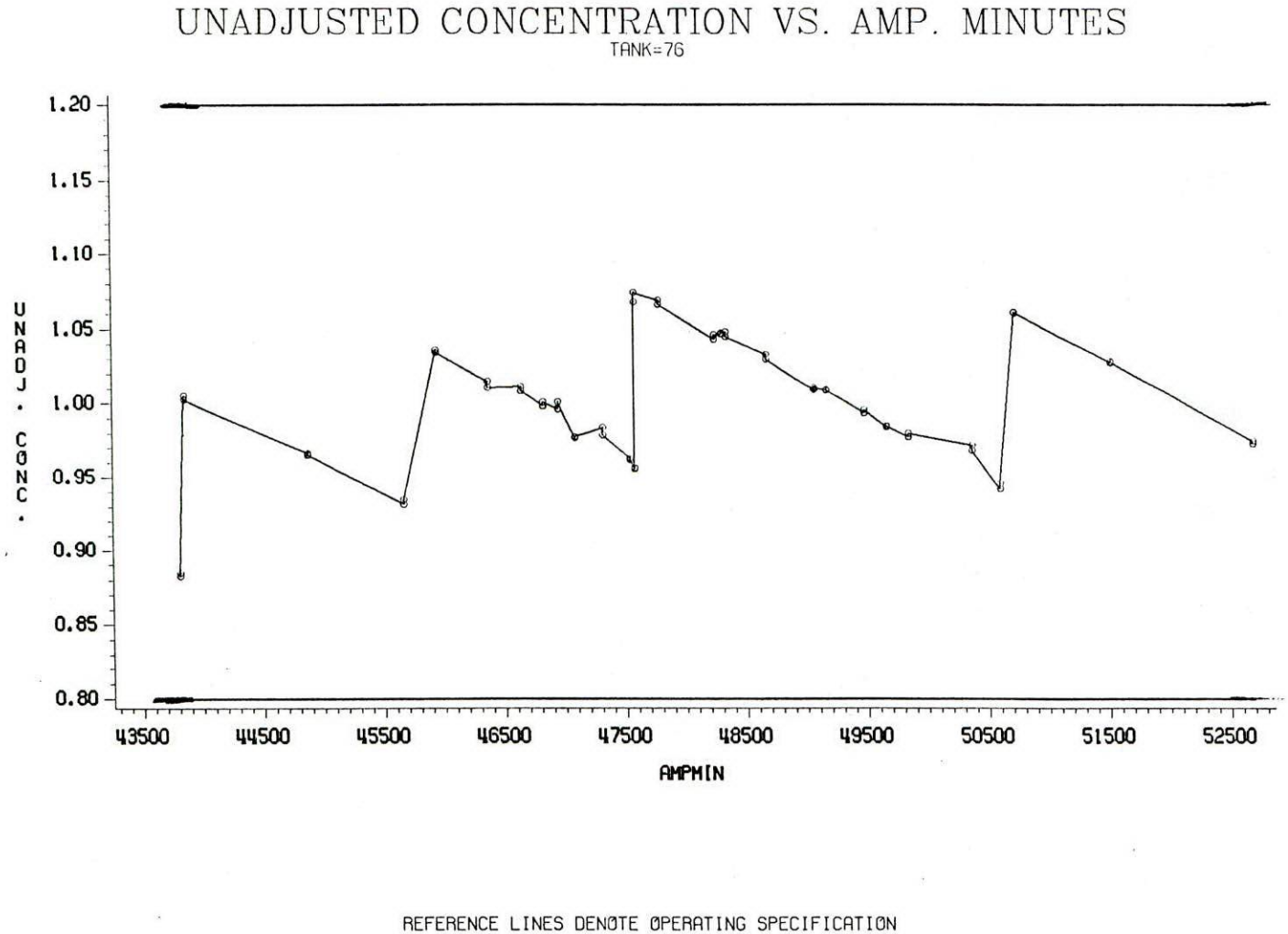

FIGURE 1 - TYPICAL TREND CHART

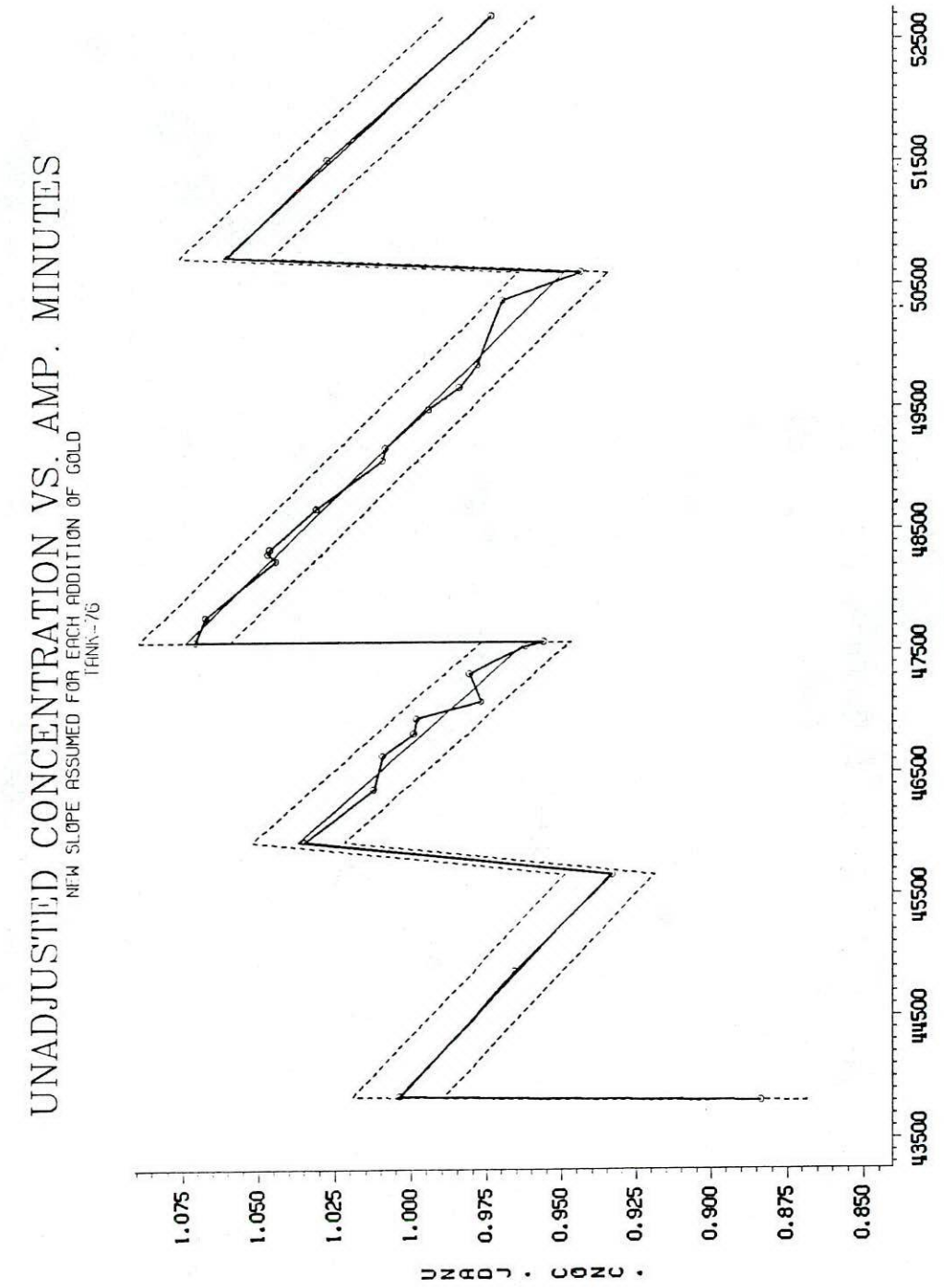

FIGURE 2 - TYPICAL TREND CHART WITH PROCESS AVERAGE AND CONTROL LIMITS

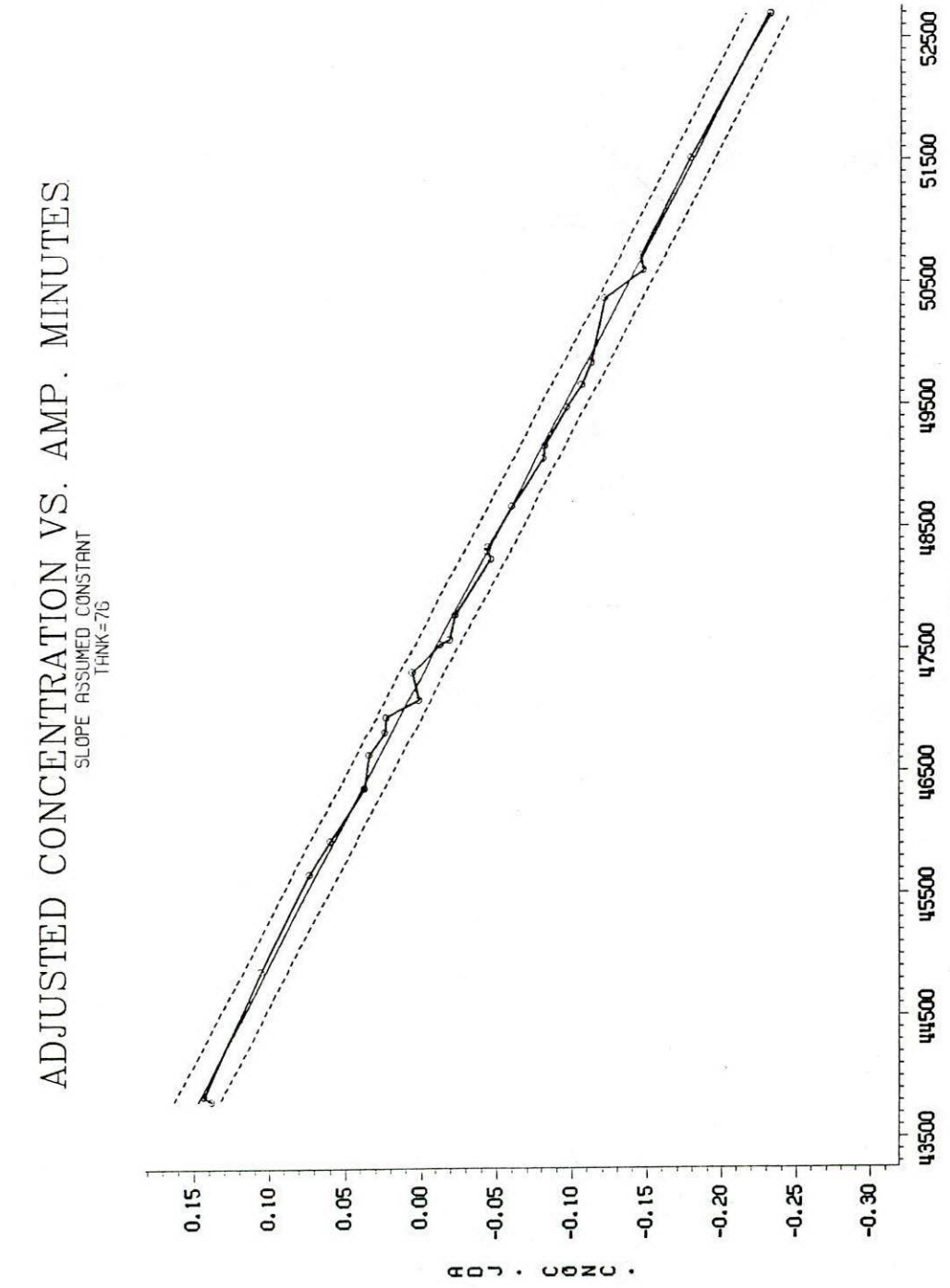

FIGURE 3 - TYPICAL ADJUSTED CONCENTRATION CHART SHOWING PROCESS AVERAGE AND CONTROL LIMITS

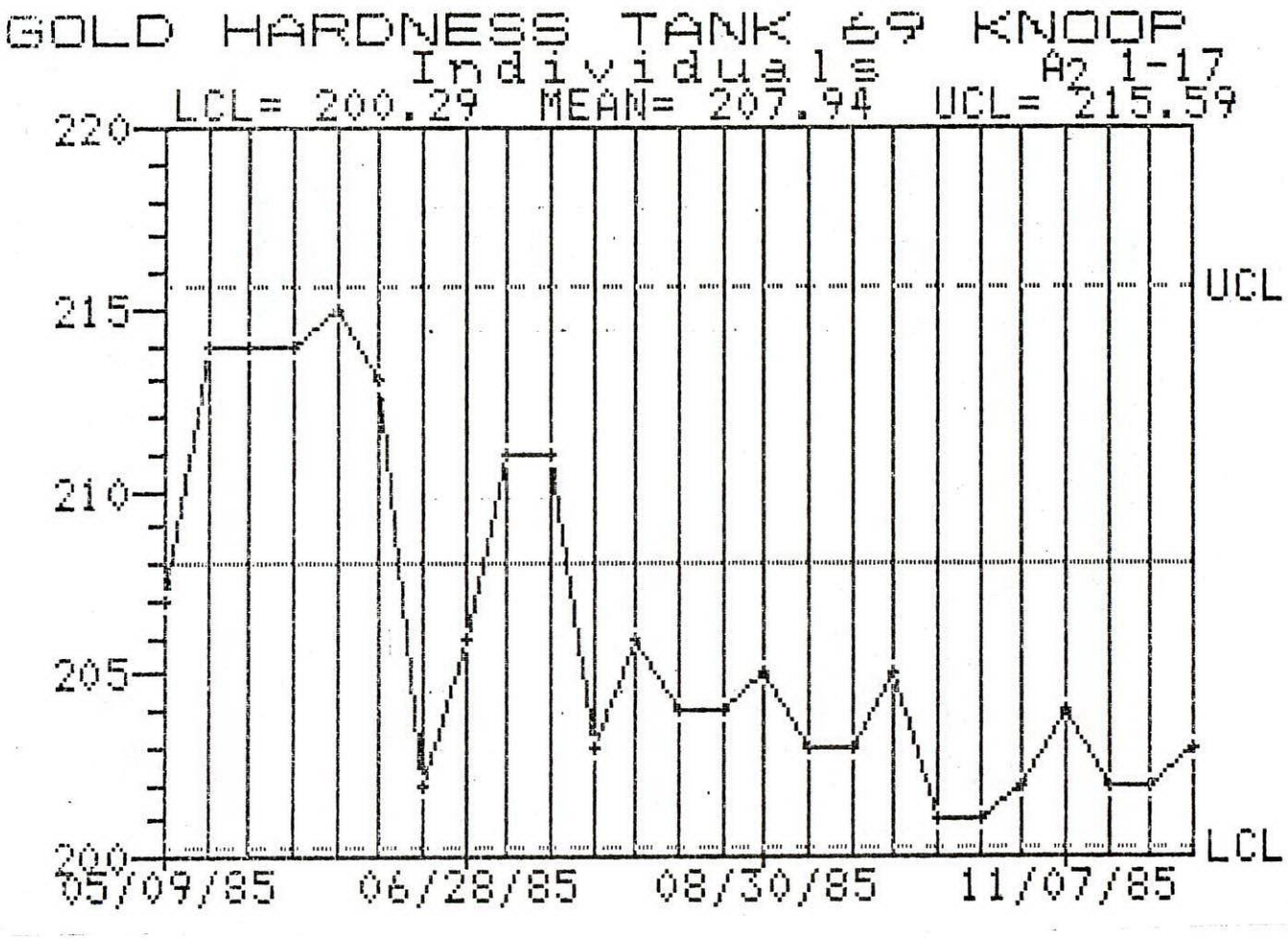

FIGURE 4 - TYPICAL GOLD HARDNESS CHART

K-1

Light Metals Finishing I
Session K

Troubleshooting of General Anodizing Problems

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TROUBLESHOOTING OF GENERAL ANODIZING PROBLEMS

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INTRODUCTION

It is difficult to present all of the potential information on the subject of troubleshooting in a few pages. In working with anodizers, many hours will be spent discussing the practices related to good anodizing. One of the most often encountered subjects is that of sources of problems and troubleshooting them. Therefore, this paper has been developed in order to present some observations on where problems arise which affect the ultimate appearance and quality of the anodized finish and how such problems might be located. This information pertains to anodizing practices in general and to all types of anodized finishes.

PERSPECTIVE

The step of anodizing is only one of many which begins with the alloying of pure metal in a cast house and does not end until the product has been in place for a number of years to show if it has been produced to give a durable finish. In between exists a multitude of opportunities for a problem to occur which can affect the appearance and durability of that finish.

The discovery of a problem should occur during inspection of finished loads at the time of unracking. Otherwise it may show up as rejected material by the customer. A proper evaluation at the time of inspection is important to determine if the problem is unique to that individual load or if something has developed in the system which will affect other loads. That evaluation is going to be dependent upon a proper understanding of anodizing.

Anodizing is the generation of an aluminum oxide film which will uniformly cover the surface of bare aluminum metal and protect it. This is done under a controlled set of electrochemical conditions. As the oxidation takes place, the quality of the film will be influenced by the physical and chemical characteristics of the aluminum base metal from which it is formed. Also, once formed, the film is transparent, and it does not have the ability to mask over metal surface

defects, even when colored. Therefore, final finish appearance will be dependent upon the uniform appearance of the base metal.

Most problems will come from one or the other of these two qualities or a combination of them, and one of the most important factors in troubleshooting is being able to visualize a problem as a result of the influence these qualities have on the physical and chemical uniformity of the film. Let us now consider some specific situations, which will exemplify the use of these two concepts as an aid to resolving anodizing problems.

SOURCES OF PROBLEMS

METAL

Casting

Taken in a normal production sequence, the first source of trouble can be in the metal itself. The more common problem is the inclusion of dross or bath particles in the ingot or billet which can be spread through the surface of the metal during rolling or extrusion. These are zones of pre-existing oxides which do not take part in the anodizing process, which will be open areas in the film, and which will appear as such after anodizing. If a color step is involved, quite often these zones will remain uncolored and appear as white or gray streaks. In the case of rolled products, the oxides may not have orignated within the metal, but from oxides rolled into the surface, however, the final anodized finshed will be the same. Cast house and rolling mill practices, which include filtration of all metal for extrusion and sheet products, have improved significantly over the years to the point that a very low percentage of problems will be a result of metal inclusions.

Alloys

The most common alloy used for anodizing is 6063 and most anodizers are familiar with its appearance after anodizing. This is not something that just happened, but has been the result of much experimentation to produce a metal surface quality that is attractive, whether in a natural or colored finish.

While the reaction of alloying ingredients is the same as that of inclusions, in that they do not oxidize during anodizing, the effect is different, in that the elemental metals are finely dispersed throughout the aluminum. As the oxidation of the aluminum takes place, the finely dispersed particles are lifted and become a part of the transparent film, or dissolve, leaving voids throughout the film, which can lead to a dull or grayish appearance. This condition becomes more pronounced with the thickness of the film or the concentration of the constituents. During the pretreatment

step of etching, these alloys can be identified by the heavier gray smut which forms. It should be pointed out that the uniformity of the film will not be affected by alloying constituents in the same manner as with non-metallic inclusions, which will not form any protective film. However, the properties of abrasion and corrosion resistance of the film can be affected, because the particles and the voids can reduce the integrity and strength of the cellular structure of the aluminum oxide film. This condition is best exemplified by the high copper containing alloys, such as 2024, which, because of the dissolution of the copper particles during anodizing, produces a characteristic dull gray finish that has a lower abrasion resistance than any other alloy outside the 2000 series.

Practically all aluminum alloys can be anodized in some form or another, but because of the effects of the alloying elements on appearance and film quality, consideration has to be given to the end use of the finish. Alloys which are to be used for extrusion and anodizing purposes are generally formulated as primary metal and controlled during casting and subsequent operations to provide the needed quality. However, it is common to encounter secondary metal which will result in a more matte or gray appearance due to higher concentrations of alloying ingredients, especially silicon and iron. Therefore, if the final anodized appearance is not the one expected, this could be an indication of improper alloy selection.

Metallurgy

The usefulness of an alloy is dependent upon its metallurgical properties. The most important is that of structural strength, which, for architectural applications, must be coupled with anodized finish quality. Both are dependent upon grain structure. If the alloying ingredients are not uniformly and finely distributed or chemically combined the resulting surface pattern after etching will be either a coarse, grainy pattern because of selective dissolution of the aluminum from around the large, non-dispersed particles or a pattern having the appearance of frost, as a result of a slow crystalline growth of the aluminum and its constituents. This can occur as a result of improper homogenization of billet or improper heat treatment of extruded parts. Here again, present day practices of homogenization and heat treatment have corrected many of the historical problems. However, on occasion these practices may not be properly followed, and the results will appear in the anodized finish.

A common problem encountered is the hot/cold spot, which may occur in a random or a regular pattern along an extrusion. This is usually due to contact between the part and the runout table during extrusion, which interferes with the cooling process. The cooling is generally slower at that spot, and

as a result, the grain structure is larger and the particles less dispersed. After etching, this will show up with a darker coating of smut and, after anodizing, will be a grayer and more matte spot due to the large particulate incorporated into the film. This problem can not be corrected or hidden by the anodizing process.

Heat Treatment

The designation system which relates the desired metallurgical qualities to the degree of heat treatment required is that of temper. Generally, the higher the temper the better will be the grain structure and the anodize response. This will produce a brighter, smoother, and less gray finish. There are a very variety of tempers available, because of structural requirements, and it is important to be aware of what is being anodized and what response one expects.

A final point about the metal quality factors discussed so far, is that, for in-house extruders, there is a better chance of controlling these problems or correcting them, once encountered. However, there is also a tendency to be lax, because the work is being done internally, and the thought is that the anodizing department can compensate for faulty practices. In the case of job shops who work for outside extruders and suppliers of metal, the job becomes more difficult in resolving the problems that can arise. This requires time, patience, diplomacy, and an educational process to get a supplier to understand the difficulties his practices are creating. However, with proper effort this can be achieved.

HANDLING

From the time parts are extruded or sheet is rolled several handling steps occur. The material is cut to length, stacked on carts, heat treated, stored for cool-down, dismounted, possibly stored again until ready for anodizing, and finally racked. In each step the mill-finished, unprotected metal is handled with gloves or hands, greasy or clean, stacked in contact with wood or cardboard, wet or dry, stored outside in the weather or inside close to the anodizing line with its inherent fumes, and eventually racked with similar hands, gloved or bare. An example of this occured in which a person had been working on a greasy crane motor and came over to help the rackers for a few minutes. Every piece that he handled ended up at the other end of the anodize process with his gloved finger and/or palm prints on the parts that he had handled. The grease, being not only heavy but also impregnated with fine metallic particles, left a residue and surface blemishes which the cleaner solution could not remove and the zones were subsequently selectively etched.

This is, fortunately, not a common occurrence to the extent of this example, but surprisingly enough it is not an uncommon problem. It will generally occur as an etch pattern

which, after anodizing, has the distinct appearance of finger prints or just a mottled pattern of smudges. They may occur in a batch of metal, indicating the load was mishandled; on a few random pieces, from an inexperienced helper; or in a definite repeated sequence, from contact with wooden slats during heat treatment or with the carbon slats on the conveyor of the extrusion runout table. Here again, anodizing can not hide such blemishes.

Another problem occurs with the storage of mill finish material. Over time, a normal, uniform oxide film will build up, which usually presents no problem. However, in contact with rain, a generally humid atmosphere, or anodizing fumes, the surface may become selectively more oxidized in spots. Degreasing alone can not deal with this type of oxidation, and the result after etching will be pitting or a galvanized appearance. Once this occurs, there is little that can be done to salvage the metal. Passing the load to the desmut solution and using it as a deoxidizing solution prior to degreasing can significantly reduce the incidence of this problem. It is not, however, a cure-all for poorly handled or stored metal.

RACKING

The most important thing to remember about racking is that it is for making electrical contact, not just for suspending parts in order to pass them through the various solutions. Good mounting practices can not be overemphasized. The contact, once made, has to endure severe attempts to break it loose, not the least of which occurs in the anodizing step with the tremendous force exerted by the growing aluminum oxide film, which can then act as an electrical insulator. The results of poor contact are readily measureable by coating thickness testers or by the physical appearance of the contact point or the end of the part, which will either be burned or gray-looking from overheating. Nonuniformity of coating thickness on a load of parts is an indicator of random contact with the rack. With electrolytic coloring this will be readily visible as color variation of the pieces or "light ends".

Another common problem is spacing of parts. Anodizing followed by coloring requires certain rules of spacing which must be met in order to achieve uniform coating thickness and color. This can either be done in a single-spline format or a doublespline format, optionally with a center cathode in the anodize and color tanks, depending on the process. For clear anodizing, the racking is much denser with multiple parts across. This leads to a situation of nonuniformity of film thickness because the inside parts receive less energy for film growth with distance from the cathodes and from shielding by the outside pieces. Thus, the parts in the center will have significantly less film than those at the outside. For

most applications of commercial and residential clear products, the thickness may be adequate to protect the aluminum, although it may not actually meet the specifications required. This type of racking will not be adequate to produce uniform color in the electrolytic coloring step.

Returning to the idea of electrical contact, a significant problem which can occur in a very random pattern, depending upon the operator's attention to details, is that of stripping racks thoroughly between loads, especially if Class 1 and Class 2 architectural films are being produced. If any film is left on the spline, it will act as an insulator. This can prevent contact altogether or cause a higher resistance contact point, which can result in the same burning or discoloration problems discussed before.

CLEANING/PRETREATMENT

Having presented some of the things that can happen to the mill finished parts prior to reaching the anodize line, it is possible to recognize the importance of the pretreatment steps prior to anodizing. The normal sequence of pretreatment steps in the anodizing line is degrease, etch, and desmut.

Deoxidize

As pointed out, if problems occur with handling or storage of metal, it would be a good idea to add the deoxidize step at the beginning of the sequence.

Degrease

The degrease step often gets overlooked as to its importance in the chain of events. If the temperature is too cold, the concentration of the soap additives too weak, or the formulation is not correct for the needs of a plant, proper cleaning will not be done. This will result in selective etching, which will leave mottled patterns on the metal surface. If allowed to become too old and contaminated, the soap solution can cause a pitting action, if the load is left for more than 5 minutes. When working properly, loads should be able to be left for up to 30 minutes without problem.

Degreasing agents are formulated to be non-etching, but either slightly basic (caustic), which are common for architectural anodizing, or slightly acid, which usually are for special applications, such as in automotive anodizing where buffing compounds are difficult to remove. Most additives are proprietary and have been formulated over a period of time based on experience. If you have any questions or problems, it is wise to contact your supplier and work with him to come up with a formulation and operating conditions for your particular operation.

Etch

The basic purpose of etching is to dissolve the surface of the metal in order to: 1. remove impurities ground into it, 2. reduce or eliminate extrusion die lines and mild scratches, 3. give a generally smooth uniform appearance, and 4. reduce the natural brightness to a "matte" condition. The important criteria to do this are caustic and additive concentrations, temperature, air agitation, and rate of load transfer. Variations in chemical concentrations and temperature can result in insufficient etching, apparent by brightness and die lines, to overetching, which will result in a very grainy texture and too dull a finish. Air agitation and transfer time, can cause streaking from an abrasive action of the air bubbles traveling upward or from rundown and continued etching during the transfer. It is important to use well-distributed, low-pressure air, to keep the temperature moderate to avoid dry-on during transfer, and to transfer quickly. If "dry-on" is allowed to occur, the result will be salt deposits, specifically aluminum hydroxide, which will not be removed in the rinse tank or in the desmut solution. These not only look bad on the finished product but are areas where anodizing will not occur (similar to metal inclusions) and can become corrosion zones upon exterior exposure. Many new etch formulations, referred to as "never-dump" solutions, are designed to function with a high rate of dragout to control the buildup of aluminum in the solution and allow for a rapid transfer operation.

Recognizing the cost factor of propriety etches, many anodizers still use their own systems of liquid caustic and an additive such as sodium gluconate. This system, with stringent control and frequent dumping, has been adequate over the years, but with the better proprietary formulations and additives developed, here again by experience, the etching process has been improved to provide a smoother finish which is uniform from day to day or when it becomes necessary to rerun material. Working with a supplier, one can develop an etch that serves the needs of a particular operation.

Desmut

Most of the principal alloying constituents, Si, Fe, Cu, and Mn, are not soluble in or reactive with the etch solution. As a result, there is left on the surface, particles of these elements in a form called "smut". It is necessary to remove these particles before anodizing or they will contaminate the anodize tank. The solution designed to do this has its basis in nitric acid, which will readily dissolve all but the silicon. This seems straight forward and is probably the least problem step in the process. However, the other function it has is to neutralize the caustic residues after rinsing. If thorough rinsing is not done before entering the desmut solution, the reaction between the acid and the caustic can result in formation of a scum of aluminum hydroxide, which

will entrap the smut particles. At the least, this increases the time in the desmut to dissolve the smut. At the worst it can leave a film, which in the anodize solution will selectively dissolve, leaving insoluble particulate, such as silicon, on the surface. This will not prevent anodizing, as it is not in the metal surface, but it will not dissolve in the anodize solution and it is not incorporated into cellular structure of the film, so it ends up as a film or residue on the anodized finish. With the standard anodizing quality alloys the silicon concentration is controlled, such that the silicon is removed with the other elements in the desmut solution. However, primary alloys, such as 6061, or secondary alloys, which have a high concentration of silicon, and which have been heavily etched, can develop this problem. Clear finishes may not show this residue, or they may show a slightly gray appearance, but it can be a serious problem for colored finishes, and it is difficult to remove.

As with degreasing and etching formulations, there are also proprietary formulations for desmut solutions. However, be careful that the additives of one supplier's etch bath are compatible with another supplier's desmut solution.

ANODIZING

In the real estate business it used to be that the three most important factors in property investment were location, location and location-now it's financing, financing and financing. Well, the anodizing step has it's three most important factors, also, and they are contact, contact, and contact. Being that it is an electrochemical process, it is important to understand and maintain the proper contacts within the circuitry, and there are, indeed, three contact locations to be considered.

Contact

The first one has been discussed briefly under RACKING. There has to be good contact between the parts and the splines, between the splines and the flight beam, and between the flight beam and the power saddles located on the tank. This constitutes the load.

The load has to receive power from the rectifier via bussing, which may have several connections between it and the power saddle. This constitutes the supply.

The load has to pass the power on, through the electrolyte, which carries out the electrochemical oxidation to form the anodized film, to the cathodes, which are connected to a system of bussing, which, also, having several connections, returns the power back to the recitifier, thus completing the circuit. This constitutes the return.

Breakdowns at any of the connection points will cut off the circuit and no power will flow. The obvious result is no anodizing, resulting in immediate measures to get the power flowing again to continue production. However, there is a far

more subtle problem, which can be called the "insulation effect", which can lead to serious and varied coating uniformity problems.

Coating Thickness/Film Distribution

One of the simplest and most useful tools in anodizing is the coating thickness detector, which is non-destructive and can be used right on the anodizing line. With it one can determine if there is enough film and how it is distributed over the load. The most common problems will be more coating on one load than another, coating variation from top to bottom and/or from end to end, and from inside to outside. Some of these have been discussed as being a result of racking techniques, but they can readily occur as a result of contact problems in the anodizing circuitry.

Current Distribution

Coating variations within a load are generally a function of how the current is distributed once the load is in the tank and the power is on. The current flows off the load through the electrolyte to the cathodes, which have to be properly prepared to receive it. It must be understood that the current doesn't care where it goes. It will simply follow the path of lowest resistance.

One of the most common problems is that of higher coating thickness at the bottom of a load. In this situation, the anodize tank is usually lead lined or there is a considerable amount of cathode surface area at or near the bottom of the tank. Having a large amount of metal near the bottom will draw more current through the parts located near the bottom of the load, which will then generate a heavier film in those parts. One of the earliest practices to render a tank inert was lining with lead, which will work for that purpose. However, when used as the cathode, it is necessary to mask off or cover the bottom, ends, and portions of the side walls to obtain a better distribution of the current. In designing newer systems, the tank lining is usually a special inert rubber, synthetic plastic, or fiberglass, and experience has shown that the cathode area, properly distributed along the side walls, can be 1/3 the size of the surface area of the largest routine load and still be sufficient for most anodizing needs. In cases where film uniformity is critical for inside surfaces, a center cathode can be added.

Another problem which is not as common, but far more serious when it occurs, is that of end to end and/or totally random film thickness. The cause of this is usually in the contact between the cathodes and the bussing along the top of the tank. Acid solution aspirated by the air agitation from below or dripping off of loads passing overhead can penetrate between the two surfaces and form oxides which will ultimately insulate the connection so that current flow is reduced or cut off entirely to that cathode section. The

current, seeking the path of lowest resistance, will flow from the load in the zones closet to the cathode areas which are functioning better. Quite often this type of insulation will develop at the end where most of the dragout drainage occurs and on the side over which the load passes for rinsing. This problem has been encountered in plants trying to produce Class 1 films of 0.7 mil, and the loads came out with an end to end variation of 0.3 mil at the drainage end to 1.2 mils. at the opposite end. In one particular case, a check of the cathode plates demonstrated that less than half were functioning properly. This problem was a result of no protection of the cathode/buss connections from the acid drainage of the loads.

To located this partucular problem, place a load in the tank and allow it to stabilize, with air agitation, in the anodize cycle for about 5 minutes. Then, shut off the air agitation and observe the evolution of the gases from the cathodes, which should be uniform from all surfaces opposite the load and which should show a flowing action equally from both sides to the center of the solution. If this does not occur, it indicates that the cathodes are not connected properly or are partially or totally insulated.

Regardless of whether this problem occurs or not, steps should be taken to protect and regularly maintain the cathode/buss connections, as well as all others in the anodizing circuit, to prevent this "insulation effect" from occurring.

Constant Current

Many anodizers operate by the practice of constant voltage control, which is used exactly the same on every load, regardless of size or shape. The assumption is that the result will be the same each time. For some applications this may be adequate, but will certainly not give the same results. The problem is that the total system of supply, load, and return is thought of as an integral unit which has one large voltage drop. Actually, the system, as described so far, is a series of small voltage drops which begin at the rectifier and accumulate as the current passes through every connection point. The connections which are in a fixed position can be attacked by the solutions splashed during transfer or from fumes and can suffer from the "insulation effect". Over time, resistance will build and the amount of current available for anodizing will slowly be reduced. If the anodizing practice is control by constant voltage, then the anodizing time will have to be increased or the coating thickness will gradually diminish as current flow is reduced.

In the same system there are many connections, such as in racking, which change with every load. If those connections do not have the same voltage characteristics each time, there will be a variation of current from load to load and subsequent variation of film thickness. Since the electrochemical oxidation occurs as a function of current and

not voltage, maintaining the same current concentration to each load and freeing the voltage to respond to the resistance variations results in a more unifrom film from one load to another. Control by constant current is based on a predetermined amount of current per unit surface area, such as square feet, and requires a calculation of the total area of the load. This is a somewhat tedious process to start and is probably the reason the industry has been using constant voltage control. However, if an operation has the problem of load to load uniformity, it may be advisable to consider changing to control by constant current, even if making load area calculations may not be the easiest way to go. It is interesting to review some of the historical practices of anodizing and find that this has generally been the recommended method. While seemingly tedious at the outset, once put into practice as a routine and normal part of the job, it can become a very effective tool.

SEALING

Once a uniform anodized film has been generated to the specified thickness, it is necessary to seal it, since the film is a porous structure of cellular aluminum oxide. Left in the unsealed condition it would quickly become stained by subsequent handling. Also, its corrosion resistance would be jeopardized, if its natural tendency to seal itself is interfered with by exposure to an unprotected atmosphere.

The sealing process requires contact with hot water which hydrolyses the aluminum oxide to form a hydrate which increases the volume of the cell structure. This effectively closes the pore and prevents penetration of the film by staining or corrosive materials. The factors which affect a good seal are the quality of the water used, the pH of the water, the temperature, and the time. Lack of control of any of these factors will impair the final seal quality as well as generate some appearance problems.

Smut

If the temperature and the pH are too low, less than 200°F and 5.80, respectively, the hydrate which forms is not the desired one, which is hard, smooth, and clear. Instead, the one that forms is soft, rough, and chalky or hazy. If the surface is wiped, it will turn into a white powder, which is practically impossible to remove, and which, if removed, would cause the loss of a considerable portion of the film. This is true seal "smut" and is a direct result of sealing problems. In recent years, with an understanding of this particular problem, conditions have been controlled or low-temperature nickel acetate seals have been substituted which have almost eliminated it. As a result, the term "smut" has come to be used to describe two other surface problems, which do not necessarily relate to control of the pH or the temperature.

Residue

The deposit of silicon, which can be left on the surface in the desmut step, will end up as a residue on the film after sealing (as discussed in CLEANING/PRETREATMENT-Desmut). This is not a smut and was not generated by poor seal conditions, but could be confused with such. The difference is that it usually is uniformly deposited over all surfaces of the parts and can be removed by wiping. The surface underneath, if sealed properly, will be hard and smooth. However, if this is confused with seal smut, then the proper corrective measures will not be taken.

Another source of residue comes from the dissolved solids, salts, or minerals, which remain on the surface after drying. These can accumulate in the seal tank through drag-in contamination or prolonged use of the seal water. This, also, is removable by wiping. The surface underneath may be properly sealed, or, because of the mineral content, it may only be partially sealed, but it will still be hard, clean, and smooth after wiping. This condition would indicate need of an immediate change of the seal water.

Powder

The other type of deposit which can occur is loose powder, which wipes off with very little effort. This results from undissolved solids, which, depending on the type of processes in the line, come from the neutralization of dissolved salts to form insoluble hydroxides in the rinse tanks. This can, also, be a problem with the precipitation of nickel hydroxide in low temperature seal baths, if conditions are not properly controlled.

RINSING

Rinsing may be the least considered part of the line operation, except for how much water is consumed and the quality of it leaving the plant. Not enough water flow leads to many of the residue and powder problems discussed, as well as, contamination of the various working solutions. Too much water flow is a waste and may result in unnecessarily high water and sewer charges. Most of these situations can be avoided or reduced by using counterflow practices and conductivity probes in the rinse tanks to control the chemical concentrations as a function of the pH of the rinses. For example, many of the hydroxides remain water soluble at a pH of 2.5-3.0, which is clean enough for a first rinse after most operations. This can be followed by a second, cleaner rinse, maintained at a pH of 5.5 to 6.5, which counterflows into the first rinse. The water flow through both tanks is then controlled by placing a conductivity probe in the first rinse to signal a valve which adds water to the second rinse.

Besides the residue problems, rinse tanks, which become too contaminated, can lead to metal surface problems, such as, pitting or galvanic corrosion, because of chemical interaction

between the salts and the bare unprotected aluminum. Also, because rinse tanks are considered to be inert, loads will sometimes be left hanging on the crane without having been electrically isolated or left touching metallic parts of a tank. This can set up a galvanic action which can destroy the surface condition of the metal in a very few minutes. Most practices have eliminated these problems, but they can still occur on a random basis and cause a great deal of frustration in trying to locate the cause of a finish problem.

AUTOMATIC CONTROLS

Many of the problems discussed have been know for years, while many can be considered more recent due to changes of standard practices to accommodate the need for economy and productivity. As a result, the greatest improvements to the anodizing process have not come from new practices, but from new controls, which can free the operator from many of the human variables that have made anodizing an "art" instead of a science for many years. New instrumentation allows the operator to more consistantly control his line and to free him to handle more effectively the manual steps, which can not be readily controlled automatically. Such controls can aid in good rinsing practices, in better temperature control of solutions, improved time and electrical input control to the anodizing step, and to improved product flow through the line.

TESTING FOR FILM QUALITY

There are many tests available to determine the quality of the final finish, which have been included in pamphlet no. 46 from the Aluminum Association. As mentioned, coating thickness testing, which is non-destructive, is probably the most useful tool on the line. Another test, which is destructive, utilizes a solution of chromic acid and phosphoric acid, which, at different temperature conditions, can determine seal quality and coating weight. Also, this test can be used to determine if a problem is in the anodized film or in the metal, as it will dissolve the film without acting on the metal. If the problem disappears, the problem relates to something that affected film growth. If the problem remains, then the metal may have an inherent defect, or it was not pretreated properly. This test can easily be set up in a plant lab and can be an important method of quality control.

TROUBLESHOOTING

OBJECTIVE IDENTIFICATION

Now that a multitude of problems have been considered (and by no means all of them), how is a problem determined, located, and eliminated? First and most important of all, the anodized (and colored) load must be examined and tested carefully, and objectively, to accurately define the problem.

This has to be done without looking to place blame on any particular person, or persons, or department. This is mentioned here, because many situations have been encountered which were made more difficult to resolve, because of an unwillingness to accept blame and, therefore, responsibility that a problem was occurring in a particular area. This can seriously interfere with making a good assessment of the problem.

SOURCE DETERMINATION

Once determined, the location or source of the problem must be identified. This can be done by taking note of the steps that can generate the problem. For instance, for pitting of the metal under the final finish, at least four locations have been discussed, before and during anodizing, where pitting can occur. The type of pitting, such as star shapes, sharp pits, or galvanic frost, can give a clue, but not the answer. The first step is to run another load. It may seem expensive to sacrifice a load of metal in this manner, but if something is changed at this point, it will be difficult to determine if the condition was a one-time occurance due to poor practices, or if a change occured in the system which could affect all subsequent loads. If the problem does not repeat, be careful and watch to see if it recurs in a random pattern. An unresolved and sporadic problem can lead to an increase of rework material. If the problem repeats, it becomes necessary to start changing variables and running more loads. Do not change more than one variable at a time. This will only lead to confusion over which change corrected the problem. Start with the most apparent first.

With respect to a pitting problem, obtain good, fresh metal, and process it. If it still shows pitting problems, then look to the sources of pitting in the anodizing line. Run a check of the rinses and the solutions, and check for possible points of electrical contact between the load and ground. If it comes clean, run some more loads. If they, also, come OK, then look to your metal storage practices and age of the metal, and consider using the deoxidize step before processing.

EXAMPLE OF TROUBLESHOOTING

One plant had a pitting problem, which was occuring in a totally random pattern. The operator was observed for most of a day, but in no way interfering with his normal handling of the line. Most of the time, after transfer of a load, he would leave it in a rinse tank to go move another load. This was the practice for the loads after desmut and before anodize, when he generally had a load in the anodize tank. However, on occasion an anodize load would end before the next load was ready, so that after desmut he would have an empty

anodize tank to which he could go right after the desmut rinse. In this circumstance, he would allow the load to remain suspended from the crane for the time specified for rinsing, which was five minutes. In good clean water this probably would not have been a problem, but a concentration of dissolved salts and a low pH in the desmut rinse, in combination with the fact that the load had electrical contact with the crane, was producing star pitting. Since this was only occuring on those loads which were handled in this manner, the problem was a random one. The fault was not the operator's, as either rinse practice, under proper conditions, should have been acceptable. It was a problem, which required cleaning up the desmut rinse and insulating the crane hooks from the crane so that a galvanic circuit was not formed. This effectively eliminated the problem.

PATIENT INVESTIGATION

It should be noted from the EXAMPLE that an important factor to properly resolving a problem is patience. When a plant is under pressure to maintain production, sometimes the problem is dealt with in haste and will rarely be correctly resolved. Troubleshooting requires time and a stepwise investigation. Once the source and location of the problem have been determined, take steps to eliminate it. Don't leave it in the hands of the operator to have to deal with it by telling him to be careful when he comes to that particular step, unless it is only a temporary period to obtain controls or equipment to correct the problem. Remember that the operator is human and that in any anodizing line when all is well, he will have plenty to do. Unless the problem is properly and completely corrected, one cannot expect to eliminate it.

CONCLUSION

This paper can not begin to deal with all the potential sources of anodizing problems, but it is hoped that it will provide some specific examples of problems, and will also provide a systematic pattern for evaluating, locating, and correcting problems. If further information or detail is desired, the reader is referred to the Publications List included.

PUBLICATIONS DEALING WITH THE ANODIZING OF ALUMINUM

RECOMMENDED READING SOURCE	SUGGESTED PURCHASING SOURCE
1.The Surface Treatment and Finishing of Aluminum and It's Alloys. (2 Vols.) S. Wernick and R. Pinner 4th Edition, 1972	Metals and Plastics Publications, Inc. One University Plaza Hackensack, N.J. 07601
The Technology of Anodizing Aluminum. A.W. Brace & P.G. Sheasby Technicopy Limited 66 High Street, Stonehouse Gloucestershire, g. L10ZNA England, 2nd. Edition, 1979	Metals and Plastics Publications, Inc. (see above) or AES Book Department 1201 Louisiana Avenue Winter Park, FL 32789
Aluminum Finishes Process Manual. Reynolds Metals Company Richmond, Virginia 1973	R.A.I.S.I P.O. Box 27002 Richmond, VA 23261 Attn: Don Rose
Aluminum Standards and Data. Publication No. 1 (1983) Designation System for Aluminum Finishes. Publication No. 45 (1980) Standards for Anodized Architectural Aluminum. Publication No. 46 (1978)	The Aluminum Association 818 Connecticut Ave., N.W. Washington, D.C. 20006
Anodized Aluminum. ASTM Special Technical Publication No. 388 A Symposium Presented in Cleveland, Ohio on February 9, 1965	University Microfilm International P.O. Box 1467 Ann Arbor, MI 48106
Aluminum Finishing Seminar Technical Papers, VOL. 1. Aluminum Finishing Seminar March 30-April 1, 1982 St. Louis, Missouri	The Aluminum Association (see above)

PUBLICATIONS DEALING WITH THE ANODIZING OF ALUMINUM

RECOMMENDED READING SOURCE	SUGGESTED PURCHASING SOURCE
SUR/FIN `83, Session J:Light Metal Finishing I & Session L:Light Metal Finishing II. 70th Annual Technical Conference of the American Electroplaters' Society June 26-30, 1983 Indianapolis, Indiana	AES Book Department (see above)
Anodizing Respones of Aluminum Finishes. S.B. Wyman Reynolds Metals Company Technical Paper Presented at 57th Annual Convention of The AES in Montreal, Canada on June 22, 1970	AES Book Department (see above)
Process Factors Affecting Finish of Aluminum Alloy Extrusions. Edmund C. Franz Alcoa Research Laboratories Technical Paper Published in Metal Progress Magazine June 1970 Issue, pp.80-82	Metal Progress Reader Service Deparment P.O. Box 1979 Clinton, Iowa 52735 or University Microfilm International (see above)

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K-2

Light Metals Finishing I
Session K

Anodizing Aluminum Alloys for Aircraft Wheels and Brakes

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ANODIZING ALUMINUM ALLOYS FOR AIRCRAFT WHEELS AND BRAKES

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Abstract

The design of large, commercial aircraft wheels and brakes is dependent upon extensive use of high strength aluminum alloys. However, these wheels and brakes operate in potentially corrosive environments which necessitate the use of protective coatings. Although paint systems are included in these protective coatings, anodic films form the basis for corrosion resistance of aluminum alloys. Thin anodic films from sulfuric and chromic acid baths, as well as thicker hardcoats, are applied depending upon the design needs of each component. This paper is intended to provide an understanding of the anodic processes used in aircraft wheel and brake components, and includes a discussion of design, processing, and service history of these parts.

Introduction

Large commercial aircraft, such as those operated by the major airlines, have long depended on aluminum alloys due to their light weight and mechanical strength. This is particularly true of the wheel and brake assemblies where aluminum alloys are used extensively to offset the massive weight of the heat sinks employed in the brake. In addition to light weight, resulting in fuel economy, aluminum alloys offer promise for corrosion protection through extended warranteed periods. Corrosion protection can take many forms, but usually consists of a combination of anodic films and paint systems.

The aircraft wheel and brake assembly, as depicted in Figures 1 and 2, contains several components that are manufactured using heat treatable aluminum alloys. These components are the wheel halves, brake housing, pistons, and piston bushings. 2000 series aluminum alloys are used primarily for the wheel halves and brake housings, while both 7000 series and 6000 series alloys are used for the pistons and piston bushings depending on the loads encountered during operation.

Airlines operate in a variety of environments including high humidity, salt, snow, sand, and extremely low temperatures, which demand coatings to protect the base material from degradation under adverse conditions. In addition, the assembly and operation of some of the components require

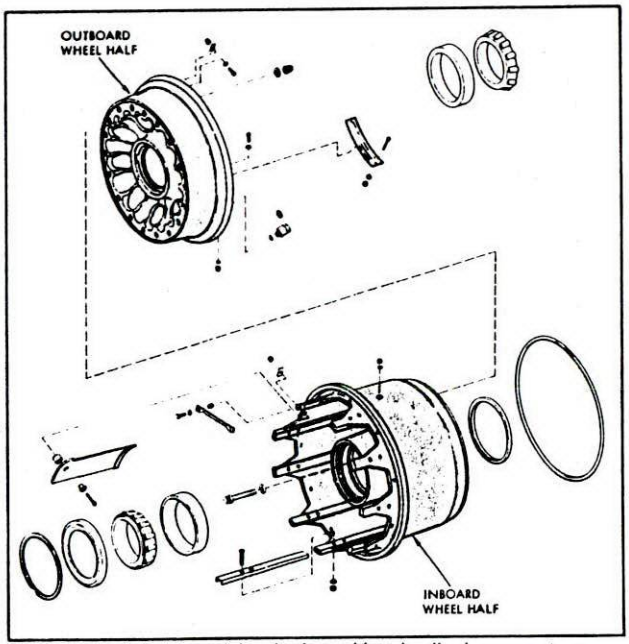

Figure 1 - Exploded view of the wheel assembly. Anodized components are labeled.

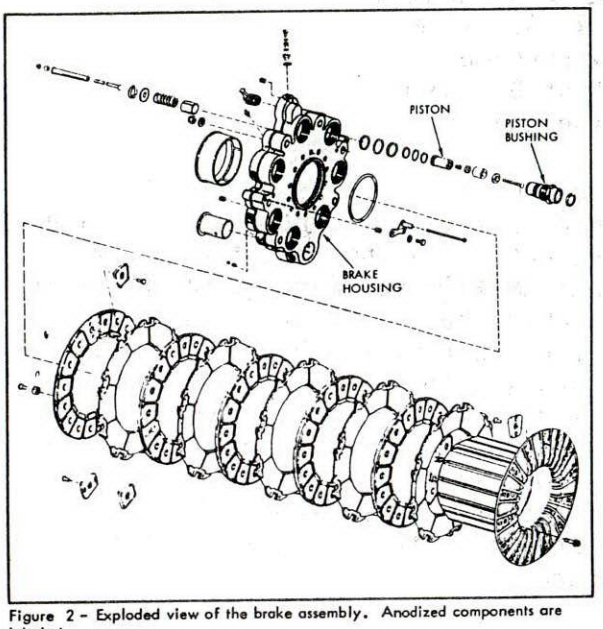

Figure 2 - Exploded view of the brake assembly. Anodized components are labeled.

protection from wear and galvanic corrosion. Wheel halves are the main structural component in these assemblies and are subjected to high cyclic loading. Protection from environmental and galvanic corrosion is paramount in order to increase the life by reducing the incidence of corrosion-induced fatigue. Thinner chromic acid anodizing is preferred where fatigue strength is the life limiting factor, whereas sulfuric acid anodized coating is more corrosion resistant and has an additional measure of wear resistance. This additional wear resistance is important in that tire and mating components can wear away anodic films. Brake housings are usually subjected to greater cyclic loading than wheel halves, so chromic acid anodic films are applied prior to application of a paint system.

Unlike the wheel halves and brake housings, wear resistance is more critical for the pistons and piston bushings. Pistons are designed to slide against the bushings when the brake is actuated. A hardcoat anodic film provides a combination of wear and corrosion resistance that is desirable for these components. Hardcoat is used unsealed for additional wear resistance and lubricity due to entrapment of the hydraulic fluid in the crack pattern.

In all aluminum components that receive an anodic film, the electrical contact points are specified to be located in nonfatigue critical areas, or in areas that can tolerate a potential arc burn. These are protected with a chemical conversion coating. Chemical conversion coatings are also used to repair areas damaged after anodizing.

Processes Used

Chromic Acid Anodizing

The process of applying an anodic film to wheel halves and brake housings from a chromic acid bath is shown schematically in Figure 3. This method involves a precleaning step to remove dirt and oily substances, such as cutting oils, which would inhibit the formation of the anodic film. This is accomplished with the use of an alkaline cleaner and degreasing operation. The alkaline cleaner is inhibited to prevent pitting of the aluminum base metal.

Anodizing is carried out in a steel tank using a 3% solution of chromic acid in deionized water. Current is applied at 9 amps per square foot, and voltage is increased incrementally up to 40 volts. Generally, for the size of the loads processed, a time of 30 minutes is considered optimum for obtaining a chromic acid anodic film conforming to the specification. The temperature of the bath is maintained at 91°F-99°F (32.7°C-37.2°C), and it is air-agitated to maintain uniform concentration and

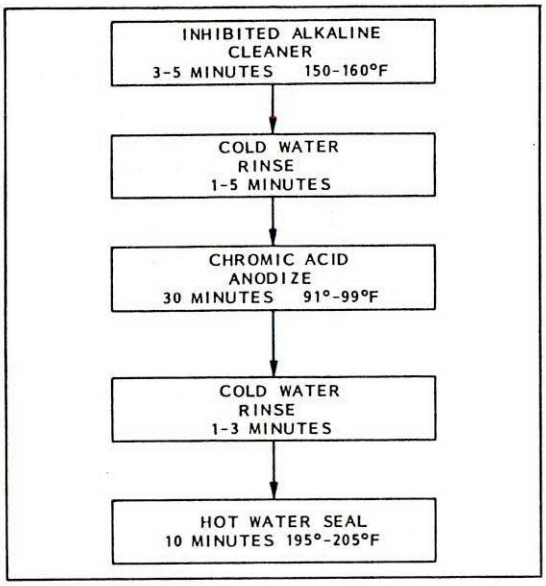

Figure 3 - Chromic acid anodize flow chart

temperature. The fixturing used for anodizing are either titanium or aluminum alloys.

After anodizing, the parts are immediately removed from the acid bath and rinsed in cold running water. After rinsing, the chromic acid anodizing process is completed by sealing in hot deionized water for ten minutes. The temperature of the hot water is maintained at 195°F-205°F (90.5°C-96.1°C). This bath is kept slightly acidic by additions of chromic acid. Not only does this operation seal the anodic film but it also facilitates drying of the parts.

The anodic film, as applied by this process, produces a coating thickness of about 0.00004 inch, which is adequate for corrosion protection without a significant reduction in fatigue strength. However, since it is a relatively light coating, it is extremely sensitive to handling damage. Localized damage is repaired by applying a chemical conversion coating, or by stripping and reapplying the anodic film if the damage is extensive.

Sulfuric Acid Anodizing

The process of applying an anodic film to wheel halves from a sulfuric acid bath is shown schematically in Figure 4. Precleaning is similar to the chromic acid process in that it utilizes an inhibited alkaline cleaner to remove dirt, and, if necessary, a vapor degreaser to remove grease and oil. In addition, the precleaning step in the sulfuric acid process includes a deoxidizer to remove inherent surface oxides. The deoxidizer is a dilute solution of hydrofluoric acid, so care is exercised to limit the component exposure time and to monitor deoxidizer bath chemistry due to the highly corrosive nature of hydrofluoric acid on aluminum alloys. Both the alkaline cleaner and deoxidizer baths are air agitated to maintain uniform concentration.

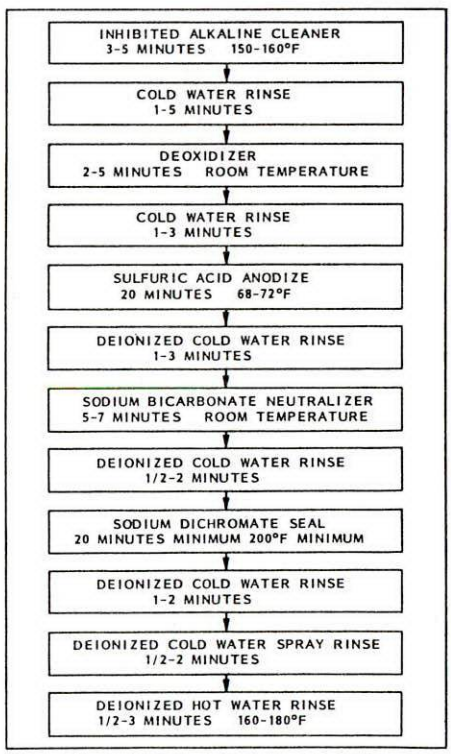

Figure 4 - Sulfuric acid anodize flow chart

After precleaning, the parts are transferred to the sulfuric acid bath. This bath is made up of 16-20% sulfuric acid in deionized water, which is air agitated and kept in a lead-lined steel tank fitted with cooling coils capable of maintaining a bath temperature of 68°F-72°F. The parts are suspended at an angle so as to minimize air pockets. Titanium or aluminum alloys are used for fixturing. Current is applied at 9 amps/ft^2, and the voltage is raised to 18-20 volts for 2000 series alloys, and 16-18 volts for any 7000 series alloys that might be processed with sulfuric acid anodic films. 2000 series alloys are anodized for 20 minutes and 7000 series alloys are anodized for 15 minutes. 7000 series alloys require less voltage and time due to their inherent ability to produce thicker anodic films than the 2000 series alloys. These times and voltages are designed to produce an anodic film 0.0003-0.0005 inch thick.

The electrolyte is routinely controlled. Dissolved aluminum in the bath is maintained at 9 grams per liter and the chloride concentration at 0.2 grams per liter maximum. Aluminum and chloride contents are controlled by discarding a portion of the solution and replenishing with fresh sulfuric acid solution.

Once the anodic film has formed, the parts are immersed in a 5% solution of sodium bicarbonate to neutralize the acid retained on the surface. This bath is air agitated and is maintained at room temperature. The parts are neutralized for 5-7 minutes, and care is exercised to limit the exposure since localized attack of the part may occur.

Once neutralization is complete, the parts are sealed in a sodium dichromate solution. Although sulfuric anodic films may also be sealed by nickel acetate or hot water, sodium dichromate has proved to exhibit the most corrosion resistance for this application. The bath contains 5% sodium dichromate in deionized water, and the temperature is maintained at 200°F minimum. Parts are sealed for 20 minutes, producing a characteristic deep yellow appearance. A cold rinse and a hot rinse, which facilitates drying, completes the anodic film process. This is followed by the application of chemical conversion coating to the contact points.

Hardcoat Process

The process of applying a hardcoat anodic film to pistons and piston bushings is shown schematically in Figure 5. The only precleaning necessary is a vapor degreasing operation to remove grease and oil.

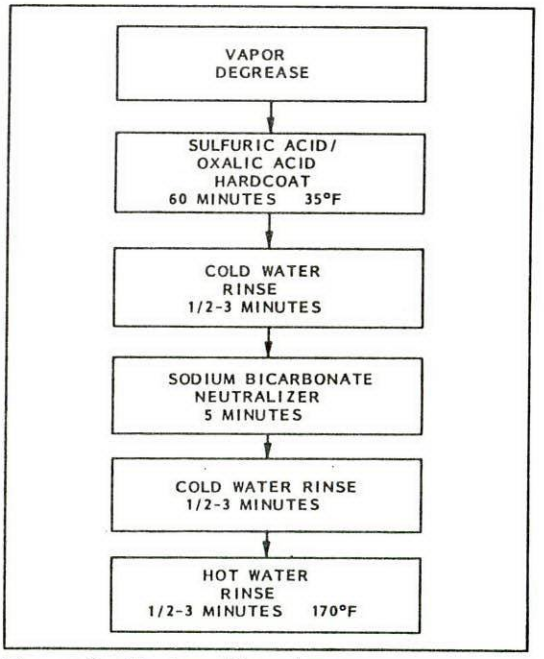

Figure 5 - Hardcoat flow chart

The hardcoat bath is made up of 15% sulfuric acid, 1% oxalic acid in deionized water. It is contained in a lead-lined steel tank fitted with cooling coils capable of maintaining

a temperature of 30-40°F, and is mechanically stirred to ensure uniform concentration. The parts are suspended with titanium hooks at an angle to minimize air pockets. Current is applied at 36-37 amps per square foot, and the parts are anodized for a time necessary to produce an anodic film thickness of 0.001-0.003 inch thick, which for the 6000 series alloys is approximately 60 minutes. The thickness is determined by the use of a control rod that is anodized with the parts. The bath is routinely controlled as is the aluminum concentration which is maintained at a maximum of 9 grams per liter.

Since this coating is used in the unsealed state for improved wear resistance, the parts are rinsed in cold and then hot, 170°F, water to facilitate drying. Although prolonged exposure to hot water will tend to seal anodic films, this bath is kept at a temperature which is lower than necessary to seal the coating for the expected exposure time. The anodic process is completed by applying a chemical conversion coating to the electrical contact areas.

Coating Inspection and Test Procedures

Quality control is maintained by periodic coating weight and corrosion tests. Anodic coating weight is determined by measuring weight loss of an aluminum panel that has been anodized with production pieces and stripped in a mixture of chromic acid and phosphoric acid. Coating weights are closely monitored to meet the specification requirements. Corrosion resistance of coatings is measured by exposing test panels, which have been anodized with production parts, in a salt spray cabinet. The panels are inclined at six degrees and subjected to a spray containing 5% sodium chloride for 336 hours. Coatings should not exhibit more than five isolated pits of 0.03125 inch maximum in diameter.

In addition to coating weight and corrosion resistance, hardcoat films are also subjected to an abrasion test using a Taber abrador. Abrasion resistance is determined by calculating weight loss after subjecting the coating to 10,000 cycles under a 1000 gram load. Weight loss should meet the customer's specifications.

Finally, anodic coatings are visually inspected to ensure that they are continuous, smooth, adherent, and uniform in appearance and color. They are to be free from powdery areas, loose films, and discontinuities such as breaks, scratches, burned areas, and other damage.

Problems Associated With Anodizing

Due to the variety of aluminum alloys and processes used in the production of anodic films for aircraft wheels and brake systems, several problems are encountered in the production and operation of components.

Surface preparation is a major problem in the formation of anodic films. If the parts are not properly cleaned, surface contaminants can interfere with oxide growth. Although the alkaline cleaner is intended to remove dirt, some of the processing operations preceding anodizing, such as shot peening and deburring, have caused contaminants to become entrapped on the part surface. In addition, the chemicals used to prepare the surface can be detrimental to the surface finish of fatigue critical parts. Therefore, care has to be exercised to minimize the exposure of these parts to such chemicals and to properly maintain the chemistry of each bath.

Formation of the anodic film can also be limited by improper acid concentration and impurities, such as dissolved aluminum and chlorides, which can cause a disruption in the anodic film. Although the chemistry of the acid and seal tanks are critical to ensure corrosion protection, contaminants in other baths, especially final rinse tanks, can effect the subsequent paint operation. In one case, steam used to maintain the temperature of the chromic acid anodize hot water seal tank generated organic contaminants that coated the parts and caused difficulties with paint adhesion. Subsequently, steam heaters were replaced with electric heaters.

Other problems associated with the production of an anodic film are poor electrical contact, air pockets, handling damage, operator error, and poor alloy identification. Improper electrical contact by either insufficient clamping force or by improperly cleaned anodes can cause arc burns or insufficient coating thickness. Air pockets are caused by improper racking or by insufficient agitation of the bath. Handling damage can normally be repaired by application of the chemical conversion coating; operator error and poor alloy identification often necessitates stripping of the anodic film and reprocessing.

The anodic films, as applied by the recommended procedures, exceed the requirements of various military and commercial specifications. However, if the airlines' overhaul facilities do not conform to the manufacturer's codes, difficulties can arise in the breakdown of anodic coating and poor corrosion resistance. This has a bearing on the warrantees offered by the manufacturer.

Aside from the problems associated with the control of anodic processes, the design and operation of the wheel and brake assembly can cause breakdown of the anodic film. This breakdown is caused by contact from mating parts which wear away paint and anodic film and establish galvanic cells. Figures 6 and 7 illustrate the damage that can occur when two components, in this case the wheel and a key boss cap, come into contact. The protective films were worn away, resulting in a galvanic cell and intergranular corrosion. A fatigue crack initiated from corrosion pits and propagated until the air pressure was released from the tire.

Figure 8 is an example of the wear damage to the wheel half at the tire contact area. Typically, the tire heal reinforcing material wears away the protective coating, thus making the base metal vulnerable to crevice corrosion. Damage of this kind can be prevented by periodic inspection at each tire change.

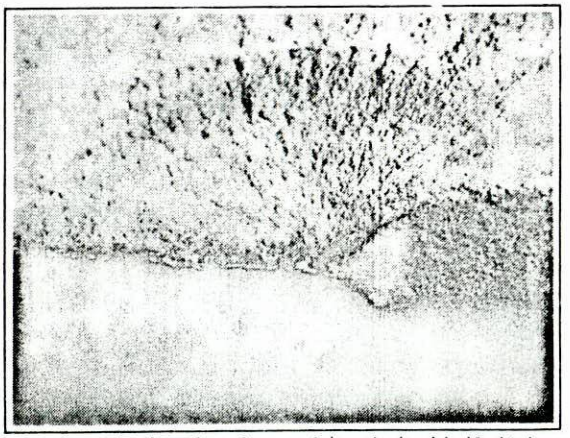

Figure 6 - Crack surface from an inboard wheel half which clearly illustrates fatigue beach marks and a corrosion pit at the origin. Magnification: 6X

brakes can be complex, it has become an integral part of the manufacturing process for improved corrosion and wear resistance. The need for a clean surface prior to anodizing, proper sealing procedures, and painting have extended the life of these parts exposed to a variety of hostile environments.

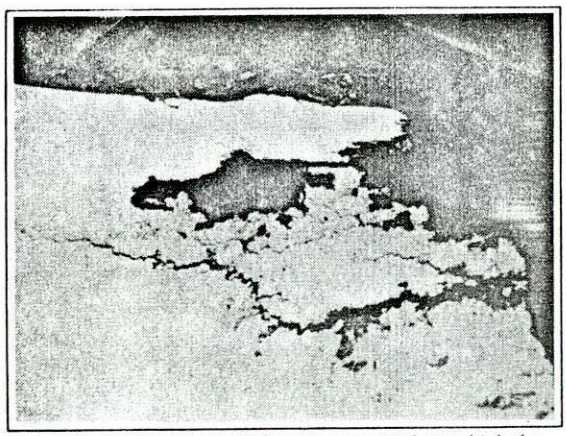

Figure 7 - Section through the corrosion pit from which the fatigue crack originated. Magnification: 200 X

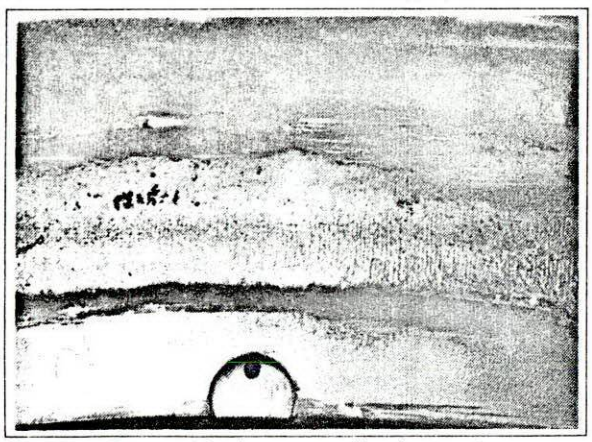

Figure 8 - Erosion of the base material by the tire after removal of the anodic film. Magnification: 1X

Conclusions

Although the application of anodic coatings on components that are assembled into aircraft wheels and

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Light Metals Finishing I Session K

Sealing of Anodized Aluminum - Hot, Lukewarm and Cold

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Paper not received in time for publication

K-4

Light Metals Finishing I
Session K

Progress Report
Technology & Economics of Gold Conversion Sealing

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PROGRESS REPORT

TECHNOLOGY & ECONOMICS OF COLD CONVERSION SEALING

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CREDITS

A PART OF THE MATERIAL REPORTED HERE IS BASED ON WORK UNDERTAKEN BY DR. WALTER DALLA BARBA, WHO IS TECHNICAL DIRECTOR FOR ITALTECHNO IN MODENA, ITALY AND BY DR. FRELY SACCHI, WHO IS EDITOR OF THE MAGAZINE "ANODIZING AND PAINTING TODAY". THIS SEEMS APPROPRIATE SINCE MOST, IF NOT ALL, OF THE COLD CONVERSION SEALING DONE IN EUROPE AND THE UNITED STATES DERIVES FROM THE TECHNICAL WORK OF THESE MEN AND THEIR ASSOCIATES. THE BALANCE OF OF THE MATERIAL IS BASED ON AEROMARINE'S EXPERIENCE AND OBSERVATIONS IN WORKING WITH COLD CONVERSION SEALING IN THE UNITED STATES AND, TO A LESSER DEGREE, IN EUROPE.

DEFINITIONS

IT IS USEFUL TO PROPOSE SOME DEFINITIONS FOR SOME OF THE LANGUAGE WHICH WILL BE USED HERE. IT IS WELL KNOWN THAT NEWLY FORMED ANODIC COATINGS ON ALUMINUM ALLOYS ARE UNDESIRABLY SORPTIVE AND SUSCEPTIBLE TO STAINING AND PERMANENT DISCOLORATION. MOST SUCH COATINGS ARE SUBJECTED TO ONE OR MORE FURTHER PROCESS STEPS TO SEAL THE COATING. AFTER SUCH PROCESS STEPS ARE SUCCESSFULLY COMPLETED, THE ANODIC COATING POSSESSES A MUCH IMPROVED RESISTANCE TO STAINING, CHEMICAL ATTACK AND CORROSION, AND IS SAID TO BE "SEALED". MORE SPECIFICALLY, THE WORD "SEALED" AS USED HERE WILL REFER TO AN ANODIC COATING WHICH HAS PROPERTIES CAPABLE OF PASSING THE ASTM B136-77 MODIFIED DYE STAIN TEST AND WHICH EVIDENCES A WEIGHT LOSS OF LESS THAN 2.6 MILLIGRAMS PER SQUARE INCH WHEN TESTED IN ACCORDANCE WITH THE ISO 3210 INTERNATIONAL ACID DISSOLUTION TEST.

THE CONVENTIONAL METHOD OF SEALING ENTAILS IMMERSION OF THE ANODIZED ALUMINUM ALLOY IN EITHER WATER OR AN AQUEOUS SOLUTION OF METAL SALTS AT ELEVATED TEMPERATURE. DEIONIZED WATER AT NEAR BOILING TEMPERATURE IS USED BY SOME OPERATORS. OTHERS USE SOLUTIONS OF NICKEL ACETATE OR OTHER CHEMICALS AT TEMPERATURES IN THE RANGE OF 170 TO 210 DEGREES FAHRENHEIT. IT IS GENERALLY ACCEPTED THAT THE PRINCIPAL MECHANISM OF SUCH SEALING PROCESSES IS THE HYDRATION OF THE ALUMINUM OXIDE IN THE ANODIC COATING. THE TERMINOLOGY "HYDRATION SEALING" IS USED HERE IN REFERRING TO SUCH PROCESSES, ALTHOUGH IT MUST BE RECOGNIZED THAT THERE EXIST WIDE VARIATIONS IN THE TEMPERATURES, SEALING TIMES AND QUALITY OF SEAL RESULTING FROM SUCH PROCESSES AS CURRENTLY PRACTICED IN THE ANODIZING INDUSTRY IN THE UNITED STATES. THAT IS, MANY HYDRATION SEALED COATINGS DO NOT MEET THE RIGOROUS STANDARDS USED IN THE DEFINITIONS SET FORTH ABOVE.

LOW TEMPERATURE CONVERSION SEALING IS A DIFFERENT MATTER

ENTIRELY AND AGAIN SOME DEFINITION OF TERMINOLOGY IS USEFUL. LOW TEMPERATURE SEALING, OR COLD SEALING, IS USED HERE IN REFERENCE TO SEALING BATHS WHICH ARE COLD TO THE TOUCH. THE TERM "CONVERSION SEALING" WILL REFER TO A SEALING PROCESS WHICH, BY CHEMICAL REACTIONS WITHIN THE COATING, CREATES NEW CHEMICAL SPECIES WHICH ARE DIFFERENT FROM THE CHEMICAL COMPOSITION OF THE CONVENTIONAL HYDRATION SEALED COATING. THAT IS, THE MECHANISM OF SEALING IS ENTIRELY DIFFERENT FROM THE PRINCIPAL MECHANISM OF HYDRATION SEALING IN THAT IT ENTAILS A CHEMICAL REACTION OF THE SEALANT ACTIVE SPECIES WITH THE ALUMINUM OXIDE OF THE ANODIC COATING. THIS REACTION TAKES PLACE WITHIN THE POROUS STRUCTURE OF THE ANODIC COATING.

THERE ARE A NUMBER OF COLD CONVERSION SEALS PRESENTLY AVAILABLE TO ANODIZERS OF ALUMINUM. THESE PRODUCTS ARE PROPRIETARY TO THE COMPANIES WHICH DISTRIBUTE THEM AND ARE RELATIVELY NEW IN THE U.S. MARKETPLACE. INFORMATION ABOUT THESE VARIOUS PRODUCTS, HOW WELL THEY OPERATE, AND HOW THE ANODIC COATINGS PERFORM IN SERVICE IS NOT WELL DOCUMENTED NOR WIDELY KNOWN. PRODUCTION EXPERIENCE WITH THE COLD CONVERSION SEALS IS RELATIVELY LIMITED COMPARED WITH THE INDUSTRY'S EXPERIENCE WITH HYDRATION SEALS. IN THESE CIRCUMSTANCES IT IS DIFFICULT TO GENERALIZE AND WHAT IS WRITTEN HERE ADDRESSES POSSIBILITIES, CHARACTERISTICS AND RESULTS THAT MAY NOT APPLY EQUALLY TO ALL SUCH PRODUCTS.

BACKGROUND

THE THEORETICAL BASIS FOR COLD CONVERSION SEALING DATES BACK AT LEAST TWENTY YEARS TO WORK UNDERTAKEN BY DR. FRELY SACCHI AND OTHERS AT THE EXPERIMENTAL INSTITUTE FOR LIGHT METALS AT NOVARA IN ITALY. AT THAT TIME A COMPARISON WAS MADE OF CONVENTIONAL SEALING IN BOILING DEIONIZED WATER WITH PRACTICAL SEALING IN NICKEL SALT SOLUTIONS AS CARRIED OUT IN ITALIAN INDUSTRIAL PLANTS. TYPICAL RESULTS ARE ILLUSTRATED IN FIGURE 1. IT WAS FOUND THAT SEALING IN WATER GAVE EXCELLENT RESULTS ONLY IF THE WATER WAS VERY PURE, ALMOST BOILING, AND THE SEALING TIME WAS AT LEAST EQUAL TO THE ANODIZING TIME. SEALING IN HOT NICKEL SALT SOLUTIONS GAVE GOOD RESULTS WITH LOWER TEMPERATURES AND SHORTER SEALING TIMES, AND DID NOT REQUIRE THE HIGH DEGREE OF WATER PURITY NEEDED FOR HOT WATER SEALING. IT WAS ALSO OBSERVED THAT THE QUALITY OF SEALING CARRIED OUT IN NICKEL SALTS CLEARLY IMPROVED AFTER AGING FOR A FEW DAYS. AS A CONSEQUENCE OF THESE OBSERVATIONS THE RESEARCHERS CONCLUDED THAT NICKEL SALT SEALING CONSISTS OF TWO PHENOMENA: SOME HYDRATION OF THE ANODIC COATING ANALOGOUS TO THAT ACHIEVED IN HOT WATER SEALING, TOGETHER WITH SOME PRECIPITATION OF A NICKEL COMPOUND IN THE PORES OF THE ANODIC COATING. SUCCEEDING STUDIES SHOWED THAT THE PHYSICAL COMPONENT OF NICKEL SEALING, THAT IS THE PRECIPITATION OF NICKEL COMPOUNDS IN THE PORES OF THE ANODIC COATING AND THE AGEING EFFECT, COULD BE IMPROVED BY USING MORE REACTIVE SALTS, REGULATING THE CONCENTRATIONS AND THE PH OF THE SEALANT BATHS, AND ADDING SURFACE ACTIVATORS TO FACILITATE THE PRECIPITATION.

OPERATIONAL CHARACTERISTICS

FIGURE 2 SHOWS A COMPARISON OF COLD SEAL OPERATIONS WITH OPERATIONS TYPICALLY USED IN HYDRATION SEALING. COLD CONVERSION SEALS HAVE NOW EVOLVED TO THE POINT WHERE IT IS POSSIBLE TO OBTAIN A HIGH QUALITY SEAL IN FROM 5 TO 12 MINUTES AT TEMPERATURES IN THE RANGE OF 85 TO 95 DEGREES FAHRENHEIT WITH THE PROVISION THAT THE SEAL BE PERMITTED TO AGE FOR 4 HOURS OR LONGER PRIOR TO TESTING. OUR EXPERIENCE IS THAT THE COLD CONVERSION SEALED ANODIC COATING WILL TYPICALLY PASS THE CONVENTIONAL DYE STAIN TEST WITHIN MINUTES OF THE COMPLETION OF THE SEALING PROCESS, BUT REQUIRES 4 HOURS OF AGING TO PASS THE MODIFIED DYE STAIN TEST.

THE ITALIAN RESEARCHERS ALSO FOUND THAT SEALING IN BOILING SOLUTIONS FORMED A SUPERFICIAL LAYER OF DUST, OR SMUT, WHICH WAS AN INSEPERABLE SIGN OF EFFICIENT HYDRATION OF THE ANODIC COATING. THIS SMUT WAS FOUND TO BE EXTREMELY TENACIOUS AND DIFFICULT TO REMOVE.

COLD CONVERSION SEALING CAN, HOWEVER, PROVIDE FOR COMPLETE PHYSICAL SEALING BY CHEMICAL MEANS SO THAT LITTLE IF ANY HYDRATION OF THE ANODIC COATING IS NEEDED. EXPERIENCE HAS CONFIRMED THAT THE COLD CONVERSION SEAL CAN BE ENTIRELY FREE OF SEAL SMUT ALTHOUGH THIS MAY NOT BE UNIVERSALLY TRUE OF ALL COLD SEALS. IT HAS ALSO BEEN OBSERVED THAT SMUT, DISCOLORATION OR STAINING OF ANODIZED ALUMINUM CAN ORIGINATE AT A VARIETY OF STEPS IN THE PREPARATION, ANODIZING AND SEALING OF ALUMINUM ALLOYS. IF SUCH CIRCUMSTANCES OCCUR PRIOR TO COLD CONVERSION SEALING, IT IS LIKELY THAT THE SEALING WILL MAKE IT MUCH MORE APPARENT. AS A RESULT OF THESE OBSERVATIONS WE HAVE CONCLUDED THAT CERTAIN KINDS OF PRE-SEAL SMUT CAN OCCUR WHICH MIGHT BE REMOVED IN A HOT SEAL BUT NOT IN A COLD ONE. AS A CONSEQUENCE, THE UTILIZATION OF A COLD SEAL MAY REQUIRE CLOSER ATTENTION TO PREPARATION PROCESSES SUCH AS CLEANING, ETCHING, AND DE-OXIDIZING THAN MIGHT OTHERWISE BE THE CASE.

QUALITY CHARACTERISTICS

A TECHNICAL COMPARISON OF THE PROPERTIES OF COLD CONVERSION SEALED ANODIC COATINGS WITH SIMILAR HYDRATION SEALED COATINGS IS SET FORTH IN FIGURE 3. THE COLD SEAL DATA ARE NECESSARILY FOR A SPECIFIC SEAL AND MAY NOT BE REPRESENTATIVE OF ALL SUCH SEALS. FOR THIS CASE, SAMPLES OF CLEAR, BRONZE AND BLACK ELECTROCOLORED CLASS I ARCHITECTURAL ANODIC COATINGS WERE SUBJECTED TO A VARIETY OF TESTS TO EVALUATE PROPERTIES OF DURABILITY AND CORROSION RESISTANCE.

WITH RESPECT TO HARDNESS, THE ITALIAN RESEARCHERS FOUND THAT HYDRATION SEALING REDUCES THE HARDNESS AND WEAR RESISTANCE COMPARED TO THE QUALITIES OF AN UNSEALED ANODIC COATING. COLD CONVERSION SEALING, ON THE OTHER HAND, CAN RESULT IN A DECIDED

IMPROVEMENT IN HARDNESS AND WEAR RESISTANCE.

THE TESTS INCLUDED EXTENDED EXPOSURE IN THE ASTM B117 SALT SPRAY TEST, WHICH IS GENERALLY ACCEPTED BY THE AEROSPACE INDUSTRY AND DEPARTMENT OF DEFENSE AS THE MOST MEANINGFUL TEST FOR CORROSION RESISTANCE. WHATEVER THE SHORTCOMINGS OF THIS TEST, AND THE TIME NEEDED TO GET CONCLUSIVE RESULTS IS CERTAINLY ONE OF THEM, IT PROBABLY HAS A LONGER HISTORY OF CORRELATION WITH RESPECT TO OUTDOOR EXPOSURE THAN ANY OF THE MORE RECENTLY DEVELOPED TESTS. AS SHOWN HERE, THE CONVERSION SEALED SAMPLES SHOWED NO EVIDENCE OF CORROSION AFTER 5000 HOURS EXPOSURE WHEREAS THE HYDRATION SEALED SAMPLES WERE BADLY CORRODED AFTER ONLY 1500 HOURS.

THE COPPER ACCELERATED SALT SPRAY TEST, WHICH IS A VERY AGGRESSIVE TEST OF AN ANODIC COATING, WAS ALSO PERFORMED ON SEALED SAMPLES. AFTER 72 HOURS EXPOSURE, THE HYDRATION SEALED SAMPLES EVIDENCED OVER TEN THOUSAND PITS PER SQUARE METER WITH PITS HAVING AN AREA OF OVER TWO SQUARE MILLIMETERS. THE CONVERSION SEALED SAMPLES HAD AN ORDER OF MAGNITUDE FEWER PITS WITH AN ORDER OF MAGNITUDE SMALLER PIT AREA.

THESE DURABILITY RESULTS WERE CONFIRMED BY A 5 CYCLE KESTERNICH TEST. HERE AGAIN THE HYDRATION SEALED SAMPLES SHOWED SEVERE DISCOLORATION WHEREAS THE CONVERSION SEALED SAMPLES SHOWED NO EVIDENCE OF DISCOLORATION.

A FURTHER PROPERTY OF THE CONVERSION SEAL WHICH IS NOT SHOWN ON THE SLIDE IS THE COMPATIBILITY OF THE SEALED ANODIC COATING WITH OTHER MATERIALS. THE CONVERSION SEAL DISCUSSED ON THE PREVIOUS SLIDES HAS BEEN SHOWN TO RENDER AN ANODIC COATING SOMEWHAT MORE RESISTANT TO ALKALINE ATTACK THAN TYPICAL HYDRATION SEALS. THIS IS BORNE OUT BY THE EXPERIENCE OF PRODUCERS OF ARCHITECTURAL ANODIC COATING WHO USE THIS SEAL. SEVERAL HAVE REPORTED A NOTICEABLE INCREASE IN THE TIME REQUIRED TO STRIP RACKS. ALSO, SOME U.S. USERS HAVE RUN INDEPENDENT TESTS TO ESTABLISH THAT THE SEAL IS COMPATIBLE WITH VARIOUS GLAZING SEALANTS AND SERVES ALSO AS AN ACCEPTABLE PAINT BASE. WITH RESPECT TO THESE LAST TWO CHARACTERISTICS, THE COLD SEAL IS NOT REPORTED TO BE SIGNIFICANTLY DIFFERENT THAN A HYDRATION SEAL.

ECONOMIC CHARACTERISTICS

IN ADDRESSING THE ECONOMICS OF CONVERSION SEALING, PARTICULARLY IN COMPARISON TO HYDRATION SEALING, IT HAS TO BE RECOGNIZED THAT THE COST OF SEALING VARIES WIDELY AMONG THE MANY ANODIZERS WHO USE THESE PROCESSES. THIS IS DUE TO THE WIDE VARIATIONS IN TEMPERATURES AND CHEMICAL PRODUCTS BEING USED, WITH RESULTING VARIATIONS IN CHEMICAL COSTS, SEALANT USEFUL LIFE, AND WATER REQUIREMENTS. THERE ARE ALSO VARIATIONS IN SEAL QUALITY IN THAT NOT ALL ANODIZERS HAVE TO MEET THE SPECIFICATIONS FOR ARCHITECTURAL ALUMINUM. IN VIEW OF THE MANY VARIABLES INVOLVED, NO

DIRECT COMPARISON OF THE ECONOMICS OF COLD CONVERSION SEALING AND HYDRATION SEALING CAN BE VERY MEANINGFUL. INSTEAD, THE FACTORS WHICH MOST INFLUENCE THE COST OF COLD CONVERSION SEALING ARE REVIEWED, AND THE AREAS WHERE SAVINGS CAN BE MADE ARE INDICATED. ALSO, THE COLD CONVERSION SEAL CHEMICAL COSTS ARE IDENTIFIED SO THAT THOSE WHO ARE SO INCLINED CAN MAKE MORE DIRECT COMPARISONS FOR SPECIFIC INSTALLATIONS OF INTEREST.

MORE OFTEN THAN NOT THE COLD CONVERSION SEAL IS CONSIDERED AS A REPLACEMENT FOR AN IN-PLACE, IN-OPERATION, HYDRATION SEAL. IN THESE CIRCUMSTANCES CERTAIN PREPARATIONS, WITH ATTENDANT COSTS, MAY HAVE TO BE UNDERTAKEN. IT MAY BE NECESSARY TO INSTALL A NEW TANK OR RE-LINE AN EXISTING TANK, OR AT LEAST CLEAN AN EXISTING TANK, SINCE THE TANK FOR A CONVERSION SEAL IS REQUIRED TO BE STAINLESS STEEL OR PLASTIC LINED AND MUST BE INITIALLY CLEAN TO AVOID CONTAMINATION OF THE SEAL. THE COSTS FOR THESE PREPARATORY ACTIONS WILL DEPEND ON THE FACILITIES TO BE CONVERTED. ALSO, SINCE FILTERING OF THE CONVERSION SEAL IS USUALLY RECOMMENDED TO PROLONG THE SEAL'S USEFULNESS, IT MAY BE DESIRABLE TO INSTALL SOME FILTERING EQUIPMENT WITH ASSOCIATED PLUMBING. THESE PREPARATION ACTIVITIES ENTAIL SOME DOWN TIME AND COSTS FOR LABOR AND EQUIPMENT. THESE ITEMS CAN USUALLY BE HANDLED SATISFACTORILY BY THE IN-PLANT MAINTENANCE PERSONNEL AND TYPICALLY REQUIRE NO MORE THAN ONE SHIFT OF DOWN TIME FOR AN EXISTING SEAL TANK. A SUITABLE FILTER INCLUDING PUMP AND MOTOR SHOULD COST NO MORE THAN $400 FOR A MEDIUM SIZE SEAL TANK.

ACTUAL INSTALLATION OF THE COLD CONVERSION SEAL IN A READIED FACILITY REQUIRES NO MORE THAN A COUPLE OF HOURS. COST OF CHEMICALS FOR THE COLD CONVERSION SEAL AT TODAYS PRICES SHOULD BE IN THE RANGE OF 20-25 CENTS PER GALLON OF INSTALLED SEALANT.

SINCE A CONVERSION SEAL MAY BE DAMAGED BY PROLONGED EXPOSURE TO ELEVATED TEMPERATURES, IT MAY BE ADVANTAGEOUS TO DOWN-SIZE OR OTHERWISE PARTIALLY DISABLE THE SEAL TANK HEATING SYSTEM. THIS WILL AVOID INADVERTANT OVERHEATING OF THE SEAL, WHICH ON AT LEAST ONE HAPPENING RESULTED IN THE SEAL BEING DAMAGED BEYOND RECOVERY.

THE MECHANISM OF SEALING WITH THE COLD CONVERSION SEAL IS SUCH THAT THE CHEMICALS IN THE SEAL ARE DEPLETED WITH REPEATED USE AND THEREFORE HAVE TO BE REPLACED IN ORDER TO MAINTAIN THE SEALANT AT ITS OPERATIONAL CONCENTRATION. THIS REPLENISHMENT COST WILL ALSO DEPEND ON DRAGOUT, OR MORE SPECIFICALLY, ON THE CARE AND TIME TAKEN TO MINIMIZE DRAGOUT. IF REASONABLE CARE IS EXERCISED WITH RESPECT TO DRAINING PROCEDURES, REPLACEMENT CHEMICAL COSTS CAN BE EXPECTED TO FALL IN THE RANGE OF $2000 TO $2500 PER MILLION SQUARE FEET OF ALUMINUM PROCESSED.

IF PROPERLY MAINTAINED THE COLD CONVERSION SEAL CAN BE A VERY DURABLE PROCESS. SOME TANKS HAVE BEEN IN OPERATION IN EUROPE FOR NEARLY FIVE YEARS. SOME TANKS HAVE BEEN OPERATIONAL IN THE U.S FOR OVER TWO YEARS. THIS IS NOT TO SUGGEST THAT THE

PROCESS IS INDESTRUCTABLE. PROLONGED EXPOSURE TO TEMPERATURES IN EXCESS OF THE ESTABLISHED OPERATIONAL RANGE MAY DAMAGE THE SEAL. ALSO, AS WITH ANY SEAL, CARE MUST BE TAKEN TO AVOID THE INTRUSION OF CONTAMINANTS INTO THE SEAL TANK. IN THIS CONNECTION, MOST OF THE LIKELY DAMAGING CONTAMINANTS HAVE BEEN IDENTIFIED AND METHODS HAVE BEEN DEVELOPED FOR RECUPERATING A COLD CONVERSION SEAL THAT HAS BEEN CONTAMINATED. THE UTILITY OF THIS METHODOLOGY IS LIKELY TO VARY WIDELY DEPENDING ON THE CHARACTERISTICS OF THE SPECIFIC SEAL AND ON THE SPECIFIC CONTAMINANT. IN THIS CONNECTION, IT IS NOTED THAT ALL SEALS ARE SUBJECT TO DAMAGE BY INTRUSION OF CONTAMINANTS. THE COLD CONVERSION SEAL, IN GENERAL, HAS NOT BEEN FOUND TO BE MORE SUSCEPTIBLE TO CONTAMINATION THAN HYDRATION SEALS AND IS PROBABLY LESS SUSCEPTIBLE TO SUCH DAMAGE THAN A DEIONIZED HOT WATER SEAL. HOWEVER, IN THE CASE OF THE CONVERSION SEAL, CORRECTION OF THE PROBLEM MAY BE MUCH MORE EXPENSIVE THAN REPLACEMENT OF A HYDRATION SEAL.

INSTALLATION OF A COLD CONVERSION SEAL IN AN OPERATING ANODIZING LINE MAY ENCOURAGE SOME PROCEDURAL CHANGES TO AVOID SMUT AND THE ATTENDANT COSTS OF SMUT REMOVAL. IT IS WELL KNOWN THAT SMUT CAN OCCUR AT A VARIETY OF STEPS IN THE ANODIZING PROCESS. PUT SIMPLY, IF THE PRODUCT HAS FOREIGN MATERIAL ON IT WHEN IT GOES INTO A COLD CONVERSION SEAL, IT WILL IN ALL LIKLIHOOD BE SMUTTY AFTER IT IS SEALED. MORE OFTEN THAN NOT SUCH SMUT WILL NOT BE VISIBLE UNTIL THE PRODUCT IS DRY. IT SOMETIMES TAKES REAL DETECTIVE WORK TO FIND AND ELIMINATE THE SOURCE OF THE SMUT. THIS HAS BEEN EXPERIENCED IN A NUMBER OF INSTALLATIONS, AND IT HAS USUSALLY BEEN FOUND THAT THE SMUT WAS BEING FORMED IN THE PREPARATION PROCESSING AND NOT BEING REMOVED PRIOR TO ANODIZING. IT IS ALSO WELL KNOWN THAT SMUT CAN ORIGINATE IN THE ELECTROCOLORING PROCESS, SO THAT ALL OF THESE POSSIBILITIES NEED TO BE EXAMINED BEFORE THE APPROPRIATE CORRECTIVE ACTION CAN BE TAKEN. IF SMUT IS ENCOUNTERED AND THE PROBLEM IS ADDRESSED IN A BUSINESSLIKE WAY BY AN EXPERIENCED TECHNICIAN, THE COST OF SMUT AVOIDANCE IS USUALLY FOUND TO BE MINIMAL. HOWEVER, IT IS EMPHASIZED THAT THE MEASURES TO BE TAKEN TO AVOID SMUT WILL DEPEND ON THE CHARACTERISTICS OF THE SPECIFIC CONVERSION SEAL.

ANOTHER CHANGE WHICH MAY BE DESIRABLE IS RELATED TO THE TANK HEATING SYSTEM. GIVEN INSTALLATION OF A COLD CONVERSION SEAL IN AN EXISTING PLANT, IT IS GENERALLY FOUND THAT IN SUBSEQUENT OPERATIONS THE HEATING SYSTEM MAY BE OPERATING AT A RELATIVELY SMALL FRACTION OF ITS RATED OUTPUT. THIS CAN AFFECT THE EFFICIENCY OF THE HEATING SYSTEM AND RESULT IN ENERGY SAVINGS LESS THAN MIGHT OTHERWISE BE OBTAINED. UNDER THESE CIRCUMSTANCES IT MIGHT BE USEFUL TO REVIEW THE SITUATION TO DETERMINE IF WAYS CAN BE FOUND TO IMPROVE HEATING SYSTEM EFFICIENCY.

ALSO, INSTALLATION OF A CONVERSION SEAL, IN THE ABSENCE OF OTHER CHANGES, RESULTS IN THE FINAL PRODUCT COMING OUT OF THE LINE COLD AND IT THEREFORE TAKES LONGER TO DRY. MOST OPERATORS SIMPLY ADJUST TO THIS CIRCUMSTANCE. OTHERS USE A HEATED FINAL

RINSE WHICH SPEEDS DRYING AND PROMOTES CURING OF THE SEAL, OR USE FANS TO BLOW-DRY THE PRODUCT. EITHER OF THE LATTER ACTIONS WILL ENTAIL SOME COSTS FOR MODIFICATION OF FACILITIES.

COLD CONVERSION SEALS ARE NEW ON THE SCENE AND AT LEAST ONE SUCH SEAL IS THE SUBJECT OF AN ISSUED U.S. PATENT. THE USERS OF SEALS COVERED BY PATENT MAY BE OBLIGED TO PAY ROYALTIES FOR A GRANT OF IMMUNITY FROM INFRINGING A PATENT. IT CAN REASONABLY BE EXPECTED THAT ROYALTY PAYMENTS, IF ANY, WOULD BE A SMALL PART OF THE TOTAL COSTS OF USING A COLD CONVERSION SEAL.

COLD CONVERSION SEALS TYPICALLY OPERATE IN THE RANGE OF 85-95 DEGREES F AND THEREFORE THERE IS A COST FOR SUPPLYING HEAT TO THE SEAL. THIS IS ORDINARILY A SMALL FRACTION OF THE COST OF HEATING A HYDRATION SEAL. THIS SAVING IN ENERGY COSTS, AS ILLUSTRATED IN FIGURE 4, IS MOST OFTEN THE PRINCIPAL ECONOMIC BENEFIT OFFERED BY THE COLD CONVERSION SEAL. HOWEVER, THE NUMBERS HAVE TO BE CONSIDERED ON A SPECIFIC CASE BASIS. IF THE COLD CONVERSION SEAL IS BEING CONSIDERED AS A REPLACEMENT FOR A 170 DEGREE NICKEL ACETATE SEAL IN A COVERED INSULATED TANK HEATED BY AN EFFICIENT SYSTEM IN AN AREA WHERE FUEL PRICES ARE LOW, THE ENERGY COST REDUCTION MAY NOT BE ENOUGH TO JUSTIFY THE HIGHER CHEMICAL COSTS. HOWEVER, IF THE SEAL TO BE REPLACED IS OPERATED AT NEAR BOILING TEMPERATURES IN AN OPEN UN-INSULATED TANK, THE POTENTIAL ENERGY SAVING CAN BE VERY ATTRACTIVE INDEED. FIGURE 4 SHOWS THE RESULTS OF A COMPUTER ANALYSIS OF A SPECIFIC TANK IN OPERATION IN A WEST COAST PLANT. THE GENERAL SHAPE OF THE CURVE IS SOMETHING OF A FACT OF LIFE. AS WATER APPROACHES THE BOILING POINT THE VAPOR PRESSURE INCREASES DRAMATICALLY AND CONSEQUENTLY MORE HEAT IS LOST IN THE EVAPORATION OF WATER. AT 212 DEGREES FAHRENHEIT AT SEA LEVEL, THE CURVE GOES NORTH. IN ONE INSTALLATION ON THE WEST COAST WHERE THE TANKS ARE HEATED BY A GAS FIRED SYSTEM, THE ENERGY SAVINGS ATTENDANT TO THE INSTALLATION OF A COLD CONVERSION SEAL RESULTED IN A 65% REDUCTION OF THE GAS BILL. IN A SECOND INSTALLATION WHERE THREE HOT WATER SEAL TANKS WERE REPLACED BY TWO COLD CONVERSION SEAL TANKS, THE PLANT MANAGER REALIZED NET SAVINGS OF OVER $125,000 PER YEAR. IN MANY CASES THE SAVINGS POTENTIAL IS MUCH LESS DRAMATIC. THE SAVINGS POTENTIAL JUST HAS TO BE EXAMINED IN THE CONTEXT OF ALTERNATIVES FOR THE SPECIFIC APPLICATION.

THE SHORTER SEALING TIME NEEDED FOR THE COLD CONVERSION SEAL, AS COMPARED TO THE TYPICAL HYDRATION SEAL, OFFERS OPPORTUNITIES FOR ENHANCED PRODUCTIVITY. AS IN THE CASE CITED EARLIER TWO COLD SEAL TANKS MAY BE USED TO REPLACE THREE HOT SEAL TANKS. ALSO, IT MAY BE POSSIBLE TO REPLACE TWO HOT SEALS WITH A SINGLE COLD SEAL, THUS MAKING A TANK AVAILABLE FOR OTHER USES.

COLD CONVERSION SEALING CAN OFFER INTERESTING ECONOMIES WHEN INTRODUCED INTO NEW PLANT CONSTRUCTION. DOWN-SIZING THE HEATING SYSTEM AND REDUCING THE NUMBER OF TANKS CAN ASSIST IN REDUCING THE CAPITAL INVESTMENT AND DEBT SERVICE.

ALSO, THERE MAY BE ECONOMIES IN THE USE OF WATER OFFERED BY THE COLD CONVERSION SEAL. HYDRATION SEALS TYPICALLY DEGRADE WITH USE UNTIL THEY EITHER FAIL TO SEAL OR PRODUCE AN UNACCEPTABLE DEGREE OF SMUT. THE USEFUL LIFE OF A HYDRATION SEAL VARIES FROM PLANT TO PLANT. PERIODIC REPLACEMENT OF A HOT SEAL USUALLY MEANS LOSS OF WATER, TOGETHER WITH ANY CHEMICALS USED, AND ALSO LOSS OF HEAT ENERGY.

LIMITATIONS

A COLD CONVERSION SEAL, DEPENDING ON THE PARTICULAR PRODUCT USED, MAY HAVE LIMITATIONS WHICH CAN ADVERSELY AFFECT SEALING COSTS. AS MENTIONED EARLIER, THE COLD CONVERSION SEAL WORKS BY CAUSING CHEMICAL REACTIONS BETWEEN THE SEALANT COMPOUNDS AND THE ANODIC COATING. THESE REACTIONS TAKE PLACE IN THE ANODIC COATING. IT IS REASONABLE TO EXPECT THEN, THAT THE PRESENCE OF THESE REACTIONS BOTH DURING SEALING AND THE CURING STAGE AFTER SEALING, AS WELL AS THE RATES OF THESE REACTIONS, MAY DEPEND ON THE CHEMISTRY OF THE ANODIC COATING ITSELF. THE CHEMISTRY OF THE ANODIC COATING DEPENDS ON THE ALLOY, THE ELECTROLYTE AND NUMEROUS OTHER PARAMETERS CONTROLLING THE ANODIZING PROCESS.

THERE ARE CIRCUMSTANCES WHERE ONE SHOULD BE CAUTIOUS WITH RESPECT TO COLD CONVERSION SEALING. FIRST, COLD CONVERSION SEALING HAS BEEN USED MOSTLY WITH SULFURIC ACID ANODIZING. COATINGS FORMED IN OTHER ELECTROLYTES MAY GIVE DIFFERENT RESULTS. IN AT LEAST ONE INSTANCE THE APPLICATION OF A COLD CONVERSION SEAL TO A PROPRIETARY INTEGRAL COLOR PROCESS PRODUCED SOME ANODIC COATINGS WHICH CHANGED APPEARANCE WHEN EXPOSED TO SUNLIGHT. IN AT LEAST ONE INSTANCE A COLD CONVERSION SEAL FAILED TO WORK AT ALL ON COATINGS FORMED IN PHOSPHORIC ACID. THUS, FOR OPERATIONS WHERE ANODIZING WITH ELECTROLYTES OTHER THAN SULFURIC ACID ARE UNDERTAKEN OR CONTEMPLATED, IT MAY BE FOUND THAT THE COLD CONVERSION SEAL IS NOT A SUITABLE REPLACEMENT FOR A CONVENTIONAL HYDRATION SEAL. THIS SAME LIMITATION MAY APPLY TO OPERATIONS WHERE ANODIC

COATINGS ARE COLORED BY USE OF ORGANIC DYES.

THE APPLICATION OF A COLD CONVERSION SEAL TO ANODIC COATINGS ON ALLOYS OTHER THAN 6063 SHOULD ALSO BE APPROACHED WITH SOME CAUTION. THERE IS EVIDENCE THAT THE CURE RATE FOR THE SEAL MAY BE LONGER WITH OTHER ALLOYS. THERE IS ALSO EVIDENCE THAT A COLD CONVERSATION SEAL MAY CAUSE UNWANTED DISCOLORATION WITH SOME 2000 AND 7000 SERIES ALLOYS AND THE DEGREE OF DISCOLORATION MAY BE RELATED TO COATING THICKNESS. HERE AGAIN, THE COLD CONVERSION SEAL MAY NOT BE A CANDIDATE REPLACEMENT FOR A HYDRATION SEAL.

DEPENDING ON THE SEAL PRODUCT SELECTED, A COLD CONVERSION SEAL MAY HAVE CRITICAL SENSITIVITIES TO ONE OR MORE SPECIFIC CONTAMINANTS. SUCH CHARACTERISTICS COULD SERIOUSLY IMPAIR THE SEAL'S COST-EFFECTIVENESS FOR USE WITH SPECIFIC PROCESSES SUCH AS CHEMICAL BRIGHTENING OR ELECTROCOLORING. THESE KINDS OF INCOM-

PATIBILITIES ARE READILY AVOIDABLE BY PROPER TEST AND EVALUATION OF CANDIDATE CONVERSION SEALS BEFORE A SELECTION IS MADE.

HOWEVER, WITH RESPECT TO ARCHITECTURAL ANODIC COATINGS FORMED IN SULFURIC ACID, THE TESTING AND PRODUCTION EXPERIENCE TO DATE HAVE PROVEN THAT THE COLD CONVERSION SEAL CAN RESULT IN SEAL QUALITY WHICH IS IN NO WAY INFERIOR AND IN MANY RESPECTS SUPERIOR TO THAT ACHIEVABLE WITH THE MORE CONVENTIONAL HYDRATION SEALS. FURTHER, AND OF EQUAL IMPORTANCE, THE COLD CONVERSION SEAL CAN OFFER A NUMBER OF WAYS TO CUT ANODIZING COSTS AND IMPROVE ANODIZING PLANT PRODUCTIVITY. THESE ATTRIBUTES ARE CAUSING GROWING INTEREST IN THIS TECHNOLOGY. COLD CONVERSION SEALING IS NOW WIDELY USED IN THE PRODUCTION OF ANODIZED ALUMINUM FOR BUILDING AND CONSTRUCTION MARKETS IN EUROPE, AND USED TO A SOMEWHAT LESSER DEGREE IN THE UNITED STATES, THEREBY DEMONSTRATING THAT THE PROCESS IS ACQUIRING A SIGNIFICANT DEGREE OF ACCEPTANCE BY THE ANODIZING INDUSTRY ON AN INTERNATIONAL SCALE.

WEIGHT LOSS IN $H_2 SO_4$
vs.
HOURS OF AGING

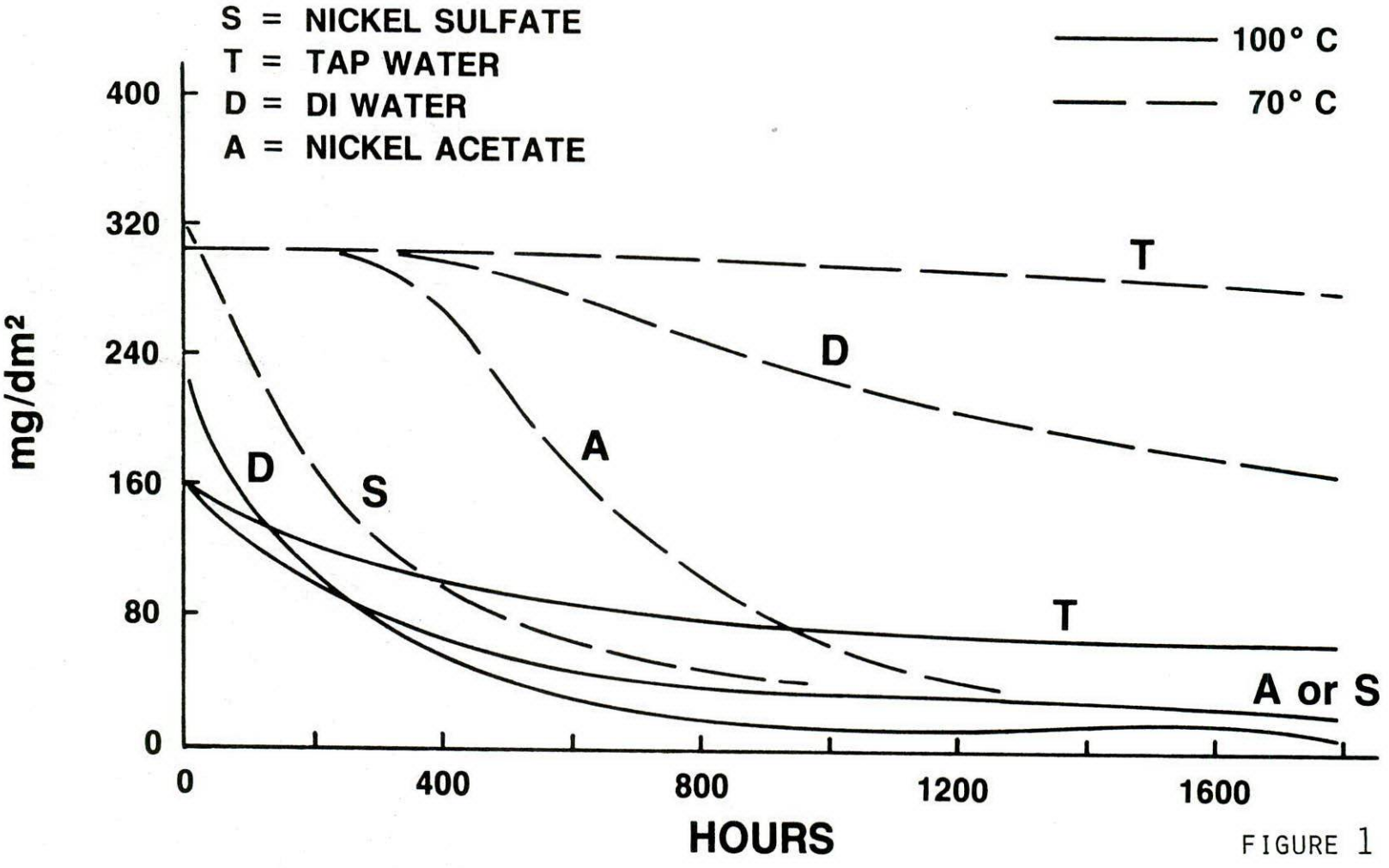

FIGURE 1

Data courtesy of Italtechno, s.r.l.

OPERATIONAL COMPARISON

CRITERIA	HYDRATION SEAL	ITALTECHNO* COLD SEAL
TEMPERATURE	180° - 210° F	85° - 95° F
TIME	30 - 45 min	5 - 12 min
CURE TIME	N/A	4 hrs
SMUT	FREQUENTLY	NONE

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* Data courtesy of Italtechno s.r.l.

FIGURE 2

QUALITY COMPARISON

CRITERIA	HYDRATION SEAL	ITALTECHNO* COLD SEAL
HARDNESS (VICKERS)*	280 - 300	540 - 560
SALT SPRAY ASTM B-117*	< 1500 hrs	> 5000 hrs
CASS-72 HRS ASTM B-368*	$> 10^4$ pits/m^2 > 2.0 mm^2 AREA	$< 2.5 \times 10^3$ pits/m^2 < 0.5 mm^2 AREA
KESTERNICH 5 CYCLES*	DISCOLORED OPAQUE	UNAFFECTED
TABOR WEIGHT LOSS (10,000 CYCLES)	> 20 mg	< 5 mg
WEIGHT LOSS ISO 3210*	1.5 - 2.6 mg/in^2	< 0.5 mg/in^2

* Data courtesy of Italtechno s.r.l.

FIGURE 3

TYPICAL SEAL ENERGY/WATER COST

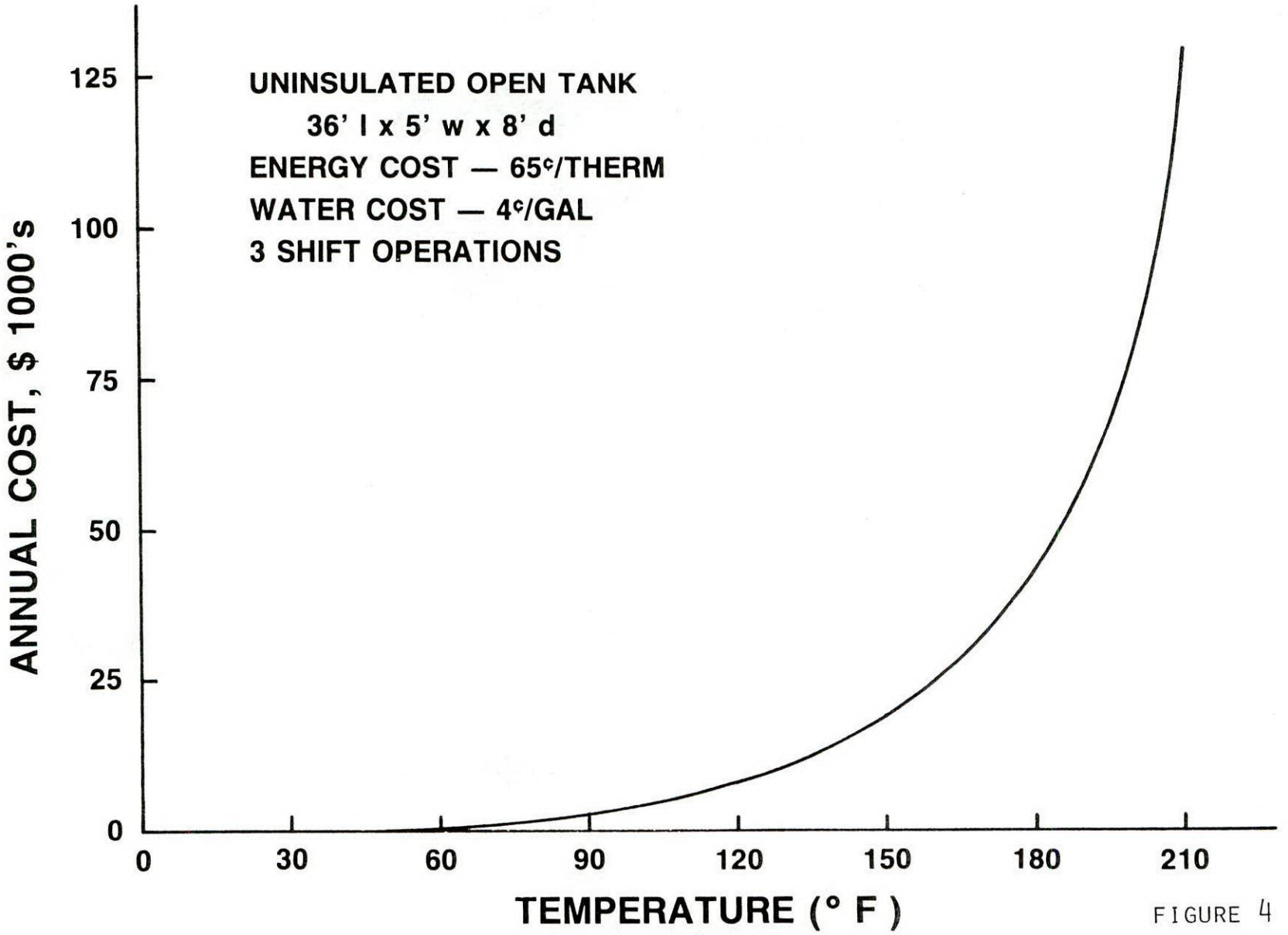

FIGURE 4