PLATING RESOURCES, INC. ®PLATERS

"Surface Finishing Technology"

DuraChrome Hard Chromium Plating

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Chapter 1
CHROMIUM PLATING

Introduction

Chromium is bluish-white and lustrous metal that is resistant to corrosion in most atmospheres. Chromium plating, therefore, is extensively used as a final finishing operation. There are two principal classes of chromium plating: "decorative, in which thin coatings serve as a non-tarnishing, durable surface finish; and industrial or "hard" chromium, where heavy coatings are used to take advantage of the special properties of chromium, which include resistance to heat, wear, corrosion, erosion, low coefficient of friction and anti galling.

Decorative chrome is almost always plated on top of either nickel or a copper and nickel-plated layer. These sub-layers of copper and nickel tend to seal off the substrate so that the micro-cracking chrome deposit does not present corrosion problems. Decorative chromium deposits are used on such items as automobile bumpers and trim, household appliances, furniture and many other articles that require a bright and aesthetic appearance. The normal thickness for decorative chromium is in the range of 0.000020'1 - 0.000070". The total deposit including the copper and nickel under-layers is typically 0.0005" thick. The Dura catalysts used in decorative chrome plating promote deposition at higher speeds, greatly increase the throwing power of the deposit and activate the sometimes passive nickel under-layer. Chromium plating baths in general tend to have very poor throwing power and the deposits may appear burned on the edges and may show a lack of plating or discoloration in the very low current density areas (those areas furthest from the anodes). These problems are overcome with the use of the Dura catalysts, proper racking techniques, anode control and maintenance of optimum bath composition.

Our concern for the rest of this paper, however, will be with hard chrome plating. Chromium is the hardest of the most commonly deposited metals. Hard chrome is used as a wear resistant coating not only on steel but also on a wide variety of other metals. Hard chromium differs from decorative chromium not only because of its use but also because of the difference in deposit thickness. A typical hard chrome deposit is in the range of 0.0005" - 0.0100" thick.

In some cases Thin-Dense hard chrome is used which is typically 0.0002" thick. Other types of specialty hard chrome include Crackless and Multi-Phase deposits which alter and control the microcrack structure.

The electro-deposition of hard chrome is a recognized means of prolonging the life of all types of metal parts subjected to wear, friction, abrasion and corrosion. These parts can be protected when newly manufactured, or they can be salvaged when they are worn and would otherwise be scrapped. As an example, it is much less expensive to reclaim worn hydraulic components by rebuilding tolerances with a hard chrome deposit than it is to buy or fabricate the part from scratch. Hard chromium, because it has a low surface energy, is more often deposited on sliding or revolving parts and is, therefore, used on things like engines, pumps, compressors, hydraulic and pneumatic rods, etc. The hard chromium deposit is also highly resistant to corrosion, and a large number of applications where it is used to protect parts from corrosion are in popular demand. Another attribute of the process is that it is a relatively cold one and can, therefore, be used to impart a very hard surface onto delicate parts without fear of distortion or changing the substrates properties. Thus, it can be regarded as a means of "surface hardening".

Hard chrome deposits have a hardness range from 56 - 74 R.C. depending on the bath type used. Obviously, the higher the R.C. (Rockwell C) number the longer the service life will be provided to the component. Deposit hardness is a function of the bath chemistry used. Thus it is best to use a plating process that provides the highest R.C. value. Standard 100:1 sulfate baths only provide a R.C. value of 56-60, while the Dura-100 and Dura-3000 baths provide a R.C. value of 70-74. A component with a surface hardness exceeding 70 R.C. will provide the longest possible service life.

Decorative chromium deposits have the same hardness range as hard chrome. However, industrial chromium tends to be harder only because of the greater thickness of deposit. A deposit of at least 0.002" must be used before the surface entirely reflects the properties of the chromium metal and not the substrate.

All hard chrome deposits, however, have a tendency to reduce the fatigue limit of the part. Shot peening of steels harder than 40 R.C. is used prior to plating to avoid this effect and prolong the life of the part. The Dura baths deposit is compressive and therefore provides less stress that the standard 100:1 sulfate bath which has a tensile deposit.

History

The commercial process of chromium plating resulted principally from the work of C. G. Fink and C. H. Eldridge, in 1923 and 1924. Lieblich also made similar discoveries more or less simultaneously in Germany, but confused them by overemphasis on the supposed importance of the trivalent chromium also present in the chromic acid-sulfate bath. Udy also discovered a workable process, but his results were not made public until much later. The hard chrome process using the original standard 100:1 sulfate bath was in commercial use around 1930.

A noteworthy improvement in chromium plating, from the original standard 100:1 sulfate bath using only chromic acid and a sulfate catalyst, came with the introduction of the Dual Catalyst bath in 1949. These baths, using a double catalyst system of both sulfate and a fluoride, offered improvements in hardness, wear resistance, corrosion resistance, and the rate of deposition. The Dura-100 is one such "high-fluoride" bath, which still offers the maximum micro-crack structure of any hard chrome process available today.

One fluoride bath formulation was the older self-regulating type where a partially soluble catalyst was used. The purpose of this was to avoid the need for periodic bath analysis by attempting to self-control the amount of catalyst present. In reality this never worked properly as the undissolved catalyst formed a hard mud on the tank bottom that required constant probing to keep it in the proper concentration. As a result the bath never had the correct level of catalyst present and the resulting deposits were disappointing at best. The Dura Additives overcome this by using a totally soluble liquid catalyst system.

High-fluoride baths, however, have one significant drawback. The fluoride ion is very aggressive to equipment like anodes, bath heating & cooling equipment and even tank linings. This can be overcome by using special alloys for the anodes, Teflon for the heating & cooling equipment and special tank linings. The high fluoride baths are also aggressive to unplated areas of exposed parts that are not stopped off. Bath contact with these surfaces will slowly dissolve the substrate, in some cases damaging them, but which also adds iron and other metallic contaminants to the bath. This is more pronounced in the low current density areas due to the lack of chrome coverage, and is known as low current etching.

However, not all dual catalyst baths use a high fluoride level. Low fluoride baths are very beneficial to the deposit quality while avoiding the problems of etching. Low fluoride baths are easy to control and are very user friendly. Some of the Dura Additives are the low fluoride type.

Plating Resources, Inc. also developed a new triple catalyst system that avoids the problems with fluoride, yet still provides the maximum hardness value and related deposit properties. The Dura-3000 bath offers a very high plating speed, an excellent micro-crack structure and a very hard deposit, all without the problems associated with low current etching. One unique feature of the Dura-3000 bath is its ability to maintain the fast plating speed with high levels of bath contaminants.

Principles

Chromium cannot be deposited from a solution containing only chromic acid (CrO_3) and water. There must also be at least one or more acid radicals present to act as catalyst and aid in the cathodic deposition of chromium. Those most commonly used are sulfate and fluoride, the latter generally in the form of a complex fluoride. Chlorides have also been tried as catalysts along with a few other halogen radicals but drawbacks of these are a more precise need to control their level and problems with severe etching of parts. Chlorides are now regarded as major contaminants and care must be exercised to keep chloride contamination out of the chrome bath. For successful operation, the ratio of chromic acid to total catalyst acid radicals must be maintained within definite limits, preferably about 100:1 in the case of sulfate and other ratios for fluoride and related catalyst ions.

It is generally immaterial what other substances the catalyst is combined with when it enters the bath or from what sources it may be derived, but the material must be soluble. Some sulfate is ordinarily present in all chromium plating baths, since it is contained in even the best commercial grades of chromic acid. Sulfuric acid is the most common sources of sulfate.

Although the current efficiency in chromium plating baths is low (generally in the range of 10 to 25% for a bright plate), a fairly high rate of deposition is obtained owing to the relatively high current densities that one can use. The voltages required are higher than in most other electroplating processes: generally 4 - 10 V, depending on operating conditions. Consequently, the electrical energy required for chromium plating is higher than that for most other metal plating, but this disadvantage has not seriously hindered the widespread use of the process.

The throwing power of the chromium plating is relatively poor relative to other metals like copper or nickel. Nevertheless, remarkable coverage can be achieved, even when plating irregular shaped articles, if the optimum ratio of chromic acid to total catalyst is carefully maintained. A buffering type additive like Dura-76 also helps tremendously with throwing power. Special auxiliary and conforming anodes are sometimes used to cover deep holes or recesses and to obtain a uniform deposit thickness. Such auxiliary/conforming anodes are designed in accord with well-known and long-established principles of ample size for current-carrying requirements and proper spacing for uniform distribution of current.

The maximum conductivity (current carrying ability) of a chromic acid solution is not achieved until a concentration of 50 - 60 oz/gal is reached. Commercial chromium plating generally uses baths containing 20 - 35 oz/gal chromic acid to get as good a conductivity as practical along with good current efficiency for satisfactory deposits. Small amounts of trivalent chromium (Cr III) and metallic contaminants like iron and copper decrease conductivity. The specific gravity (density) of the baths provides a rough measure of the concentration of chromic acid, especially if allowance is made for the contaminants present in the bath.

Theory

Very little was known about the role of sulfate in the chrome plating bath until 1979 when a mechanism was finally elaborated by Hoare which described the complexing role of the sulfate ion. It has long been known that the electrolysis of pure chromic acid solutions produces only hydrogen evolution under most conditions. In fact, hydrogen evolution at the cathode and oxygen evolution at the anode are two reactions that can be achieved when any conductive liquid has an electric current passed through it. The diagram below shows these reactions for an aqueous solution of sodium chloride (NaCl).
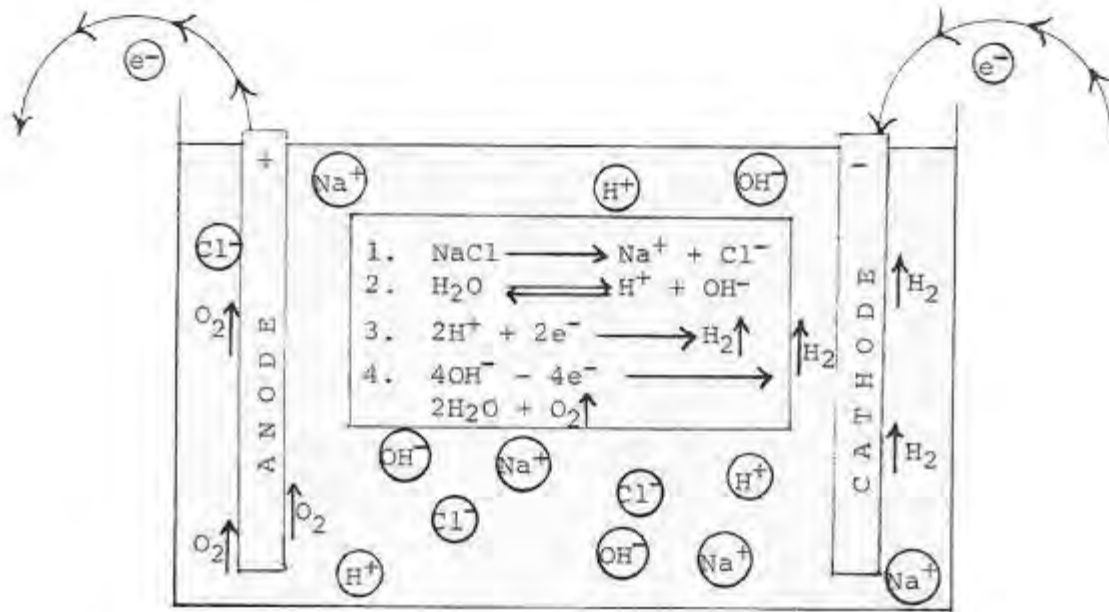
Fig. 1

The first two reactions show the disassociation of NaCl and H2O. These reactions occur in any aqueous solution. The double arrow indicates the reaction can go in either direction. Reactions #3 and #4, however, can only occur under the influence of an electric current where electrons flow from the cathode to the anode. The third reaction shows how two positive hydrogen ions and two electrons produce the neutral hydrogen molecule that leaves the solution as a gas. The fourth reaction shows how four negatively charged hydroxide ions loose their four electrons to produce two water molecules and the neutral oxygen molecule, which also leaves the solution as a gas.

The chemical reactions in a chrome plating system are not quite that simple. Besides oxygen and hydrogen evolution, a positively charged chromium complex is reduced to chromium metal on the cathode surface; some Cr (VI) is also partially reduced to Cr (III) at the cathode surface. Hoare's proposed mechanism describes how the sulfate and other catalytic ions play a dual role in the reduction of Cr (VI) to Cr metal. First, it acts as a blocking agent so that the desired chromic-dichromate complex can be formed. Second, it catalyzes the reduction of Cr (II) to Cr metal, which cannot be obtained without the formation of chrome-sulfate complexes. The distribution of these chrome-catalyst complexes (some of which can be reduced to Cr metal and some of which cannot) depends on the concentration of the catalyst. Hoare's mechanism shows through chemical equations that the best distribution of these complexes, (if one's object is to arrive at a metallic chrome plate) is achieved by employing an l00: l chromic acid to sulfate ratio. This is indeed the ratio that was arrived at many years ago using experimental methods.
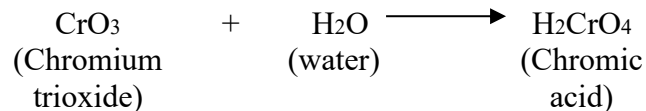
The definition of a catalyst in any chemical equation is "an agent which allows the reaction to proceed toward its desired end but is not itself used up on the reaction." The sulfate ion (SO4) in the chrome-plating bath acts as a true catalyst in that it is regenerated continuously and the only way its concentration decreases is through drag-out. Other catalyst ions, like fluoride, are consumed in the electrolysis so in reality they are not true catalysts, but act like catalysts.

Besides the desired reaction of metallic chromium formation, many undesired side reactions occur. One of these, as mentioned above, is the formation of hydrogen gas, which can become entrapped causing stress and later cracking as it seeks an escape route out of the deposit. A chrome deposit with a large macro-crack structure promotes rapid corrosion of the underlying substrate metal. However, under the right conditions, a chrome deposit with a truly microscopic crack structure (micro-cracking) can actually improve the corrosion resistance of the part because of current flow patterns set up at each crack interface. As a matter of fact, one of the advantages of fluoride type catalysts is that they tend to produce this truly microscopic crack structure.

A second reaction involves the formation of Cr (III) which cannot be reduced to Cr metal and is, therefore, considered a contaminant in the solution. While it forms continuously at the cathode surface in any chrome-plating bath, fortunately, with sufficient anode area, it can be oxidized back to Cr (VI) just as swiftly at the anode surface. Cr (III) also contributes to the resistance of the solution to current flow. In other words, more voltage will have to be supplied by the rectifier to achieve the desired amperage. This contributes to the additional side reaction of excess heat evolution.

To give some insight into the processes involved, let us look at some of the simple reactions taking place, uncomplicated by additional side reactions.

Chromic acid as sold is not truly chromic acid - it is actually chromium trioxide or chromium anhydride and is not an acid until it is dissolved in water.

$$CrO_3 \quad + \quad H_2O \longrightarrow H_2CrO_4$$
$$\text{(Chromium} \qquad \text{(water)} \qquad \text{(Chromic}$$
$$\text{trioxide)} \qquad\qquad\qquad \text{acid)}$$

Actually, the $CrO_4^=$ ion is in equilibrium with $Cr_2O_7^=$. Deposition probably occurs the latter.

$$2CrO_4^= \quad + \quad 2H^+ \rightleftharpoons Cr_2O_7^= \quad + \quad H_2O$$
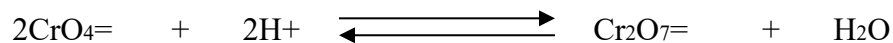
First, let's consider the reaction at the cathode. The electrons supplied to the work piece reduce the complex salt (here even further simplified) of chromium to metallic chromium. The equation can be written as follows:

$$Cr_2O_7^= \quad + \quad 14H^+ \quad + \quad 12e^- \longrightarrow 2Cr \quad + \quad 7H_2O$$
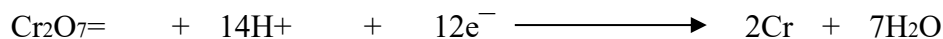
The valence of the Cr in $Cr_2O_7^=$ is +6. As mentioned before, an additional side reaction is the partial reduction of Cr(VI) to Cr(III) also occurring at the cathode surface. At the insoluble lead anode surface, however, Cr(III) reacts with oxygen to reform hexavalent chromium in its complex salt. The equation may be expressed as follows:

$$2Cr^{+3} \quad + \quad 7H_2O \longrightarrow Cr_2O_7^= \quad + \quad 6e^-$$
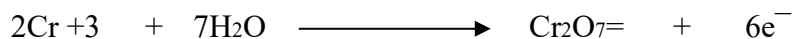
The chromium lost from the bath by plating on the work piece, or drag-out, is replenished by adding chromic acid. Chromium must be present as the complex salt in order to plate satisfactorily. Metallic chromium does not dissolve to form this salt when used as the anode and, consequently, this is one of the reasons why insoluble lead anodes are used instead. Also, if pure chrome anodes were used the bath would continuously build-up in Cr as the anode would dissolve at 100% efficiency while the deposit only takes place at 15-35% efficiency, depending upon the bath type used.

Hoare's theory fits in nicely with visual observations that have been made over the years showing the initial formation of an insoluble film on the cathode, known as the cathodic diffusion layer, which is quite gelatinous. A film of this type prevents the deposition of chromium from pure chromic acid. The deposition of chromium when sulfate or other anions are added is felt to result from modification of this film. Apparently, catalyst anions keep the film from growing too thick, and inhibits hydrogen evolution, thus favoring chromium deposition. For a smooth adherent, bright plate, the solution layer immediately adjacent to the cathode must have mixed activation and passivation tendencies. Thus, if the cathodic diffusion layer were too thin, or completely nonexistent, chrome would tend to re-dissolve in the strongly acid electrolyte. Conversely, if the cathodic diffusion layer were too thick it would tend to plate dull and in the form of non-adherent layers flaking from each other, as frequently occurs when there are current interruptions. Such current interruptions become less harmful as the catalyst concentration and the temperature are increased.

Unfortunately, many other questions on theory are still left unexplained. The exact function of fluoride and other catalyst anions is unknown as fluoride by itself produces dark dull deposits, unless sulfate is present.

Also unknown is why the current efficiency varies so widely with temperature, current density, chromic acid concentration and the proportion of catalyst anions, and why the addition of fluoride and other catalysts increases the hardness of the deposit.

Practice

There are only two essential constituents in conventional chromium plating baths: chromic acid, and one or more catalyst radicals. Chromium Trioxide (chromic acid) is a reddish-brown, hygroscopic (water absorbing) chemical, easily soluble in water to give a solution containing both H_2CrO_4 and $H_2Cr_2O_7$ as mentioned earlier. Many manufacturers, now aware of the effect of even small amounts of catalyst acid radicals, furnish a pure grade of chromic acid especially suited for chromium plating. This chromic acid, known as HCP Grade, is made to meet specifications which require that it contain not more than a small fraction of a percent of sulfate and be free from other contaminants such as chloride and iron. Special precautions have to be taken in its manufacture since sulfuric acid is used in the production of chromic acid from raw chromium ores and carryover of sulfuric acid to the end product could easily happen.

A 25-oz/gal chromic acid solution contains about 13 oz/gal of chromium metal. With complete utilization and no losses, 13ozs. of chromium would be sufficient to cover about 22 ft2 of surface with a deposit 1 mil thick (0.001").

To convert a pure chromic acid solution to a chromium plating bath, at least one catalyst is needed. With a given set of conditions of bath temperature, current density, and chromic acid concentration, too small an amount of catalyst will result in either no plate or in brown oxide stains. Too high a catalyst content will result in either partial plating with poor throwing power or no plate at all, owing to depolarizing action or easy formation of chromium (III) at the cathode. The proper ratio of chromic acid to sulfate in a standard plating bath is 100:1 as mentioned before. Baths that contain an additional catalyst, of course, operate at a higher chrome to sulfate ratio because part of the effect of the catalytic action of the sulfate is provided by the second catalyst ion.

As mentioned before, insoluble lead alloy anodes are used as opposed to chromium anodes because 1) chromium dissolved from anodes does not enter the solution in the proper form to make it available for plating, 2) chromium anodes would dissolve at an uncommonly high rate, continually increasing the concentration of chromium in the solution and 3) lead or lead alloy anodes provide a surface for the re-oxidation of trivalent chromium. A typical anode alloy is 7% tin and 93% lead. This alloy provides for the best conductivity and oxidation properties. Long anodes, over 6', or configurations that tend to sag must be fabricated of 6% antimony and 94% lead. This alloy provides the additional stability needed in such situations. During plating the anodes tend to form a crust or scale, which has detrimental insulating properties. This scale should be removed in an AnoBest-104 solution periodically so that it is able to conduct the proper current.

In order to understand the ins and outs of hard chrome plating, it is essential to have knowledge of the three basic bath types in use. These types are:

Standard Bath

Chromic Acid	33 oz/gal
Sulfate	100:1 ratio
Temperature	130°F
Cathode Current Density	2 ASI

High Efficiency Non-Etch

Chromic Acid	20 – 50 oz/gal
Sulfate	120:1 ratio
Dura-3000 Additive	3% by volume
Dura-3500 Booster	2 oz/gal.
Temperature	130 - 140°F
Cathode Current Density	1-10 ASI

High-Speed Fluoride

Chromic Acid	20-50 oz/gal
Sulfate	215:1 ratio
Dura-100 Catalyst	3% by volume
Temperature	130 - 140°F
Cathode Current Density	1-10 ASI

The following chart illustrates typical speeds and hardness values for these baths:

	Rate of deposit/hr. at 2 ASI	Hardness
Standard Bath	0.00060"	56-60 R.C.
High Efficiency Non-Etch	0.00125"	70-74 R.C.
High-Speed Fluoride	0.00120"	70-72 R.C.

The solid line in Fig. 2 outlines the area where a bright plate can be achieved over a range of certain temperatures and current density areas. This chart holds true only for standard chromic acid-sulfate baths. If we look at the current densities that can be achieved with the other two bath types, however, we see that using more modern chemistry can substantially increase the bright plating range with the added advantage of a faster plate and harder deposit.
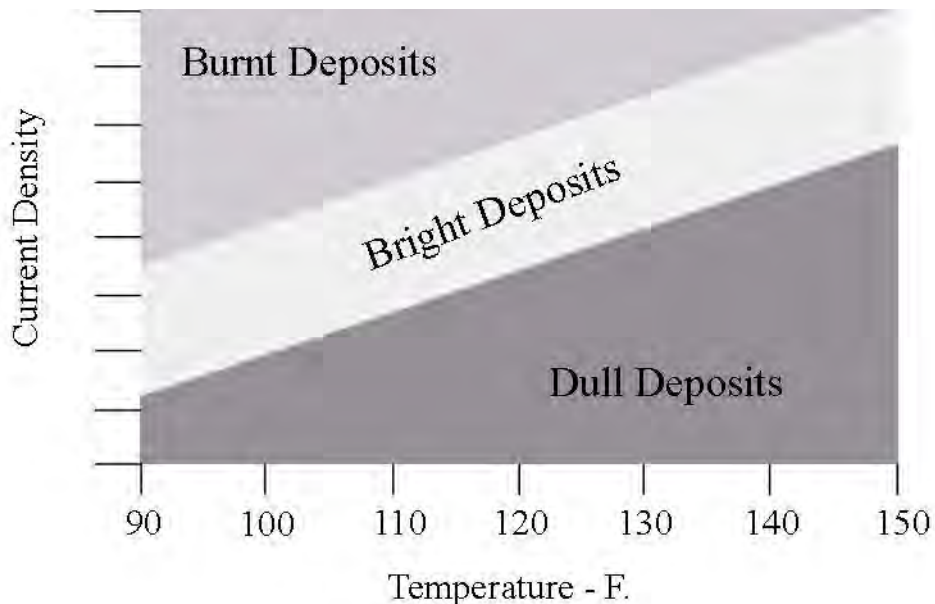

Fig. 2

More information on these baths can be found in the product technical literature at www.plating.com.

Chapter 2
PLATING LINE

Introduction

Set-up of an entire chromium plating line involves much broader knowledge and much more information than that needed simply to show how a chrome plating bath works. The information presented in the last chapter could just as easily be used to set-up a 267ml Hull Cell in a laboratory as to describe how a 2,000-gallon chrome plating bath works "on the line". To take a rough fabricated part from the end of the production line to a finished product gleaming with a bright chrome plate, honed to specifications, requires knowledge all the way from basic geometry and electricity to pollution control and problem solving. Steps along the way include knowledge of grinding, polishing and buffing; how to properly rack parts; what cleaning and activation procedures are necessary; rinsing and drying processes; stripping procedures, if necessary; solution control of the various baths; and testing of the final plate for hardness, corrosion potential, and adhesion.

The basic information on all these various procedures is easily presented but, in the end, there is no substitute for human alertness and common sense. Workers on the line should be able to spot a problem in the making before it becomes a production stoppage and most importantly relay the information to someone in authority who can investigate ways to solve the problem. Plating supervisors must be able to track the problem to its source and apply corrective measures. They must also be able to determine what parts may require extra care in preparation and plating and what parts require less preparation. This is important in terms of the cost of the finished product. A clean working area is not only healthier for the people on the line but also one of the best ways to prevent contamination problems in the various baths. Inspection of the line periodically can do much to prevent problems in the first place. Making sure all electrical connections are clean and secure can solve many problems before they occur. Checking racking and masking procedures on parts not only insures a better deposit but can also help eliminate contamination problems in the plating bath.

Plating Resources, Inc. is available for consultation on problems that may not have a readily obvious solution and for detailed analysis of the baths themselves.

With these things in mind, the rest of this chapter will be devoted to information on how to take a raw fabricated part from the end of the production line to a finished product.

Basic Geometry

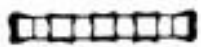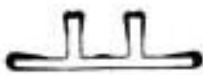| Design Feature	Influence on platability	Better Design
	Convex Surface. Ideal shape. Easy to plate to uniform thickness, especially where edges are round.	
	Flat Surface. Not as desirable as crowned surface. Use 0.015-in.-per-in. crown to hide undulations caused by uneven buffing.	
	Sharply Angled Edge. Undesirable. Reduced thickness of plate at center areas: requires increased plating time for depositing minimum thickness of durable plate. All edges should be round. (Edges that contact painted surfaces should have a 1/32 in. min. radius.)	
	Flange. Large flange with sharp inside angles should be avoided to minimize plating costs. Use generous radius on inside angles, and taper abutment.	
	Slots. Narrow, closely spaced slots and holes cannot be plated properly with nickel and chromium unless corners are round.	
	Blind Hole. Must usually be exempted from minimum thickness requirement.	
	Sharply Angled Indentation. Increases plating time and cost for attaining a specified minimum thickness and reduces the durability of the plated part.	
	Flat-bottom Groove. Inside and outside angles should be rounded generously to minimize plating costs.	
	V-shaped Groove. Deep grooves cannot be plated satisfactorily. Shallow, rounded grooves are better.	
	Fins. Increase plating time and costs for attaining a specified minimum thickness and reduce the durability of the plated part.	
	Ribs. Narrow ribs with sharp angles usually reduce platability; wide ribs with rounded edges impose no problem. Taper each rib from its center to both side and round off edges. Increase spacing, if possible.	
	Deep scoop. Increases time and cost for plating specified minimum thickness	
	Spearlike Jut. Buildup on jut will rob corners of electroplate. Crown base and round all corners.	
	Ring. Platability depends on dimensions. Round corners; crown from center line, sloping toward both sides.	
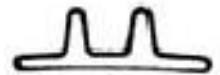
Table I

The design engineer has to select from numerous substrates, the base metal to fabricate the part from. He should have some basic knowledge of chrome electroplating if the process is to proceed from there. Table I illustrates design styles that can have a definite influence on the ease of plating a particular part (and, therefore, the final cost) or even whether the part can be plated at all.

The chemical balance, operating variables, types of anodes and design of fixtures or racks must all be considered to insure successful plating of complex shapes. The chromium plating process lacks the ability to produce uniformly thick metal deposits on all areas of an irregular or internal surface. This is mainly because of the drop in cathode current efficiency with a decrease in current density. For example, if one area of the part being plated is farther from the anode than another area, the area farther away receives less deposited metal, not only because of lower current density, but also because of lower cathode efficiency at the reduced current density.

Moreover, although some metal is deposited at low current densities in most other plating solutions, in chromic acid solutions there is a minimum current density for a given solution at a given temperature below which no metal is deposited. Hence, if an area of internal or irregular shape receives less than this minimum current density, no deposition of metal will occur in this area. This explains why it is so difficult to chromium plate recesses and internal shapes without special anodes. On the other hand, special hardware in the form of "thieves" or "shields" is required for lowering the current density on areas such as edges, in order to prevent excessive buildup (or burning) of the deposit.

It thus becomes apparent that in order to minimize plating problems, we must go all the way back to the fabrication of the part itself to insure that it can indeed be easily plated.

Electroplating is a process in which a metal is deposited onto a metallic substrate. Since the quality of the plate, and indeed, whether the part receives a plate at all depends on current density (which is current per some square area), we must know rather precisely the area of the surface to be plated. Table II lists calculations for determining the surface area of various geometrical shapes.

Table II

Geometrical Figure	Calculation of Surface Area
square	a^2 (where "a" is the length of a side)
rectangle	ab (where "a" and "b" are the lengths of the sides)
triangle	$\dfrac{hb}{2}$ (where "b" is the base and "h" the altitude)
circle	pie r^2 (where "r" is the radius and pie is 3.1416)
sphere	4 pie r^2
cylinder	Pie D H (where pie = 3.1416, D = diameter and H = height)

Surface Preparation

After fabrication, the part may contain numerous surface defects in the form of scale, pits, mold marks, grinding lines, tool marks or scratches. These defects must be removed prior to plating if a satisfactory finished part is to be expected. Polishing and buffing are operations that are frequently employed to remove these surface defects. After fabrication, the part is processed in the following sequence as may be required depending on the surface defects that may be present.

  1) Grinding

  2) Polishing

  3) Buffing

Grinding is considered a machining operation and is used to remove a substantial amount of metal from the surface. Most grinding operations will leave the surface with a finish of 20 micro-inches or rougher.

Polishing is an abrasion process that is used to remove grinding lines as well as numerous other defects. Polishing is accomplished with either an abrasive belt or with a cloth wheel to which a suitable abrasive medium has been bonded. Polishing will also remove a substantial amount of metal from the surface but will leave the articles virtually free from undesirable defects. Common abrasives used in polishing include silicon carbide and aluminum oxide with grain sizes ranging from #60 to #320 depending upon the amount of metal to be removed.

Buffing is also an abrasion process but with much finer abrasives being used. The purpose of buffing is to produce a bright smooth and scratch-free surface. Articles are buffed just prior to the chrome plating sequence as the brightness and surface reflectivity of the part after buffing will exactly equal the brightness and surface reflectivity after the chrome plate.

Besides the type of throwing power we have been discussing so far, that has to do with the distance of the part from the anode determining thickness of deposit or whether there is any deposit at all, a second type of throwing power comes into play here. "Macro" throwing power is basically a property of anode to cathode spacing. "Micro" throwing power has to do with the ability of the plated metal to fill the small grooves and scratches left after the buffing operation. Fig. 3 shows the three types of "micro" throwing power possible in different plating baths.
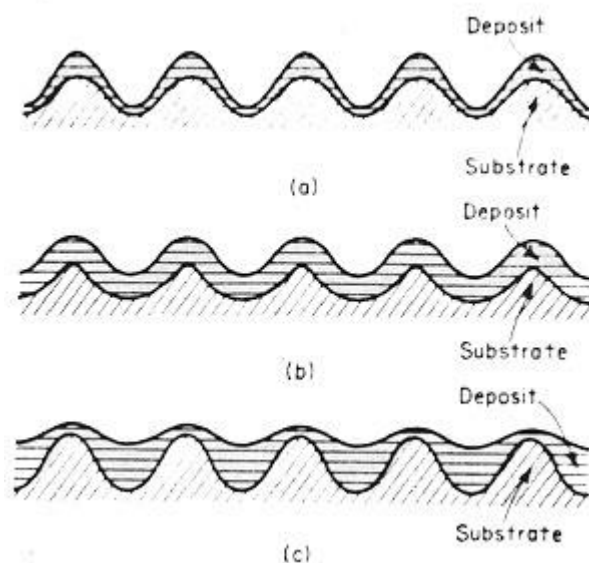

Fig. 3
Types of microthrowing power:
(a) negative microthrow, (b) geometric leveling, (c) true leveling.

True leveling is achieved in nickel plating. Geometric leveling is a characteristic of chrome plating. Thus, it can be seen that the smoothness of the surface after buffing is of primary importance to achieve a bright plate after the chrome plating operation. Only when post-plating steps such as grinding, honing or polishing is employed does the importance of the "as plated" chrome surface become less critical.

The buffing operation uses cloth wheels to which a compound is applied. These compounds usually contain glue or binder as well as an abrasive. The abrasives used in buffing are similar to those used in polishing but are of a much finer mesh size. Typical abrasives grits used in buffing range from #240 to #600 or finer. The selection of proper compounds, abrasives, wheel types, wheel speeds and pressure are of great importance in order to produce the desired finish.

Most polishing and buffing operations are performed by hand with the operator processing each individual part. Automated equipment is used where the volume of a particular run warrants the expense.

Mass finishing is also used to remove surface defects on parts and can be used in place of polishing and/or buffing for large volumes of small parts. The parts to be processed are held in either barrels that rotate or in tubs that vibrate. In addition to the parts these containers also hold abrasive media of proper composition, size and shape for the particular application. The selection of proper media also depends on whether it is a polishing or buffing operation, what the metallic composition of the part is, and the desired surface appearance. In addition, the barrels or tubs also contain specifically formulated detergent-type compounds that 1) act as buffers between the parts and the abrasives; 2) remove surface oils from the parts; and 3) keep removed metallic particles away from part surfaces. The mass finishing process can, therefore, also act as a cleaning operation.

The only limiting factors in mass finishing are the size of the parts, their mass and the effect that sharp edges may have on other parts as they tumble or vibrate against each other and against the abrasive.

Mass finishing is a much less expensive way to remove surface defects, where it can be used, than the manual operations of polishing and buffing. As used on smaller parts, it can lower costs by reducing labor requirements as well as not requiring a highly specialized operator. Higher productivity per hour and fewer rejects are additional benefits of mass finishing.

Electricity, Generators, Rectifiers, and Buss Bars
The physical embodiment of an electroplating process consists of four parts: 1) the external circuit, consisting of a source of direct current (DC), a means of conveying this current to the plating tank; 2) the negative electrodes or cathodes, which are the material to be plated, along with means of positioning the work in the plating solution so that contact is made with the current source; 3) the plating solution; 4) the positive electrodes, the anodes, usually of the metal being plated but sometimes of a conducting material which serves merely to complete the circuit, called inert or insoluble anodes. Steel sheets, for example, are used as inert anodes in electro-cleaning baths, and lead alloys are used as inert anodes in chrome plating baths. Fig. 4 illustrates the electroplating layout.
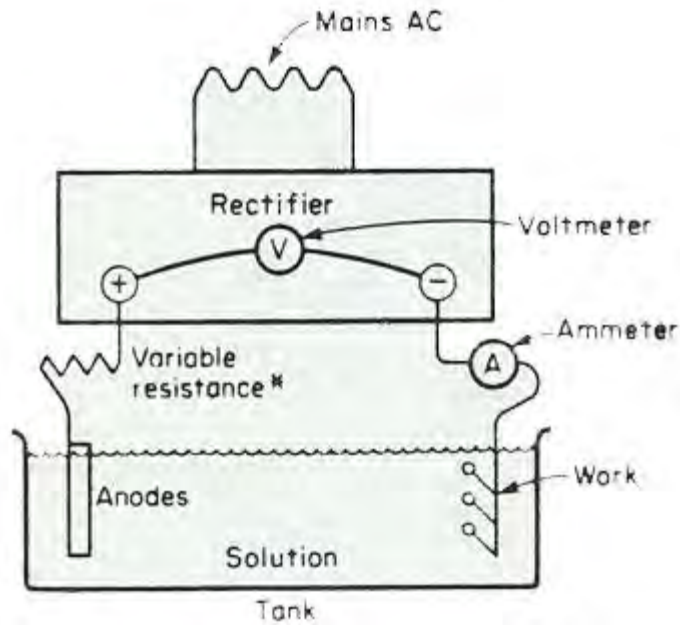
Fig. 4
Schematic of an electroplating layout.

A variable resistance is required only if the rectifier serves two or more tanks in parallel, otherwise the voltage is regulated at the rectifier. The typical plating tank will have three bare copper conductors running down its length: these are called bus bars, and they must be insulated from the tank itself by various means such as ceramic insulators. They must be fabricated both to withstand the current flow and to support the weight of the anodes and parts. The two outside bars are connected to the positive side of the DC source, and on them are hung the anodes, usually by means of hooks (Fig. 5). The central bus bar is connected to the negative side of the DC source and holds the work, usually held on racks which are similarly hung on the cathode bar by hooks.

Fig. 5
Cutaway view of typical plating tank.

In an electrical circuit, electric current is said to flow from the "positive" to the "negative" terminal: we connect the positive (plus) terminal of a battery, rectifier, or generator to the anodes or anode bar of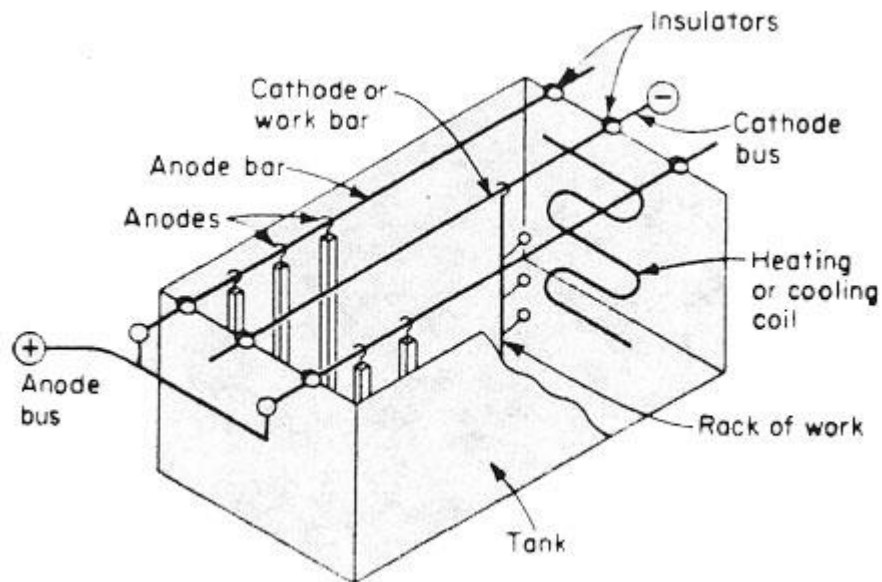 the plating tank, and the negative (minus) terminal to the cathodes or cathode bus bar. This nomenclature was firmly set before it became clear that in metallic conductors the actual flow of electrons was in the opposite direction; the "negative" terminal provides electrons and the "positive" terminal collects them or acts as an "electron sink".

There are two basic types of electric current: unidirectional, direct current, or DC, in which the direction of flow is constant; and alternating current, or AC in which the direction of flow reverses at definite, usually very short, intervals. For obvious reasons, the only type of current useful to the electroplater is direct current, or DC, and certain minor variations of it. Alternating current would have no net effect in either direction and would accordingly be useless for plating.

Electricity as generated by power companies and transmitted over the country, however, is almost always in the form of alternating current, and for economic reasons it is transmitted at high voltages. These voltages are extremely high in cross-country transmission lines and they are "stepped down" at local power stations. In most parts of the USA, the power supplied to residences is 220V 60-cycle AC, which is further reduced to 110 or 120 V at the house for lighting and driving the various appliances upon which modern living depends, although some appliances operate at 220 V.

Most electroplating processes require voltages much lower than the 110-440 V supplied by the power company, and at amperages much higher than the 15-30 A for which the usual house wiring is fused. These processes also require that the alternating current be changed into unidirectional or direct current (DC).

Time-honored, but still useful instructionally, is the analogy between the flow of water and of DC electricity.

$$\text{Rate of Flow} = K \; \frac{\text{pressure}}{\text{resistance}}$$

The rate of flow (gallons per minute) is directly proportional to the pressure; and is inversely proportional to the resistance of the system. The resistance of a pipe can be increased by increasing its length or reducing its cross section, and to some extent by roughening its inside surface. K is proportionality constant. The quantity of water, in gallons, that flows will be equal to the product of the rate of flow and the time of flow.

$$\text{gals. per minute X min.} = \text{gal.}$$

In a direct-current (DC) circuit, the potential, expressed in volts (V), corresponds to the pressure in the hydraulic analogy. The obstruction that a wire or other conductor introduces to the flow of current is known as the resistance of that part of the circuit and is measured in ohms. The smoothness of the inside of the pipe in hydraulics can be compared (very roughly) to the individual characteristics of various conductors. Some metals like copper and aluminum are "smoother" and oppose the flow less than others of the same dimensions. Lead and steel on the other hand are "rougher" and oppose the flow more; ie: copper is a much better conductor than steel. The same laws hold: the resistance of any given conductor is directly proportional to its length and inversely proportional to its cross-sectional area.

$$\text{Current} = K \; \frac{\text{potential}}{\text{resistance}}$$

or

$$I \text{ (current)} = E \text{ (volts)} / R \text{ (ohms)}$$

This relationship is known as Ohm's law and is the fundamental expression of current flow. In any circuit the current is directly proportional to the potential and inversely proportional to the resistance. It is important to distinguish between the current I, the rate of flow of electricity, and the total quantity of electricity. The unit of current is the ampere, while the unit of quantity of electricity is the coulomb (the quantity of electricity delivered by one ampere flowing for one second).

$$coulomb = amps. \times seconds$$

However, in plating, we usually don't bother to actually calculate the number of coulombs used, though we do control amps on the rectifier and time on a clock.

As stated, the electric power as purchased from utility companies is almost always in the form of alternating current (AC), usually 50-60 Hz, which as the name implies reverses its direction 60 times each second, as diagramed in Fig. 6. Such power is delivered to the user at voltages nominally varying between 110 and 440 V, and may be 1 or 3-phase. Such power is not useful for electroplating purposes, and must be rectified, i.e., transformed into direct, unidirectional current.
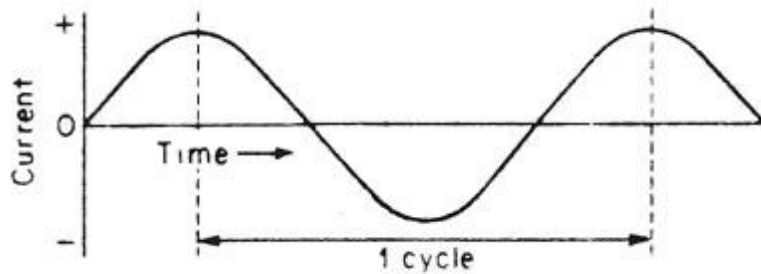

Fig. 6
Typical alternating current.

Ideal unidirectional current, such as that provided by a battery, has the form shown in Fig. 7. Furthermore, the mains voltage is too high for most metal-finishing operations, and its amperage is too low, so that apparatus for transforming AC into DC also amplifies the amperage available.
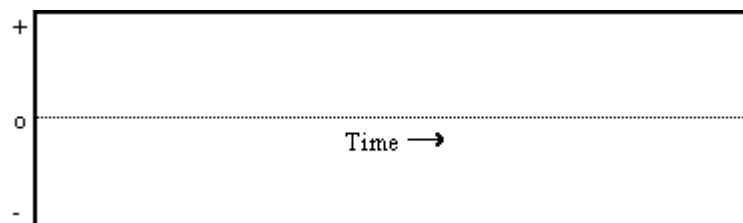
Fig. 7
Ideal direct current from a battery.

Alternating current may be changed into direct current in several ways; formerly motor-generator sets were used for this purpose. Such apparatus are rugged, possess long life if not abused, and withstand considerable overloads; they also provide, in general, purer DC than rectifiers. But owing to their high original cost, necessity for maintenance, and criticality in installation, they have been almost entirely superseded by rectifiers, at least in newer installations. Many motor-generator sets are still in operation, but few new ones are sold.

Rectifiers have the property of allowing current to flow freely in one direction but offering a very high resistance to current flow in opposite directions, thus, delivering DC at their terminals. Rectifiers also normally include step-down transformers, so that the voltage at their terminals is substantially reduced and the amperage correspondingly increased. Several materials, all classified as semiconductors, have the property that their resistance to current flow is much higher in one direction than in the other. One of the earliest to be

commercialized was copper oxide; later copper sulfide, germanium, and selenium were used. At present, the silicon rectifier dominates the field, and there are no indications that its position is being challenged.

If only single phase current is available at the rectifier, as in small bench-type rectifiers meant for use on ordinary 110 or l20-V lines, the current delivered has the wave form shown in Fig. 8.

Fig. 8
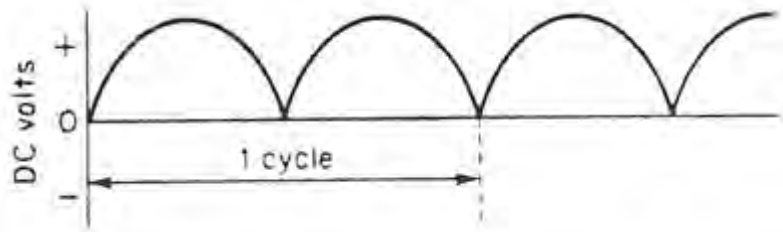Single-phase full-wave rectification.

Such rectifiers are common for small bench-top applications, and the fluctuating-current supply is generally satisfactory for small- scale and experimental use. The rapid current fluctuations appear to have little or no effect in most electroplating operations, with the exception of chromium plating and a few other specialized applications. But for practical larger-scale shop use, the AC fed to the rectifier is 3-phase, and all three phases are rectified, leading to a DC output of much smoother form, as shown in Fig. 9. By proper internal wiring, rectifiers can be made to deliver DC almost as constant as that from a battery. The extent to which the DC deviates from the ideal is known as ripple. Ripple is normally of little importance in electroplating operations. It is usually important, however, that the ripple of rectifiers supplying current to a chrome plating tank be less than 5 per cent.
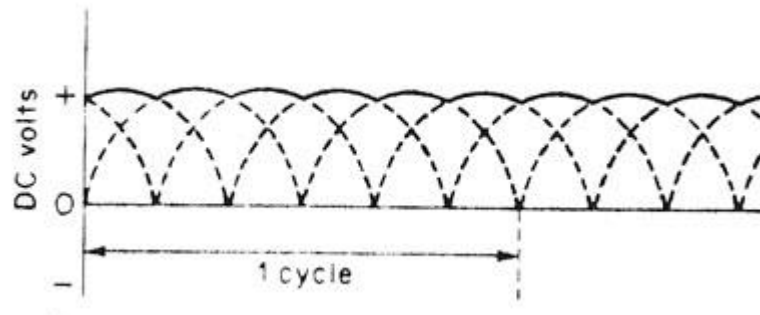
Fig. 9
Three-phase full-wave rectification.

Depending on the process, the current supplied by the rectifier is in the range of 6 - 12 V with various amperages depending on the surface area of the cathode. A typical current density for hard chrome plating operations is 2 ASI (amperes/sq. inch) of area to be plated. Hence, a cathode area of 1,000 square inches would require a current of 2,000 A. In actual practice, for production plants, rectifiers with a capacity of 5,000 - 20,000 amps are very typical.

The working parts of rectifiers consist of; transformers, to reduce the voltage; diodes to convert the current to dc; voltage and current controls for the output; over load protection; and a cooling device to remove heat generated in the rectifier. Rectifiers are either air or water-cooled.

Another factor to be considered when specifying a rectifier is the current waveform. A rectifier may be built to deliver either a half-wave or full-wave current. It is important to use only a full-wave unit as many of the processes, especially chromium plating, will not operate properly with half-wave rectification.

All rectifiers used in electroplating have a variable output control. Both tap switches and infinitely variable controls can be used. Fixed output units are available, that are somewhat less expensive, but are obviously not desirable due to ever changing plating load factors.

Other controls that are available on modern rectifiers include automatic voltage, current and current density controls. These special options are becoming increasingly more popular as they provide a consistent output control for the plater.

Tanks, Ventilation, Heaters and Related Equipment

Plain steel tanks can be used for alkaline cleaning and alkaline stripping baths. Alkali resistant plastic or plastic lined tanks are also suitable. Rinse tanks should have a suitable lining.

A separate reverse etch tank is recommended for chrome plating lines as it prevents the buildup of trivalent chromium and iron contamination in the main plating tank. The reverse etch and the chrome-plating tank should be lined with a suitable material such as plastisized PVC. When plastisized PVC linings are used, they should have a minimum thickness of 3/32 on the sidewalls and 3/16 on the bottom with a 3/16" thickness at the solution level. Supported molded polyethylene linings may be used in certain applications, but polypropylene linings must be avoided due to the tendency of stress cracking and welded seam separation. Lead linings should also be avoided due to corrosion and conductivity (stray current) concerns.

Exhaust ventilation is recommended on the stripping tank and, of course, with both the reverse etch and the chrome plating tanks. The large volumes of hydrogen and oxygen evolved during chromium plating causes chromic acid spray to be given off which, if permitted to escape into the plating room, is damaging to the surroundings, can be a source of contamination to other baths in the area, and constitutes a health hazard to the workers. The chromic acid mist is sharply irritating and corrosive to the mucous membranes of the nose and throat. This spray, therefore, requires removal or suppression to protect the workers and equipment, and adequate exhaust facilities should be provided for the purpose.

As of 5/30/06 the maximum allowable exposure to dusts and mists from hexavalent chromium, measured as Cr(VI), is currently 5 ug/m3 of air, with an OSHA action level of 2.5 ug. Generally, fumes are exhausted from a chromium plating tank by means of lateral exhaust hoods along both long sides of the tank. For narrow tanks (up to 24" wide), a lateral exhaust on one side of the tank should be adequate unless strong cross drafts exist. The velocity of the air at the lateral exhaust hood slots should be 2000 ft. per min., or more. The minimum ventilation rate should be 250 CFM per sq. ft. of solution surface area.

Mist eliminators should be used to capture bulk chrome mists for return back into the tank. Fume scrubbers with various densities of mesh pads are also used to clean the air stream before it's discharged to the atmosphere. A special polyvinyl chloride (PVC) material is generally the construction material used for all parts of these ventilation systems. Current environmental laws regulate the maximum amount of Cr(VI) discharge allowable.

Several methods can be used to control the chrome mist to lower the amount that reaches the ventilation system or escapes into the shop. Special floating polypropylene balls and/or fume suppressants can reduce this misting by as much as 99.9%.

Heating of the various baths and rinse tanks is usually done with titanium or Teflon electric immersion heaters, all of which have an automatic temperature control. Steam heating is also used for some larger installations. Cooling coils for the chrome bath are likewise typically made of titanium or Teflon. The best materials of construction, however, are dependent upon the individual bath chemistry being used.

Temperature control should begin with selecting the proper volume of the plating bath. An ideal volume is one gallon (or more) of chrome solution for each 50 watts of plating power. About 60% of this plating power (30 watts) produces heat and will maintain the solution at temperature in an un-insulated tank. Power applications in excess of 50 watts per gallon will require cooling of the plating bath.

Air or mechanical agitation is used in the tanks to maintain chemical and temperature balance. The chrome-plating bath should be agitated periodically, and particularly when the bath is being started, to prevent temperature stratification. Air agitation is very effective, but a separate oil-free blower should be used to prevent contamination of the tanks. A perforated CPVC pipe is used to distribute the air at the bottom of the tanks.

Anodes

All electrical process steps in the chrome plating operation require anoding. An electro-cleaner may be part of the process line if heavy soils are present on the parts. Alkaline electro-cleaners usually use type 304 stainless steel for the anodes, or cathodes if it is an anodic cleaner. The plain steel tank wall can also be used as the electrode, but this is not good practice as it obviously makes the electrodes impossible to remove for cleaning, and also increases the chances of stray currents. Type 304 stainless steel cathodes are also used in the alkaline electrostrip tank. These should be cleaned periodically as some type of chrome deposit will inevitably plate out on them.

Anodes used in the reverse etch and the chrome plating should be made of special lead alloys. Pure lead anodes are attacked by the solution and cause the formation of excessive amounts of lead chromate sludge.

A typical alloy is 93% lead - 7% tin, except where the length and weight of the anode is a problem. In these cases, anodes are usually 94% lead - 6% antimony. Tin-lead anodes have better conductivity and last longer, but antimony-lead anodes are more rigid. Anodes used in high fluoride baths should use the tin-lead alloy, as antimony-lead alloys will have a poor life expectancy and form an abundance of corrosion products. Also, when tank type anodes are used in high fluoride baths, they should be of the solid smooth variety and not hollow or ribbed.

| Oval | Rectangle | Round | Gear-tooth | Fluted |
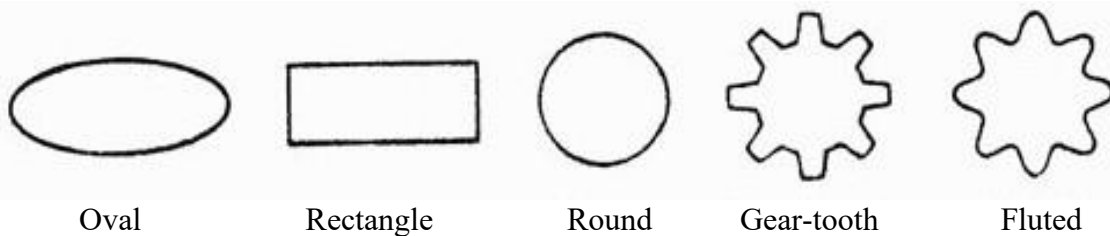
Fig. 10
Cross sections of anode shapes

Fig. 10 shows cross-sectional shapes for several types of anodes that can be used in chrome plating solutions. It is important to use thick enough anodes and a large enough number of them to conduct the high currents required. Anodes that are too thin will overheat and tend to corrode and warp excessively. Troublesome overheating of the bath might also occur if the total anode area is so small that resistive heating becomes a factor. Anodes of round cross section are most commonly used. When maximum anode area is desired, ridged, and multi-edged anodes are employed. The round anode is a favorite because its surface is active on its entire circumference, and it is thus able to carry higher amperage at lower voltage. The absence of inactive areas on this type of anode minimizes the formation of lead chromate film, thus reducing maintenance requirements.

If the weight of the anode presents a problem, hollow round anodes are sometimes used. Such anodes provide a 25 to 40% reduction in weight; however, their current-carrying capacity is less than that of solid anodes.

Round tank type anodes are normally manufactured by extrusion. A copper hook is homogeneously burned to the extruded anode, which extends down into the anode, provides contact with the bus bar. A heavy plastisol coating for protection against corrosion should cover the hook and the top of the anode. Conforming anodes are most frequently made of cast lead alloys.

Many anode materials other than lead alloys have been tried, but nothing better has been found. It is perhaps worthy to note that pure iron is corroded less as anode than steel. Iron anodes have occasionally been used, particularly in special instances where greater strength and rigidity are required. Their continued use, however, leads to the accumulation of iron and chromium (III) in the bath. Where iron anodes are used, it is recommended that they be coated with lead whenever feasible. Small platinum wire anodes can also be used for special purposes, such as plating the inside of very small openings, but they too will form chromium (III) in the bath. Copper, nickel, stainless steel and titanium should never be used for chrome plating anodes.

Dura-Core anodes are designed specifically for use where maximum conductivity and rigidity are required. Dura-Core anodes are constructed of a one-piece solid steel, copper or aluminum hook and core using a special P-190 alloy. This resists hard shell scale and maintains the re- oxidation of trivalent chrome. They also operate cooler due to their superior conductivity and this helps to prevent anode "curl". Dura-Core anodes typically last 100% - 200% longer than traditional anodes do.
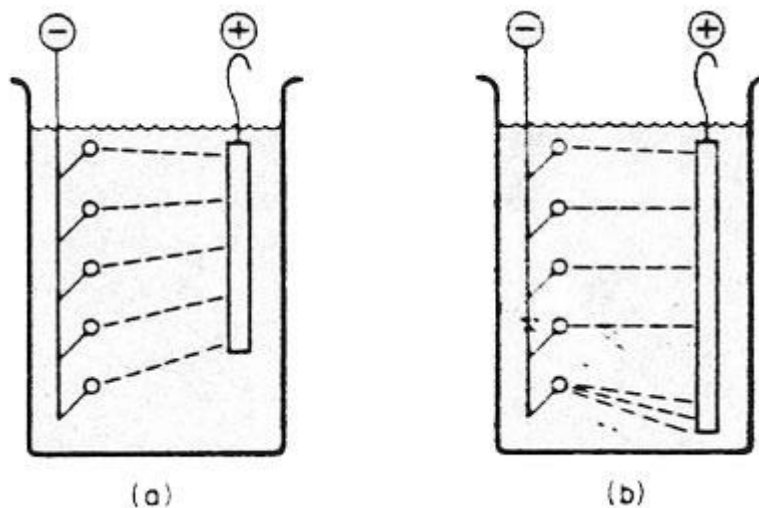
Fig. 11
Anode length

(a) anode shorter than rack of work, no excess current at bottom;
(b) anode longer than rack of work, excess current at bottom of rack.

For most plating situations, the anodes are usually shorter than the cathodes. This tends to decrease the excess current that would otherwise flow to the work at the bottom of the rack (see Fig. 11). The bottom of each anode should be at least 6" above the bottom of the plating tank. When the part contains sharp, narrow recesses, such as grooves, a reduction of the anode distance may help to increase the thickness of the deposit at the bottom of the grooves. However, some parts with sharp-cornered grooves, bosses and undercuts cannot be uniformly covered unless conforming or auxiliary anodes are used. Examples of parts in this category and the areas of heavy deposits are illustrated in Fig. 12.
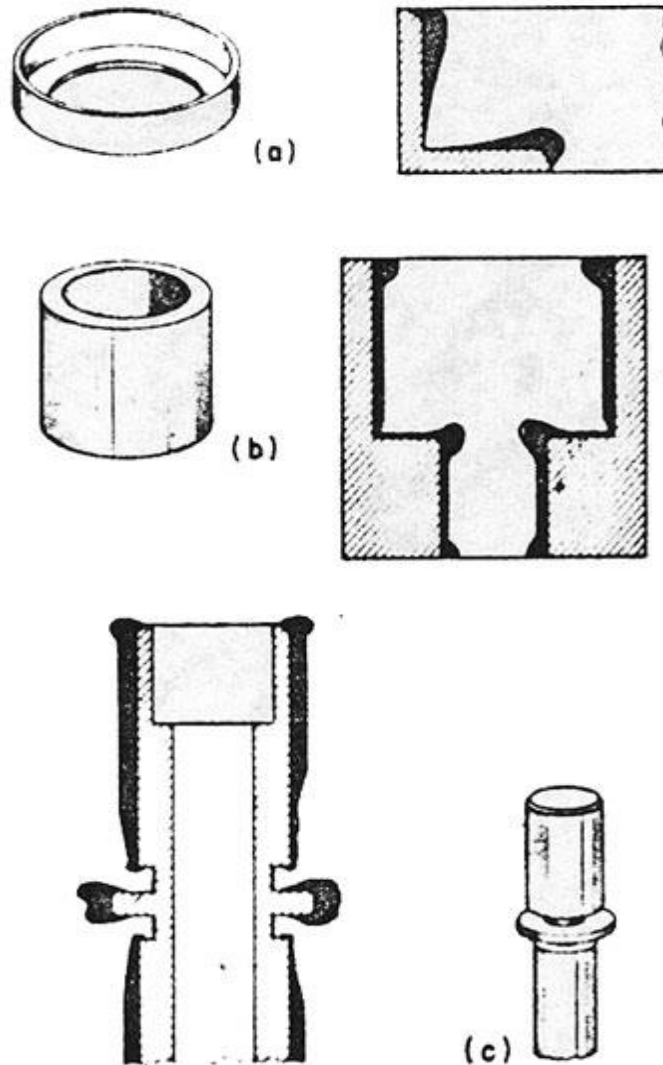
Fig. 12
Variations in plate thickness shown are approximately to scale.
<u>Examples of parts that are difficult to plate uniformly unless conforming anodes are used.</u>

The anodes used for plating deep recesses can either be directly connected to the power supply or can be bipolar in nature. The bipolar anode has no direct electrical connection and takes advantage of the fact that current will follow the path of least resistance. Therefore, because the bipolar anode will conduct electricity better than the solution, the current will pass through the anode. Thus, even though the bipolar anode has no direct electrical connection, it can be charged so that the end nearest the conductive anode becomes cathodic while the end nearest the cathode (work piece) becomes anodic. This increases the current flow in the region nearest the work piece and causes that area to be plated more readily. The use of a bipolar anode to direct current into a sharp angle is illustrated in Fig. 13.
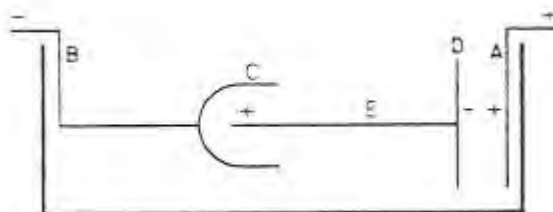
Fig. 13
<u>Diagram of bipolar anode.</u>
A=anode; B=cathode connection; C=cathode; D=collector end; E=discharge end.

When the total anode area is not 1½ - 2 times the total cathode area, build- up of trivalent chrome may become a problem. This usually occurs more frequently in hard chrome plating baths than in decorative baths, because decorative baths tend to use more anode area to plate irregular recesses. This problem is especially severe for hard chrome platers who do a great deal of inside diameter (ID) work on cylinders, where the anode is only a thin rod by comparison. Fortunately, by employing a special process culled "dummying with CR-3 Reducer", the trivalent chromium concentration can be lowered to desired levels.

Lead alloy anodes that are properly maintained have a brown-black lead peroxide film. This film protects the anodes from attack and provides a surface for the re-oxidation of trivalent chrome. But this film cannot be too heavy or irregular, or the current distribution may be affected. Lead anodes coated with lead peroxide tend to become "passive" after standing idle for some time and require electrolysis with the full tank voltage for 10-30 minutes for reactivation and to re-establish the original conductivity. This tendency is due to the insulating effects of insoluble lead compounds such as lead chromate and it is readily apparent as the anodes take on an orange or yellow appearance. Shadows and burning of the chrome plate can result from such passive anodes. The only way found to avoid this effect, aside from cleaning in an AnoBest 104 solution is to remove the anodes from the tank promptly after use. This gives good results but is not always practical.

Passivation or polarization is always present during electrolysis of a solution but is only of concern when its effect becomes excessive. It can be caused either by changes in bath concentration or changes in either the cathode or anode films. The result of excess passivation is that an increasingly higher potential (voltage) has to be applied to get the desired amperage. High excess voltage leads to excessive heat production at the anode surface and the production of abnormal quantities of trivalent chromium in the chrome-plating bath.

If the passive film is too thick then the anode must be cleaned in AnoBest-104. This is a simple soak process that removes these coatings without harm to the anodes. However, if a rigorous program of scratch brushing the anodes is followed once a week, the need for soaking in AnoBest-104 can be eliminated and most of the above-mentioned problems avoided.

Fixtures, Racking and Stop-Off Methods

The processes used in electroplating are similar for all metal plating solutions. The part to be plated has to be cleaned of all surface soils and then activated to remove oxides. Once the base metal is activated it is placed immediately into the plating solution to prevent re-oxidation on the surface of the base metal, which can result in poor adhesion. The exact cycle and times spent in the various baths will vary somewhat depending on the base metal and the type of plating to be done.

Parts to be plated are made cathodic in the plating solution. In a simplified operation these parts would be simply suspended by a hook or wire from the cathode bar. Most hard chrome operations, however, require that the parts are held and suspended from fixtures, also called racks.

A plating fixture is a device that holds the parts in a fixed position during the plating cycle. It must be highly conductive due to the necessity of connecting the part electrically to the bus bar and the DC power supply. The following general design is used for fabricating the plating fixtures:

1. They should be designed to hold work pieces in a favorable position for plating uniformly on significant surfaces and to facilitate easy racking and un- racking.

2. They should be fabricated using a highly conductive material like copper or aluminum, and have sufficient cross section to carry the current load without overheating.

3. Ideally, they will use a welded construction instead of bolting wherever practical.

4. All areas not contacting the part or the buss bars should be coated with Plastisol to prevent corrosion and bath contamination.

5. Work pieces with protruding sections should be racked so that the parts shield each other, or if this is not possible, a current "thief" or "robber" should be used to reduce the current density at the high points. Another option is to use a shield to prevent high current on edges.

6. Electrical contact with the part should be made on a non-significant surface.

7. The contact or rack tip should be rigid enough to hold work pieces securely and maintain positive contact.

8. To minimize solution losses due to drag out, and to prevent cross-contamination of solutions, the work should be hung as nearly vertical as possible, with the lower edge of the work tilted from the horizontal to permit runoff at a corner. When recessed areas cannot be racked to allow proper runoff, provision should be made for drain holes in the fabrication of the piece, or simply tilt the rack when it is being withdrawn from the solution.

An example of a "significant surface", mentioned in the first recommendation, is the journal of a crankshaft, which is to be plated with hard chrome; the adjacent web area is of no concern.

Thieves (or robbers) are metal conductors, positioned near edges and points to divert current from such areas. Proper maintenance of the thieves is important as they can be the source of large drag out losses if allowed to build up excessively. Current shields, in contrast, are non-conducting objects that are mounted on the plating rack to divert excessive current from areas of high current density, or to direct additional current into areas of low current density.

In as much as thieves receive a deposit, this represents a waste of valuable plating metal. They need to be stripped occasionally so that excessive build-up is avoided. These factors normally make the use of thieves expensive and impractical. It is for this reason that shields are in greater use for parts with troublesome areas.

Both drainage and air entrapment should be considered when racking parts. Curved surfaces facing upward will have drainage problems, but if the surface is racked directly downward, not only may some air become entrapped as it enters the solution, but we must also remember that hydrogen is evolved at the cathode surface during chrome plating. If this curved area is to receive a significant plate, it must be tilted on the rack.

Although the design of racks and the methods of racking vary considerably, two basic types of racks are generally employed. The first type consists of a single high-conductivity bar on which suitable supports have been mounted for holding the work to be plated; this rack is the cathode side of the plating circuit.

The second type consists of two elements, the cathode and the anode, and is bi-polar in nature. The cathodic side holds the work piece, and the anodic side holds the anode. The two sides are insulated from each other. This type of rack is generally used for plating smaller parts.

Because of their high conductivity, aluminum and copper are employed for the main parts of racks; other parts, such as small spring loaded tips, are frequently made of phosphor bronze. To prevent the deposition of chromium and attack from the plating bath, most fixtures should be coated with either Plastisol, or anther non-conductive material like PVC tape, with only the contact points bared. Racking usually occurs at the very beginning of the plating cycle, and the same fixture is carried through all the processes from cleaning to drying.

During plating, part surfaces that are not to be plated should be protected from the solution by using stop-off items, such as lacquers, foils, tapes and waxes. Stop-off mediums must adhere well to the metal surface, not become soft at the temperatures of the bath and be resistant to the solutions used for cleaning, etching and plating. Ideally, they should also be easy to remove after plating.

Special stop-off lacquer is used to prevent surfaces from being plated can be easily applied by brushing, spraying, or dipping. After plating, the lacquer can be stripped off or dissolved in an appropriate solvent. Lead

foil (or aluminum for certain baths) not only provides a positive stop-off, but can also act as "robbers" to aid in current distribution. Lead can be pounded into holes, keyways or slots and trimmed with a sharp knife.

Tapes of several kinds are also used for stop-off. They vary from adhesive tapes backed with lead or aluminum foil to tapes made of vinyl and other plastics. The lead foil tapes combine a specially compounded lead foil with a highly pressure-sensitive adhesive to provide a quick and convenient stop-off. The lead tape is useful as a "robber" in areas of high current density or it can be lacquered when used in areas of low current density for equalizing current distribution. It is soft enough to conform to various configurations. Vinyl and other plastic tapes are soft and pliable. Some have extruded edges for providing a leak-free seal on almost any contour. To prevent plating or corrosion of the basis metal, it is essential that the stop-off adhere firmly to the area being masked.

For large production runs it is convenient to make stop-off forms that can be re-used many times. CPVC sheet and certain other plastics are excellent for masking. Steel is sometimes substituted for plastic if it is desirable to equalize current distribution. In many cases these can be built right into the plating fixture.

Special stop-off waxes can also be used. This uses a heated dip tank that is controlled to maintain temperatures about 50 deg. F. above the melting point of the wax. The portion of the part to be plated can be covered with masking tape to prevent the wax from adhering; or, if desired, the whole part can be coated and the wax stripped with a knife from areas to be plated.

Cleaning, Activation & Preheating

Parts received in the finishing department cannot be plated without cleaning and activation. The deposit is expected to be adherent to the substrate, and such adhesion will not be obtained unless the parts are reasonably clean before entering the plating bath. Therefore, the parts must be pretreated in order to remove all soils and oxides.

The ideally clean surface would consist of atoms of the substrate metal, uncontaminated by any foreign material at all. Such a surface is extremely difficult to obtain, even in the laboratory, and is virtually impossible under shop conditions. A practical definition of the word "clean" is: "containing no contaminants that would interfere with satisfactory deposition of an adherent finish." The necessary steps in the cleaning cycle, then, depend on two factors: (1) the nature and quantity of the soil, and (2) the nature of the finish to be applied. The first is usually more important than the second, since sources of variation are more numerous.

Before being received in the finishing department, parts have been subjected to one or all of several operations, all of which leave residues of foreign material on them. Fabrication, stamping, grinding, polishing, buffing, and handling each contribute to the soil that must be removed before the parts can enter a finishing cycle. In addition, by merely being exposed to normal shop atmosphere, any object receives deposits of dust and airborne contaminants, and most metals acquire forms of oxides or other corrosion products. These pre-finishing operations leave heat scale, quenching coils, rust-proofing oils, drawing oils, stamping and die lubricants, and flushing oils on the parts, in addition to normal shop soil and oxide films. Polishing and buffing steps leave residues of the fats and waxes used in buffing compounds, as well as the abrasives from the compounds or from grinding. These soils will change character on standing, usually in the direction of becoming more difficult to remove.

The water break test is used as a practical method of determining if a surface is clean. This test depends on the fact that clean metal surfaces are hydrophilic and will shed water in an unbroken sheet, whereas, if traces of soil remain on the surface, the water will run off, leaving un-wetted areas, which are easily observed. These tests reveal organic or hydrophobic soils only; oxide films and other inorganic soils will not be detected. If the part retains a film of alkali, or alkaline cleaners from the last cleaning operation, the test can be easily masked to show a clean surface when that is not the fact. Therefore, before the test is applied, the part should be rinsed thoroughly after the final alkaline cleaning, immersed briefly in dilute acid, rinsed in cool clean water, and then observed.

Although there are many subdivisions, the pre-plating operations included under the general heading of cleaning are of three general types: organic solvent degreasing, alkaline cleaning and acid pickling. Usually they are applied in that order; though the last two can be reversed in the chrome plating sequence because the reverse etch is used for the final removal of oxides before chrome plating.

In special cases, parts that are highly soiled with organic oils and greases may require cleaning with an organic solvent before alkaline cleaning. The usual method for cleaning these parts is by vapor degreasing. Vapor degreasing is usually called a "pre-cleaning" stage. In this process the organic solvent is vaporized in a boiler beneath the work, the vapors condense on the work, forming a liquid, which does the cleaning and dissolves the oils, and drips back into the solvent sump. The process has the outstanding advantage over merely dipping the part in the solvent, that the solvent is being continuously distilled. Consequently, the liquid in contact with the work is always pure, uncontaminated solvent. Fig. 14 illustrates a typical vapor degreaser tank.
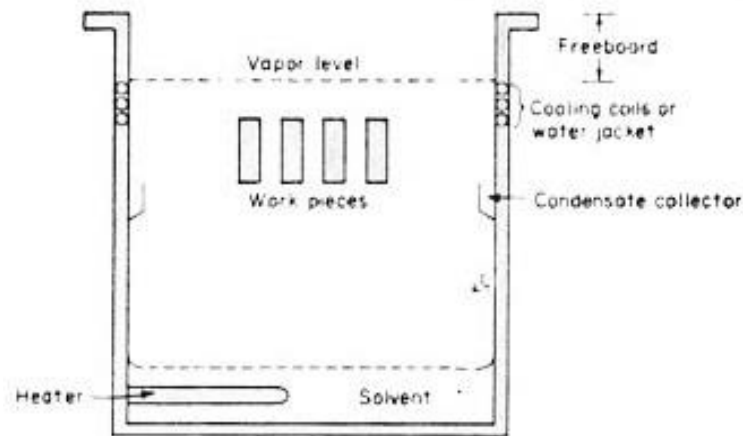
Fig. 14

Heavy rust and scale should also be removed before the metal enters the cleaning cycle. This is usually accomplished in an acid pickling bath. Depending on the base metal, almost all common acids can be used in the process in varying concentrations. Hydrochloric and sulfuric acids are the ones generally used. Dry acid salts like Actonall-210 are also used, which is much safer to handle. Actonall-210 and sulfuric acid are preferred as they don't give large amounts of noxious fumes as does hydrochloric.

The most common method of preparing large quantities of parts for chrome plating usually involves electrolytic or soak alkaline cleaners. Since these cleaners are operated at high temperatures (150 - 200 F), they can also be used as a preheat before chrome plating. Many platers are not aware of how important preheating can be to the quality of the final deposit. Unless parts enter the chrome-plating bath at approximately the temperature of the bath, non-adhesion and many other defects can result.

Alkaline cleaners remove organic type soils and have less effect on inorganic soils such as oxides, scale and rust, though many of these may also be removed if they are embedded in the organic soils because they are lifted out with them. Alkaline cleaners work through the processes of saponification, emulsification, solubilization, and preferential wetting, though saponification actually plays a very minor role in cleaning because the process is so slow. Also, saponification reactions form metal soaps which are very strongly adherent to the metal surface and very difficult to remove once they are formed. This is one reason why "natural" soaps such as those based on tall oil and fatty oils are so little used today in cleaner formulations. And, these types of soaps do not work very well in hard water areas. Synthetic detergents have largely replaced natural soaps in all metal cleaner formulations.

Alkaline cleaners should be water-soluble and their solutions should wet the surface being cleaned, and preferentially wet and penetrate the soil to be removed. They should be temporarily able to emulsify and suspend solid particles in solution without redepositing them on the metal surface; and they should be able to solubilize or bring into solution those soils capable of dissolving in a reasonable length of time. They should

be able to soften water, rinse freely, not attack or tarnish the metal surface being cleaned, have a high buffering capacity, i.e., tolerate drag-in of acid substances introduced with the metal without change of pH; and they should not form excessive foam or suds during cleaning or rinsing.

In alkaline soak cleaning, the parts are immersed in tanks of hot alkaline cleaning solution. Concentration and temperature of the cleaner should be as high as possible considering the nature of the work, in order to minimize the time for satisfactory cleaning. Agitation of the solution is helpful: the cleaning action depends on wetting and gradual emulsification of oils and greases, and occasionally saponification of these is also involved. Dirt and solid soil are bound to the surface by the oils and greases and they are removed with the binders when the latter are dislodged. Heat and agitation speed up wetting, emulsification, and saponification. The force of the moving solution aids in dislodging the soil and pre- vents it from redepositing on the work.

Soak cleaning is used to remove the bulk of the soils on the surface. Electro-cleaning done immediately after soak cleaning provides the final cleaning stage and removes the last traces of soil. Electro-cleaning adds to the chemical action of the cleaner, the mechanical action caused by copious gas evolution at the surface of the work. The gas helps in dislodging the soil and simultaneously brings up fresh solution to the surface.

In cathodic or direct electro-cleaning, hydrogen gas is evolved at the work surface. Twice as much hydrogen is evolved at the cathode as oxygen at the anode. The negatively charged work also repels negatively charged particles of dirt. In highly alkaline solutions most colloidal particles are negatively charged. On the other hand, the negatively charged work will attract positively charged metal ions, forming a metal smut. Nickel and nickel alloys must be cleaned cathodically; anodic cleaning would cause passivity, and passive nickel will not plate properly. Most other metals, however, are usually cleaned anodically.

In anodic or reverse cleaning the gas evolved on the work is oxygen; only half as much oxygen is evolved as hydrogen at the cathode so that the mechanical action is not as effective. However, the positively charged work will repel metal ions and smuts. Copper and copper-base alloys should be cleaned for only short periods anodically unless the cleaner is specially inhibited to prevent formation of tarnish films.

The use of soak and electro-cleaning is usually reserved for larger production jobs. Small lots of parts having low soil levels are usually only hand cleaned prior to chrome plating. These surfaces are degreased using a suitable solvent on a rag and then scrubbed with slurry of DuraPrep on a ScotchBrite pad The DuraPrep removes the last traces of soil and microscopic machining debris that are a common source of pitting and roughness.

The final operations before chrome plating is usually a reverse etch in either a chromium plating solution or a solution of sulfuric acid. This operation removes the last traces of oxides, left on the surface after the cleaning operation; activates the surface of the metal (remember that the initial layer of chrome plate is sometimes very difficult to deposit, and, most importantly, contributes to good adhesion of the chrome plate.

The reverse etch bath can be a straight chromic acid solution with no sulfate added or the reverse etch can be performed in the plating bath itself though this is considered a poor practice as it substantially increases the amount of chromium (III) in the bath and also dissolves iron into the solution. Sulfuric acid solutions are used at room temperature and work very well but they do not preheat the part and must be thoroughly rinsed before entering the chrome tank or sulfuric acid introduced will change the catalyst balance of the bath. Chromic acid reverse etches are operated at the temperature of the plating bath so no rinse is necessary between them. This saves time and insures that no oxides reform as might be the case if there were a rinse tank between.

There is danger on some parts of producing a rough deposit if the etch is prolonged much beyond the desired time, which is dependent upon the base metal alloy being plated. It is a good idea to briefly inspect the surface after etching to ensure that a carbon smut has not formed as can happen on high carbon alloys. The current densities used for the reverse etch are typically the same as for plating, about 2 ASI.

Rinsing and Drying Procedures

A typical process cycle for parts not overly soiled from the manufacturing and polishing operations is as follows:

1. Racking
2. Soak clean and preheat
3. Double rinse
4. Reverse etch
5. Chrome plate
6. Recovery rinse
7. Double rinse
8. Drying
9. De-racking

The importance of using the proper rinsing procedures between the various baths can't be overemphasized. When a part is transferred from one bath to another, or when it leaves the final bath, it carries with it some of the solution in which it was immersed. This adhering solution must be removed before the part enters the next step in the sequence. To accomplish this, the parts must be rinsed free of this adhering solution.

The use of sprays to rinse the parts is a method that can be used to replace immersion in a rinse tank. Applicability of sprays is limited by the design of the parts. Parts having hidden pockets or deeply recessed areas may simply trap the spray, which may not run off freely.

ChromeKill-318 can be used in the final rinse tank to remove the last traces of the chrome bath, which can later bleed out and stain the parts. Time of contact between the work and the rinse must be sufficient to remove all chemical films; for immersion rinses with air agitation this is usually around 30 - 60 seconds. Another advantage of using ChromeKill-318 as the final rinse is that it operates hot and therefore the parts air dry quickly without requiring a separate drying operation.

Water is the main ingredient in all of the baths used and its quality will effect the various operations. Impurities present in most water supplies may include dissolved mineral salts; organic compounds; suspended solids and microorganisms. The water quality concern is dissolved mineral salts, the most common are calcium and magnesium found in hard water. Although water quality is often expressed in terms of hardness, many ions do not contribute to hardness but may nevertheless be detrimental to the plating operation. Ions such as sodium, potassium, and ammonium do not precipitate soaps and, therefore, do not count as hardness; yet they may produce undesirable effects in some processes. Therefore, the total dissolved solids level is a more informative measure of water quality. Most water supplies, even city water, should be treated for use in a chrome plating operation. Either reverse osmosis or ion exchange can be used to remove all anions and cations. A detailed analysis of the water available in a particular area will show whether water purification equipment is necessary.

The Plating Bath

The initial set-up of a chrome bath involves cleaning and leaching of the tank; dissolving the proper amount of chromic acid; adding the proper amount of sulfuric acid and the Dura Catalysts. A sample of the bath should then be analyzed as small additions or adjustments, particularly sulfate, may be needed.

Electrolysis of a new solution is very helpful for the initial break in period. This electrolysis is performed using regular production anodes but with dummy cathodes. Generally, one to two hours is all that is needed for a new solution.

During operation, routine analysis and care in keeping contamination out of the chrome bath will make it last indefinitely. Following is a typical maintenance schedule for a hard chrome-plating tank.

Daily	Check temperature. Check concentration of bath by density measurements. Clean the bus bars and electrical connections.
Weekly	Analyze for chromic acid and sulfate contents.
Monthly	Perform a complete bath analysis to include the chromic acid, sulfate, trivalent Cr, iron, copper and chloride levels.
Semiannually	Check tanks for leaks and condition of lining. Clean and inspect the rectifiers.

The chromic acid and sulfate contents are relatively easy to control. Excess sulfate can be precipitated with barium carbonate. Dummying can be used reduce excess trivalent chrome levels. But, buildup of metallic contamination such as iron and copper can seriously affect the life of the bath. There is no easy or inexpensive way to remove large amounts of metallic contamination once it has built up. Smaller amounts can be treated using porous pots along with CR-3 Reducer. The only alternative for larger amounts of metallic contamination is ion exchange or electrodialysis, both of which are time consuming and expensive. The importance of contamination control in the chrome-plating bath, therefore, cannot be overemphasized.

As the plating process continues and the deposit becomes increasingly thicker, there is a tendency to produce excess growth around edges and other high current density areas. These growths are commonly called "trees" or "nodules", and are, of course, undesirable. Trees are a deposit growth normally forming around edges and are quite angular in appearance actually looking like a tree with its many branches. As the tree grows, its distance to the anode decreases, it is plated at a higher current density, and its growth is accelerated. A tree has a very thin structure at its base and will break off if touched, sometimes causing a pinhole at its base. These pinholes can be especially obvious if a grinding or honing procedure follows chrome plating. Nodules appear as small rounded hills on the surface of the chrome deposit and are usually much more firmly attached at the base. Both types of deposit are undesirable and can usually be eliminated by proper anode to cathode spacing, solution control, current density control and the use of a suitable Dura catalyst.

Post Plating Treatments
Post-plating treatments are not commonly used on chromium plate, as the great passivity and tarnish resistance of the metal make them unnecessary under most circumstances.

Factors that increase susceptibility to hydrogen embrittlement are hardening of the steel, grinding, surface defects, pickling, cathodic cleaning, and the depth of plate relative to the thickness and hardness of the part being plated. Unless hydrogen absorbed during pickling and cathodic cleaning is removed, subsequent plating will further embrittle the part to such an extent that breakage can occur. This effect becomes more prevalent with increasing hardness of the steel and on parts of thin cross section. One way to reduce hydrogen embrittlement is to relieve stress in the part before it enters the chrome plating line. If the hardness of the steel is less than 40 Rockwell C, it is unlikely that any damaging effect will occur as a result of stress. Steel parts with hardness above 40 Rockwell C should be baked at 375 F for 4 hrs after plating, to ameliorate the effects of hydrogen embrittlement. This treatment should be started as soon as possible (preferably within 15 minutes) after plating.

Stripping
In view of its passivity and usefulness, chromium is remarkably easy to strip. It is only necessary to select a solution in which the basis metal suffers little attack from the stripping action.

Simple immersion in 10-40% (by volume) hydrochloric acid at room temperature will dissolve a thin decorative chrome plate in a few seconds. For thicker hard chrome deposits, the action tends to slow down or stop where the deposit is thickest, and becomes corrosive to the base metal. Using Inhib-All in the hydrochloric acid strip prevents these difficulties and stops attack on the exposed base metal. Hydrochloric acid strippers give off nasty and very corrosive fumes that must be controlled. They also have a relatively short life and must be disposed of regularly as the stripping action slows down drastically as chrome builds-up

in the solution. The hydrochloric acid strip solution, however, is the only one suitable for brass, bronze, copper, Ferrotic or nickel alloys.

For steel alloys, the use of an alkaline electrolytic stripper like Polystrip-26 is best. This solution is non-damaging to exposed steel and the parts can be left in the bath indefinitely without damage. This bath also has an extremely long service life as it has the ability to hold a tremendous amount of chrome in solution. It is therefore much more economical to operate for steel substrates. The part being stripped is made the anode and current densities of around 1 ASI are used to provide a fast stripping rate of around 0.003"/hour.

Pollution Control

Pollution control in a chrome plating line begins with reclaiming and reusing as much of the chrome bath as possible. This is accomplished by using recovery rinses after plating that then replenish the chrome bath as water evaporates from it. ZERO Discharge Recovery (ZDR) was developed by Plating Resources, Inc. as an effective alternative to waste treatment. This is usually accomplished without the use of special evaporators, concentrators or other expensive devices. With ZDR there is are no liquid discharge, no drain connections and no need for waste treatment. ZDR reclaims and reuses the chrome rinse water at 100% efficiency. This provides a significant savings on chemical costs and reduces the overhead. It also eliminates the liability associated with hazardous waste storage and the need to dispose of the hydroxide sludge. The ZDR system is easy to operate and inexpensive to maintain.

The ZERO Discharge Recovery method, as developed by Plating Resources, encompasses all areas of environmental concern. The inherent value is derived from a combination of regulatory compliance and operational cost reductions. The proper application of ZDR involves maximizing natural bath evaporation and optimizing rinse water usage. Each ZDR System is custom-tailored to a specific need. This typically includes reducing the rinse water requirements, recycling the remaining rinse water, overflow and spill protection, segregation of bath chemistries, preventing bath contamination, extending bath life, reuse of ventilation wash-down, subsoil protection and back up provisions.

A typical chrome shop that originally used waste treatment had an annual waste cost of $187,000 per year. After installing ZDR they were able to reduce their overheard by $179,000.

<p align="center">**Chapter 3**</p>
<p align="center">**Quality Control**</p>

Introduction

Quality control includes all of the steps needed to ensure a continued high quality chrome deposit. Specific categories include bath sampling, solution analysis and deposit testing. The chrome bath can be operated over an indefinite period of time and seldom if ever requires discarding, if it is properly maintained.

Chromium plating baths are relatively forgiving when compared to other processes. In general, the bath chemistry does not change drastically with relation to the amount of chrome plated. This is not to say that chromium baths do not require routine analysis and frequent bath additions. Quite the contrary, chromium-plating baths need regular analysis and bath additions in order to maintain the chemistry within fairly narrow limits if repeatable high quality deposits are expected.

Chemicals and additives are consumed as the plating bath is used. Replenishment of these chemicals is needed to maintain their desired concentrations. The chromium plating solution may become unbalanced during continued operation due to:

1. Depletion of metallic ions through plating.
2. Incomplete reactions.
3. Decomposition of ingredients.
4. Drag-in from previous solutions.
5. Drag-out of the plating solution.
6. External contamination.

Other process baths on the line including cleaners and strippers will also require analysis periodically to insure that the baths are operating properly. By maintaining a constant bath composition, variations in the chrome deposit will be eliminated. The advantages of routine analytical control of process baths are as follows:

1. Rejects are minimized with a resulting savings in time and rework.

2. A reduction in the amount of chemicals consumed.

Analysis Frequency

The value of optimizing quality control with regularly scheduled bath analysis and maintenance additions cannot be overstated. The result is a much higher deposit quality, fewer rejects that need stripping and re-plating with the resulting increase in profits.

The optimum frequency for solution analysis is dependent upon the total number of ampere hours plated and the bath volume. The ideal is to maintain the desired bath ingredients to within 5 % of the concentration range; actually a 2% range is even better. Another objective of bath analysis is to determine the level of contaminants that are present in the chrome bath, typically trivalent, iron, copper and chloride.

It is recommended that most operations provide bath analysis as follows:

> Weekly: Test in-house for chromic acid and possibly sulfate.
>
> Monthly: Send a sample to Plating Resources, Inc. for a complete analysis.
>   This includes all bath ingredients and the normal contaminants.

In addition to the monthly outside bath testing outlined above, the following is also recommended for optimum quality control:

Expanded Analysis: Should be performed <u>every 6-12 months.</u> This is a detailed analysis of all contaminants present in the bath, both organic and inorganic. This test also checks bath conductivity, surface tension, bath pH and organic residue.

Bench Testing: Should be performed <u>every 12 months</u>. This includes an expanded analysis as well as deposit evaluation. A steel mandrel is plated to 0.005" thick and subjected to metallurgical analysis for bright range, throwing power, edge burning, adhesion, crack structure, pitting tendency, hardness and plating speed. A one (1) gallon bath sample is needed for bench testing.

The cost of sending samples to Plating Resources, Inc. is repaid many times over by not needing a highly paid on-staff technician, as well as the resulting optimum control of the process. Shops that follow this procedure find that their overall costs are lower, their baths last longer, their customers are more satisfied and their workload is reduced.

More frequent testing, both in-house and at Plating Resources, Inc., may be needed for operations with a very high production requirement or a small tank with respect to the amount of chrome plated. Plating Resources, Inc. can make recommendations as to the optimum analytical frequency based upon the degree of concentration changes.

The facility needed for in-house testing does not need to be large, elaborate nor expensive. A simple 8-10' long counter top with a sink and good lighting is adequate. Plating Resources, Inc. can provide the needed reagents, test equipment, procedures and even training of the personnel.

<u>Bath Sampling</u>
The following procedure should be followed when sampling the chrome plating solution. This is best done at the end of a work shift when the tank is empty; it is also best to make chemical additions at this time.

1)   Fill the bath to its normal operating level with water if necessary. If water was added, allow the bath to air agitate for 30 minutes before sampling. If no water is needed, agitate the bath for 15 minutes.

2)   Take a sample at three (3) points in the tank as a minimum.

3)   Allow the sample to cool, then tighten the bottle cap and rinse the bottle thoroughly with water, then dry with a towel.

4)   Apply a label to the bottle indicating the tank number, date, bath volume, bath type and other critical information.

     If sending the sample to Plating Resources, Inc. continue as follows:

     i.   Apply vinyl plating tape around the cap to prevent leaking.

     ii.   Insert the sample bottle into a poly. bag and seal it.

     iii.   Insert the bottle and tag into a heavy duty (275 lb.test) inner carton. Place this carton into another 275 lb test outside shipping box and seal thoroughly. Use plastic peanuts or bubble wrap, as needed. Do not cushion with paper or rags as this is combustible should a leak occur.

     iv.   Ship to Plating Resources, Inc. by Federal Express or UPS, ground transportation, following all requirements for hazardous materials. Other carriers may be used as needed.

The DOT shipping nomenclature is as follows:

Chromic Acid Solutions
Chromic Acid Solution
HC 8, UN 1755, PG II
Corrosive

Acid - Alkali Stripper Solutions
Corrosive Liquids, NOS
(enter generic chemical name, ie:
Hydrochloric Acid or Sodium Hydroxide)
HC 8, UN 1760, PG III
Corrosive

If needed, Plating Resources, Inc. can also provide the recommended sample bottles.

Chrome Bath Analysis

The following procedures are used to analyze hexavalent chromium plating solutions. These procedures were developed by Plating Resources, Inc. and are an improvement over other methods used in the industry. These improvements include accuracy of the results obtained, clarity of titration endpoints and speed in obtaining the results.

Standardization Of FAS Solution

FAS is a solution that is used to titrate the chromic acid in order to determine its concentration. The exact strength of the FAS must first be determined by titration against a known chromium standard that is traceable to the NBS. The FAS solution will gradually loose strength over time, hence the need for this procedure.

1) Pipette a 20 ml. aliquot of 0.100 Normal Potassium Dichromate Standard into a 250 ml. Erlenmeyer flask. Place a Teflon coated stir bar into the flask.

2) Add approx. 125 mls. of Cr Titration Diluter.

3) Place on a lighted magnetic stirrer and adjust the speed for thorough agitation without splashing.

4) Add 5-6 drops of Ferroin Indicator (do not add more than this).

5) Titrate with the FAS solution to a clear bright orange endpoint.

6) Calculate as follows; Normality of FAS Equals: $\dfrac{2.0}{\text{Mls. of FAS}}$

7) Enter the normality in the FAS normality log.

Notes:

A) The FAS solution should be standardized weekly, as a minimum.

B) During titration the solution will gradually turn cloudy green, then clear blue, then a hazy gray and, finally, to a bright orange endpoint. This endpoint is very distinct and just 1 - 2 drops past the hazy grey color.

C) The orange endpoint should last for five (5) seconds minimum. If not, then add 1 - 2 drops more until the color stays fast.

D) The same brightness of the orange endpoint should be used for the chromic acid Titration.

FAS Normality Log

Date	Normality	Eppindorf Factor (= N x 9.21886)

Chromic Acid Titration

1) Pipette a 0.5 ml. (500 ul) aliquot into a 250 ml. Erlenmeyer flask using an Eppendorf micropipette. Be certain that there are no air bubbles in the tip.

2) Add approx. 125 mls. of Cr Titration Diluter, and place a Teflon stir bar into the flask.

3) Place on a lighted magnetic stirrer and adjust the speed for thorough agitation without splashing.

4) Add 8-10 drops of Ferroin Indicator.

5) Titrate with the FAS solution to a clear bright orange endpoint. Use the same technique and endpoint color as with the FAS standardization.

6) Calculate as follows: oz./gal. Chromic Acid Equals:

mls. of FAS titrant x Eppendorf Factor

(or: mls. of titration x Normality of FAS x 9.21886)

Note: The use of the Eppendorf micropipette in step # 1 above saves considerable time. An option is to pipette a 10 ml. aliquot of the bath into a 250 ml. volumetric flask and dilute to 250 mls. with DI water. Using a second pipette, take a 10 ml. sample of this dilution and transfer it into the 250 ml. Erlenmeyer flask. In this case, the calculation is: mls. of titration X normality of FAS X 11.27.

Density Testing
Density tests can be used as a rough field measurement of the chromic acid concentration, in lieu of titration, for operations that wish to minimize their laboratory size. The density of the bath, measured in either Baume' or specific gravity with a hydrometer, shows a ballpark concentration of the chromic acid level. The exact concentration of chrome is dependent upon the amount of bath contamination present, typically trivalent, iron and copper. These contaminants are also measured with the hydrometer and if not accounted for will end up showing a higher reading of chromic acid than is actually in the bath. Older baths typically will show a significant difference between the density reading and the actual amount of chromic acid present.

Procedure
Pour a sample of the bath into a hydrometer jar and allow it to cool to 60 deg. F.
Place a hydrometer into the jar and allow it to float to a steady point. Read the density in either Baume' or specific gravity. Compare the reading to the chart below.

A bath sample should still be sent to Plating Resources, Inc. on a monthly basis so the actual chromic acid reading is known. Determine the difference between the actual analysis and the density reading, then deduct this amount from the density reading in order to obtain a more accurate level of chromic acid present in the bath.

Baume'	Specific Gravity	oz/gal Chromic Acid
10	1.074	13.6
11	1.082	15.2
12	1.090	16.7
13	1.099	18.3
14	1.107	19.9
15	1.115	21.6
16	1.124	23.3
17	1.133	25.0
18	1.142	26.7
19	1.151	28.5
20	1.160	30.3
21	1.169	32.2
22	1.179	34.1
23	1.189	36.0
24	1.198	37.9
25	1.208	39.8
26	1.219	41.8
27	1.229	43.9

Baume'	Specific Gravity	oz/gal Chromic Acid
28	1.239	46.0
29	1.250	48.2
30	1.261	50.3
31	1.272	52.5
32	1.283	54.8
33	1.295	57.1
34	1.306	59.5
35	1.318	62.0

Extrapolate for numbers between the values shown. Cooling the solution to 60 deg. F. is important. Subtract the contaminant equivalent from the chromic acid level found to obtain a more accurate reading.

Sulfate Analysis
This procedure uses a special four (4) place electric centrifuge, with aluminum tube retainers and poly. cushions. The centrifuge tubes used are also special in that they have a narrow tip end that is calibrated to read directly in oz/gal. sulfate concentration. Each head position as well as the individual tubes should be marked with numbers #1 - #4.

Important:
For accurate results it is critical that the tubes be calibrated against a bath standard. It is common for factory supplied tubes to have variances in the tube diameter and the scale placement. Such tubes will produce erratic results. Plating Resources, Inc. provides special tubes that have been calibrated for accuracy.

Procedure:

1) Allow any bath solids to settle in the sample before proceeding. Then, Transfer 5 mls. of 5N Hydrochloric Acid into each tube.

2) Pipette a 20 ml. aliquot of the bath into a numbered tube. When pipetting, be sure that the tip does not reach the bottom of the sample so as to avoid picking up any solids. Place a #0 rubber stopper into the centrifuge tube. Remove the tube and shake vigorously for 30 seconds. Return the tube to the appropriate numbered holder.

3) Centrifuge for 5 minutes at 1,000 rpm. Remove the tube and check for solids at the bottom. Record this reading if any are found.

4) Transfer 5 mls. of 30% Barium Chloride into each tube. Stopper and shake vigorously for 60 seconds. Return the tube to the appropriate numbered holder. Allow to stand for 5 minutes, minimum.

5) Centrifuge again for 5 minutes at 1,000 rpm.

6) Remove the tubes and note the reading. The tubes read directly in oz/gal of sulfate with a scale of 1 - 6 and five subdivisions. Each number represents 0.1 oz/gal and each subdivision represents 0.02 oz/gal. If desired, a third decimal can be extrapolated.

Gently tap the tube end should the precipitate be at an angle. If this does not level the reading, then rotate the tube in the holder 180 degrees.

7) Repeat step # 5 centrifuging two (2) more times as a minimum, noting the reading each time. It is common for this reading to decrease, but sometimes it will increase if the sulfate precipitation was not complete in step # 4. Continue until the readings are the same for a minimum of two (2) times.

8) Subtract any solids found in step # 3 from the final reading in step # 7.
The result is the sulfate concentration in oz/gal.

Notes:
It is best to run dual samples with the tubes opposite each other for balancing. The results should be averaged. When running only a single sample the opposite tube must be filled with an equal volume (or slightly more) of DI water for balancing. It is possible to run four (4) individual samples, or two (2) dual samples at the same time.

Should the sulfate reading be above the 0.60 oz/gal level at the top of the tube, then start over using only a 10 ml. sample. In this event, add 10 mls. of DI water in step # 2 and mix well. The reading obtained would then be multiplied by 2 to obtain the sulfate level.

The tubes are quite delicate. It is suggested to have several spares on hand.

This centrifuge method is actually more accurate, when properly performed, than the precipitation and weigh method is. This is due to the uncertainty of complete precipitation, complete washing and complete drying, which causes significant errors in the old method.

Ratio Determination
Chromium baths require a specific ratio be maintained of the chromic acid to the sulfate levels in the bath. The exact ratio is dependent upon the bath type and to a lesser extent the operating conditions. Refer to Plating Resources, Inc. technical bulletins for the optimum ratios. Maintaining the optimum ratio is needed for proper bath operation and high quality deposits.

 A bath with 30.0 oz/gal of chromic acid and 0.25 oz/gal of sulfate would have a ratio of 120:1, which is calculated as follows:

$$\frac{\text{Chromic acid concentration}}{\text{Sulfate concentration}}$$

The ratio can be adjusted by either increasing or decreasing the chromic acid or the sulfate levels. There are advantages and disadvantages to both; Plating Resources, Inc. can provide assistance should questions arise as to the best approach.

Trivalent Chrome Analysis
This method uses a simplified colorimetric test that is both fast and fairly accurate. It uses a diluted bath sample that is compared to a color standard with a known trivalent level. Hexavalent chrome solutions become darker in color with increasing trivalent levels, hence the simplicity of this procedure.

Procedure:
1) Analyze the bath for chromic acid concentration. Then determine the dilution amount by dividing 133.5 by the chromic acid oz/gal. The result is the amount of mls. to be used in step # 2. Example: a chrome level of 30 oz/gal would use 4.5 mls. of bath sample.

2) Transfer this amount of the bath sample into a 10 ml. test tube, using a graduated pipette.

3) Fill the tube to the 10 ml. mark with DI water, stopper and agitate thoroughly.

4) View the diluted sample with known color standards in a comparator test block in front of a strong light source. When the color is matched, the percentage shown on the standard equals the bath trivalent level in relation to the chromic acid. Half percentage points can be extrapolated.

Notes:
This test is accurate down to 13 oz/gal of chromic acid. A more accurate method , which uses a similar dilution involves the use of a spectrograph. Another method, which is much more complicated and involved, is by direct titration using an excess of ceric sulfate and back titrating with sodium nitrate while using potentiometric titration techniques.

Dura Catalyst - Additive Analysis
The Dura Catalyst and Additive levels are determined using specially modified specific ion meters with combination electrode attachments. This analytical unit is calibrated against 1 % and 5% standards each time the test is performed. This procedure is reserved for sophisticated laboratories due to the high cost of the instrumentation and the technical skills required for operation. As such, it is not usually practical for field applications. In addition, the procedures used are proprietary, but can be provided on request.

Routine Catalyst/Additive bath additions should be made based on the process technical bulletin. This is usually based on the amount of ampere hours of operation, but can also be based upon the amount of chromic acid consumed.

Plating Resources, Inc. can make recommendations on optimum Catalyst/Additive addition rates. It is also recommended that a bath sample be sent to Plating Resources, Inc. laboratory, on a monthly basis, for catalyst and a complete bath analysis.

Chloride Analysis
Chloride is a very common contaminant in chromium solutions, and rather insignificant amounts have a very negative impact on the quality of the deposit. The chloride level must be kept below 50 ppm, preferably below 20 ppm.

Similar to the Dura Catalyst - Additive analysis, chloride is tested using a specific ion meter with a combination electrode attachment. Plating Resources, Inc. tests for chloride as a routine on all bath samples submitted for analysis.

Iron And Copper Analysis
Iron and copper, as well as other heavy metal contaminants, are analyzed using an Atomic Absorption / Emission Spectrophotometer operated in the absorption mode. This rather sophisticated instrument is calibrated against known standards using a chromic acid background.

As with the specific ion meters, this expensive instrument is not usually suited for field use. Plating Resources, Inc., Inc. tests for iron and copper as a normal routine on all bath samples submitted for analysis.

Bath Performance Testing
Small-scale bench plating tests are used to check the deposit quality. Two such tests are; the Hull Cell Test and the Mandrel Test.

Hull Cell Testing
A Hull cell, typically 267 ml., is a device where the cathode is angular to the anode. This provides a known and variable current density. This test is for visually observing the brightness and coverage at various current densities. It's then easy to observe where burning starts at the high current density and where coverage stops at the low current density. The Hull cell is only used when current density or brightness is an issue.

A typical Hull cell is shown below. The ones for testing chrome baths are made of polyethylene and are perforated for solution flow and to stabilize the temperature. This is placed inside of a Pyrex container that is fitted with a temperature control for heating & cooling and an agitator.
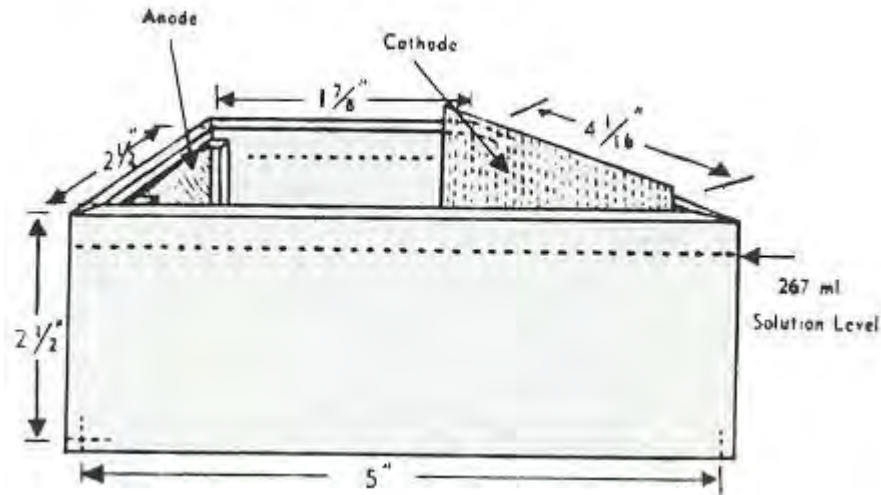
Mandrel Testing
The mandrel test is used to test the plating speed and metallurgical properties of a chrome baths deposit at a fixed current density. It duplicates conditions found in the shop and isolates the bath chemistry from the equipment and techniques used. This is a great tool for problem solving and for annual verification of the deposits metallurgical properties.

Observations that can be made with the Mandrel Test are deposits brightness, smoothness, pitting tendency, crack structure, hardness and adhesion.

This test consists of plating in a 4 liter beaker under controlled conditions using a conforming anode. The test pieces are usually 0.5" diameter x 6" long #4140 TG&P mandrels. The beaker is fitted a temperature control for both heating & cooling, and agitation. Generally, a current density of 2 ASI is used.

Metallurgical Testing
The plated mandrels from the above test can then be cross-sectioned and polished by various metallographic techniques for microscopic observation of the thickness, crack structure (surface & cross section), for adhesion and for deposit hardness with a DPH tester. Other properties that can be similarly tested include coefficient of friction, internal stress and ductility, and wear resistance.

Wear or abrasion resistance is often confused with hardness, and it is true that many hard materials are also resistant to the loss of thickness caused by wear and rubbing. But this correlation is by no means universal, and if the application involves actual wear (as in bearing surfaces), abrasion resistance itself should be tested. No standard test is universally accepted, but the Taber Abraser is widely used. In this instrument the test panel is rotated while two abrasive wheels held by weighted arms produce a rubbing action. An annular ring of wear is produced on the specimen by the abrasive wheels, and the degree of wear can be observed visually or measured by weight loss. Various types of wheels are available and the load weight can be varied.

Corrosion Resistance Testing
Corrosion is the result of the reaction of metals with various chemicals in the environment. The compounds so formed, called corrosion products, are usually either oxides or salts; their nature often influences the course of the reaction and may determine whether additional protection is required. The most widely used metal, iron, unfortunately, is little protected by its natural corrosion product, rust, and so usually requires some form of

corrosion protection. Corrosion control is based on preventing or slowing down the reaction of a metal with its environment. This aim may be approached through controlling the environment, the nature of the metal, or the nature of the interface between the two. Controlling the nature of the interface is the object of chromium plate or any deposit for that matter.

A decorative chrome plate with its underlying nickel and copper layers has a unique way of doing this. Both nickel and chromium tend to become passive in most environments, and thus behave cathodically; steel is the anode in the resulting corrosion cell, and the conductive medium may be provided by moisture if nothing else. Thus, the usual protective system consists of not one metal, but usually at least two, nickel and chrome; often of three, copper, nickel and chrome; and sometimes effectively of even more than three, since nickel can be deposited in several different conditions, some of which are more active than others. Fig. 15 illustrates the simple system: nickel/chrome on steel. Here chrome is cathodic and steel anodic, with nickel intermediate. Chromium, however, can be deposited in a form known as micro discontinuous, which has many microscopic cracks or pores. This is usually achieved, as mentioned before, with the use of a dual catalyst system. The nickel, anodic to the chromium, corrodes laterally by galvanic action and since much more of it is available, eventual penetration to the base steel is much delayed. The development and understanding of this process makes decorative chrome-plated bumpers much more serviceable today than 25 years ago.
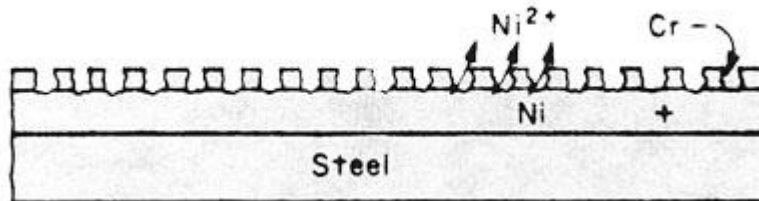

Fig. 15
Micro discontinuous chromium; corrosion is distributed over a large area of nickel.

In hard chrome plating, the passivity of the metal is still important. Passivity is a result of chromium forming a very thin oxide film on its surface. This film is so stable and self-healing that it protects the metal underneath from further air oxidation. However, the chemical resistance of the chromium plate is not so great and it can't be attacked by certain acids. The chemical resistance of the chromium plate may be used to the best advantage only if the underlying metal is completely covered. For this reason, hard or industrial chromium deposits for corrosive service should be at least 1 or 2 mil thick. This ensures that the cracks are not continuous to the base metal. Another way of achieving this protection, is by depositing a Crackless deposit or filling the cracks with MicroTuff.

Corrosion testing should be carried out in an environment that simulates that in which the part will be used. Many accelerated corrosion tests have been devised, with the aim of speeding up the process while at the same time simulating its effects. Such tests include the following:

Neutral Salt Spray (Fog) Widely used and specified, the test consists essentially of spraying the specimens with a mist of 5% or 20% sodium chloride solution in a closed cabinet, under strictly specified conditions of temperature and spray rate.

Acetic Acid Salt Spray (Fog) test. Similar to the above, with the mist solution acidified with acetic acid for faster action.

Copper-accelerated Acetic Acid Salt Spray (CASS) Test. Similar, but with the addition of copper salts to the mist solution.

Corrodkote Test. The specimen is coated with a slurry of kaolin containing copper nitrate, ferric chloride, and ammonium chloride. The slurry is allowed to dry and the coated specimen is placed in a humidity chamber; it is removed, cleaned and examined after stated intervals of time.

Electrochemical Corrosion Test (ECT). The specimen is made anodic in a specified electrolyte; under carefully controlled conditions, corrosion is stated to occur within a few minutes.

Sulfur Dioxide Test. The specimen is suspended in a closed chamber in the presence of sulfur dioxide gas.

The corrosion engineers usual method of expressing corrosion rates is in weight loss per unit area per unit time, such as milligrams per square decimeter per day. Measurements of this type normally are not practical for the chrome plater. Evaluation of corrosion depends on the use for which the coating was applied. It cannot be overstressed that actual service is the final test of corrosion resistance of any material, whether finished or not. The various corrosion tests can give approximations, sometimes fairly close, of how the part will fare in service. The nearer the test conditions approach actual service conditions, the better will be the approximation to actual experience.