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ELECTROPLATING

Electroplating is the process of applying a metallic coating to an article by passing an electric current through an electrolyte in contact with the article. The ASTM (1) adds some quality restriction by defining electroplating as electrodeposition of an adherent metallic coating on an electrode such that a surface having properties or dimensions different from those of the basis metal is formed. Two other related plating processes are electroforming, an adaptation of electroplating wherein the deposit is removed from the basis material for use as a separate part, and autocatalytic plating, more commonly referred to as electroless plating (qv). This latter is a form of metal plating wherein dissolved metal is reduced to its metallic form on an article using a chemical reducing agent instead of externally applied electric currents, yielding plate thicknesses of any desired level. In immersion plating the plate is very thin, and the replacement reaction ceases when the active surface is completely coated (see also METALLIC COATINGS; THIN FILMS).

The science of electroplating technology has followed the art. As late as the 1930s, platers depended on unpublished trade secrets for much of their craft. Solution formulas often were contained in the platers' jealously guarded little black books. Plating solutions of that period often produced dull, rough, pitted deposits that needed much hand finishing and buffing. During this time, some

materials were discovered that produced improved deposits when added to the plating bath. Many of these secret additives were food products and some of the modern proprietary electroplating additives have been derived from analyses of the active ingredients of these grocery additives.

The first basic book on the principles of electroplating and electroforming (2) was published in the United States in 1924. An electroplaters society, American Electroplaters Society, now known as American Electroplaters and Surface Finishers Society, was formed soon after. Chemical suppliers to the plating industry formed and began developing specialty chemicals and additives designed to improve the quality of the electroplating processes. The specialty chemical and anode suppliers contributed significantly to the advancement of electroplating technology (see also METAL ANODES).

Progress in electroplating is also linked to improvements in materials of construction (see BUILDING MATERIALS, SURVEY), power supplies and other plating equipment, purer industrial chemicals and anodes, and improved analytical test and control methods. The quality of electroplating is dependent on the basis metal surface. Cleaner, less porous castings and better casting alloys, and improved steel (qv) and steel finishes have helped significantly (see also METAL SURFACE TREATMENTS; SURFACE AND INTERFACE ANALYSES).

Materials

Surfaces. Essentially any electrically conductive surface can be electroplated, although special techniques may be required to make the surface electrically conductive. Many techniques are used to metallize nonconductive surfaces. These are well-covered in the literature (3) and can range from coating with metallic-loaded paints or reduced-silver spray, to autocatalytic processes on tin–palladium activated surfaces or vapor-deposited metals. Preparation steps must be optimized and closely controlled for each substrate being electroplated.

Although metals and alloy substrates account for much of the volume in electroplating, there is a large and growing amount of plastic surfaces being plated, both for decorative trim and for electronic shielding applications. On a smaller scale, other materials that are plated include wood (qv), plaster, fibers (qv) and cloth materials, and plant and animal tissue, such as leaves, leather (qv), paper (qv), and seashells.

Electroplated Metals and Alloys. The metals electroplated on a commercial scale from specially formulated aqueous solutions include cadmium, chromium, cobalt, copper, gold, indium, iron, lead, nickel, platinum-group metals, silver, tin, and zinc. Although it is possible to electroplate some metals, such as aluminum, from nonaqueous solutions as well as some from molten salt baths, these processes appear to have achieved little commercial significance.

In addition to the metals listed above, many alloys are commercially electroplated: brass, bronze, many gold alloys, lead–tin, nickel–iron, nickel–cobalt, nickel–phosphorus, tin–nickel, tin–zinc, zinc–nickel, zinc–cobalt, and zinc–iron. Electroplated alloys in lesser use include lead–indium, nickel–manganese, nickel–tungsten, palladium alloys, silver alloys, and zinc–manganese. Whereas

tertiary and many other alloys can feasibly be electroplated, these have not found commercial applications.

Composites. Another type of electrodeposit in commercial use is the composite form, in which insoluble materials are codeposited along with the electrodeposited metal or alloy to produce particular desirable properties. Polytetrafluoroethylene (PTFE) particles are codeposited with nickel to improve lubricity (see LUBRICATION AND LUBRICANTS). Silicon carbide and other hard particles including diamond are co-deposited with nickel to improve wear properties or to make cutting and grinding tools (see CARBIDES; TOOL MATERIALS).

Economic Aspects

Electroplating is done both in job shops, where a customer's work is plated, and in captive (in-house) shops. There were reported to be about 7500 plating plants in the United States (4) in 1992. This is a decrease from the ca 12,000 reported by the same source in 1980. The reduction, particularly in the number of smaller job shops, is related to the problems in meeting the waste regulations imposed on plating shop effluents.

The plating industry is relatively small. In the United States, the American Electroplaters and Surface Finishing Society (AESF) had about 9000 members in 1992. No colleges or universities offer full courses specifically in electroplating, although a very few offer a degree in electrochemical engineering. Special courses are available from other sources, however (5), and two technical societies, AESF and American Society for Metals (ASM), offer intensive courses on electroplating.

Many captive-plating shops exist, and the value added by electroplating in captive shops can far exceed plating costs. For example a $10,000 part, scrapped because of wear or mismachining, may be salvaged using $10 or less of plated metal. The 10 largest electroplating job shop plants in the United States estimated annual sales totalling $178–217 million with ca 3100 employees (6). Twenty-nine of the next larger shops reported 3300 employees.

One indicator of business in the plating industry is anode sales to electroplaters; however, anode costs are only a varying portion of the prices used by electroplating shops, because no standard pricing practice seems to exist. The total value of the plating industry is estimated to be in the area of several billion dollars. Job shop plating sales could be about a billion dollars.

Cadmium. In 1989, U.S. consumption of cadmium for coatings was 1474 t (7), compared to 1552 t in 1970, 2089 t in 1979, and 1230 t in 1985. Cadmium plating amounts to about 15% of total cadmium production (see CADMIUM AND CADMIUM ALLOYS). Of the cadmium being plated in 1989, 30% was for automotive parts, over 22% for electronics, and 18% for industrial fasteners. Because of cadmium's high and well-publicized toxicity and very tight waste restrictions, there are considerable efforts to develop alternative materials, and the quantities of cadmium used in electroplating are expected to decrease. The price of cadmium anodes in early 1993 was about $1/kg.

Chromium. Worldwide consumption for functional uses of chromium is estimated at 13,600 metric tons. From 3630–4080 t of this is used in the United States; Europe is estimated to use about 3600 t; and the remainder is divided

among Far Eastern and Third World countries. For functional applications, chromium is used for its hardness and wear properties.

Decorative plating primarily over bright nickel is estimated to consume about 2270 t worldwide. Some 60% of this is used in North America, and about 900 t in Europe. A relatively new method in decorative chromium plating is based on trivalent instead of hexavalent chromium, and this is estimated to total about 10% of the decorative market and is expected to increase. Chromic acid, which cost about $2.76/kg in early 1993, is the hexavalent chromium source for plating solutions (see CHROMIUM AND CHROMIUM ALLOYS; CHROMIUM COMPOUNDS).

Copper. Copper (qv) consumed in electroplating and electroforming in the United States and Canada is estimated to be 136,050 t/yr including, since 1983, the U.S. Government copper plating of the zinc penny used for coinage. This usage averages about 870 t/yr and could range up to 1360 t/yr. In early 1993, copper prices were on the order of $3.65/kg (see also COPPER ALLOYS).

Gold. Used both in decorative and electronic electroplating applications, about 27.5 t of gold were consumed in the United States in 1990 (8) (see GOLD AND GOLD ALLOYS).

Silver. About 72.3 t of silver were electroplated in the United States (8) in 1989. Silver is used in dinnerware and hardware or functional applications. This usage is reported to be fairly stable (see SILVER AND SILVER ALLOYS).

Nickel. Worldwide, nickel used in electroplating has averaged about 63,500 t annually from 1980–1990 (9). The United States uses about 18,000 t/yr, and Europe about the same quantity; Japan consumes about 9,000 t, and another 9,000 t is used by the other Pacific rim countries. Canada and South America are reported to use about 4500 t annually. Electroforming applications consume another 4500 t of nickel worldwide. About half of this electroforming is done in the United States and Canada. Nickel deposited from autocatalytic solutions was estimated to account for 1600 t of nickel on a worldwide basis (10) in 1990. Nickel averaged ~ $3.65/kg in early 1993 (see NICKEL AND NICKEL ALLOYS).

Tin. Application of tin on strip steel for can stock has decreased. Nevertheless, tin plating is still done in large volume, and tin plate for can stock was estimated at 11,750 t in 1990 (11). Additionally, 603 t of tin anodes were used for electroplating in electronic applications in the United States in 1990. The use of tin in solder manufacture is reported to exceed that used in can stock (12). The cost of tin in early 1993 was $7.50/kg (see TIN AND TIN ALLOYS).

Zinc. Suppliers of zinc electroplating chemicals have reported that zinc electroplating volumes continue to grow. More recently, electroplated zinc alloys have been promoted. Zinc was priced at $1.50/kg in early 1993 (see ZINC AND ZINC ALLOYS).

Other Materials. The amount of plastic substrates plated in 1991 for both decorative and electromagnetic shielding applications was estimated to be about $4.3–5.4 \times 10^6$ m^2 (13).

Uses

Electroplated materials are generally employed for a specific property or function. There is, of course, some overlap; for example, decorative use certainly requires

some degree of corrosion resistance. The various usages and the principal plating metals employed are as listed. There are also smaller amounts of other metals and alloys used for specific applications.

Property/Function	Principal plating metals
decorative	chromium, copper, nickel, brass, bronze, gold, silver, platinum-group, zinc
corrosion resistance	nickel, chromium, electroless nickel, zinc, cadmium, copper and copper alloys
wear, lubricity, hardness	chromium, electroless nickel, bronze, nickel, cadmium, metal composites
bearings	copper and bronze, silver and silver alloys, lead–tin
joining, soldering, brazing, electrical contact resistance, conductivity	nickel, electroless nickel, electroless copper, copper, cadmium, gold, silver, lead–tin, tin, cobalt
barrier coatings, antidiffusion, heat-treat, stop-off	nickel, cobalt, iron, copper, bronze, tin–nickel
electromagnetic shielding	copper, electroless copper, nickel or electroless nickel, zinc
paint/lacquer base, rubber bonding	zinc, tin, chromium, brass
manufacturing; electroforming	copper, nickel
manufacturing; electronic circuitry	electroless copper, copper, electroless nickel, nickel
dimensional buildup, salvage of worn parts	chromium, nickel, electroless nickel, iron

Decoration. Decorative chromium plating may be the most familiar electroplating application. Colloquially referred to as chrome, chromium finishes are composed of multiple coatings, either nickel or copper and nickel undercoats, having relatively thin (0.2–0.6 μm) coatings of chromium as the top coat. Work by the automobile manufacturing companies, the specialty chemical plating suppliers, and others have led to improvements in the corrosion resistance and appearance of chromium-plated finishes, and in improved processes. Corrosion protection has been extended such that plated bumpers have been found rust-free in some exposure tests after 15 years (14). The improved processes require more complicated plating systems, but these have been adopted where better corrosion protection is a requirement.

To plate a smooth, highly decorative finish on base materials requires special processing. For the roughest surfaces, mechanical finishing such as polishing and buffing are needed. Copper is more easily polished than steel, and because copper flows well with buffing, rougher parts are often copper-plated to substantial thicknesses and then polished and buffed. For smoother surfaces, it is sometimes possible to avoid mechanical finishing. A sufficiently smooth surface may be achieved by the use of adequate thicknesses of copper and nickel deposits from higher

leveling plating solutions. The term leveling is applied to that property of a plating process that produces a plated surface smoother than the original surface. Leveling may be positive, the surface gets smoother; or negative, in which the surface gets rougher. The ability to level is a function of the individual metal being plated and the additives, usually proprietary, used in the particular plating solution. In some plating solutions, such as alkaline copper cyanide, leveling can also be enhanced by d-c power manipulations (15). Improvements in the leveling capabilities of plating processes have reduced the need for mechanical finishing, especially when combined with improved casting surfaces. For some applications, the need for polishing and buffing is, however, expected to remain. The quality and performance of the plated surface depends substantially on the finish and quality of the substrate material. Thus the basis material has to be considered an important variable in the plating process.

Other decoratively plated coatings produced in quantity are copper and copper alloys. Copper-plated hardware for cabinetry, lighting fixtures, household trim, and other uses is protected using a top coat of clear lacquer. Copper plating finishes are available with a variety of post-treatments to simulate antique or rustic appearances.

Bright brass plating for decorative purposes is usually produced much like chromium; ie, it is plated over a bright nickel plate. The brass is very thin, amounting to only a flash of as little as 0.05 μm. Thicker deposits tend to be duller. For bright brass electrodeposits of greater thicknesses, proprietary brighteners are added to the brass plating solution, but often thicker deposits require buffing to obtain full color and brightness.

Bronze, copper–tin alloy, electrodeposits can be produced in thicker deposits using proprietary brightening additives in the plating solution, especially over a smooth bright substrate. The brightest deposit with better corrosion resistance is attained when bronze is plated over a bright nickel plate. However, direct plating over steel is not an uncommon practice.

Decorative plating of jewelry using gold and silver is one of the oldest uses of electroplating and the first electroplating process to be patented (16). Bright nickel plate is used as an undercoat, especially for gold-plated jewelry, and the gold can be as thin as 0.05 to 0.10 μm.

Decorative silver plating is used with or without a bright nickel plate as an undercoat. When used on jewelry, plating can be thin, 1 or 2 μm, and requires a clear lacquer top coat to retard silver tarnishing. Decorative silver plating as used in plating flatware (eating utensils) and hollow ware such as bowls, pots, urns, and trays, accounts for considerable quantities of silver. The silver plate thickness on flatware varies according to the specific grades used in this industry, and ranges from about 3.5 to 32 μm (17).

A small amount of the platinum-group metals is also used in jewelry. The high cost of these metals is an obvious deterrent.

Although zinc is not usually considered a decorative plating metal, advances in plating processes have resulted in the production of very bright zinc deposits, matching the appearance of bright nickel–chromium. Bright zinc does not, however, withstand the more severe exposure to corrosive environments. Chromated zinc deposits can also be dyed a variety of colors. These may be decorative, and

are given a clear lacquer top coat. Brass-like colors are being produced on parts used in protected environments, such as inside homes and offices.

Functional Plating. Plating for engineering purposes encompasses all the other purposes for electroplating. Plating for functional properties has grown to surpass decorative applications. Platings for functional properties are extremely varied and are present in almost every industry. Work is plated in a variety of shapes and forms, but the simpler shapes are less troublesome in achieving adequate plate thickness distribution.

Plating Method. Strips. Materials such as strip steel are plated on machines where coils of steel are unrolled on a continuous, high production basis, fed through a sequence of preparation steps, and into the plating tank(s) on a series of rolls and rollers. Short plating times, high current densities, and relatively thin deposits are the rule. Current is supplied to the moving strip through contact with the rolls entering and exiting the plating tank. The large installations are electrogalvanizing (zinc plating) lines, tin plating lines, and the so-called tin-free lines (a form of chromium). Some strip lines have been started up in several countries to plate zinc alloys, primarily zinc–nickel and zinc–cobalt, which are being promoted for making the body steel for automobiles more corrosion resistant.

Wire. In electroplating wire is uncoiled from spools or reels, passed through the processing and plating steps as individual strands, and then recoiled. Several spools can be plated simultaneously through multistrand machines. More flexible wires can be handled by a multipass arrangement where the plated wire is directed back and forth through the plating tank. Wire has also been plated in loose coils without uncoiling, but the plating quality is less. Wire is plated commercially with several metals. Among these are copper and copper alloys, zinc, iron and iron alloys, nickel and nickel alloys, gold, and silver. Special machines are available to plate wire, and come in many sizes from desk top to shop size models.

Stampings. Stampings, moldings, and castings are usually mounted onto specially designed plating racks to allow rigid and proper positioning of the part. Some plating shops prefer to hang parts on universal hooks, or wire parts onto hooks using copper or steel wire, but this does not allow maximization of plate distribution. The positioning and the spacing of the parts on the rack is an important factor in plate thickness distribution. The plating rack is designed to have sufficient electrical contacts and current-carrying ability to provide current without generating excessive heat from high electrical resistances. The electrical current flow between the part and the anode is such that areas of the part closest to the anode get the most plate, and deeply recessed areas may get little or no plating. Additionally, current attracted to the edges and sharp corners of parts and plate thicknesses is greater in these areas. Plating racks are coated with inert plastic materials except for the necessary electrical contact areas. This prevents waste and allows improved current distribution. Racks can also be provided with inert plastic shields to help direct current flow to desired areas. Racks can be designed to provide auxiliary or intermediate anodes, attached to, but insulated from, the rack. These anodes are used to direct current flow to deeply recessed areas of a shaped part. A rack design and supply industry is active and caters to the plating industry. Properly designed racks are important to production of good quality plated ware.

Barrel Plating. When the parts to be plated are small enough, bulk plating methods may be used. Although some work may be electroplated in dipping baskets, plating barrels are effective. Plating barrels come in many shapes, sizes, and styles. All are capable of turning while going through the process, are shaped to tumble small parts so these are continually mixed, and are equipped with holes to allow for passage of current and exchange of solutions. Plating barrels are made of inert plastic materials with means for electrical contact to the parts and the d-c power source. Sizes range from beaker-size to barrels that hold hundreds of kilograms of parts. Parts most acceptable to barrel plating are those that tumble well and do not stick together or nest. Voltages required for barrel plating processes are higher than those required for rack plating because of the added resistance from the small open-hole area through the barrel.

Brush Plating. When parts are large and only smaller areas of the part require plating brush plating is employed (18). Other terms used for this method include selective, contact, swab, and out-of-tank plating. Specially designed plating tools, which are essentially shaped-anode materials covered with some absorbent material saturated with a plating solution, are used. The anode tool is electrically connected to a d-c power source, and the part to be plated connected as the cathode. The circuit is completed by contacting the wet anode-tool to the part to be plated. Tools can be handheld, kept saturated and in motion, or can be fixtured to do rotating parts such as shafts. This technique finds use in plating of large parts, for touch-up and repair, and has been particularly helpful in the aircraft industry.

Automation. Handling of racks or barrels through the process tanks in a plating line can be done manually, or it can be fully or partially automated. A variety of automated styles are used: a return-type conveyor system transports the racks or barrels from a loading station through the sequence of tanks without backtracking; the conveyor returns through the second half of the process cycle off to the side of the first half so that in no case does the work drip solution drainage into previous process tanks in the cycle. A straight-line cycle could provide the same sequence, but the load and unload stations would be widely separated and require additional load–unload equipment or additional personnel if manually loaded and unloaded. Another style tries to place process tanks such that those most sensitive to drippage problems and cross-contamination are placed in parts of the in-line layout where they would be least troublesome. The transport system is then programmed to take the work in a nonsequential order, skipping over stations and backtracking in order to complete the plating cycle. The carrying of work over other bars tends to leave salt buildup on the superstructure of the work bars, and potential contamination of any and all tanks in the line depending on which station the salt buildup eventually drops into.

Fundamentals of Electroplating

The essential components of an electroplating process are an electrode to be plated (the cathode); a second electrode to complete the circuit (the anode); an electrolyte containing the metal ions to be deposited; and a d-c power source. The electrodes are immersed in the electrolyte such that the anode is connected to the positive

leg of the power supply and the cathode to the negative. As the current is increased from zero, a minimum point is reached where metal plating begins to take place on the cathode. The physics of this process has been the topic of many studies, and several theories have been proposed. A discussion of these theories can be found elsewhere (19).

Plate Thickness. In plating processes, plate thickness can be predicted knowing the cathode efficiency of a particular plating solution, the current density, and time of plating.

Plate thickness is an important factor in electroplating, in terms of both performance and economics. Corrosion resistance, porosity, wear, appearance, and several other properties are proportional to plate thickness. Minimum plate thicknesses are, or should be, specified as should the location, or check-point, where the thickness is to be measured. In some applications, such as threaded fasteners, maximum thicknesses should be specified. Root diameters of finer machine threads can be adversely affected by as little as 10 μm of plating.

A problem that affects the accuracy of the prediction of plating thickness is in estimating the actual current density. Current is not evenly distributed over the surface of the part being plated, rather, it takes the path of least resistance. Current also concentrates on sharper points, corners, and edges; even the shape of the plating tank can have an influence on the current distribution. The difference in current and, subsequently, the plate thickness distribution, is minimal when geometrically conforming anodes are part of the system, but this condition is not often achieved.

Cathode Efficiency. Faraday's law relates the passage of current to the amount of a particular metal being deposited; ie, 96,485 coulombs, equal to one Faraday, deposits one gram-equivalent weight of a metal at 100% efficiency. The cathode efficiency, an important factor in commercial electroplating, is the ratio of the actual amount of metal deposited to that theoretically calculated multiplied by 100%.

Throwing Power. It has long been observed that plate thickness distribution does not always follow the primary current distribution. Throwing power, a term used to describe the relative plate thickness distribution, was initially defined as the improvement in percentage of the metal distribution ratio above the primary current distribution ratio. A test method for the measurement and mathematical expression of throwing power, called the Haring Cell test, is available (20). Plating solutions vary widely in ability to exhibit good throwing power. As current is increased in a given plating process, a point is reached where the metal ion being deposited is not replaced in the solution film nearest the surface fast enough and a concentration polarization occurs, shifting some of the current to the unpolarized, lower current density areas. The effect is to reduce the plating rate in these higher current areas.

The values obtained using the Haring Cell test are only relative, but can be useful for comparison purposes. Copper cyanide plating solutions under a given set of operating conditions can give a throwing power value of 60%. On a particularly shaped part, the ratio of copper plate thickness was found to be less than 2:1, highest-to-lowest plate thickness. The same part, plated in a chromium plating solution having a −100% throwing power, had a thickness ratio of more than

20:1, and in an acid copper plating solution having about a 5–10% throwing power, had a thickness ratio of about 7:1.

A plating solution that exhibits a decrease in cathode efficiency with increasing current density exhibits better throwing power, ie, more even plate thickness distribution, than other solutions. Generally, the solutions having positive throwing power are those that contain some complexing agent for the metal ion being deposited. Complexing agents impede the transfer and reduction of the metal ion in the cathode film, promoting concentration polarization (see CHELATING AGENTS). Conversely, poorer throwing power is obtained from those plating solutions containing simple uncomplexed metal ion salts.

Examples of plating solutions having good throwing power include cyanide plating baths such as copper, zinc, cadmium, silver, and gold, and noncyanide alkaline zinc baths. Examples of poorer throwing power baths are acid baths such as copper, nickel, zinc, and hexavalent chromium.

Covering Power. The term covering power is often but erroneously used interchangeably with throwing power. These are two distinctively different terms (1), and a plating solution can have good covering power but poor throwing power. This is more often seen in barrel plating processes where the parts cover well but show wide thickness variations. Covering power refers to the lowest current density area where plating appears on a part. There are qualitative and semiquantitative tests for covering power, but no standard method is described by ASTM. One method simulates plating a tubular part by rolling a metal foil into a tubular shape, plating the rolled foil, unrolling, and measuring the distance that the plating covered on the inside of the foil.

Current Density. For a given electroplating process, as the current density is increased on the work, the point where the deposit becomes rough, coarse-grained, and takes on what is termed a burned and generally unacceptable appearance is eventually reached. The range from the minimum covering power to just below this burn producing current is the usable current density range. In electroplating, this range is not the same for all metal plating baths, and is influenced by metal ion concentration, chemical compositions, temperature, agitation, and anode-to-cathode spacing, as well as by the shape of the work and how it is positioned. In production plants, it is usually preferred to plate at the highest possible current density to shorten production time. This is not always done, however, especially when using lower throwing power plating baths, because increasing current decreases throwing power even further. For parts that require more even deposit thicknesses, lower current densities and longer plating times are used.

The Plating Tank. Materials of construction for the plating tank and the required auxiliary equipment are chosen either to be totally inert to the plating solution, or lined with inert material to protect the tank. In all cases, it is preferable to have a nonconductive inner surface of the tank to provide electrical as well as chemical resistance. A more recent requirement in many states is a containment surrounding the plating tank area to prevent accidental chemical spills from entering the environment (see TANKS). For alkaline plating solutions, mild steel materials are used; in acid plating solutions, other materials are used, depending on the chemical composition of the plating bath. Titanium and various

stainless steel alloys, polytetrafluoroethylene (PTFE), Karbate, Hastalloys, zirconium alloys, and others are among the choices.

Sizing. There is no limit to plating tank size. Commercial electroplating lines have varied from liter-size tanks in benchtop wire plating lines to those holding 100,000 L and more. Tanks of over 250,000 L were used by the automobile industry when large amounts of plated trim were used. Tank width should allow for adequate anode-to-cathode spacing. In strip and wire lines, where the work is of a simple shape, anode-to-cathode spacing can be on the order of several millimeters to keep voltage requirements low. For plating work on racks, consideration should be given to the size and shape of the work to be plated. More complicated parts having deeply recessed areas require greater anode-to-cathode spacing.

In the simplest tank arrangement, there is a single work lane in the center and two anode bars equidistant from the center. If only one side of a part were to be plated, there would be no need for the second anode bar. A double-lane tank arrangement has two work lanes having an anode bar between and anode bars on the outside. Each anode is equidistant to the center of each work lane. Plating lines having more than double-lane plating tanks have been used, but these are much less common. The exception is those for wire lines. No standard rules appear to be followed in sizing tanks for rack plating parts having deeply recessed areas. Most of the time the part is made to fit whatever size tank is available. Fewer control and quality problems arise using anode-to-cathode spacing of 40 cm, rather than 15–20 cm, especially when plating parts with deeply recessed areas.

Plating tank depth requirements have changed. Plating tanks were historically much deeper than the length of the plating racks used, allowing for a substantial settling zone for particles that entered the plating solution from whatever source. Deeper tanks also allow room for installing pipe lines for filter headers, solution agitation, or air lines for air agitation. Rack plating tanks having a freeboard of at least 20 cm and 30–60 cm deeper than the longest rack would reach, give a less troublesome plating tank. The length of the plating tank is related to production requirements, and whether the tank is part of a conveyorized automatic system.

Busbars. Fitting the tank for d-c power is usually accomplished using round copper busbars, both for supporting the anodes and the work or cathodes. Size of the copper bus is determined by the amount of current flow expected; 1000 amperes requires about 6.5 cm^2 of cross-sectional area. The bus is insulated from the tank, and any other sources of grounding, and connected to the d-c power supply. Shorter distances from the tank as well as fewer electrical connections keeps the voltage drop to a minimum.

Filters. Continuously filtering plating solutions are becoming much more common, except for hexavalent chromium plating solutions. Baths are filtered to remove any fine particulate matter that could codeposit with the electroplate and cause roughness. Inlets to the filter(s) are usually located near the bottom of the plating tank, often in several areas or through a perforated header-pipe. The discharge is best placed near the top of the solution and directed horizontally. The filter flow is a function of retention size among other factors. Depending on the kind of plating bath and quality requirements, the filter retention size may vary from about 25 μm down to 0.2 μm. Platers refer to filter capacity as the tank turnovers per hour; the media retention should be included. A filter turning over

five-tank volumes per hour through a 15-μm media would do less than one turnover through a 1-μm media. Filter media has to be chosen carefully to avoid introducing any soluble impurities and to avoid dissolving any of the media itself.

Heating and Cooling. In some plating tanks heating or cooling is required preferably using a means of automatic control. Heating coils, plate coils, and other forms of immersion heaters are placed along a tank wall, preferably in an area that has good solution agitation. Heating can also be accomplished using external heat exchangers where the solution is pumped from the plating tank. In-tank heaters have to be properly located and insulated to avoid becoming part of the plating electrical circuit. Smaller tanks are often heated with quartz electric heaters. Steam (qv) coils and steam-heated external heat exchangers are used in large installations (see HEAT-EXCHANGE TECHNOLOGY).

Cooling is required in some plating solutions. High currents in relatively smaller solution volumes often bring about rising temperatures and solutions which can require cooling to continue, even if heating was required to begin plating. Other solutions require cooler than ambient temperature to perform properly. Cooling can be accomplished using cooling water coils, if demand is not high, or refrigeration units, commonly called chillers (see REFRIGERATION AND REFRIGERANTS).

Temperature control is important to all electroplating baths where good quality is required, because many properties are affected with only a few degrees of temperature change. Although a given plating bath may operate over a wide temperature range, it most often has a much narrower range where the desired properties are maximized. It is common practice to specify room temperature as a plating solution's operating parameter. In most cases this is too broad a range for good consistent quality. The preferred range is 5°C or less from a set temperature. An automatic temperature control is a considerable benefit to quality plating.

Anodes. There are two types of anodes: soluble and insoluble. Most electroplating baths use one or the other specifically; however, a few baths use either or both. Chromic acid plating baths use insoluble anodes; alkaline zinc cyanide baths use both; noncyanide alkaline zincs may use either. Soluble anodes are designed to dissolve efficiently with current flow and preferably, not to dissolve when the system is idle. A plating solution having the anode efficiency close to the cathode efficiency provides a balanced process that has fewer control problems and is less costly. If the anode efficiency is much greater than the cathode efficiency and there are only small solution losses, the dissolved metal concentration rises until at some time the bath has to be diluted back or the excess metal has to be reduced by some other means. If the anode efficiency is less than the cathode efficiency, the dissolved metal decreases, pH decreases, and eventually metal salt additions and other solution corrections are required. Based on the cost of metal, it is usually considerably more economical to plate from the anode rather than add metal salt. Copper cyanide, for example, costs about twice as much to add than to dissolve a comparable amount of copper anode. Additionally, the anion added with the metal salt may build up in the plating solution.

Faraday's Law applies to the anode as well as to the cathode; ie, the total reaction at the anode is proportional to the current, and much like the cathode, the anode efficiency varies with the current density. As the current on the anode

is increased, the anode efficiency decreases, slightly at first, until it reaches a point at which the anode metal cannot dissolve fast enough through the anode film. The first stage of dissolution for the soluble anode is the oxidation of the metal followed by dissolution of the oxide. When the oxide dissolution rate is less than the oxidation rate, polarization of the anode takes place. The oxide film builds up in sufficient thickness to form an insulating coating, and the current decreases rapidly. The thick anode films can dislodge at the reduced current and remain as particulate matter until they slowly redissolve. As particulate matter, the dislodged anode films form a significant source of roughness because they can co-deposit with the metal on the work before redissolving. While the anode is polarized, oxygen and other gasses can be given off from the anode. Solutions containing chlorides or bromides can emit chlorine or bromine, which are hazardous. Anode current densities should be maintained well below the point at which polarization occurs. This can be accomplished by increasing the anode area and lowering the current.

Agitation of the solution around the anodes and some chemical variations can increase the anode current density range before polarization. Lower pH and chloride ion have been used to improve anode corrosion in acid nickel baths. Higher free cyanide, Rochelle salts (sodium potassium tartrate), and proprietary substitutes improve anode efficiency in cyanide copper solutions. Higher alkalinity improves zinc anode corrosion in the alkaline zinc solutions; lower pH increases zinc anode corrosion in acidic chloride zinc solutions. Some platers use anode bags to prevent particulate anode and anode film material from reaching the work. However, the solution flow through the bag material may be inadequate and add to the polarization problem. The weave opening of the bag material is important to maximize solution flow without passing excessive particulates. Anode bags must be replaced once plugged.

Soluble anode materials are not always a pure metal. In acid, low chloride nickel solutions, pure nickel does not corrode well, and small amounts of specific impurities are added to make the nickel more active, allowing more efficient dissolution. For example, since the early 1960s, nickel anode material containing a small amount of nickel sulfide [*16812-54-7*], NiS, has been commercially available and important in nickel sulfamate [*13770-85-3*], $Ni(H_2NO_3S)_2$, plating baths. These anodes corrode at a lower potential then pure nickel or other nickel anode materials (see NICKEL AND NICKEL ALLOYS).

Copper anodes for use in acid copper plating solutions preferably contain a small amount of phosphorus [*7723-14-0*], usually 0.03–0.04 wt %, which retards chemical dissolution of the copper and thus the subsequent copper build-up. Typically, acid copper plating solutions increase in copper and require periodic dilution. Additionally, additives for brightening acid copper baths tend to last longer in plating tanks using phosphorized copper anodes. In cyanide copper solutions, phosphorized copper anodes should not be used.

Since the 1960s titanium mesh anode baskets have been used (21), especially in nickel plating solutions. Nickel anodes in the form of small round buttons and pellets combined with the titanium anode basket allows a constant anode area to be maintained with a minimum of effort.

Insoluble anodes are used exclusively in some plating baths. Chromium plating solutions utilize lead–tin, lead–antimony, or lead anodes. Gold and other

precious metal plating processes use stainless steel anodes, keeping inventory costs down. Other plating processes make use of insoluble anodes, on occasion, either in an effort to reduce metal ion buildup or as an auxiliary anode to direct the current into recessed or low current density areas. Platinum plated titanium and platinum plated niobium insoluble auxiliary anodes are often used in decorative plating lines for plating complex-shaped parts.

Whenever insoluble anodes are used, the pH of the plating solution decreases along with the metal ion concentration. In some plating baths, a portion of the anodes is replaced with insoluble anodes in order to prevent metal ion buildup or to reduce metal ion concentration. Lead anodes have been used in acid copper sulfate baths, and steel anodes have been used in alkaline plating baths.

The use of insoluble anodes can also result in side effects. In alkaline cyanide solutions, the generation and buildup of carbonates is accelerated remarkably, along with a significant reduction in alkalinity. In acid solutions the pH decreases as well, requiring frequent adjustments. In sulfamate nickel plating solutions, insoluble anodes, and even slightly passive soluble anodes, partially oxidize the sulfamate ion to form sulfur-bearing compounds which change the character and performance of the deposit (22).

d-c Power Supplies. The Daniell cells and batteries of the mid-nineteenth century, replaced by motor-generator sets in the first half of the twentieth century, have given way to solid-state silicon rectifiers. A variety of modifications in power supplies has become available. Stepless controls, constant current, and constant voltage are popular. Automatic current manipulations are also getting more use. Current interruption cycles where the current is periodically discontinued have been used in alkaline baths. Cycles on the order of 10 seconds on to 2 seconds off have been employed (15) in cyanide copper baths using a variety of time and current density cycles. One system uses about 45–60 s at 500 A/m^2 and 15–20 s reverse polarity at about 200 A/m^2. The newer forms of current manipulation are called pulse cycles because the cycle is typically on the order of milliseconds. A number of variations are possible (23).

The d-c output from a rectifier can have a portion of modulation from the a-c input, called ripple. Modern rectifiers usually have 5–10% or less ripple at full load. High ripple can have some bad effects, especially in chromium plating where ripple can cause dullness and poor coverage. The exact amount of ripple to cause the problem varies with the chemical composition, and a finite figure is difficult to set. However, there is usually some effect when ripple exceeds about 20–30%. Some dullness has been encountered using alkaline noncyanide zinc plating baths, but few of the other plating solutions have been reported as being sensitive to ripple. In all cases, the d-c power supply needs a means of control, stepless preferred, and appropriate ammeter and voltmeter. Ampere-hour recorders are convenient for making additions and keeping records.

Preparation for Plating

Preparation cycles vary depending on the particular substrate being electroplated. High carbon steels, low carbon steels, free-machining steels (lead or bismuth), HSLA steels, stainless steels, cast-iron, and high nickel alloys all require

special considerations in preplate treatments, as do the many nonferrous alloys and various plastic substrates. Often only slight variations in substrate composition significantly influence the preparation process. Heat treating variations also contribute to the complications in preparation. Determining an optimum preparation process for a given material often becomes a matter of trial and error. Some guidelines can be found in the literature (24,25) and from suppliers of proprietary preparation products. Several ASTM guides are

ASTM guide no.	Title
B253	*Preparation of Aluminum Alloys for Electroplating*
B322	*Cleaning Metals Prior to Electroplating*
	Practices for preparation of and electroplating on:
B630	*Chromium (Electrodeposits) on Chromium*
B281	*Copper and Copper-Base Alloys*
B320	*Iron Castings*
B319	*Lead and Lead Alloys*
B480	*Magnesium and Magnesium Alloys*
B629	*Molybdenum and Molybdenum Alloys*
B558	*Nickel Alloys*
B343	*Nickel (Electrodeposits) with Nickel*
B727	*Plastic Materials*
B242	*Steel, High Carbon*
B183	*Steel, Low Carbon*
B254	*Steel, Stainless*
B481	*Titanium and Titanium Alloys*
B482	*Tungsten and Tungsten Alloys*
B252	*Zinc Alloy Die Castings*

Poor preparation of the substrate can result in loss of adhesion, pitting, roughness, lower corrosion resistance, smears, and stains. Because electroplating takes place at the exact molecular surface of a work, it is important that the substrate surface be absolutely clean and receptive to the plating. In the effort to get the substrate into this condition, several separate steps may be required, and it is in these cleaning steps that most of the problems associated with plating arise.

Cleaning Methods. The soils encountered in electroplating processes can be organic, eg, oils, greases, and other cleaning compounds, and also inorganic, such as oxides and heat-treat scales. Some plating baths can clean surfaces and thus tolerate minimally cleaned surfaces; others need surfaces cleaned to near perfection. Chromium plating from chromic acid solutions is a good example of the former. In practice, some hard-chromium platers depend on the strong oxidizing nature of the chromic acid to remove residual oils. A short period of reverse current before plating provides an etched surface, often clean enough to plate. Another plating bath that possesses good cleaning properties is the high cyanide zinc plating solution. Historically little or no cleaning was used when barrel-plat-

ing in high cyanide zinc (or cadmium) plating solutions. Work would be tumbled without current in the plating solution until clean enough to plate. Quality, however, was not always guaranteed. Use of high cyanide zinc solutions has been in decline since the late 1960s primarily because of environmental regulations and the high cost of waste management.

The majority of plating baths require excellent cleaning. Substrate surfaces have to be free of even the slightest of soil-containing films or oxides as the work enters the plating solution. No simple, universal cleaning cycle exists for electroplating. Several methods and cleaning solutions may be used in a single-plating process (26,27).

Mechanical Cleaning. Parts should go through an alkaline cleaning step to remove organic soils before mechanical cleaning, which employs some form of abrasion. Dry blasting uses sand, aluminum oxide or silicon carbide grits, glass beads, or similar abrasives (qv). Wet blasting, vapor honing, wet tumbling with abrasive media, and vibratory finishing are also used. These methods are often required to remove heavier heat-treat scales. Alternatively, a strong pickling acid treatment, which has the severe disadvantage of promoting hydrogen embrittlement especially in hardened steels, must be used.

Solvent Cleaning and Vapor Degreasing. Heavy organic soils of many types including waxes are removed by solvent cleaning and vapor degreasing. The latter also results in dry parts, but because solvents such as the chlorinated hydrocarbons and chlorofluorocarbons (CFCs) are employed, usage has declined and is expected to continue to decline (see CHLOROCARBONS AND CHLOROHYDROCARBONS). In many cases, aqueous cleaning is being substituted. Vapor degreasing equipment for preventing loss of the volatile solvents has been undergoing improvement, however, in an effort to allow continued use. The 1990 Clean Air Act in the United States has set a timetable for unilaterally eradicating such materials as the CFCs and the chlorinated hydrocarbons, eg, methyl chloroform [*71-55-6*] (1,1,1-trichloroethane). In 1989, 50,000 vapor degreaser installations in the United States used about 260,000 metric tons of chlorinated solvents of which 60% was methyl chloroform (28). The number of degreasers used only in electroplating is not known, but most plating plants had at least one vapor degreaser or solvent cleaning tank available.

Diphase Cleaning. Use of an organic solvent top layer over a mild aqueous cleaner solution was popular for aiding in the removal of buffing compounds, especially on zinc base die castings. Use of this diphase cleaning has declined with the decline in buffed zinc castings.

Spray Cleaning. The advantages of spray cleaning are high agitation and physical force. The limitations are in focusing the sprays to hit all surfaces and in having to limit spray composition to nonfoaming constituents. Spray cleaning use has also declined because of the decline in plating of buffed substrates.

Ultrasonic Cleaning. Both organic solvents and aqueous cleaners can be used in ultrasonic cleaning tanks. Ultrasonic rinsing has been helpful in processing porous substrates. Although the chemical costs can be low, equipment costs are not. The use of ultrasonics (qv) has grown, but not significantly.

Soak Cleaning. A common method in plating plants is soak cleaning, which is the first immersion cleaning step on the plating line. Soak cleaners can be characterized as alkaline or acid. Alkaline is the most common. Formulations for

alkaline soak cleaners can contain some or all of the following: sodium hydroxide, sodium carbonate, sodium silicates, trisodium phosphate, tetrasodium pyrophosphate, borax, sodium gluconate or sodium heptonate, and minor amounts of chelating agents (qv) such as EDTA or NTA. In addition, formulations can contain soaps, although these are becoming less common, and other surface-active compounds. Surface-active components may be detergents, wetting agents, or surfactants (qv). Other minor constituents may include defoamers (qv), dispersants (qv), which prevent redeposition of soil; and materials that aid in rinsing, solubilizing, or inhibiting attack on the substrate. Some formulations substitute potassium salts for the sodium for increased solubility at an increase in cost. Whereas typical formulations can be found in the literature, most plating plants utilize proprietary cleaning compounds formulated by suppliers specializing in cleaning compounds for the plating industry.

Soak cleaner formulations have been modified over the years. Older formulas contained higher caustic contents and required operation at high concentrations and high temperatures, often at a rolling boil. For some stubborn soils such as waxes (qv), this type of cleaner still finds use. Generally, the trend has been toward greater use of surfactants, lower temperature operation, and lower caustic contents. Most of the time, the plating plant has no control over the type and quantity of soil on the work received. These soils are usually neither single compounds, nor easily identifiable. Besides dirt, typical soils are metal-working compounds such as rust preventatives, forming compounds, cutting fluids, die lubricants, and stamping oils. Soils introduced from improved metal-working often require new cleaner formulations.

Cleaning is accomplished by one or more of several mechanisms, eg, saponification, solubilization, emulsification, wetting, sequestration, and deflocculation. In soak cleaner formulations, there is usually both an inorganic portion and an organic one. Optimum concentrations and operating temperatures exist for the various cleaner blends in a working bath. Higher temperatures have an expected benefit in removing soils because of increased activity of the components and increased reaction rates. The maximum performance of a cleaner, however, is not necessarily at the highest temperature. Surfactants are typically less soluble in solutions having higher salt contents and at higher temperatures. When the solubility limit of the surfactant is exceeded, some of the surfactant separates and the solution becomes turbid. Under these conditions, the separated surfactant agglomerates and usually collects in oily appearing masses on the surface of the cleaner tank. At the first sign of turbidity, the cleaner is said to behave almost as a diphase cleaner, the surfactant acting more like an oil-loving solvent. It is at just below this cloud point that most cleaners perform best and most economically.

The Water-Break Test. It is the nature of surfactants to be substantive, ie, have high attraction to solid surfaces. Additionally, oils are very substantive. Thus, concentration of surfactant on the surface of the work is greater than in the body of the solution. The surfactant is also tenacious and difficult to rinse. In the course of removing organic, oil-like soils from the work surface, some of the soil is solubilized by the surfactants, but the resultant oil–surfactant mixture still retains some of the substantive properties of the surfactant, ie, it has become water-soluble, but clings. A common visual test to determine cleanliness of the work is to observe how the surface rinses; if the surfaces drain evenly when rinsed

using clean water, holding a sheet of water, it is said to be water-break-free and clean. If rinse water beads up in droplets on the part surface or does not hold a sheet of water as it drains, it is said to water-break and is in need of additional cleaning. However, if this test is run on surfaces having surfactant-solubilized oil films, the water-break test is not definitive. Thus, the part has to be thoroughly rinsed, acid dipped in clean acid, and thoroughly rinsed again before using the water-break test. Neither does the water-break test reliably detect inorganic films. Thus, the water-break test indicates when a part is dirty, but not necessarily when it is clean.

Controlling Soak Cleaners. The relationship of an optimum temperature-concentration value for good cleaning requires better temperature control and more frequent analysis and adjustments than is the rule in many plating plants. Larger soak cleaner tanks are typically heated with internal steam coils; smaller tanks may be electrically heated. Direct-fired tanks are becoming much less common. Heating a solution is much more efficient if the solution is agitated, avoiding localized overheating, temperature stratification, and resulting in improved heat-transfer. External heat exchangers having adequate pumping rates are much preferred over still tanks. An added benefit is the improved cleaning action with agitation.

Automatic temperature controllers are recommended, and should be capable of holding a set temperature within a range of 4°C or less. Concentrations of cleaning solutions can be controlled through simple titrations. Many suppliers of proprietary cleaners provide simple test kits that can be used at tankside by unskilled help. Frequency of analyses depends on the usage of the cleaner tank and the drag-out. It should be frequent enough so that required additions should be less than 10% of the set concentration. This could occur once per day with high usage, or once per week at lower use. Additions should be kept reasonably small and spaced out over a reasonable period to avoid sudden changes. When using dry, powdered, or crystalline cleaning compounds, additions to hot cleaner tanks can react violently, spewing hot alkali out of the tank. It is safer to make additions at the end of a shift, when the solution can be cooled and additions sprinkled in slowly using good agitation. The use of liquid cleaner concentrates eliminates this hazard, and probably accounts for much of the increased interest in liquids.

Improvements. Soak cleaner tanks equipped with an overflow weir and a sump, plumbed through the bottom of the sump to a recirculating pump provide several benefits, including extra agitation of the solution; aid in heat transfer; minimal temperature stratification throughout the tank; a constant level; aid in keeping a more constant cleaner concentration; an area for collecting and removing separated oils (in the sump) and an area to install an oil-separating device; and an area for making cleaning compound additions.

Further, more attention is being given to the oil content of cleaner wastes. This attention is expected to increase substantially in the near future as tighter environmental regulations come into play.

Cleaners. Cleaner formulations can be classified with respect to the ability to emulsify oils, keep them in solution; or to reject oils, split them out of solution. The latter type loosens the oil, and the separated oil does not dissolve but is rejected, and usually floats to the top of the cleaner solution. For the cleaner that rejects oil, the tank needs to be skimmed constantly. This is most easily accom-

plished using the overflow weir, sump, and recirculating pump arrangement. Oil-rejecting cleaners last longer.

When using emulsifying soak cleaners, a limit is reached in use where the oil-holding capacity is exceeded. This capacity varies with the formulation, but eventually the contaminated cleaner begins to act as a soil. Some emulsifying formulations are capable of rejecting some oil after reaching the limit on emulsifying, and properly skimmed, some of these cleaner tanks have lasted for years. Purification of oil-laden cleaners has been carried out successfully in production tests. Comparative tests run in the 1950s using periodic activated carbon treatment on one cleaner line resulted in increased cleaner tank life on that line.

Acid Soak Cleaners. Benefits in processing steel using acid soak cleaners include the ability to both clean and derust in the same tank. Acid soak cleaners, which are less popular, more expensive, and more corrosive than alkaline cleaners, have found use in some lines when plating on aluminum alloys and copper alloys. Formulations for acidic soak cleaners have not shown high soil-load capacity, and are used for relatively clean stock. More common formulas are based on phosphoric acid mixtures with surfactants and organic emulsifying agents. Acid soak cleaners for aluminum may contain nitric acid mixtures. Excellent rinsing is required after these to prevent any carryover into sensitive plating solutions.

Removing the soak cleaner film from the work, whether it is alkaline or acid, takes a good portion of the preplate process cycle. If the soak cleaner has performed well, the organic soils have been solubilized completely, and the water-insoluble soil film originally on the work has been replaced with a surface-active but water-soluble film. This film now contains the elements of the cleaner along with the cleaner–soil constituents. Rinsing in clean water is essential to reducing this tenacious film.

Electrocleaning. Application of a low voltage d-c current through a conductive alkaline cleaning solution using the work as one electrode and usually steel suspended from busbars on either side of the work as the other, is called electrocleaning. The equipment and process has many of the elements of the electroplating process. When the work is connected to the positive pole of the rectifier, the process is referred to as anodic or reverse cleaning, ie, it is reverse to electroplating. Oxygen generated in copious quantities on the work provides agitation at the immediate surface of the soil–part interface. Anodic cleaning is used primarily on steel. Special precautions and milder conditions are used when cleaning zinc-based die castings and copper or copper alloys.

Cathodic or direct cleaning uses the work as the cathode; hydrogen is generated at the work surface. The reducing environment on the part often helps in loosening stubborn scales. Direct current prevents attack of the substrate, but metallic impurities in the cleaning solution may deposit as nonadherent smuts. Direct cleaning is used in the preparatory process for many difficult-to-plate metal substrates. Copper and copper alloys do not tarnish with cathodic cleaning. Thus direct cleaning is sometimes used for most of the time cycle, then the polarity switched to anodic cleaning for the last 30 seconds.

Cathodic cleaning of hardened steels can lead to excessive hydrogen embrittlement. Usually, cathodic cleaning has been avoided on steels having a Rockwell hardness (HRC) greater than about 40 HRC; more recently, this has been lowered

to 35 HRC. Hydrogen embrittlement can be relieved by baking for a minimum of 3 hours at 190 ± 15°C (29). This baking process is required after plating hardened steel regardless of how the part was cleaned, but it is considered good practice to minimize the introduction of hydrogen wherever possible. The ASTM guides, such as those for engineering chromium (30) and autocatalytic nickel–phosphorus (31), give explicit baking times and temperatures. Specifications applicable to each particular process should be followed.

Surfactants in Electrocleaners. Surfactants typically consist of a long-chain hydrocarbon molecule having a solubilizing or water-loving group which can be anionic, cationic, or nonionic when solubilized. Thousands of surfactant products are marketed, usually under trade names (32). In commercially formulated electrocleaners, surfactants are usually anionic, and often mixtures of anionics and nonionics.

Many plating plants use electrocleaners both anodically and cathodically through the use of reversing switches or in two separate tanks. Not all anionic surfactants do well in cathodic cleaning. Proprietary electrocleaners are commonly used and highly recommended.

Operation and Function. Overheating electrocleaner solutions can result in surfactant loss, as for soak cleaners. Tank construction and electrodes can be steel. Current distribution is easier to optimize and control when the inside of the electrocleaner tank is lined with an inert, nonconductive lining. An overflow weir, sump, and recirculating pump are recommended. When plating barrels are used electrocleaning can take 10 minutes or more compared to 1 minute on a plating rack. Higher voltages are also needed.

When an electrocleaner follows a soak cleaning step, its main function is to remove the soak cleaner film left on the part. If the soak cleaner has done its job, the soil remaining on the part has been made more soluble. There are some significant differences in the chemical compositions of electrocleaners and soak cleaners. Electrocleaners are not usually designed to remove heavy organic soils, and are formulated using much lower concentrations of surfactants. Excess surfactants should be avoided, because the more surfactant, the harder it is to rinse. The goal is to get the cleaned part to the plating tank without any residual wetting agent films.

A secondary function of the electrocleaner is to aid in removing light smuts or scale. Complexing agents may assist in this function, but the possible effect on the waste treatment process has to be considered. Cyanide, an effective smut remover, is no longer used. Heavier carbon smut, especially that from etching of steel substrates, is difficult to remove. This problem is more pronounced in high carbon steels. It is preferable to minimize etching.

Electrocleaners are used cathodically to activate normally passive substrates such as nickel, nickel alloys, and stainless steels. When cleaned anodically, these materials become much more difficult to activate. Unless fully activated, little or no adhesion is obtained. Anodic cleaning dissolves chromium and is commonly used for stripping chromium deposits. The presence of dissolved chromium in the electrocleaner is undesirable and causes uneven etching, leaving patterns that are still visible after plating. Sodium hydrosulfite in small quantities is sometimes used to reduce the chromium. Proprietary compounds based on reducing sugars are safer. Chromium is a common impurity in nickel–chromium decorative

plating lines because the plating rack carries the chromium, either as the solution or as chromium-plated contact tips or both, back through the cleaning cycle. Less well-known but capable of causing problems, stainless steels can be anodically attacked, albeit slowly, in strong alkaline solutions and chromium dissolved from the alloy surface. Stainless steel anodes in alkaline solutions are sometimes, erroneously recommended; mild steel is usually adequate.

Alkaline Derusting. Adding highly alkaline solutions that can dissolve light rust is a form of electrocleaning dealing with inorganic soils on steel. Applying a d-c current increases this capability to a practical degree. Further improvements in the rate of removal are possible with the addition of certain complexing agents and the use of periodic current reversal cycles. A typical formulation for an alkaline deruster is about 80% caustic soda and 20% sodium gluconate of which 100–250 g/L are used. Elevated (65–90°C) temperatures aid conductivity and reaction rates. Current density should be 500 A/m^2 or more with current cycles of about 60 seconds with the work anodic and 30 seconds cathodic. Work is removed on the anodic cycle. Time depends on several factors, and can be as long as several minutes. Some rust scales may require acid pickling to remove them completely.

Cleaning Cycles. Cleaning cycles usually start with a soak cleaner followed by electrocleaning. If work is heavily soiled, however, a precleaning step may be required. Buffing compound residues fall into this class. Solvents, diphase mixes, power washers, and other presoaks are used. If instead work is received in a fairly clean state, the high surfactant soak cleaner is omitted from the cleaning cycle. The electrocleaner formulation has less tendency toward leaving substantive films and is preferred. In some plating lines, there are more problems removing the soil-remover than in removing the soil.

Combination soak-and-electrocleaner products are touted for use when normal soak cleaner is too much and a normal electrocleaner is too little. These combination cleaners are often electrocleaners with additional surfactants. The results are often hard-to-rinse electrocleaner or a low capacity soak. The term heavy-duty, often used to describe cleaners, can refer to high caustic content or to good soil-removing, high soil-load capacity.

Rinsing. Rinsing is extremely important to the overall operation of a plating line. Work traveling from a processing solution carries a film on its surface from that solution. This amount of drag-out varies with the shape and surface area of the part, along with the nature of the solution. Drag-out can reach considerable quantities, eg, from 20–80 mL/m^2 (33).

To reduce costs of the more expensive plating solutions and decrease the amount of hazardous or regulated material in a waste stream, recovery and reuse of the drag-out is a common practice. This is done by closing off the water flow to the first rinse tank following the process tank, and periodically returning the accumulated solution to the process tank. Used after nickel plating, a single saver-rinse can recover 60% of the nickel dragged out. This increases to 80% if two saver-rinses are used. In precious metal plating lines, there are several nonflowing rinse tanks (saver-rinses) following the plating tank. In chromium plating, the drag-out is processed through an evaporator before returning it to the plating tank.

Recycling drag-out losses can have the unwanted effect of concentrating impurities in the plating tank. Thus, it is good practice to purify the drag-out before returning it to the process tank. Filtration (qv) through activated carbon is helpful on most nonchromium solutions; cation exchange has been useful with chromic acid drag-out solutions, before it is evaporated. The impurity concentrating potential makes it even more important to use effective prerinsing with good quality water, ie, before work enters the process tank. Each processing solution is a serious contaminant to the next.

Good rinsing requires good water, not too cold, vigorous agitation, and time. Many seasonal plating problems, especially in northern climates, can be traced to colder winter rinses. Water at 5–7°C is a poor rinse; water at 30–35°C gives a good rinse. Time and agitation allow the rinse water to penetrate, to dilute, and remove the often substantive films. A two-minute dip in each agitated rinse has often produced good work having good adhesion, when one minute dips failed.

Dual- or triple-rinse tanks follow most process solutions. Additionally, many lines utilize counterflow or cascade rinsing with the multiple tanks plumbed so freshwater flows from one tank to the next counter to the direction of the work. This method of conserving water is recommended procedure for all plating lines. A double counterflow rinse of 70 L/h could give equivalent rinsing to 2250 L/h using a single rinse in reducing a concentrated solution of 2200 g/L to 7.5 g/L. For a triple counterflow rinse, the rate dropped to 30 L/h (34).

An example of rinse stages in a relatively simple plating cycle for plating an engineering nickel on a common, low carbon steel having varying soil conditions is shown in Table 1. On the longer suggested cycle for heavily soiled, rusted stock, 13 of the 19 stations are some form of rinse.

Spray rinsing can be efficient because of the impingement; misting at the exit of a processing tank can reduce drag-out. Barrel plating lines need much more rinsing time and special consideration because of the relatively high drag-out rates.

Acid Dips and Acid Pickles. Acids are used to remove inorganic soils. A distinction is made between acid dips and acid pickles. Where there is no rust or scales, a dilute acid dip is used for activation and as a rinse aid. Caustic residues from cleaners are notoriously difficult to remove with water rinsing alone. By contrast, strong acid pickles are used to remove rust and scale.

The most commonly used acids in preplate processes are hydrochloric acid, HCl, more common for rust and scale removal, and sulfuric acid, H_2SO_4 (see HYDROGEN CHLORIDE; SULFURIC ACID AND SULFUR TRIOXIDE). Usually 30–60% by volume of 20° Bé hydrochloric acid is used. At room temperature, hydrochloric acid removes complex iron oxide scales in a shorter time than sulfuric acid, produces a smoother, whiter surface, and holds more iron in solution. On the negative side, hydrochloric acid is more volatile and gives off corrosive fumes even at room temperatures. Ventilation is required. Hydrochloric acid pickles are operated at room temperature, always below 40°C. Sulfuric acid solutions increase in pickling rate with concentration up to about 25% strength; rates then decrease to essentially zero at full strength sulfuric acid. The pickling rate of 5% sulfuric acid is about 10 times faster at 60°C than at 18°C; at 10% sulfuric acid, this increases to 15 times faster (35).

Table 1. Processing Cycle for Engineering Nickel on Low Carbon Steel[a]

Station	Heavy soil rust and scale	Heavy soil no rust or scale	Light soil no rust
1	soak clean[b]	soak clean[b]	
2	rinse	rinse	
3	electroclean	electroclean	electroclean
4	rinse	rinse	rinse
5	rinse	rinse	rinse
6	acid pickle[c]	acid dip[c]	acid dip[c]
7	rinse	rinse	rinse
8	rinse	rinse	rinse
9	electroclean[d]	[d]	[d]
10	rinse		
11	rinse		
12	acid dip, mild		
13	rinse		
14	rinse		
15	nickel plate	nickel plate	nickel plate
16	saver-rinse	saver-rinse	saver-rinse
17	rinse	rinse	rinse
18	rinse	rinse	rinse
19	hot rinse and dry	hot rinse and dry	hot rinse and dry

[a]For high carbon (0.4% C and more), the desmutting steps 9–14 are required.
[b]Preclean, option before soak.
[c]For high carbon steel, keep mild as possible.
[d]Alkaline desmut option.

Heat scales and rust on steel are not of even composition or thickness, and parts are subject to uneven pickling. To minimize over-etching, inhibitors are sometimes used to slow the attack on the clean steel. Many inhibitors produce strong adverse effects if carried into the plating solution. A second electrocleaning step is used after the pickle when inhibitors are employed.

Acid dips are more likely to be dilute sulfuric acid, 2–5% by volume of 66° Bé sulfuric acid. The hazards of handling and diluting sulfuric acid have spurred use of proprietary dry acid salts, a common ingredient of which is sodium bisulfate. Proprietary compounds may contain wetting agents that require good rinsing to remove. Other acids have been used for specific substrates. Leaded steels and leaded brasses use pickles and acid dips of fluoboric acid (see FLUORINE COMPOUNDS, INORGANIC). Sulfuric acid should be avoided on leaded alloys. Free-machining steels having about 0.5% lead in the surface are treated with 10–20% by volume of 42 wt% fluoboric acid to avoid formation of insoluble lead salts. When strong pickling action is not required, citric acid [77-29-9] and proprietary citric-based products work well for leaded steel and copper alloys. Modified citric acid dips are being used successfully on steels such as chromium–molybdenum and nickel–chromium–molybdenum steels. Citric acid has been used in processing zinc-base die castings. Sulfamic acid, a strong acid which forms soluble lead compounds, is often mentioned for use on lead or lead-containing alloys. Sulfamic acid

tends to bring out smut when used on high (>0.4%) carbon steels, and strong solutions decompose with time.

Acids containing fluoride, or mixtures of other acids and fluoride salts, are used on silicon-containing alloys. Sulfuric acid and ammonium acid fluoride mixtures are used on high silicon steels; nitric acid with ammonium acid fluoride is common in processing high silicon–aluminum alloys. Higher magnesium-containing aluminum alloys often are treated with dilute sulfuric acid; other aluminum alloys with nitric acid.

Chromic acid is seldom used in preplate acid dips, but has had special applications in other preplate treatments. Chromic acid pickles or prepickles are part of some processes for plating on certain magnesium alloys. Chromic acid-containing bright dips are sometimes part of the preplate treatment on copper alloys; and to a less extent on zinc-base die castings. In plating on plastic substrates, strong chromic acid solutions are used to etch the base for providing adhesion. Whenever chromic acid is used in the preplate process, it is important that no residual hexavalent chromium remains on the surface. Only a very small amount of chromic acid can yield poor adhesion and blistering, or stop the plating completely.

Electropickling. At times, electrolytic pickling is used; steel can be treated anodically in strong sulfuric acid, 70%. If the sulfuric acid is too dilute, anodic etching can be severe. In bright nickel plating of steel, pretreatment in a cathodic 5–10% sulfuric acid has reduced subsequent pitting of the nickel. Cathodic treatment prevents etching of the steel.

Cathodic treatment of steel parts in acids could be expected to contribute significantly to hydrogen embrittlement of the part if the steel has been previously heat treated to over 40 HRC. Cold-worked steel is susceptible at a lower hardness. Some work shows more embrittlement from the plating bath than from preplate treatments (36).

When plating any substrate less noble than copper, only a few mg/L of dissolved copper in the acid baths can adversely affect adhesion. Coatings can be too thin to be visible, yet contribute to poor adhesion. Small additions of thiourea have been used to prevent copper immersion, but it acts as a potent inhibitor, and work should be re-electrocleaned after the acid. Work should be exposed to the mildest acid treatments possible. Over-etching should be avoided.

Properties, Specifications, and Test Methods

Standard test methods are required to measure the properties of electroplated materials. Documents on plating specifications for many phases of the plating process are published by such organizations as the Federal government, the military, ASTM, ISO, SAE, etc. An excellent cross-index of these is available (37).

Plate Thickness. Thickness of the plate should always be specified as should the locations on the work where the thickness is to be measured. Generally, thicker deposits perform better, but there are notable exceptions. Mating parts, eg, fasteners having fine machine threads, are not usable if over plated. Machine-threads are usually plated to 10 μm or less, depending on tolerances. Additionally, gold-plate over nickel does not solder well if too thick; thus, gold is usually 1–2

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