ELECTROPLATING

1. Introduction

Electroplating is a specific type of surface finishing. Everyone has at one time or another, seen and handled electroplated objects, even if they were not aware of it. Some typical examples include kitchen and bathroom faucets, inexpensive jewelry, and the trim on some automobiles. There are thousands of other examples. There are three basic reasons for surface finishing/electroplating: (*1*) To improve appearance, (*2*) To slow or prevent corrosion (rust), and (*3*) To increase strength and resistance to wear (in the case of “engineering” finishes). An object may be processed for any or all of these reasons. The term electroplating means what it sounds, ie, the coating of an object with a thin layer of metal by use of electricity. The metals most often used are gold, silver, chromium, copper, nickel, tin, and zinc, but many others are used also. The object to be plated is usually made of different metal, but can be the same metal or a nonmetal, such as a plastic grille for an automobile.

Electroplating usually takes place in a “tank” of solution containing the metal to be deposited on an object. This metal is in a dissolved form called ions. An ion is an atom that has lost or gained one or more electrons and is thus electrically charged. One cannot see ions, but the solution may show a certain color; a nickel solution, eg, is typically emerald green. The deposited metal, however, will be metallic gray or silver in appearance.

Simply put, when those metallic chemicals dissolve in water, the metal atoms of these chemicals are freed to move about, but lose one or more electrons (negative charges) and, as a result, are positively charged. The object to be plated is negatively charged and attracts the positive metal ions, which then coat the object to be plated and regain the lost electrons to become metal again.

A practical example of this process may be the experiment that may be easily performed in which a key is plated with copper. The key (the cathode) is connected to the negative terminal of a battery and is placed in a solution of vinegar, a weak acid. The positive terminal of the battery is connected to a piece of copper (called the anode—and may be just a copper wire), which is placed in the solution. The acid slowly dissolves the wire, producing copper ions that are then attracted to the key, regaining their lost electrons and becoming copper metal again, but now in the form of a thin coating on the key. The battery forces all this to happen and prevents the deposited copper from redissolving.

Electroplating has, over recent decades, evolved from an art to an exact science. This development is seen as responsible for the ever-increasing number and widening types of applications of this branch of practical science and engineering. Some of the technological areas in which means and methods of electroplating constitute an essential component are all aspects of electronics: macro and micro, optics, optoelectronics, and sensors of most types, to name only a few. In addition a number of key industries such as the automobile industry (that uses, eg, chrome plating to enhance the corrosion resistance of metal parts) adopt the methods even where other methods, such as evaporation, sputtering, chemical vapor deposition (CVD), and the like are an option. That is so for reasons of economy and convenience. By way of illustration, it should be noted that modern electroplating equips the practitioner with the ability to predesign the properties of surfaces and in the case of electroforming those of the whole part. Furthermore, the ability to deposit very thin multilayers (less than a millionth of a cm) via electroplating represents yet a new avenue of producing new materials.

2. History

Before continuing with more detailed discussion of the subject at hand, a brief history of electroplating will be presented here. The early history of electroplating may be traced back to ~1800. A university professor, or in modern terms: a chemist, Luigi Brugnatelli is considered as the first person to apply an electrodeposition process to electroplate gold. Brugnatelli was a friend of Allisandro Volta (after whom the electric unit "volt" has been named) who had just a short time before discovered the chemical principles that would make possible the development of "voltaic" electrical cells. Volta's first actual demonstration of that was called "Voltaic Pile." As a consequence of this development, Brugnatelli's early work using voltaic electricity enabled him to experiment with various plating solutions. By 1805, he had refined his process enough to plate a fine layer of gold over large silver metal objects. He wrote in a letter to the *Belgian Journal of Physics and Chemistry* (later reprinted in Britain), which reads:

> *"I have lately gilt in a complete manner two large silver medals, by bringing them into communication by means of a steel wire, with a negative pole of a voltaic pile, and keeping them one after the other immersed in ammoniuret of gold newly made and well saturated."*

Unfortunately for Brugnatelli, a disagreement or falling out with the French Academy of Sciences, the leading scientific body of Europe at the time, prevented Brugnatelli's work from being published in the scientific journals of his day. His work remained largely unknown outside of his native Italy except for a small group of associates. By 1839, however, scientist in Britain as well as in Russia had independently devised metal deposition processes similar to those of Brugnatelli's for copper electroplating of printing press plates. By 1840, this discovery was adapted and refined by Henry and George Elkington of Birmingham, England for gold and silver plating. Collaborating with their partner John Wright and using formulas developed by the latter for potassium cyanide plating baths, the Elkingtons were able to have the first viable patents for gold and silver electroplating issued on their name. From Great Britain, the electroplating process for gold and silver quickly spread throughout the rest of Europe and later to the United States.

With the burgeoning knowledge and understanding of the subject of electrochemistry and its importance in understanding the processes of "electrodeposition" came the ability to deposit other metals. By the 1850s electroplating methods of bright nickel, brass, tin, and zinc were commercialized and were applied for engineering and specific commercial purposes. In time, the industrial age and financial capital had expanded from Great Britain to the rest of the world. As a result, electrodeposition processes were expanding in scope and found more and more usage in the production of a variety of goods and services.

While this expansion was taking place, no significant scientific discoveries were made until the emergence of the electronic industry in the mid 1940s of the last century. The only exceptions to this were improvements made to direct current power supplies that were/are used instead of batteries. Thus it is said that the years from 1870 to 1940 were a quiet period as far as electroplating was concerned, significant only in gradual improvement in larger scale manufacturing processes, anodic and cathodic reaction principles and plating bath formulas. During the later years of the 1940s, rediscovery of heavy gold plating for electronic components took place. In comparison to that, during the mid- to later-1950s, the usage of new and more "user friendly" plating baths based on acid formulas (rather than strongly poisonous cyanide based ones) were developed and introduced for large scale commercial use. In closing, this brief historic summary, one is to note that today a number of regulatory laws (enacted mainly in the 1970s), eg, concerning waste water emission and waste disposal, set the tone/direction for the electrodeposition/electroplating industry for the next 30 years.

Today, with the impressive progress and deeper understanding of the underlying electrochemical principles of electrodeposition, sophisticated plating baths formulas have been developed and are being routinely employed. Those provide much greater control over the working characteristics of the deposition process than hitherto. Layer thickness, performance of electroplated finishes is among the attributes that have been brought under strict control. New developments enable greater plating speed, better throwing power (the ability of a plating solution to produce a relatively uniform distribution of metal thickness upon a cathode of irregular shape), as well as reliable plated finishes. In addition, electroplating of materials such as platinum, osmium, and ruthenium are now broadly used in electronics for connectors, circuit boards, contacts, etc. The writer believes that new and innovative electroplating technology will facilitate the rapid expansion of the telecommunication industry. In general, the growth of the electronics industry as a whole, and the demand to support the expansion of its underlying infrastructure will continue to drive improvements worldwide in the electrodeposition/electroplating industry. To illustrate the possible directions of progress, we mention the need for further refinement and control of dc power supplies. Such progress should lead to further achievements in the electroplating and metal finishing industry. Last, but certainly not least, safer manufacturing methods and processes including wastewater recycling should reduce work place exposure to dangerous chemicals and waste by-products.

There has been a recent upsurge of interest in electrodeposition, which is due to three main factors/technologies:

- Metal deposition for the fabrication of integrated circuits.
- Deposition of magnetic recording devices (heads, disks).
- Deposition of multilayer structures.

By way of illustration we mention here that electrodeposition of copper for integrated circuit fabrication has been successfully used since 1997 for the production of interconnection lines down to $< 0.02\,\mu$ (micron $(\mu) =$ one-millionth of a meter) width. Electrodeposition methods represent a very attractive alternative to the hitherto conventional fabrication methods. As an aside it may be commented that the ASTM (1) chooses to make the very definition of electroplating somewhat restricted.

To put the foregoing in context, it is typical of this field that the first basic book (2) on the principles of electroplating and electroforming was published in the United States in 1924. An electroplaters society, The 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.

Progress in electroplating, particularly on the larger dimension objects, is also linked to improvements in materials of construction, 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 and steel finishes have helped significantly. Last, but not least, as mentioned above, the recent great strides toward full understanding of the detailed atomic level processes responsible for electroplating, makes it possible to apply the technics to ever more and more complex systems (eg, nanotechnology).

3. Materials

In general, any electrically conductive surface can be electroplated, however, specific techniques may be required to make a given surface electrically conductive. Many techniques may be used to metallize nonconductive surfaces and thus render them conductive and so receptive of electroplating. 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 a good portion of the volume in electroplating, there is a large and rapidly growing amount of plastic and other surfaces being plated, both for decorative trim as well as for many modern electronic applications. On a far smaller scale, other materials that are plated include wood, plaster, fibers and cloth materials, and plant and animal tissue, such as leaves, leather, paper, and seashells.

The metals commonly though not exclusively 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 have achieved only limited commercial use due to the stringent conditions (such as high temperature) required for successful results not to mention severe enviromential restrictions.

In addition to the metals listed above, many alloys are commercially electroplated, those include 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 somewhat lesser use include lead–indium, nickel–manganese, nickel–tungsten, palladium alloys, silver alloys, and zinc–manganese. Ternary and many other alloys can feasibly be electroplated, these have of late found commercial applications in the area of lead free solders (eg, Sn Ag X systems with X standing for one of the noble metals).

Still 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. Thus, eg, silicon carbide and other hard particles including diamond are codeposited with nickel to improve wear properties or to make cutting and grinding tools.

4. Economic Aspects

Electroplating is done less and less in job shops, where a customer's work is plated, and more and more in captive (in-house) shops. There were reported to be $\sim$7500 plating plants in the United States (4) in 1992. This is a decrease from the $\sim$12,000 reported by the same source in 1980. The reduction, particularly in the number of smaller job shops, is further evident from the 1997 number, which was down to 3399. This still continuing tendency is the consequence of a number of factors. Chief among those 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 $\sim$9000 members in 1992. That number stands at $\sim$7000 in 2003. Only a small number of colleges or universities offer full courses specifically in electroplating, a few do offer a degree in electrochemical engineering. Special courses, have been available from other sources, however (5), and the two technical societies, AESF and the American Society for Metals (ASM), offer intensive courses on electroplating.

Many captive(in-house) 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. To put matters in perspective, even back in 1997, the 14 largest electroplating job shop plants in the United States estimated annual sales totaling \$165 million, with $\sim$5300 employees. Ninety-four of the next larger shops reported 13,000 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 likely be $>$ \$1 billion.

4.1. Cadmium. In 1998, U.S. consumption of cadmium for coating was $\sim$300 t. Compare that to 1989, when U.S. consumption of cadmium for coatings was 1474 t (6), compared again to, 2089 t in 1979. Cadmium plating in 1989 amounted to ~15% of the total cadmium production. In 2000, it constituted only 8% of the total. Of the cadmium plated in 1989, 30% was for automotive parts, >22% for electronics, and 18% for industrial fasteners. Because of cadmium's high and well-publicized toxicity and very tight waste restrictions, there have been considerable efforts to develop alternative materials, and the quantities of cadmium used in electroplating are expected to decrease even further. The price of cadmium anodes in early 1993 was ~$1/kg. In 2000, it was ~$0.40.

4.2. Chromium. Worldwide consumption for functional uses of chromium is estimated at 15,000 metric tons. From 4000–4500 t of this is used in the United States; Europe is estimated to use ~3500 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 ~2270-t worldwide. Some 60% of this is used in North America, and ~900 t in Europe. A now relatively popular method in decorative chromium plating is based on trivalent instead of hexavalent chromium, and this is estimated to total ~15–20% of the decorative market and is expected to increase. Chromic acid is the hexavalent chromium source for plating solutions.

4.3. Copper. Copper consumed in electroplating and electroforming in the United States and Canada is estimated to be 136,050 t/year including, since 1983, the U.S. Government copper plating of the zinc and later the stainless steel penny used for coinage. This usage averages ~1000 t/year and could range up to 1500 t/year. In early 1993, copper prices were on the order of $3.50/kg. While subject to fluctuations it remains on the same order of magnitude even in early 2004.

4.4. Gold. Used both in decorative and electronic electroplating applications, ~27.5 t of gold were consumed in the United States in 1990. By 2000, an increase of ~15% has been noted (7). The electronics industry increases the demand for this metal annually, though not all in the form of electroplating. In all, the use of electroplated gold in a variety of different functions in the electronics industry has led (8) to many advances in our fundamental understanding of the electrodeposition process and new electroplating technologies over the past 25 years.

4.5. Silver. About 72.3 t of silver (which represents 30% of the total consumed) were electroplated in the United States in 1989. By 2000, this number rose by ~10% (9). Silver is used in dinnerware and hardware or functional applications. This usage is expected to grow modestly.

4.6. Nickel. Worldwide nickel used in electroplating has averaged ~63,500 t annually from 1980–1990 (10,11). It stands now (2004) ~88,000 t. Of this, the United States uses ~24,000 t/year, and Europe about the same quantity; Japan consumes ~12,000 t, and another 9000 t is used by the other Pacific rim countries. Canada and South America are reported to use ~5500 t annually. The rest is used by all other countries. Electroforming applications consume another 5500 t of nickel worldwide. About half of this electroforming is done in the United States and Canada. Nickel deposited from autocatalytic solutions (electroless) was estimated to account for 1600 t of nickel on a worldwide basis already in 1990 and it has grown considerably since then. The price of nickel stayed at about the same level as copper during the nineties (at ~$3.50/kg).

4.7. Tin. Application of tin on strip steel for can stock has decreased. Nevertheless, tin plating is still done in relativelly large volume, and tin plate for can stock was estimated at 11,750 t in 1990 (12). Additionally, 603 t of tin anodes were used for electroplating in electronic applications in the United States in 1990. That number decreased to 9150 t in 1999. The use of tin in solder manufacture is reported to exceed that used in can stock (12,13). The cost of tin in early 1993 was $7.50/kg. The price stayed flat until 1999.

4.8. Zinc. Suppliers of zinc electroplating chemicals seemed to feel in the past that zinc electroplating volumes would continue to grow. Thus zinc was priced at $1.50/kg in early 1993 and it stood on $1.70/kg at the end of 1998. More recently, however, electroplated zinc alloys have been promoted by electroplating practitioners. As a consequence, the price of the metal stood at $1.25 in 2000.

5. Uses

Electroplated objects and materials are required for a number of specific properties or functions. There is in this, of course, some overlap; eg, a decorative use certainly requires some degree of corrosion resistance. Various usages and the principal plating metals employed are as listed in Table 1. There are also smaller amounts of other metals and alloys used for specific applications.

5.1. Decoration. Decorative deposits offer a pleasing, reflective appearance while also providing corrosion resistance, lubricity, and durability. Decorative chromium plating may be the most familiar electroplating application.

Table 1. **Uses and Typical Plating Metals**

Property/Function/Application	Typical plating metals
decoration	chromium, copper, nickel, brass, bronze, gold, silver, platinum-group, zinc
corrosion resistance	nickel, chromium, electroless nickel, zinc, cadmium, copper and copper alloys, gold
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, gold–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 electroless gold, gold
dimensional buildup, salvage of worn parts	chromium, nickel, electroless nickel, iron

Colloquially referred to as chrome, chromium finishes are typically, though not always, composed of multiple coatings, either nickel or copper and nickel undercoats, having relatively thin (<0.80 μm) coatings of chromium as the topcoat. 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 thus been extended such that plated bumpers have been found rust-free in some exposure tests after 15 years (10). The improved processes require more complicated plating systems, but these have been adopted where better corrosion protection is a requirement.

Special processing of the base materials is required in order to plate a smooth, highly decorative finish. 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 only 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 solution 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 in the plating solutions. Specifically, in case of positive leveling, solutions contain organic additives that are adsorbed preferentially at micropeaks; the resulting increase in local resistance to current flow increases the current density in microgrooves thereby promoting leveling. The detailed make up of additives used in a particular plating solution remains usually proprietary. In some plating solutions, such as alkaline copper cyanide, leveling can also be enhanced by dc power manipulations (14) ; such as periodic current reversal or pulse plating. 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 must be considered an important variable in the plating process.

Copper and copper alloys in and of themselves constitute yet another often used decoratively plated material, produced in quantity. Copper-plated hardware for cabinetry, lighting fixtures, household trim, and other uses are corrosion/tarnish protected using a topcoat of clear lacquer. Copper plating finishes are also available with a variety of posttreatments 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 in thickness. Thicker deposits tend to be duller. For bright brass electrodeposits of greater thicknesses, proprietary brighteners (often contain aromatic organic compounds) are added to the brass plating solution, but often thicker deposits require buffing to obtain full color and brightness.

Thin films made of bronze, copper–tin alloy, may be deposited in thicker forms using proprietary brightening additives in the plating solution, especially over a smooth bright substrate. The brightest deposit with better corrosion resistance is obtained when bronze is plated over a bright nickel plate. Direct plating over steel, however, is not an uncommon practice.

Electroplating of jewelry using gold and/or silver, for decorative purposes, is one of the oldest uses of electroplating and the first electroplating process to be patented (as mentioned above, see Ref. 15). Bright nickel plate is often used as an undercoat, especially for gold-plated jewelry, and the gold may be as thin as 0.05–0.10 μm.

It is cusomary to apply decorative silver plating with or without a bright nickel plate as an undercoat. When used on jewelry, plating may be as thin as, 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 ~3.5–32 μm (16). Decorative electroplating of the the platinum-group metals is also used in jewelry. The high cost of these metals, however, is an obvious deterrent.

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 topcoat. Brass-like colors are being produced on parts used in protected environments, such as inside homes and offices.

5.2. Functional Plating. Functional plating encompasses all the other than the above mentioned purposes for electroplating. Plating for functional properties has grown to surpass decorative applications. There are many reasons for this. The introduction of electroplating techniques in the ever burgeoning electronic industry has a great deal to do with this. By way of illustration, nickel coating used as diffusion barriers beneath precious metal deposits in electronic applications, nickel electroplating of strip and hardware in the production of batteries and nickel electroplated steel coin blanks are but a few specific examples of functional applications that have grown in importance. In general, 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.

5.3. Plating Methods. *Strips.* This method is rather common in the automobile industry though othes employ it as well. Specifically, 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). By way of illustrating, electrogalvanizing one side of strip up to 6 ft in width at 600 ft/min is a commercial process that would operate 24/7 and stop for maintenance, only. 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.

Wires. Wire platers were the first high speed ones with curent densities up to 2000 ASF (ampere per square foot). These high current densities are made possible by moving the wire at high speeds through plating solution causing rapid wire motion relative to solution not only parallel to the pull direction but also perpendicular as a result of wire vibration through the plating cell. Wire is an ideal cathode usually being round in cross-section and continuously uniform in shape throughout the plating operation. Wire also lend itself to multiple line platers, which is important in achieving high volume production of plated wire needed in a variety of applications. 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.

Rack Platers. Stampings, moldings, and castings are usually mounted onto specially designed plating racks to allow rigid and proper positioning of the part. Rack plating consists of attaching parts to an insulated frame and either manually or automatically moving the racks of parts through all plating steps. Manual rack plating requires an operator to transfer racks usually on a time basis. Automatic plating produces more reproducable plating and is almost always used for large scale production. Good rack design and construction is important to successful rack plating. Some platers hang parts on universal hooks, others 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. Plating racks are designed to have sufficiently good electrical contacts and current-carrying ability to provide current without generating excessive heat from high electrical resistances. The electrical current flow, which takes place along electric field lines, between the part (cathode) and the anode is uneven. The resulting current density distribution is such that areas of the part closest to the anode get the most plate, while deeply recessed areas may get little or no plating. Also, due to the nature of the field line distribution, current is attracted more 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. Barrel plating began in the post-civil war years. Barrels were the first plating devise to dramatically increase productivity. Specifically, when 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 partially or entirely immersed and capable of rotating while going through the plating process. They are shaped to tumble small parts so these are continually mixed, and are perforated 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, often with flexible probes called danglers. 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.

Brush (Decorative and Engineering) Plating. When parts are larger than the smaller areas of the part that require plating or when the part is in a fixed position away from a plating shop, brush plating may be employed (17). 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 (electrolyte) solution, are used. The anode tool is electrically connected to a dc 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. Special plating fixtures and solutions for substrate cleaning and depositing a variety of metals have been developed.

Automation. The electroplating industry has at its disposal an extensive amount of information and technology for monitoring and controlling all aspects of the plating process. Sensors have an important role in the monitoring of the status of each important parameter that must be controlled for successful plating. As new phenomena and technology are converted into practical cost-saving devices for monitoring and controlling electroplating parameters and systems, the industry has adopted them. Electric devices and in particular computers have revolutionized the convertion of sensor signals to a useful form for monitoring and control. Further, plating information can be gathered and analyzed quckly to ensure that quality is maintained at all times. The design and engineering of individual sensor devices has improved greatly in recent years. Many incorporate a microprocessor for signal conditioning, and some now can also carry out control of certain plating conditions directly without relying on a PLC (programmable logic controller) or computer. Automation of electroplating utilizing monitoring and control has resulted in lower manufacturing cost while improving quality and repruducibility of processing.

6. Fundamentals of Electroplating

Electroplating is often also called “electrodeposition,” and the two terms are used interchangeably. As a matter of fact, “electroplating” can be considered to occur by the process of electrodeposition. Electrodeposition is the process of producing a coating, usually metallic, on a surface by the action of electric current. The deposition of a metallic coating onto an object is achieved by putting a negative charge on the object to be coated and immersing it into a solution that contains a salt of the metal to be deposited (in other words, the object to be plated is made

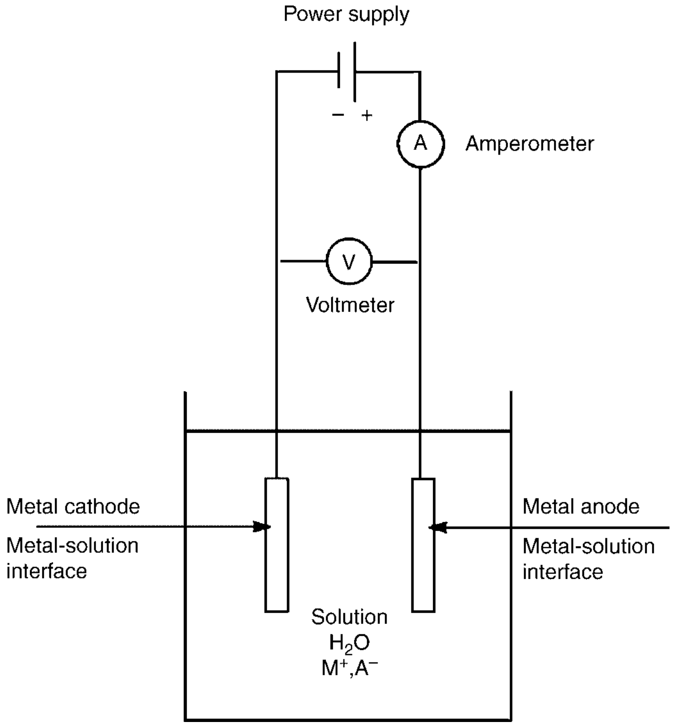

Fig. 1. Schematics of an electrolytic cell for plating metal “M” from a solution of the metal salt “MA”.

the cathode of an electrolytic cell). The metallic ions of the salt carry a positive charge and are thus attracted to the object. When they reach the negatively charged object (that is to be electroplated), it provides electrons to reduce the positively charged ions to metallic form. Figure 1 is a schematic presentation of an electrolytic cell for electroplating a metal “M” from an aqueous (water) solution of metal salt “MA.”

By now, it should be evident that electrodeposition or electroplating should be defined as the process in which the deposit of a (usually) thin layer (of metal) is formed “electrolitically” upon a substrate (that is often, but not always, also a metal). The purpose of such process may be to enhance or change the substrate’s appearance and/or attributes (such as *corrosion* resistance). Examples are the deposition of gold or silver on jewelry and utensils, and the deposition of chrome on automobile parts. Electroplating is performed in a liquid solution called an electrolyte, otherwise referred to as the “plating bath.” The bath is a specially designed chemical solution that contains the desired metal (such as gold, copper, or nickel) dissolved in a form of submicroscopic metallic particles (positively charged ions). In addition, various substances (additives) are introduced in the bath to obtain smooth and bright deposits. The object that is to be plated is submerged into the electrolyte (plating bath). Placed usually at the center of the bath, the object that is to be plated acts as a negatively charged cathode. The positively charged anode(s) completes the electric circuit; those may be at opposite edges of the plating tank, thus causing film deposit on both sides of the cathode. A power source in the form of a battery or rectifier (which converts ac electricity to regulated low voltage dc current) is providing the necessary current. This type of circuit arrangement directs electrons (negative charge carriers) into a path from the power supply (rectifier) to the cathode (the object to be plated). Now, in the bath the electric current is carried largely by the positively charged ions from the anode(s) toward the negatively charged cathode. This movement makes the metal ions in the bath to migrate toward extra electrons that are located at or near the cathode's surface outer layer. Finally, by way of electrolysis the metal ions are removed from the solution and are deposited on the surface of the object as a thin layer. It is this process to which we refer as "electrodeposition."

From the above, it would appear that the thickness of the electroplated layer on the substrate is determined by the time duration of the plating. In other words, the longer time the object remains in the operating plating bath the thicker the resulting electroplated layer will be. Typically, layer thicknesses may vary from 0.1 to 30 μ, though nothing prevents the deposition of thicker or thinner layers, as desired. The geometric shape and contour of an object to be plated affects the thickness of the deposited layer. In general, objects with sharp corners and features will tend to have thicker deposits on the outside corners and thinner ones in the recessed areas. The cause of this difference in the resulting layer thicknesses is that dc current flows more densely to sharp edges than to the less accessible recessed areas, in other words, the current distribution is not uniform. (Another, more accurate, explanation of this phenomenon involves the geometry of the electric field lines that exist between cathode and anode in the solution.) In practice, an item such as, say, a watch or similar item with sharp faceted corners are difficult (almost impossible, actually) to plate uniformly. A plating method known as "electroless plating", which is outside the scope of this article, assures uniformity of plated thickness even on highly irregular shaped objects. In the case of electroplating, judicial placement of the anode(s) as well as modifications of the current density are required to overcome the thickness irregularity effects. Electroplating processes will not, as a rule, conceal preexisting surface imperfections such as scratches, dents, or pits. Actually, the plating process will more often than not, make most surface blemishes even more pronounced. Thus it is important to remove any undesirable surface marks prior to the plating action.

Now, the electrochemical processes that occur in the deposition of a single metal has been known and utilized empirically for more than a century. In this case, it is not particularly necessary to examine the details of the mechanism and all the different (and numerous) parameters that would affect the process (and are outside the scope of this article). However, when attempting to reduce two or more different metals from a *single* solution, it is essential that the processes occurring at the cathode be considered. The most effective tool for analyzing the processes is a voltammogram, a graph of current against electrode potential (Fig. 2).

Such a curve provides all the information necessary to select the appropriate potential for the reduction of a desired metal, individually, without the

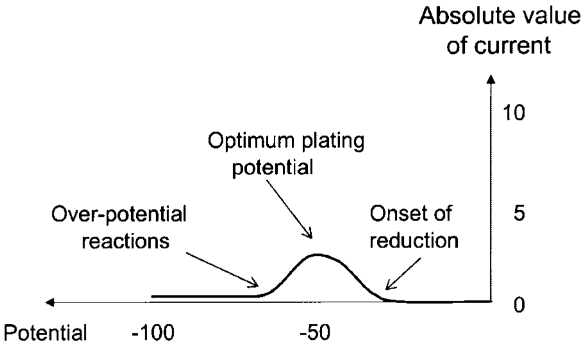

Fig. 2. Typical voltammogram for a single-metal deposition (current and potential are plotted on arbitrary scales; cathodic current is negative by international convention, absolute value is plotted for sake of simplicity).

necessity of rigorously analyzing all the interactions involved. Thus, eg, if one considered two metals "A" and "B" with metal "A" being less noble (eg, with a more negative standard potential) than "B," the voltammetric curve for either one would resemble that shown in Figure 2. For the purpose of selective deposition, the important distinction between the two metals is the onset of the reduction peaks in the voltammograms and their separation. Specifically, if the two peaks are clearly separated, one can reduce only metal "B" at some potential, while both can be reduced at a more negative potential. At the more negative potential the ratio between the amount of each metal deposited, and so present in the alloy formed, is determined primarily by their relative concentrations in the solution. On the other hand, if the two voltammetric peaks overlap considerably, only an alloy can be deposited. Another note of caution: One should not increase the cathodic potential (and current) too far to avoid parasitic reactions that may occur beyond "overpotential reactions" in Figure 2. In cases of practical applications, be it electrorefining, electrowinning, or plating, the practitioner is interested only in the weight of metal deposited on the cathode. Any current causing other changes is considered "wasted". Of course, according to Faraday's law the overall amount of chemical change produced by any given quantity of electricity can be exactly accounted for (eg, 96,485 C deposit 1 g equivalent weight of a singly ionized metal). Thus we define the current efficiency as the ratio between the actual amount of metal deposited to that expected theoretically from Faraday's law. In other words, the ratio of the weight of metal actually deposited to the weight that would have resulted if all the current had been used for depositing is called the cathode efficiency, and it is desirable to keep it as close to 100% as possible. A more thorough discussion of the fundamentals of electroplating is given in Ref. 18.

6.1. Thickness of Deposit. Thickness of the deposit may be predicted taking into account the cathode efficiency of the particular plating solution, the current density and the duration time of the plating. Plating thickness is an important parameter in electroplating from the point of views of both performance and economics. Corrosion resistance, porosity, wear, appearance, and a number of other properties are all proportional to plate thickness. Minimum or maximum plate thicknesses should be specified in different applications. For example, the former is important in plating as corrosion protection, while the latter is relevant in applications such as threaded fasteners.

Throwing Power. Note that despite what has been stated above, plate thickness distribution does not always follow the primary current distribution. Throwing power (a term used to describe the relative plate thickness distribution) was originally defined as the improvement in percentage of the metal distribution ratio above the primary current distribution ratio. 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. For comparison purposes, we note that 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 <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 >20:1, and in an acid copper plating solution having ~5–10% throwing power, had a thickness ratio of ~7:1. Finally, examples of plating solutions having good throwing power include cyanide plating baths such as copper, zinc, cadmium, silver, and gold, and non-cyanide alkaline zinc baths. Examples of poorer throwing power baths are acid baths such as copper, nickel, zinc, and hexavalent chromium. A measuring method as well as mathematical treatment of throwing power has been suggested already in 1923 (19).

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, used in the past, simulated 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. With the application of electroplating techniques in the rather sophisticated areas of electronics, angle cathodes with different angles and various side lengths, sloted cathodes, and slit cells are normally used to determine the covering power.

In Practice. In practical terms, as the current density is increased on the object to be plated, a 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 practical usable-practical 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 plated object and how it is positioned in the bath. 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 to be used.

6.2. The Plating Tank.

Materials. The materials that make up the plating tank as well as the ones for the auxiliary equipment required, are to be totally inert to the plating solution, or at the least, lined with inert material to protect the tank. In addition, it is advisable to have a nonconductive inner surface of the tank to provide electrical as well as chemical resistance. Unlined steel tanks are used, in case of alkaline plating solutions, in a number of plating outfits. However, under certain adverse conditions the steel may become susceptible to corrosion from the electrolyte. Raising free cyanide content in some electrolytes may serve to protect the steel. A recent requirement in many states is a containment surrounding the plating tank area to prevent accidental chemical spills from entering the environment. In acid plating solutions, other materials are used, depending on the chemical composition of the plating bath. Titanium and various stainless steel alloys, PTFE, Karbate, Hastalloys, zirconium alloys, and others are among the choices Tanks can be heated and cooled by lead alloy coils submerged in the solution. Titanium, tantalum Teflon, or Teflon coated stainless steel coils and heat exchangers have come to be used extensively for their extremely long life and eficient operation. Titanium coils are not the best choice for fluoride based solutions.

Tanks Sizes. Commercial electroplating lines come in practically all sizes. They vary from liter-size tanks in benchtop wire plating lines to ones holding 100,000 L and more. Tanks of >250,000 L were common in 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 (the object to be plated) is of a simple shape, anode-to-cathode spacing may 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 to achieve uniform coverage.

In case of a single work lane, it is usually positioned in the center with two anode bars equidistant from the center. If only one side of a part is to be plated, there is no need for the second anode bar. A double-lane tank arrangement requires 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, however, these are much less common. The exception is those for wire lines. No commonly accepted rules appear to be followed in sizing tanks for rack plating parts having deeply recessed areas. Rather it is recognized that electroplating inside trenches occurs preferentially on the bottom leading to void-free deposits, a phenomenon referred to as *superfilling*. Proprietary additives are used in the plating solutions to produce the superfilling properties. In most cases, the part is made to fit whatever size tank is available. Fewer control and quality problems arise using larger anode-to-cathode spacing (eg, 40 cm, rather than 15–20 cm) especially when plating parts with deeply recessed areas.

Over the years, tank depth requirements have been changing. 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. In any case, the plating tanks have to be of such size that the parts being plated are positioned 10–25 (4–10 in) from the sides and the bottom of the tank as well as from the surface. Deeper tanks allow room for installing pipe lines for filter headers, solution agitation, or air lines for air agitation In the last analysis, the length of the plating tank is related to production requirements, and whether the tank is part of a conveyorized automatic system.

Electric Connection. Connecting the tank to dc power is usually accomplished using round copper busbars. This is done both for supporting the anodes and the work (or cathodes). The size of the copper bus is determined by the amount of current flow expected; 1000-A current requires ~6.5 cm^2 of cross-sectional area. Naturally, the bus should be insulated from the tank, as well as from any other possible ground connection, and connected to the dc power supply. Short distances from the tank as well as fewer electrical connections keep the voltage drop across the busbar and so the energy losses to a minimum.

Filters and Filtration. Filtration requirements depend on the dirt load of air, any dirt brought in by the work, and the amount of detached anode sludge particles. It is possible to maintain smooth deposits with occasional batch filtration. Continuously filtering plating solutions are, however, becoming rather common, except for hexavalent chromium plating solutions and even for those filtering is recommended. Baths are filtered for the purpose of removing any fine particulate matter that could codeposit with the electroplate and cause roughness. Inlets to the filter(s) are as a rule placed at or 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 rate 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 ~25 μm down to 0.2 μm. Platers refer to filter capacity as the tank turnovers per hour; the media retention size should be included. A filter turning over five-tank volumes per hour through a 15-μm media would do <1 turnover through a 3-μm media. Filter media has to be chosen carefully to avoid introducing any soluble impurities and to avoid dissolving any of the filter media itself.

Temperature Control. Electrolyte and tank heating or cooling is required in some plating operations. This is accomplished, preferably using the means of automatic temperature control. Solution temperature can be monitored with a thermocouple, thermistor, RTD (resistance temperature detector) or silicon integrated circuit device. Many sensors for plating parameters are temperature sensitive and the output signal must be compensated for an acurate measurement. This is often done with an on-board silicon integrated device that senses temperature and corrected the parameter measurement. 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 a common practice, eg, 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 to be defined as 5°C or less from a set temperature. Cooling rather than heating may be required in some plating solutions. High currents in relatively smaller solution volumes may bring about rising temperatures and the solution may require cooling to continue, even if heating may have been 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.

Heating coils, plate coils, and other forms of immersion heaters, discussed above, may be fastened along the 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 and then returned. In-tank heaters have to be properly located and must be insulated to avoid becoming part of the plating electrical circuit. Smaller tanks are often heated with quartz electric heaters. Steam coils and steam-heated external heat exchangers are used in large installations.

Anodes. Anodes are sometimes referred to as "anticathodes". In the electroplating process, there are two types of anodes possible: soluble (made of the metal being deposited) and insoluble (made of inert material). Soluble anodes are designed to dissolve efficiently with current flow and preferably, not to dissolve when the system is idle. The majority of electroplating baths use one or the other for best results; however, a few baths may use either or even both. Chromic acid plating baths use insoluble anodes; for a number of reasons. Chief among those is the fact that chromium metal disolves with much higher anodic efficiency (85–100%) than the prevailing cathode current efficiency (12–24%), and hence rapidly increasing the chromium content of the bath. Alkaline zinc cyanide baths use both; noncyanide alkaline zincs may use either. 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, as is the case in chromic acid plating, 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, on the other hand, 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, eg, 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.

The total reaction at the anode in a given period of time is proportional to the current. This is so, since Faraday's law applies to the anode just as well as to the cathode. 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 anodic surface related 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 itself takes place; the oxide film builds up in sufficient thickness to form an insulating coating, and the current decreases rapidly. The thick anode films may dislodge at the reduced current and remain as particulate matter for a while until they slowly dissolve. As particulate matter, the dislodged anode films (anode sludge) form a significant source of roughness because they can codeposit with the metal on the work (the cathode) 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/or lowering the current, both of which lower the current density.

Electrolyte agitation around the anodes and some bath chemical variations may increase the anode current density range before polarization sets in. Lower pH and chlorides in nickel baths have been used to improve anode corrosion. Higher concentration 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. To avoid excessive polarization at any type anode in copper sulfate solution the anode current density should not be more than ~ 5 A/ dm^2 in unagitated solutions. With vigorous agitation the limit current density is >17 A/ dm^2. 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.

Anode materials, even in case of soluble ones, need not always be made of the pure metal that is being deposited. Rather, eg, in acid, low chloride nickel solutions, pure nickel does not corrode very well, leading to having to maintain low current density values. Small amounts of specific impurities may be added to make the nickel more active, allowing more efficient dissolution allowing higher current density values. For example, nickel anode material containing a small amount of nickel sulfide, NiS, has been commercially available for some time and those are widely used in nickel sulfamate, $Ni(H_2NO_3S)_2$, plating baths. These anodes corrode at a lower potential than pure nickel or other nickel anode materials.

The tenacity of the anode film is improved, and the number of particles that become detached from anode surfaces in air agitated acid copper plating solutions is decreased, by adding 0.02–0.04% phosphorus to cast copper. The films on phophorized copper anodes are responsible for the slight polarization of ~ 0.5 V. Rolled copper anodes containing at least 0.004% phophorus are customarily recommended by the vendors of brighteners for plating bright copper in copper sulfate solutions. It is observed that additives brightening acid copper baths, tend to last longer in plating baths using phosphorized copper anodes. Chunkes of pollarized copper are frequently in titanium anode baskets. Bagged copper anodes of phosphorized copper are frequently used in acid copper plating of printed wiring boards to minimize sludge formation and to produce better anode corrosion. Phosphorized copper anodes should, however, not be used in cyanide copper baths.

For some nickel plating solutions, it was suggested back in 1967 (20), to use titanium mesh anode baskets. Those were to contain small round buttons and pellets of nickel. This allowed a constant anode area to be relatively easily maintained.

As noted above, insoluble anodes are used (exclusively) in some plating baths such as chromium plating solutions that utilize lead–tin, lead–antimony, or lead anodes. Lead and lead alloys serve two key functions in the chromic acid plating bath: (*1*) They provide effective current distribution and (*2*) reoxidize Cr(III) to Cr(VI). Lead peroxide film, which forms on those anodes during use, causes continuous reoxidation of the chromium (III) forming chromic acid thereby keeping its concentration at a low acceptable value (21). Gold and other precious metal plating processes use stainless steel anodes, keeping precious inventory costs down. Platinum plated titanium and platinum plated niobium insoluble auxiliary anodes are often used in decorative plating lines for plating complex-shaped parts.

The consequence of insoluble anodes usage is (*1*) the pH of the plating solution decreases, (*2*) along with the metal ion concentration. In some plating baths, therefore, 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 are being used in acid copper sulfate baths, and steel anodes in alkaline plating baths.

Insoluble anodes can cause undesired side effects. In alkaline cyanide solutions, eg, generation, buildup of carbonates is accelerated significantly, together with a reduction in alkalinity. Also, in acid solutions the pH decreases, which requires 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 that change the character and performance of the deposit (22).

6.3. Power Supplies. A variety of power supplies is available to the plater at the opening of the twenty-first century. Continuous controls, constant current, and/or constant voltage are common place. As electroplating is becoming more and more an excact science, preprogrammed automatic current manipulations are also getting more use. Current interruption cycles where the current is periodically discontinued are used. Cycles on the order of 10 s on to 2 s off have been employed and patented (14) for cyanide copper baths using a variety of time and current density cycles. 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. There is now increased interest in pulse deposition techniques because of recently published data on the beneficial use of pulse plating in the fabrication process of integrated circuits (23).

The dc output from a rectifier can have a portion of modulation from the ac input, called ripple. Modern rectifiers usually have ~5% or less ripple at full load. 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 an accurate figure is difficult to set. However, there is usually some effect when ripple exceeds ~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, ie, even whan one uses an old fashioned dc power supply it needs a means of control, stepless preferred, and appropriate ammeter and voltmeter. Ampere-hour recorders are convenient for making additions and keeping records.

7. Preparation for Plating

Note that success of electroplating or surface conversion depends on removing contaminants and films from the substrate. Organic and nonmetalic films interfere with bonding to cause poor adhesion or even prevent deposition. Precleaning ways and methods vary depending on the particular substrate to be electroplated. Ferrous alloys are attacked by acids, withstand very alkaline cleaners and have a nonprotective oxide. It is important to protect iron alloys from oxidizing between plating steps. Copper and its alloys require a milder cleaner than many other metals. A copper cleaner may be built on a reducing acid, with complexing and wetting agents and a corrosion inhibitor. More often than not, slight variations in substrate composition significantly influence the preparation process. Determining an optimum preparation process for a given material often becomes a matter of trial and error. The literature of metal cleaning for electroplating is extensive. Guidelines can be found in the literature (24–26) and from suppliers of proprietary preparation products. Several relevant ASTM guides are listed in Table 2.

As noted above, inadequate precleaning of the substrate to be plated, can result in poor adhesion, pitting, roughness, lower corrosion resistance, smears, and stains. Since electroplating takes place at the single molecular surface layer of an object, it is mandatory that the substrate surface be absolutely clean and receptive to the plating. In the effort to get the substrate into this

Table 2. **ASTM Guides**

ASTM guide no.	Title
B253-87 (1999)	*Preparation of Aluminum Alloys for Electroplating*
B322-99 (1999)	*Cleaning Metals Prior to Electroplating*
	Practices for preparation of and electroplating on:
B630-98 (2001)	*Chromium (Electrodeposits) on Chromium*
B281-88 (2001)	*Copper and Copper-Base Alloys*
B320-60 (2003)	*Iron Castings*
B319-91 (1997)	*Lead and Lead Alloys*
B480-88 (2001)	*Magnesium and Magnesium Alloys*
B629-77 (2003)	*Molybdenum and Molybdenum Alloys*
B558-79 (2003)	*Nickel Alloys*
B343-92a(1998)	*Nickel (Electrodeposits) with Nickel*
B727-83 (1995)	*Plastic Materials*
B242-99 (1999)	*Steel, High Carbon*
B183-79 (1997)	*Steel, Low Carbon*
B254-92 (1998)	*Steel, Stainless*
B481-68 (2003)	*Titanium and Titanium Alloys*
B482-85 (2003)	*Tungsten and Tungsten Alloys*
B252-92 (1998)	*Zinc Alloy Die Castings*

condition, several separate steps may be required, and it is in these cleaning steps that most of the problems associated with plating arise.

7.1. Cleaning Methods. Surface contamination can be extrinsic, comprised of organic bebris and mineral dust from the environment or preceeding processes. It can also be intrinsic, one example being a native oxide layer. Some plating baths can in and of themselves clean surfaces. 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 (anodic cleaning). Another plating bath that possesses good cleaning properties is the high cyanide–zinc plating solution. Historically little or no cleaning was used when barrel plating 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 in the recent decades primarily because of environmental regulations and the high cost of waste management.

Despite the foregoing, the majority of plating baths require extreme degree of cleaning. Substrate surfaces have to be free of even the slightest of soil-containing films or oxides as the work enters the plating solution. It is important to understand that there is no universal cleaner. Moreover, no simple, universal cleaning cycle exists for electroplating. Several methods and cleaning solutions may have to be used in a single-plating process (26,27).

What has changed in recent decades regarding cleaning are as follows:

1. The growing requirement for efficient cleaning process with no environmental impact.
2. Databases to recommend best cleaning alternatives for a given substrate, surface condition, and subsequent plating.
3. Analysis tools to determine the actual degree of cleanliness.

In fact, the principles of cleaning are well known and the key is knowing which combinations of metals and processes are effective in specific situations.

Mechanical Cleaning. This type of cleaning employs some form of abrasion. However, parts should go through an alkaline cleaning step to remove organic soils before mechanical cleaning. Dry blasting, eg, uses sand, aluminum oxide or silicon carbide grits, glass beads, or similar abrasives. Wet blasting uses 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. While 1,1,1-trichloroethane has been banned for its role as an atmospheric ozone depleter, solvent cleaning is still possible within the current environmental and safety/health regulations (27). Three replacements without ozone depletion capability are methylene chloride, perchloroethylene, and trichloroethylene. Hydrofluoroethers are also available as alternatives to CFCs (chlorofluorohydrocarbons). These solvents must still be kept out of liquid waste disposal systems and bellow predetermined thresholds in the work place. All solvent-based cleaning must now be closed-loop and zero-discharge. Solvents must be kept relatively clean for both vapor degreasing and soak degreasing. When solvent is dirty, the contaminants can be redeposited on the part.

Aqueous Cleaners. Aqueous cleaners normally contain surfactants, builders—such as alkali for neutralizing acid—to assist in cleaning, binders to hold the ingredients together, and buffers to help neutralize the surface activity of the parts (28). Surfactants by having the hydrophobic tail seek the oil. The negatively charged metal repels the negatively charged end and the oil is gradually lifted from the surface. Sodium ions enhance the function of the surfactant. Acid cleaners attack the metal substrate to remove the intrinsic film and they also can facilitate removal of extrinsic soils (29).

Semiaqueaus Cleaners. Semiaqueaus cleaners are an alternative to solvent cleaning. These cleaners are made of synthetic organic solvents, surfactants, corrosion inhibitors, and othet additives. Water is used in some portion. For water-immiscible cleaners, the active ingridients are held as an emulsion. For water miscible cleaners, the water is actually filler to reduce volatile organic compounds emmission. This class of cleaners still has some potential for volatile organics, acquatic toxicity, flammability, and human health effects.

Soak Cleaning. Soak cleaning is the first immersion cleaning step on the plating line. Soak cleaners are categorized as alkaline or acid. Alkaline seem most common. Formulations for alkaline soak cleaners may 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 such as ethylene diamine tetraacetic acid (EDTA) or nitrilo triacetic acid (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. Other minor constituents may include defoamers, dispersants, 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 ones for increased solubility at an increase in cost. While typical formulas may be found in the literature, most plating plants utilize proprietary cleaning compounds formulated by suppliers specializing in cleaning compounds for the plating industry.

The plating plant has usually 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.

The cleaning itself is done effecting one or usually more of several mechanisms, ie, saponification, solubilization, emulsification, wetting, sequestration, and deflocculation. In soak cleaner formulations, there is usually both an inorganic component and as well as 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 bath. 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. A common visual test to determine the 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, it means that the water-break test indicates when a part is dirty, but not necessarily when it is clean.

Controlling Soak Cleaners. Functional dependency between temperature and concentration assures an optimum temperature-concentration value for efficient cleaning. This makes good temperature control and more frequent analysis and adjustments a must. This, however, has not been practiced, in previous decades, in too many plating plants. Larger soak cleaner tanks are typically heated with internal steam coils; smaller tanks may be electrically heated. Heating a solution is much more efficient if the solution is also agitated, avoiding localized overheating, temperature stratification, and resulting in improved heat transfer. External heat exchangers having adequate pumping rates are much preferred over quiescent tanks.

Temperature controllers are common place nowdays, and those should be capable of automatically holding a set temperature within a range of $\pm 2^\circ$C or less. Concentrations of cleaning solutions may be controlled through spectrophotometric techniques. Old fashioned titration may also be acceptable. Many suppliers of proprietary cleaners provide simple test kits that can be used at tankside even 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 ±5% of the set concentration. 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 is recommended practice by many consultants.

Cleaners. Close attention should be given to the oil and other contents of cleaner wastes. This attention has to increase substantially in the future as tighter environmental regulations come gradualy into play (30).

Formulations of cleaners may 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 accomplished using overflow weir, sump, and recirculating pump arrangement. Oil-rejecting cleaners last longer.

As is the case with solvents, using emulsifying soak cleaners, a saturation limit is reached, in use, where the oil-holding capacity is exceeded. This capacity (saturation limit) 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.

Acid Soak Cleaners. Acid cleaners attack the metal substrate to remove intrinsic films. The 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. Thorough rinsing is required after these to prevent any carryover into sensitive plating solutions.

Soak cleaner film removal from the work, whether it is alkaline or acid, must take a good portion of the preplate process cycle. If the soak cleaner has done its job 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. This type of cleaning, which is comprised of the application of a low voltage dc current through a conductive alkaline cleaning solution using the work itself as one electrode and usually steel suspended from busbars on either side of the work as the other, is known as electrocleaning. The equipment and process has the characteristic 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 have to be used when cleaning zinc-based die castings and copper or copper alloys as those may end up developing a fresh layer of metal-oxide as a result of the anodic type process.

The direct cleaning uses the work as the cathode (hence, the name cathodic cleaning); hydrogen is generated at the work surface. The cathodic-type reducing environment on the part helps in loosening stubborn scales and/or loose particles of the metal itself. 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, say, 30 s or even less.

By its nature of hydrogen generation at the cathode, cathodic cleaning of hardened steels can lead to excessive hydrogen embrittlement. That in turn refers to fracture phenomena having a common relationship to the presence of hydrogen in the bulk. Steel seems particularly prone to hydrogen embrittlement. Consequently, cathodic cleaning is being avoided on steels having a Rockwell hardness (HRC) greater than ∼40 HRC; more recently, this has been lowered to 35 HRC and even 30HRC. Hydrogen embrittlement can be relieved by baking for a minimum of 3 h at 190±15°C (31). Actually, 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 (Ref. 32) and autocatalytic nickel–phosphorus (Ref. 33), give explicit baking times and temperatures. Specifications applicable to each particular process should be followed.

The Nature of Surfactants. Surfactants (soaps) typically consist of a long-chain hydrocarbon molecule having a solubilizing or water-loving (hydrophiling) group that can be anionic, cationic, or nonionic when solubilized. Thousands of surfactant products are on the market, usually under trade names (34). In commercially formulated electrocleaners, surfactants are usually anionic, while often mixtures of anionics and nonionics.

Electrocleaners are often used anodically and cathodically during the same plating operation. This is done by either reversing switches or in two separate tanks. However, not all anionic surfactants do very well in cathodic cleaning. Proprietary electrocleaners seem to have the best performance.

Operation and Function. Care should be exercised as overheating electrocleaner solutions can result in surfactant loss, as for soak cleaners. Processing tanks and electrodes may be steel, but current distribution is easier to optimize and control when the inside of the electrocleaner tank is lined with an inert, nonconductive lining. In any case, an overflow weir, sump, and recirculating pump are recommended. When plating barrels are used electrocleaning can take considerably longer compared to the case in a plating rack. Higher voltages are also required for the former.

Important differences are present in the chemical compositions of electrocleaners and soak cleaners. Electrocleaners are not designed to remove heavy organic soils, rather they are formulated using much lower concentrations of surfactants. Excess surfactants should be avoided, because the more surfactant, the harder it is to rinse. The electrocleaner should follows a soak cleaning step, as 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.

The aim is to get the cleaned part to the plating tank without any residual wetting agent films.

Another function of the electrocleaner is to aid in removing light smuts or scale. Complexing agents may assist in this function, but the effect on the waste treatment process must be considered. Thus, eg, cyanide, an effective smut remover, may no longer be 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 altogether.

By and large, electrocleaners are used cathodically. The result of this is to activate (remove oxides) normally passive (oxide covered) substrates such as nickel, nickel alloys, and stainless steels. When cleaned anodically, which promotes passivation, these materials become much more difficult to activate. Unless fully activated, have bare metal on the surface, little or inferior adhesion is obtained. Anodic cleaning dissolves chromium and is thus used for stripping chromium deposits. The resulting presence of dissolved chromium in the electrocleaner is undesirable and causes uneven etching, leaving patterns that are still visible after plating is done. Sodium hydrosulfite in small quantities may be used to reduce the chromium. Proprietary compounds based on reducing sugars are far safer. As is known, chromium is a common impurity in nickel–chromium decorative plating lines because the plating rack itself usually 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 is the fact that 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 adequate, instead.

Alkaline Derusting. Highly alkaline solutions that can desolve rust is in itself a form of electrocleaning dealing with inorganic soils on steel. Applying a dc current increase this capability to a practical degree. Some rust scales may require acid pickling to remove them completely, however.

7.2. Cleaning Cycles.

Depending on the nature of the object to be plated, the cleaning cycle 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. Plating in the modern electronics industry is often performed in “clean rooms” and the work requires no prior cleaning at all.

Soak-and-electrocleaner combined products are promoted for use when normal soak cleaner is too much and a normal electrocleaner is too little. These combination cleaners are often nothing more than electrocleaners with additional surfactants. The undesired 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 soak.

7.3. Rinsing. Postdeposit rinsing is extremely important to the overall integrity of the plating operation. Work transferred 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, it is estimated to be from 20–80 mL/m^2 (35).

To reduce costs of the more expensive plating solutions and to decrease the amount of hazardous or regulated material in the waste stream, recovery and reuse of the drag-out is a common practice This is done simply by closing off the water flow to the first rinse tank following the plating 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.

On the down side, it is important to note that recycling drag-out losses can have the unwanted effect of concentrating impurities in the plating tank. Thus, it is considered a good practice to purify the drag-out before returning it to the process tank. Filtration 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. The rule that is important to remember is, that each processing solution is a serious contaminant to the next.

Rinsing requires “good” water. The water should not be too cold, vigorous agitation, and time must be provided. Many, so-called, 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 2-min dip in each agitated rinse has often produced good work having good adhesion, when 1-min dips failed.

In practice, dual- or even triple-rinse tanks follow process solutions. Additionally, many plating 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 a strongly recommended practice for plating lines. Thus, eg, 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 2200–7.5 g/L. For a triple counterflow rinse, the rate may be expected to dropp to $\sim$30 L/h.

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 3. On the longer suggested cycle for heavily soiled, rusted stock, 13 of the 19 stations are some form of rinse.

It is customary in some plating operations to employ spray rinsing. It can be efficient because of the impingement; misting at the exit of a processing tank can reduce drag-out. Barrel plating lines, such as in the production of coinage in a

Table 3. **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.

number of countries, need much more rinsing time and special consideration because of the relatively high drag-out rates.

7.4. Acid Dips and Pickles. Acids should be used to remove inorganic soils. An important distinction is to be made between acid dips and acid pickels. Where there is no rust or scales present, a dilute acid dip is sufficient 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 should be used to remove rust and scale.

The two kinds of acids most in use for preplate processes are, (*1*) hydrochloric acid, HCl, used mainly for rust and scale removal, and (*2*) sulfuric acid, H_2SO_4. 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 debit side, hydrochloric acid is more volatile and gives off corrosive fumes even at room temperatures, and so ventilation is required. Hydrochloric acid pickles are operated at room temperature, always $<40^\circ$C. Sulfuric acid solutions increase in pickling rate with concentration up to $\sim$25% strength; rates then decrease to essentially zero at full strength sulfuric acid. The pickling rate of 5% sulfuric acid is $\sim$10 times faster at 60°C than at 18°C; at 10% sulfuric acid, this increases to 15 times faster. Acid dips may be expected to be 2–5% by volume of 66° Bé sulfuric acid.

Other acids should be used for specific substrates. Leaded steels and leaded brasses use pickles and acid dips of fluoboric acid. Sulfuric acid should be avoided on leaded alloys. Free-machining steels having ~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 and proprietary citric-based products may work well for leaded steel and copper alloys. Modified citric acid dips are reported as 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 that forms soluble lead compounds, is often used 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. 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.

Electropickling. Electrolytic pickling is used in some instances; 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 may be expected to contribute significantly to hydrogen embrittlement of the part if the steel has been previously heat treated to >40 HRC. Cold-worked steel is susceptible at a lower hardness. Some early work showed more embrittlement from the plating bath than from preplate treatments (36).

When plating any substrate less noble than copper (eg, nickel), even a few milligrams per liter of dissolved copper in the acid baths may adversely affect adhesion. Coatings can be too thin to be visible, yet may 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 reelectrocleaned after the acid. Work should always be exposed to the mildest acid treatments possible. Overetching should be avoided.

Uranium is a fine example to use to demonstrate how pickling in concentrated acids can help provide adhesion in some cases. If proper procedures are used, it is posible to obtain suitable mechanical adhesion between uranium and electrodeposited coating. The most successful techniques involve chemical pickling of the uranium in concentrated acid solution containing chloride ions, eg, 500-g/L nickel chloride plus 340-mL/L nitric acid, folowed by the removal of the chloride reaction products in nitric acid before plating. This treatment, it ought to be understood, does nothing more than provide a much increased surface area with many sites for mechanical interlocking or ‘interfingering’ of the deposit. However, extremely good adherence can be obtained (37).

8. Properties, Specifications, and Test Methods

It is customary to apply standard test methods to determine the relevant parameters of electroplated materials. Documents on plating specifications for many phases of the plating process are published by a number of organizations, eg, the Federal government, the military, ASTM, ISO, SAE, etc. An excellent cross-index of these is available (38).

8.1. Deposit Thickness. Reference 39 is recommended as source for the selection of plate thickness test methods.

Various wet chemical methods are available for measuring the electrodeposit thickness: coulometric, dropping test and spot test. A disadvantage of these tests is that the part used generally becomes scrap. A nondestructive thickness test is usually preferred. There are several methods available, and most have been automated as stand alone instruments or incorporated into on-line monitoring and control plating systems. The method used include beta backscatter, X-ray fluorescence, eddy current, and magnetic field measurement.

The thickness of the plated film 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 important 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 μm or less. Chromium, plated for decorative purposes from the conventional chromic acid bath, tends to macrocrack when above ~0.7−1.0 μm. Reference 40 is a good guide for the selection of plate thickness test methods as those may vary with the purity and electrochemical activity of the deposit.

Some standard ASTM test methods for determining plate thickness are listed in Table 4.

8.2. Corrosion. Metallic coatings are one method of preventing corrosion. Deposits applied by electrodeposition or electroless plating protect substrate metals three different ways; (*1*) cathodic protection, (*2*) barrier action, and (*3*) environmental modification or control. Cathodic protection is provided by sacrificial corrosion of the coating, eg, cadmium and zinc coating on steel. Barrier action involve the use of a more corrosion resistant deposit between

Table 4. **ASTM Test Methods**

ASTM guide no.	Title
B487-85(2002)	*Microscopical Examination of a Cross Section*
B499-96(2002)	*Magnetic Method for Nonmagnetic Coatings on Magnetic Basis Metals*
B504-90(2002)	*Coulometric Method*
B530-02(2002)	*Magnetic Method for Nickel Coatings on Magnetic and Non-magnetic Substrates*
B555-86 (2002)	*Guide for Measurement of Electrodeposited Metallic Coatings by the Dropping Test*
B556-90(2002)	*Guide for Spot Test for Thin Chromium Coatings*
B567-98(2003)	*Beta Backscatter Method*
B568-98(1998)	*X-Ray Spectrometry*
B588-88(2001)	*Interference Microscope Technique*
B659-90 (2003)	*Guide for Measuring Thickness of Metallic and Inorganic Coatings*
B748-90 (2001)	*Measurement of Cross Section with a Scanning Electron Microscope*
B767-88 (2001)	*Guide for Determining Mass per Unit Area of Electrodeposited and Related Coatings by Gravimetric and Other Chemical Analysis Procedures*

the environment and the substrate to be protected. Examples of this include zinc alloy automotive parts and copper–nickel–chromium and nickel–chromium systems over steel. An example of environmental modification or control coatings in combinations with a nonimpervious barrier layer is electrolytic tinplate used in food packaging. Corrosion is affected by a variety of issues associated with coatings. These include structure, grain size, porosity, metallic impurity content, interactions involving metallic underplates and cleanliness or freedom from processing contaminants. For these reasons, the environment to which a plated part is to be exposed should be a part of any definition of corrosion resistance. Problems arise in testing a part in its intended environment in part because of the long time period required.

In many plating processes, corrosion resistance/protection is directly proportional to the plate thickness, so a specification of plate thickness is a much faster method of indirectly measuring corrosion resistance. In specifying a corrosion resistance requirement for the production of plated goods, accelerated tests are used especially if plate thicknesses cannot be related to corrosion protection.

Corrosion test methods, useful for comparison purposes, usually have no correlation to actual corrosion resistance in atmospheric exposure.

Salt Spray Test. One of the older accelerated corrosion tests is the salt spray test (41). Several modifications of this very imperfect test have been proposed, some of which are even specified for particular applications. The neutral salt spray test persists, however, especially for coatings that are anodic to the substrate and for coatings that are dissolved or attacked by neutral salt fog. For cathodic coatings, such as nickel on steel, the test becomes a porosity test, because nickel is not attacked by neutral salt fog.

The CASS Test. In the copper-accelerated acetic acid salt spray (CASS) test (42), the positioning of the test surface is restricted to $15\pm2^\circ$, and the salt fog corrosivity is increased by increasing temperature and acidity, pH ~3.2, along with the addition of cupric chloride dihydrate. The CASS test is used extensively by the U.S. automobile industry for decorative nickel–chromium deposits, but is not common for other deposits or industries. Exposure cycle requirements are usually 22 h, rarely >44 h.

Electrolytic Corrosion Test. Also developed for use on nickel–chromium and copper–nickel–chromium decorative automobile parts is the electrolytic corrosion (EC) test (43). Plated specimens or parts are made anodic in a corrosive electrolyte under controlled conditions for ~2 min, and then tested for penetration to the substrate.

8.3. Adhesion Tests. Adhesion itself is defined as the measure of the force required to separate the plated coating from the substrate. The bond between the two can be metallurgical/chemical, mechanical, or both. When plating metal-on-metal, with good metallurgical bonding, the adhesive strength is greater than the strength of the weaker metal. Plating on surfaces is an atom-to-atom process. Even smooth-appearing surfaces can be relatively rough on a submicroscopic basis, resulting in a physical keying/anchoring effect that adds to the adhesion. This microanchoring is the primary source of mechanical adhesion. Plating on plastics and other nonconductors depends on this microetch for adhesion. Adhesion tests can be broken into two categories: qualitative and quantitative. They vary from simple scotch tape test to complicated flyer tape test which require precision machined specimens and a very expensive testing facility. Quantitative [such as peeling (44)] tests have been developed for coatings on plastics (45), but not to the same extent for metal-to-metal systems. The quantitative testing systems in limited use, mainly in the electronics industry, are not commonly present in production plants, but have been used to aid in process development (46–48). For quality control purposes, qualitative tests for metal-to-metal adhesion (49) are usually adequate. The adhesion of some plated metal parts is improved with baking for 1–4 h at relatively low (120–320°C) temperatures. Many of the qualitative adhesion tests vary with the plate thickness. Adhesion appears better for thinner deposits. That has to do with the stress that is present in deposited films. A specified plating thickness should be a given parameter requirement for adhesion testing.

8.4. Ductility Tests. It is important to note that tensile strength and ductility of thin films/deposits are very much influenced by the thickness of the test sample. The ductility of plated metals differs considerably from the corresponding thermally cast metals. Typically, tensile test data are high for thin deposits and then decrease as a function of thickness before reaching some steady value. In addition, ductility that is an important property if parts are to be deformed after plating, varies with the chemical composition of the plating solution, as well as the operating conditions of a given plating process. Ductility can also be important when plated parts are stressed in use. Some metal deposits have coefficients of thermal expansion significantly different from the substrate. Brittle deposits can crack with modest temperature changes.

Ductility of plated coatings/films is often measured by bend tests (50), ie, if the plated part can be bent. If not, a foil can be prepared by plating on a nonadherent substrate, removed, and then subjected to a bend test (51). Foils are also tested by conventional tensile testing machines where the foil is pulled apart. Results of these tests have been shown to be affected by the proportionality of specimen thickness to its length and width. Better data are obtained when this is considered. In other words, a better indicator of ductility is measurement of the reduction of area of the sample rather than elongation. Reduction of area is largely a measure of the inherent ultimate ductility of a material. Significant ductility differences have been found when foils are still attached to substrates. Ductility of foils is also measured by either mechanical or hydraulic bulge-testing techniques. Data obtained by bulge testing vary with plate thickness (52,53) as do most of the deposit properties.

8.5. Hardness Test. Indentation resistance, in thin films/coatings, is usually measured on a microscopic scale, and hardness then becomes microhardness. Hardness, as related both to wear resistance and to ductility, is often a specified characteristic for plated coatings. The hardness of plated metals is higher than thermally cast metals. A fine grain size is the primary reason for the higher strength of the electrodeposits as compared with their wrought counterparts. Hardness varies with the additives, chemical composition, and operating conditions of each plating solution. Measurements are performed by forcing an indentor of specific shape into the test material with a given force, for a given time. For relatively thin-plated coatings, low forces are required, and microhardness values do vary according to the force. Because of this, the force used has to be specified along with the microhardness number and the indentor style (54).

Thus, proper expression for a microhardness value of 450 using a Knoop indentor and 0.981 N (100 gf) is 450 HK_{100}.

The accuracy of microhardness testing has been questioned at times: a wide range of values seem to appear in the literature for a given plated deposits, especially in hardness extremes. Attempt at establishing a standard test of microhardness is given in Ref. 55.

8.6. Porosity Test. A void/hole that extends through the deposit to the substrate is referred to as a pore. Porosity should also be defined by size. Very fine porosity is present in all deposits; it is only when the porosity is large enough to admit water and corrodents that porosity becomes an issue. Large enough to see, porosity is called pitting. Pits do not always extend through the deposit. Pitting is an intermittent, albeit common, problem. Excess porosity results in decreased service life. There are, however, occasions where porosity is desired in a coating, eg, porous chromium deposits from specially formulated solutions provide for improvred lubricating properties. Porosity tests for gold, as used for electrical contacts, are available (56,57), as are porosity tests of deposits over copper and copper alloys (58), and a general guide to porosity test selection (59,60).

8.7. Hydrogen Embrittlement. Hydrogen embrittlement is a generic term used to describe a wide variety of fracture phenomena having a common relationship to the presence of hydrogen as a solute or as a gas in the atmosphere (61). Electrodeposition and electroless deposition and their associated processing steps including acid pickling and electrocleaning can generate hydrogen that can enter substrates in the atomic form and cause hydrogen embrittlement. If not removed, the atomic hydrogen can have serious embrittling effects on the base metal. This effect is more pronounced with hardened, high strength steels and stainless steels, especially when the hardness is over $\sim$40 HRC, or lower if cold-worked. However, hydrogen embrittlement is not specific to just high strength steels. Relief is accomplished by baking. Generally, the harder steels require longer baking times (62,63), up to 23 h at 190°C. Shot peening before plating has also been shown to reduce or even prevent the absorption of hydrogen.

Analysis methods for hydrogen absorbed in the deposit have been described (64,65), and instruments are commercially available to detect hydrogen in metals. Several working tests have been devised that put plated specimens under strain and measure the time to failure. A method for cadmium-plated work has been described (66) as has a mechanical test method for evaluating treatments on AISI 4340 Steel (67). Additional information on testing for hydrogen embrittlement is also available (68).

8.8. Fatigue. By definition, the phenomenon leading to fracture of a part under cyclical stresses at values less than the tensile strength of the part, is called fatigue. Fatigue fractures are progressive, and grow with the cyclical loads. Electrodeposits have been known to reduce the fatigue strength of plated parts. The reason for this include (*1*) hydrogen pickup resulting from the cleaning/plating process, (*2*) surface tensile stress in the deposit, and (*3*) lower strength of the deposits compared to the basis metal leading to cracks in the deposit that subsequantly propagate through to the base metal. The greatest loss occurs when the deposit has a high tensile stress. Because a crack cannot propagate in a compressively stressed surface, deposits having higher compressively stresses have much less effect on fatigue life losses. Fatigue tests are run on specially treated test specimens in machines that apply cyclical loads. One type of machine uses round test bars that are rotated under adjustable loads. The number of cycles until failure occurs (N) is plotted against the load (S) to obtain an S−N diagram. Unplated control specimens must be run alongside the plated specimens. Fatigue strength loss is an important consideration when plating parts subject to high reciprocating forces. In the aircraft overhaul and rebuilding industry, the effects of plating on fatigue strength are a prime concern. Premature failure of critical parts can be catastrophic.

8.9. Internal Stress. This is present to a degree in just about all plated metals. Internal stress is either compressive or tensile in nature. It is compressive if the deposit tends to expand, being that it is compressed. Tensile if the deposit tends to contract to relieve the stress, being that it is stretched. High tensile stresses can lead to cracking and flaking as well as to serious reduction in life. High compressive stress can lead to blistering when the compressive stress exceeds the adhesion strength. High stress of either nature can lead to warpage where substrates are thin. Stressed deposits can be considerably more reactive than the same deposit in an unstressed state. On occasion stress may be useful, eg, in the production of magnetic films for computer memory storage media. Stress in ferromagnetic films (Fe, Ni, or Co) will bring about preferred directions of easy magnetization and other related effects.

Internal stress varies with the deposited metal, the basis material, thickness of deposit, conditions of preparation, operating conditions, and chemical composition of the plating solution. When plating on a dissimilar metal, initial stresses in the first few layers of deposit can be very high perhaps because of epitaxy and/or the tendency of the deposit to try to match the grain boundaries of the substrate. Other causes for internal stress are minute inclusions of impurities, solid and gaseous, within the deposit or within the grain boundaries, and subsequent changes in the parameters of the crystal lattice.

While internal stresses in electrodeposited chromium, nickel, and iron are usually tensile; in zinc, lead, and cadmium those are usually compressive. Again, while copper deposited from an acid sulfate bath has low tensile stress; copper deposited from a copper cyanide solution has high tensile stress. In all, additives can be used to change the nature of the stress. For illustration purposes, an example of the influence of additives on stress in nickel deposits is being presented here; small quantities of (<0.1 g/L) most sulfur bearing compounds rapidly reduce stress in nickel deposits.

Chromium, as deposited from hexavalent chromium systems, develops high tensile stress during plating that can exceed the tensile strength. In such cases, the deposit cracks while plating, and subsequent plating fills in the crack. The cycle repeats as the thickness increases and results in a deposit that can vary from microcracked appearance to macrocracked; where the cracks are completely filled in, it becomes essentially crack-free.

Several methods are being used to measure internal stresses (69,70). Most, however, are based on measuring the deformation of a flexible cathode (in the form of a long narrow strip) after plating. The cathode is either masked and plated on only one side, or one side is masked after plating on both sides and the plating stripped chemically to produce the same effect. The spiral contractometer method (71), which is less common, utilizes a flat cathode wound in the shape of a helix connected to a dial through a system of gears. The helix is coated with a thin flexible insulating plastic on the inside (72). The rigid strip method uses a flexible metal strip, usually in a nonconductive fixture, to hold the strip in place and to prevent plating on the backside. Methods that involve plating on strain gauges have been described, and more recently, a strain gauge method was used to monitor changing stresses. The actual stress in a plated part has been measured by X-ray techniques. Note that correlation of internal stress values using different test methods is difficult.

Internal stress values, as measured by deformation, are also influenced by the differences in thermal expansion between the deposited metal and the cathode, especially when plating solutions are used at elevated temperatures and where the deposit has a higher thermal coefficient of expansion than the substrate, the deposit shrinks more on cooling and adds a tensile stress component to the overall stress. In the reverse case, a compressively stressed component is added. Depending on the relative thermal properties, the same solution may yield deposits tensilely stressed on one substrate and compressively stressed on another (73). To obtain the stress of the deposit independent of the thermal properties of the substrate, the spiral contractometer can be effectively used by measuring both the initial and final deflection values at the operating temperature of the plating solution. This is termed intrinsic stress of the deposit.

9. Environmental Aspects of Electroplating

Presently, in the United states, the leadership for controlling the environmental consequences of most technologies rests with the Environmental Protection Agency (EPA). The EPA was created in 1970 to be the federal watchdog for the environmental consequences of human activities through a series of laws and regulations. These laws and regulations are constantly amended and in addition local governments issue their own regulations. In instances of conflicts or differences, the most stringent regulation applies. As a natural outcome of the foregoing, it may be said that no single topic is as important to the plating industry as waste management, which has, over the recent decades, become the key to economic survival. Waste management includes recycling, waste reduction, and waste treatment and disposal. Metal finishers (electroplaters) are regulated under a Federal EPA program, National Pollutant Discharger Elimination System (NPDES), often administered by the State. Fortunately, today the Internet offers a convenient information link that provides the opportunity for a continuous monitoring of EPA ‘regulations’, publications, proposals, etc, as well as technical help from companies that are willing and able to be subcontracted to handle the waste disposal aspects of the electroplater.

Document 40 CFR (Code of Federal regulations) of the clean water act (may be recorded from the EPA Internet site) describes the general provisions for the electroplating industry. Examples for the requirements are shown in Tables 5 and 6.

Table 5. **Discharging Limits for Facilities Discharging $<$38,000 L/Day**

Pollutant	Maximum for any 1	Average daily values (in mg/L) for
CN	5.0	2.7
Pb	0.6	0.4
Cd	1.2	0.6
TTO (total toxic organic)	4.57	

Since the limits in the table are in concentration, Section 413.14 adds "No user introducing waste-water pollutant into a publicly owned treatment works under the provisions of this subpart shall augment the use of process waste-water or otherwise dilute the waste-water as a partial or total substitute for adequate treatment to achieve compliance with this standard". To put it differently, dilution is not a solution. All new facilities are subject to the same New Source Performance Standards (NSPS) regardless of size, type of facility, or type of discharge. The Resource Conservation and Recovery Act (RCRA), is the most comprehensive pollution control law for metal finishers. One requirement assigns cradle to grave responsibility for waste to the generator, ie, the plater. Unless the waste is made into another form or recycled as another product, the original generator is still responsible for future treatment or liability costs. The treatment of electroplating waste-water as mandated by the national pretreatment standards requirements will result in two streams : an affluent that must comply with regulations for acceptable polutant discharge, and residue (sludge) containing a high concentration of the substances that the waste-water regulations prohibit discharging. Other requirements of RCRA include a generator's license, proper waste containers, labels, and manifest shipping documents, licensed haulers, record maintenance, and an annual waste minimization report. One could write an environmental impact statement for every single metal. Many of the issues, however, are similar and can be extrapolated from one metal to the next (74–76).

For the foreseeable future, the plating industry has to expect tighter restrictions and more regulation of recovery and recycling operations. Solid

Table 6. **Limits for Facilities Discharging 38,000 L or More Per Day**

Pollutant	Maximum for any 1 day	Average daily values (in mg/L) for 4 consecutive
CN	1.9	1.0
Cu	4.5	2.7
Ni	4.1	2.6
Cr	7.0	4.0
Zn	4.2	2.6
Pb	0.6	0.4
Cd	1.2	0.7
Total metals	*10.5*	*6.6*
TTO	2.13	

wastes, the sludge from waste treatment processes, have to pass stringent leaching tests to be allowed in landfills, and costs for the disposal of solid wastes are increasing dramatically. Some earlier legislation (eg, the Clean Air Act of 1990), is concerned with air pollutants. This act restricted chromium in air exhausts from chromium-plating and chromic acid anodizing plants to 0.01–0.03 mg/m^3. Also, the Pollution Prevention Act of 1990 stressed reduction of chemicals that could enter the waste stream before treatment.

In Figure 3, a schematic outline of a conventional on-site waste disposal procedure taken in industrial electroplating setting is presented.

To have things in perspective, already back in 1991, EPA started a voluntary program for industrial plants to reduce releases and off-site transfers of 17 specific chemicals, including the following: benzene, Cd/Cd compounds, carbon tetrachloride, chloroform, Cr/Cr compounds, CN-compounds/HCN, Pb/Pb compounds, Hg/Hg compounds, methylene chloride, methyl ethyl ketone, methyl isobutyl ketone, Ni/Ni compounds, tetrachloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, and xylenes.

The target at that time was a 50% reduction by 1995. The goal was, and still is, pollutant prevention rather than treatment at the end of the pipe. Substitutes

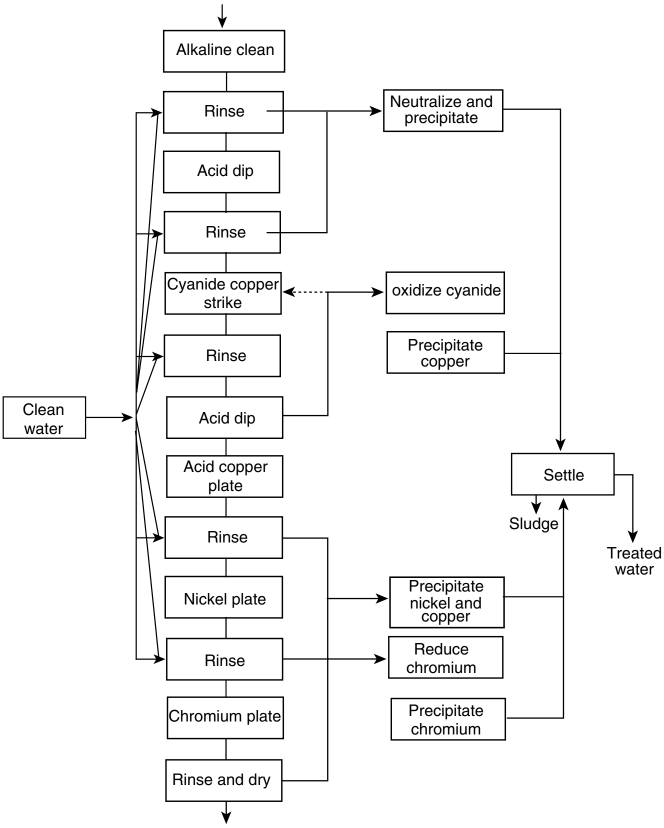

Fig. 3. Schematic outline of the conventional on-site waste disposal procedures taken in industrial electrodeposition setting.

are constantly being sought for the heavy metals on the list, and in some applications, substitution can be done without loss in performance. For example, zinc-alloy plating is replacing cadmium in some applications. Additionally, other zinc-plating solutions have been replacing cyanide zinc baths. In other cases, no suitable substitute may exist.

By way of summary, the main sources of waste from a plating line come from rinse waters, process solution dumps, solution losses from leaks, spills, purifying treatments, and filter changes. Waste reduction occurs with the use of more dilute process solutions, less rinse waters, fewer solution dumps, less filtering, and fewer purification treatments, each of which can be contradictory on many plating lines. For example, because most process solutions act as effective contaminants in the following process solution, poorer rinsing results in shorter process solution life and more frequent purification treatments say nothing about quality. The amount of process chemicals getting into the waste stream can be reduced, however, by longer drain times over the process tank, lower surface tension, more dilute process solutions, misting rinses as parts are being withdrawn, and reuse of the saver-rinse.

Minimizing Solution Dumps. While all process solutions usually have a finite life, this life may be extended when extra care is taken to reduce drag-in of contaminants, reduce breakdown products, and avoid reuse of drag-out chemicals unless purified before being returned to the process tank. Yet, another common method of extending the life of electroplating solutions involves purification. The bulk of solution dumps come from dumping cleaners and acids, not electroplating solutions. Methods to increase the tank life of these preplate solutions can have a significant impact on waste prevention in most plating operations.

Some plating plants have adapted a bleed-and-feed process where a calculated quantity is withdrawn to waste treat each day and replaced with an equivalent amount of fresh solution. Using cleaners that reject oils can be effective if proper equipment is available. Stripping racks and reject parts off-line helps extend the life of cleaners and acids. Ultrafiltration of cleaners, in limited use, is gaining interest. This technique has the capability to remove oils and greases from some cleaning solutions. Improved rinsing between cleaners and acids extends acid life significantly. Inhibitors reduce acid attack and the buildup of dissolved metals in pickle tanks. Continuous filtration, not commonly in use on cleaners and acids, is helpful, packed with activated carbon, filters can keep acid tanks free of oil thus extending the lifetime.

Finally, it ought to be stressed that technical and legal specialized knowledge and experience are required to ensure that goals are to be met when selecting waste treatment methods. There are a host of methods for waste treatment. Thus, eg, cyanide may be treated by ozone oxidation, peroxide/formaldehyde treatment, and electrolytic oxidation. A procedure using sulfur dioxide/air oxidation has also been proposed to destroy cyanide and permit removal of most of the metal-cyanide complexes in copper-plating solutions (77). A support industry concentrating on waste treatment process and equipment has developed.

Economic Considerations. It is not easy to arrive at cost numbers that will clearly define the costs that are associated with disposal. Typical numbers for the electroplating industry run at ~3% of total expenditure with a standard deviation of ~2%. Table 7 provides the cost data that were associated with

Table 7. **Comparison of Annual Operational Costs and Capital Investment for CN Process with Alkaline Noncyanide (ANC) and ANC with Recovery/Recycle (R/R*) System**

Process operation	CN costs ($)	ANC costs ($)	ANC + R/R* costs ($)
bath makeup	1,771	1,860	1,860
bath maintenance	22,325	21,225	19,425
water usage			
1. use at $7.56/7480 gal	1,213	1,213	364
2. sewering at $5.59/7480 gal	897	897	269
waste-water treatment			
1. cyanide oxidation	14,000	0	0
2. metal precipitation	69,000	69,000	20,700
3. labor at $15/hr	7,500	7,500	2,250
sludge disposal at $209/yd^3	2,600	2,600	1,820
total operating expenses	119,306	104,295	46,688
capital investment		36,000	87,822

experimental alternatives for the cyanide plating of zinc, with alternatives similar to common ones for copper. The data in Table 3 can be interpreted as requiring between 60 and 87.5% of costs dedicated to waste disposal. The cost accounting in Table 7 is provided in support of the claim that the most environmentally friendly processing is also the most cost effective.

Most developed countries spend between 1 and 2% of their gross domestic product on environmental protection, and that proportion is likely to rise. In the United States, it was estimated that the 1990 effort was 1.9% of gross nation product (GNP), and that grew to ~2.7% by the year 2000.

Regulation is by far the most common tool of environmental policy. Market driven economic environmental instruments fall into two categories:

1. "Green taxes" that put price on pollutants that in principle reflect the cost they impose on society.
2. "Marketable permits" that are based on absolute quantity of pollution that is to be allowed, and then give or sell polluters right to pollute up to that given level. Polluters can trade these rights with each other.

One relevant quantitative support for such regulations is the fact that in the year 2000 the water consumption by manufacturing industries in the United States is only about one-third of what it was in the year 1977, mainly because of the increased costs of disposing of wastewater.

10. Plating Bath Formulations

The specific formulations of plating baths is flexible in some systems while, very sensitive to variation in others. Many of the more recent changes in bath formulations have resulted from waste treatment and safety requirements. Besides the ability to deposit a coating having acceptable appearance and physical properties, the desired properties of a plating bath would also have to include some or all of: high metal solubility, good electrical conductivity, good current efficiencies for anode and cathode, noncorrosivity to substrates, nonfuming, stable, low hazard, containing, low anode dissolution during down-time, good throwing power, good covering power, wide current density plating range, ease of waste treatment, and economical to use. Few formulas have all these attributes. Only a few plating solutions are, as a consequence, commercially used without special additives, but chemical costs often constitute a relatively low percentage of the total cost of electroplating. Additives are used to brighten, reduce pitting, or otherwise modify the character of the deposit or performance of the solution. Preferred formulations are normally specified by the suppliers of the proprietary additives.

10.1. Plating Bath Purification. Once a plating bath is in use, purification is required periodically to maintain the plating solutions useful service. Alkaline zinc plating solutions are, eg, sensitive to a few milligrams per liter of heavy-metal contamination, which may be precipitated using sodium sulfide and filtered out. Nickel plating solutions may contain excess iron as well as unknown organic contaminants. Iron is removed by peroxide oxidation, precipitation at a pH of $\sim$5, then filtered out. The more complex, less water-soluble organic contaminants along with some trace metals are removed with activated carbon treatments in separate treatment tanks. About 5 g/L of plating-grade activated carbon is mixed in the plating solution for at least 1–2 h, usually at warmer temperatures.

Common purification treatment used both on new and used plating solution is “dummying.” In this, heavy-metal impurities are removed by electrolyzing, usually at moderate current densities, using large disposable steel cathodes. Good agitation and lower (acid) pH speed the process. In alkaline plating solutions, dummying is naturally more effective at higher pH; eg, zinc is dummied out of cyanide copper plating baths faster after caustic additions.

10.2. Testing. Analysis and testing are required whenever a new plating solution is made up, and thereafter at periodic intervals (78–80). Frequency of analyses and testings should be adjusted so that corrections can be held to 10% or less from established concentrations. Many variables may be tested with small plating cells such as Hull cell (81–83). Sophisticated automatic analytical machines are commercially available and the expense of obtaining those is well justified.

11. Individual Plating Baths

11.1. Cadmium and Cadmium Compounds. Suggested makeup of cadmium plating baths are shown in Table 8. Whereas cadmium provides better corrosion resistance to steel and other substrates than zinc when exposed to marine environments, zinc is better in industrial, sulfur-bearing atmospheres. Resistance of cadmium is improved with chromate conversion coatings; bright, yellow iridescent, olive drab, and black finishes are used. Cadmium is readily solderable, provides lubricity on threaded fasteners, and has been used as a high temperature protective coating in the aircraft industry when diffused into nickel plating. Olive-drab chromated cadmium plate is used on nickel-plated aluminum

Table 8. **Cadmium-Plating Solutions**[a]

Parameter	Cyanide	Acid sulfate	Fluoborate
Cd metal, g/L	20–30	15–30	75–150
NaCN, g/L	90–150		
Na_2CO_3, g/L	30–60		
H_2SO_4, g/L		45–90	
NH_4BF_4, g/L[b]			60–120
NaOH, g/L	10–20		
pH	12.5–13.5	very acid	2.5–3.0
anodes	Cd and steel	Cd and graphite	Cd
temperature, °C	15–40	18–23 max	10–40
current density, A/m^2	50–900	300–800[c]	100–600

[a] Addition agents for all three plating solutions are as required.

[b] Some baths contain 20–30 g/L $NaBF_4$ and 20–30 g/L H_3BO_3 instead of NH_4BF_4.

[c] Current densities from 100–200 A/m^2 are used for barrel plating.

electrical connectors to extend salt spray resistance. For diffusion processes, for low hydrogen embrittlement, and for plating directly on cast iron, cadmium–cyanide plating solutions are used without brighteners; in other applications, brighteners produce attractive lustrous deposits.

The future of cadmium plating is in some doubt because of cadmium toxicity (84). Cyanide-free cadmium plating systems, however, have experienced some limited growth. Acid cadmium, based on cadmium sulfate compositions, is replacing some cyanide baths in the United States. The fluoborate cadmium is reported in use in the United Kingdom, especially in barrel plating. Cadmium plating is covered by ASTM (85), U.S. government, and ISO specifications (86).

While, as indicated above, the future of cadmium plating is in some question, the interest and activity in electroplating of semiconductors of the CdX type, with X = Se,S,Te, etc. and similar, is growing. Thus, eg, CdTe can be deposited by pulse, potentiostatic, and galvanostatic electrode position. Cadmium telluride thin films are currently employed in a broad range of optoelectronic devices including solar cells and infrared detectors. This material is one of the more extensively studied semiconductors in terms of deposition by electrochemical means. Most CdTe electrodeposition makes use of an acqueous cadmium sulfate, tellurium dioxide sulfuric acid electrolyte, and either cathodic or anodic methods may be employed. The former make use of the codeposition of higher valent metal and chalcogenized metal. The latter methods are based on the corrosion of the metal in a chalcogenide environment (87).

11.2. Chromium. Electroplated chromium deposits rank among the most important plated metals and is used nearly exclusively as the final deposit on parts. Without the physical properties offered by electroplated chromium deposits, the service life of most parts would be much shorter due to wear corrosion and the like. Thus, chromium plating can be separated into two areas: hard chromium, also called functional, industrial, or engineering chromium, and decorative chromium. The plating bath compositions may be the same for both. In most cases, the differentiating factor is plate thickness. Decorative chromium is usually less than ~1 μm; hard chromium can be from ~1–500 μm or more.

Table 9. **Chromium-Plating Solutions**[a]

Parameter	Conventional baths		Cocatalyzed baths	
	Range	Typical	Range	Typical
CrO_3, g/L	150–400	240–260	150–400	150–180
SO_4^{2-}, g/L	1.25–5	2.4–2.6	0.6–1.3	0.9–1.0
SiF_6^{2-}, g/L			0.3–0.8	0.5–0.6
CrO_3/SO_4^{2-} ratio	80–120:1	90–110:1	150–200:1	170–180:1
anodes	Pb-7% Sn or Pb-6% Sb		Pb-7% Sn	
current density, A/m^2	400–4000	1000–3000	400–4500	1000–3500

[a] All decorative chromium baths are run at 38–43°C; hard chromium baths at 40–60°C.

Chromium is best deposited using chromic acid solutions containing at least one anionic catalyst, which is usually the sulfate ion. The weight ratio of chromic acid to catalyst is important and, for sulfate-catalyzed solutions, is maintained ~100:1. Formulations and conditions for operating hard chromium plating solutions are shown in Table 9.

Chromic acid based plating solutions differ from the other common metal-plating baths in that chromium solutions have poor current efficiencies, poor covering power, and poor throwing power, as well as a need to use much higher current densities to plate. Modifications developed in attempts to improve these weaknesses incorporate a second catalyst, and are called cocatalyzed baths. These have improved cathode efficiency: cocatalyzed systems can produce cathode efficiencies of 16–17 versus the 8–12% of the conventional baths. The second catalyst is often fluoride, or more commonly, the fluosilicate ion. In addition to the above, proprietary baths are also available and those are having self-regulating, chromic acid/catalyst ratios for ease of operation. In fact, a problem exists for the fluoride-containing catalysts in that the plating solution severely etches any steel areas exposed to the bath that are not being plated such as deeply recessed areas, inside surfaces of hollow cylinders, and other low current density areas. These nonplating areas have to be stopped-off with protective materials such as waxes, tapes, or other masking compounds. Newer proprietary compositions are available. Those claim nonetching, fluoride-free, co-catalyzed systems still having efficiencies of up to ~25%.

Regarding recommended compositions, as shown in Table 8, those can, actually, be quite flexible as long as the catalyst (anion) ratio is well controlled. High chromic acid baths produce less burning and have better conductivity but have lower current efficiency and a higher drag-out loss. Lower chromic acid baths exhibit better coverage in low current areas. Low catalyst (anion) ratio (high sulfate) baths have decreased coverage, but smoother deposits. High sulfate is reduced by barium carbonate precipitation. About two parts of barium carbonate is needed to precipitate one part of sulfate in a slow reaction that takes several hours to complete. Low sulfate (high ratio) also gives better coverage, and plating rate is decreased. Temperature control is important in all chromium plating baths, and agitation is required in most tanks to avoid temperature stratification. Higher temperatures improve conductivity of the solution, decrease burning, and decrease covering power. Lower temperatures produce slower plating rates.

Anodes used in chromic acid plating baths are best insoluble. Lead–tin or lead–antimony alloys are the most common practical anodes. Chromium anodes are not recommended for use, because they dissolve too quickly. The lead–alloy anode has an added benefit that, under correct conditions, trivalent chromium is reoxidized at the anode surface, and a damaging buildup is avoided. Lead–alloy anodes develop a dark brown oxide coating when working properly. If left idle or without sufficient current flow, the anode forms a chromate coating that decreases the current flow and is not capable of chromium reoxidation. When this yellow coating is observed, it may be necessary to remove and clean the anode. Caustic–gluconate solutions are best for anode cleaning. Proper anodic current density is important to maintaining the proper oxide; too high or too low are both detrimental. Because throwing power is quite poor, anode geometry, placement, and anode-to-cathode distances are very critical in obtaining sufficient plate thickness distribution. Anodes that conform to the shape of the plated part give the best results. Anodes should be shorter than the work. Anode-to-cathode spacing for conforming anode arrangements is usually ~10 cm (4 in.); for internal anodes in hollow cylinders smaller spacing, 1–2 cm(~0.5–1.0 in.) allows for more anode surface.

Metalic Impurities. There are two classes of impurities in a chromium bath. (*1*) Inorganic impurities such as chlorides, fluorides boric acid, etc and (*2*) metalic impurities. The latter are most common in the form of detrimental impurities such as iron, copper, and zinc. Chromic acid plating solutions are affected by metallic impurities that usually are accompanied by chromium reduction increasing electrical resistance. Iron is a common impurity that increases rapidly, say, when the chromium plating tank is used as the reverse current chromium etch tank, or when parts are accidentally dropped into the tank and not recovered. Eventually, chromium plating solutions have to be replaced because of high iron content. Reverse etching is often used to obtain good adhesion; overetching, however, should be avoided. A separate chromic acid etch tank should be used to extend the life of the plating solution. Of all impurities that can be present, chromium(III) is particularly detrimental (eventhough it is held by some (88) that in small amounts added to a new bath it has its merrits) but it can be treated by electrolytic oxidation treatments at temperatures of ~80°C and high (5000–5500 A/m^2) cathode and low (2000 A/m^2) anode current density. Limits of trivalent chromium that can be tolerated vary from 10–60 g/L Treatment using the electrolytic porous pot is used sometimes to purify chromium solutions (89).

Additional purification processes may include: cation-exchange treatments on diluted solutions followed by evaporation back to working bath strength; and electrodialysis directly in the working solution (90). Fluoride ion excess can be treated using aluminum foil but high (10 g/L) aluminum can, however, completely inhibit chromium plating in cocatalyzed baths. High chlorides, which reduce plating range and increase anode deterioration, can be removed by precipitation with silver oxide salts or by controlled dummying using an anode current density of ~200 A/m^2.

Efficient ventilation is a requirement for chromium plating operations. Chromic acid plating solutions having low current efficiencies produce large quantities of chromic acid-laden spray requiring good air scrubbers. Certain wetting agents form foam blankets on chromium-plating solutions and reduce spray losses, but some wetting agents contribute to pitting in hard chromium with plate thicknesses over ~25 μm.

Decorative Chromium. Thin (0.25 μm) bright chromium plate deposited over bright nickel gives a blue-white color, and was, in the past, thought of as only a tarnish preventative. This outermost coating or first barrier, is now understood to play a significant role in retarding corrosion, even though it has a tendency to crack. A substantial improvement in the corrosion resistance, afforded by thicker decorative chromium deposits, was made with the introduction of "duplex" or "dual" chromium plating procedures. Specifically, chromium-plated goods replated with a second layer of chromium, when the first layer was found thinner than specified, were found to have better corrosion resistance. In the second layer, many microcracks (MC) were found that extended down to the nickel plate. Moreover, less corrosion appears on chromium-plated test pieces at the ocean beach than on parts placed away from the shore, and plated ware on the front of automobiles are generally less corroded than parts on the rear. In both of these cases, the plated surface shows a microporous (MP) effect produced by the sand blasting. Additionally, increased protection has been observed when chromium is plated over satin nickel where the satin effect is caused by codepositing fine, nonconducting particles with the nickel. In this case, it was shown that the chromium was microporous and did not plate over the tiny particles. A minimum number of discontinuities is required for MC/chromium, (300 cracks/cm) and MP/chromium (10,000 pores/cm^2) to be corrosion resistant. Automotive and ASTM specifications (91) require either MC or MP/chromium on extended severe service parts. The corrosion resistance is explained as caused by the presense of many small electrochemical cells with a relatively low rate of corrosion of the nickel undercoat, and decreased tendency to basis metal corrosion.

Trivalent Chromium. Historically, trivalent chromium baths have always been the first and favorite approach to chromium plating. Use of trivalent chromium plating for decorative applications is continuing to grow. These materials have performed quite well in corrosion tests (92). One major advantage of some trivalent chromium formulations is that metallic impurities can be easily removed by directly passing the plating solution through an ion exchange. There are two types of proprietary trivalent chromium plating baths being marketed. These differ in anode systems and are compared in Table 10. Thick deposits up to ~25 μm appear to be attainable, but the use of trivalent chromium for hard chromium applications is not commercially practiced to any significant extent.

Specialty Chromium Baths. Chromic acid baths using sodium chromate and sodium hydroxide to form a tetrachromate (93) have had limited use. Porous chromium is used in lubricated wear applications, and is made by chemically etching regular chromium plate, sometimes with light grinding after the etch. Black chromium was used on solar collector surfaces but is replaced now by other more optically suitable materials. Baths are sulfate-free, and include fluosilicic acid or acetic acid.

Standard practices for chromium plating (94,95) and specifications for hard chromium (96) and decorative chromium (91) have been published (70).

Table 10. **Trivalent Chromium-Plating Systems**[a]

Parameter	Single cell	Double cell
anode material	carbon	Pb–7% Sn in diaphragm cell
maximum thickness, μm		
room temp	1.3	0.25
high temp	25 or more	
plating rate, μm/min		
room temp	0.13	0.10[b]
high temp	0.18	
deposit	MC and MP	MP
passivity of nonplated areas	needs postdip	needs postdip

[a] Both cell types utilize 5–25 g/L Cr at a pH 2.3–40 and a temperature from 20–50°C under mild air agitation. Current densities run from 430–1600 A/m^2, the rectifier voltage is from 4–15 V, and the anode to cathode ratio is 2:1.

[b] Average value.

11.3. Cobalt. In terms of quantity, the plating of this metal is of limited use because most high volume applications can be satisfied using nickel at considerably less cost. Cobalt has been used to coat tungsten carbide components that needed to be brazed and exposed to high temperatures in use; and as a barrier coating to inhibit migration of copper into gold. Cobalt is sputtered onto computer memory disks for its magnetic properties and this type of application has been constantly expanding. Cobalt is used in nickel electroforming solutions to increase strength and hardness. Cobalt plating solutions are so similar to nickel plating solutions in composition (97) that in most cases the equivalent cobalt salts can be substituted for nickel salts in published nickel bath formulations. Cobalt anodes dissolve well in sulfamate solutions, and have been used as auxiliary anodes in nickel sulfamate electroforming solutions.

11.4. Copper. Copper is the most common metal plated, exclusive of continuous strip plating and nickel (98). Major uses of electroplated copper is plating on plastics, printed wiring board, zinc die casting, automotive bumpers, rotogravure rolls, electrofining, and electroforming. Electroplated copper is playing a major role in the change from aluminum to copper in semiconductor interconnect technology. It signals one of the most important changes in materials that the semiconductor industry has experienced since its creation. Copper is electrodeposited for numerous engineering and decorative applications requiring a wide range of mechanical and physical properties. Copper plating is used as a final finish in some applications and is widely employed as an undercoat for other deposits. Of the several types of copper baths, the two most popular in the United States are the acid sulfate and the cyanide baths. Acid copper cannot be used directly over substrates that are attacked by high acidity, or over those on which the copper forms immersion deposits. Immersion deposits usually have poor adhesion to the substrate. For such substrates, an undercoat deposited from a cyanide copper solution is used.

Cyanide copper baths are, however, a target for replacement, and alkaline, noncyanide baths are becoming increasingly popular since the mid-1980s, as replacements for cyanide copper because of environmental issues. Care is needed, however, in choosing a noncyanide copper systems to avoid trading

Table 11. **Copper Cyanide Solution Formulations**

	Strike, g/L		Rochelle, g/L		High efficiency, g/L	
Constituent	Typical	Limits	Typical	Limits	Typical	Limits
CuCN	22	15–30	26	19–45	75	49–127
NaCN	33	23–48	35	26–68	102	62–154
or						
KCN	43	31–64			136	76–178
Na_2CO_3	15	0–15	30	15–16		
NaOH					15	22–37
or						
KOH					15	31–52
Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$	15	15	45	30–60		
By analysis						
copper	16	11–21	18	13–32	55	34–89
free Cyanide	9	6–11	6	4–9	19	10–20

one waste treatment problem for another. As of this time (winter of 2004), cyanide copper solutions are still being widely used, though less and less so, for plating the initial deposits on steel, zinc-based die castings, aluminum alloys, magnesium alloys, as well as other substrates.

Cyanide Copper. Solution make up for copper cyanide baths are shown in Table 11, while suggested operating conditions are detailed in Table 12. The more dilute, less efficient copper strike bath is a necessary and is an important step to obtain overall performance and appearance of the final plated part. Cyanide solutions are known for their cleaning ability, which is enhanced using the low efficient, high gassing cyanide copper strike baths. Strike tanks are, usually, small compared to the following plating tanks, allowing for rapid turnover of the solution through filters to remove particles and soil before the parts reach the large, more expensive plating tank. Strike compositions are modified usually through pH changes for striking various substrates. For use on steel, additional hydroxide improves solution conductivity and helps protect

Table 12. **Operating Conditions for Typical Cyanide Solutions**

Conditions	Strike	Rochelle	High efficiency
temperature, °C	40–60	55–75	60–80
cathode current density, A/dm^2	0.5–4	1.5–6.5	1–11
anode current density, A/dm^2	0.5–1	0.8–3.3	1.5–5
efficiency range			
cathode, %	10–60	30–90	70–99+
anode, %	95–100	50–70	
ratio of anode to cathode area	3:1	2:1	3:2
agitation			
cathode rod	optional	preferred	either or both
air			
solution voltage, V	6	6	0.75–4
limiting thickness, μm	2.5	13	>25

steel anode containers and tanks from corrosion. High concentration of potassium hydroxide is said to reduce anode efficiency, which can be beneficial in strike baths. Copper strike solutions tend to increase in copper content and eventually need dilution. If steel anodes are used along with copper anodes, the rate of copper buildup may be reduced, but the rate of carbonate formation is increased. Dilute acids have been used to lower the pH of cyanide solutions, but the safety of this practice is questionable. Contact of the work with the dc power supply is often required prior to entering the strike solution.

The presence of Rochelle salts in the solutions produce some grain refinement in the deposit. Other beneficial aspects include the reduction of the effects of some metallic contaminants, and the increase of the anode current density range before anode polarization occurs. Plating rates are slower for low metal contents. Rochelle salt copper baths are useful with higher metal contents for buffing or for heat treat stop-off applications. Higher currents densities produce harder-to-buff deposits; some proprietary additives can extend the useful current density range. Higher current density and higher carbonate content increase the deposit porosity. Carbonates, always present in cyanide copper solutions, are beneficial in smaller amounts but detrimental if too high. Acceptable carbonate limits vary widely; better results are obtained below ~120–150 g/L as sodium carbonate. High carbonate lowers the anode efficiency, which accelerates carbonate formation as well as producing rough deposits. Proprietary products are available to yield improvements in anode corrosion. Carbonate is formed normally from cyanide oxidation, but builds up much more rapidly when using insoluble or inefficient anodes. Carbon dioxide is also readily absorbed from the air to form carbonate salts. Thus air agitation of cyanide copper solutions, a common practice, is not recommended. Carbonate from a sodium-containing copper bath can be precipitated by cooling the solution. In northern climates, solutions are treated by pumping to an outside tank in the winter to freeze out the sodium carbonate. Potassium carbonate salts are too soluble to be removed in this manner, and are precipitated by addition of calcium salts.

High efficiency formulations allow use of higher current densities. These are sometimes also referred to as high speed formulation baths. Cyanide-plating baths typically decrease in cathode efficiency with increased current, which accounts for the good plate distribution.

More specifically, Cathode efficiency and throwing power can vary with chemical composition, additives, operating conditions, and impurities in the cyanide copper bath (99). In production tanks, the cathode efficiency of the so-called high efficiency bath formulations approach 100% only at low (often <50 A/m^2) current densities. Using more practical currents of 300–350 A/m^2, the cathode efficiency may drop 20%, especially with low agitation rates. As indicated above, it is this drop in efficiency with increased current that gives cyanide copper baths such good throwing power.

High speed baths having higher metal content permit the use of higher current densities, and additives extend this range, producing additional grain refinement and brightness. Certain selenium compounds, together with very small amounts of lead or thallium combinations, produce bright deposits. Sulfur compounds and selenium compounds codeposit, and the copper deposit is more chemically active and so tends to tarnish (oxidize) readily. Systems that avoid these have shown better resistance to accelerated corrosion tests when overplated with nickel and chromium. Sulfur is a common impurity in cyanide salts and plating solutions, additives are necessary to avoid sulfur codeposition. Cyanide copper baths are sensitive to small amounts of certain organic contaminants such as oils and greases; small amounts of nonionic and anionic detergents are used to eliminate the smeared or pitted appearance of the deposit. Hexavalent chromium even in as small quantities as 1 mg/L can cause blisters (stress) and dullness. In the presence of trivalent chromium, copper baths have been operated with as high as 3–4 g/L of chromium. While sulfur-bearing reducing agents have been used, proprietary sulfur-free products are preferred.

A not uncommon problem with cyanide copper is rough deposits most of which comes from anode films that slough off and settle on the work before the film particles can redissolve. Higher concentration of free cyanide produces less anode filming, but it also lowers the cathode efficiency and requires lowering the current. Along with the chemical composition and control, anode current density control, filtration, and agitation are key factors in minimizing roughness. Anode bags of suitable weave and material have been used successfully.

Leveling of copper cyanide plating baths can be obtained through dc current manipulation. Periodic reversal (PR) cycles combined with proper bath composition can change the leveling from a negative value to a typical value of $\sim$50%. Metallic brighteners and sulfur-bearing additives are avoided in the PR process.

Barrel plating of parts in copper cyanide solutions utilizes various formulations, some weaker, some stronger than the high efficiency/speed baths. When plating parts that tend to stick together or nest during the barrel rotation, the free cyanide may need to be increased. This may require 35–40 g/L free potassium cyanide or more with an equal copper concentration.

11.5. Acid Copper. Acid copper deposition was referred to as early as 1810 (100). The acid sulfate bath is by far the most widely used copper plating bath, both for plating and for electroforming and electrowinning. The fluoborate baths have been little used in spite of the high current densities possible. Additional information can be found in the literature (101). Bath compositions are shown in Table 13.

Copper foils used, in recent past and continue to an extent, to be electroformed on a continuous basis from copper sulfate baths for use in the electronics industry. A number of sophisticated methods have been developed in that industry lately, but the electroplating of copper using sulfate baths remains an important component material. The important fact is that, thick smooth, low stressed deposits that are easily buffed are obtained from these relatively simple baths, and applications are found in many engineering and decorative markets. Very bright, highly leveled deposits are plated using proprietary additives. The two main deficiencies, as compared to cyanide copper, are poor throwing power and the inability to plate directly on steel and certain other substrates. This is the reason, eg, that the U.S. “copper” penny is a coin of stainless steel first coated by nickel upon which a layer of copper is added. Or that Acid copper sulfate is also used to plate thick (175–200 μm) deposits over large nickel-plated rolls, then engraved, in one method, to electroform textile printing screens. Plates and rolls have been acid copper sulfate plated for graphic arts and rotogravure use. Bright acid copper sulfate baths are used extensively in decorative plating of

Table 13. **Acid Copper-Plating Baths**[a]

	Sulfate			Fluoborate	
Parameter	Typical	Average range	High throw	Low	High
Cu metal, g/L	57	38–64	15–23	60	120
$CuSO_4 \cdot 5H_2O$, g/L	225	150–250	60–90		
H_2SO_4, g/L	60	30–75	170–220		
Cl^-, g/L	0.05	0.20–0.12	0.05–0.10		
$Cu(BF_4)_2$, g/L				225	450
HBF_4, g/L				15	30
H_3BO_3, g/L				15	30
pH	<0	<0	<0	1.2–1.7	0.2–0.6
temperature, °C	25	20–45	20–30	18	65
cathode current density, A/m^2	300–700	300–700	300–700	800–1400	1400–3800
anodes[b,c]		0.02–0.08% PCu		OFHC Cu	OFHC Cu

[a] For all baths the anode to cathode ratio is 2:1; the baths are mechanically, hydraulically, or air agitated, and there is continuous filtration.

[b] Dynel or polypropylene anode bags are used for both types of anodes.

[c] OFHC = oxide-free high conductivity.

plastic trim found on automobiles, appliances, and household wares. Copper can be plated directly over the first metallic coating of electroless nickel or electroless copper. Very low current is to be used in the acid copper, initially, to avoid burning off the thin electroless deposit. More often, a nickel strike based on a Watt's bath is used to build up the electroless coating, before the acid copper. The good ductility and low internal stress are key features for plating on plastics (102).

The distribution/geometry of the electric field lines flowing from the anode to the cathode determine the distribution of the current density and with it the deposits thickness. One of the most common consequences of this is the "dog bone" or edge build up effect. Rolls and other relatively simple shapes make use of inert shields and thieves to avoid edge buildup and produce a more even plate thickness. For more complicated shapes having deeper recesses thicker deposits from cyanide copper baths have been used as an undercoat to the copper sulfate deposit. Acid copper baths operate near 100% efficient over a wide current density range. The cathode efficiency is usually slightly less than the anode efficiency, bringing about a slow increase in copper concentration unless drag-out losses are high.

In preaparing the plating solution, note that not all grades of copper sulfate are suitable for electroplating. Some contain significant amounts of silica and other materials used to improve the crystallization process and the free-flowing properties of the salt. Another point to remember is that sulfuric acid concentration has more effect on conductivity than does the copper sulfate. Low sulfuric acid content produces more high current density (HCD) burn and poorer leveling, low current density (LCD) produces dullness and gives more nodular deposits. High sulfuric acid content has less effect on the deposit but increases anode dissolution. Chloride ion is important, especially for baths that contain additives and brighteners because chloride inhibits rough and nodular plate, and is necessary for bright deposits. Low chloride content can cause dark deposits on edges and other HCD areas, loss of leveling, loss of brightness, pitting, and poor anode corrosion. Too high chloride content causes striations, increased brightener usage, reduced leveling and brightness in bright baths, and nodular, treed, and harder deposits. Too high chloride content can be reduced with zinc dust treatments or precipitation with silver nitrate followed by filtering to recover the silver. Zinc anode balls in a basket have been used by some platers with successive immersion and cleaning steps.

Addition agents for brightening, hardening, grain refining, surface smoothing, increasing the limiting current density and reducing trees are frequently added to acid copper sulfate solutions. Additives covered in patents granted in recent years are listed in Ref. 103.

High throw formulations, such as those in Table 8, are used on high aspect, PTH (plated-through-hole) printed circuit boards and in barrel plating where the high acid/low copper bath exhibits better throwing power. Acid copper sulfate solutions are tolerant to many metallic impurities. Iron is common, and has little effect in low concentrations; ~2-g/L iron. At higher concentration values, it decreases bath conductivity and reduces throwing power. Organic contaminants from brightener breakdown; oils, tank linings, and anode bags are removed with activated carbon treatment.

Copper Pyrophosphate. The earliest published reference to copper pyrophosphate deposition was by Roseleur in 1847 (104). The development of a commercial copper pyrophosphate was in 1941 by Stareck. Baths using copper pyrophosphate, $Cu_2P_2O_7$, shown in Table 14, are not in wide use in the United States, mainly for it being more expensive to make up than high throw acid formulations. Baths are used for printed circuits, plating on plastic, and electroforming. Although a pyrophosphate strike can be used to plate on steel, zinc-based die castings still require copper cyanide strikes for good adhesion. Waste treatment of pyrophosphate copper solutions presents also some problems. There is difficulty in precipitating the copper without hydrolyzing all the pyrophosphate. Further, many areas now restrict the amount of phosphate in the waste stream.

Copper–Zinc Alloy (Brass). As mentioned in the history section above, brass was the first alloy to be electroplated. It remains a popular decorative finish. Plated as an undercoat for nickel–chrome, brass provides good corrosion

Table 14. **Copper Pyrophosphate-Plating Baths**[a]

Parameter	Strike	Typical	Printed circuit bath
Cu metal, g/L	9–11	19–30	21–26
$Cu_2P_2O_7 \cdot 3H_2O$, g/L	25–31	53–84	58–73
$K_4P_2O_7 \cdot 3H_2O$, g/L	112–205	235–405	270–370
NH_4OH, mL/L	0.5–1.0	3.75–11.0	2.7–7.5
KNO_3, g/L	1.5–3.0	3.0–6.0	8.0–16.0
P_2O_7:Cu ratio	7–8:1	7.0–7.5:1	7.2–7.8:1
pH	8.0–8.5	8.0–8.7	8.0–8.4
temperature, °C	22–30	43–60	49–54
cathode current density, A/m^2	60–150	100–800	250–600

[a] For all baths the anode to cathode ratio is 2:1, the baths are mechanically or air agitated, and there is continuous filtration.

Table 15. **Brass-Plating Solutions**

	Yellow brass		
Parameter	Regular[a]	High speed	White brass
CuCN, g/L	32	75	10
$Zn(CN)_2$, g/L	10	5	60
NaCN, g/L[b]	50	125	100
Na_2CO_3, g/L	7.5		40[c]
$NaHCO_3$, g/L	10		
NaOH, g/L		45	38
NH_4OH, mL/L[d]	2.5–5.0		
pH	9.7–10.2		12.5–13.5
temperature, °C	25–35	70	15–20
cathode current density, A/m^2	up to 250	100–800	200–800
anodes	70:30 brass	70:30 brass	Zn or white brass, 35% Cu
Cu in deposit, %	70[e]	70	28

[a] A 70:30 yellow alloy is controlled by CN:Zn ratio; Zn should be 1/3–1/5 of titratable CN^-. Bath can be diluted to 65% for flash plating.

[b] Titratable CN^- is less than total and is used to control bath. Barrel-plating solutions are operated at higher CN^- and Zn levels.

[c] Value given is maximum.

[d] High ammonia favors Zn; low ammonia gives redder deposit.

[e] Red brass, 85:15, is obtained using higher CN^-/Zn ratio; architectural bronze, 90:10, with an even higher ratio.

protection compared to copper, especially on aluminum and zinc substrates. Over the years, there has been considerable use of brass plating on steel wire and other shapes because of improved rubber bonding characteristics. Brass (copper–zinc alloys) comes in defferent alloying ratios; the more common of those are yellow brass (~30% zinc), red brasses (10–15% zinc), and white brass (~72% zinc). Plating bath compositions are shown in Table 15 (in addition, see Ref. 105). Decorative yellow brass plating is usually made very thin, as flash coating over a bright nickel deposit. Brass plating times are usually as short as 30–60 s at 100–200 A/m^2. Subsequently, the brass is passivated in a dilute chromate and lacquered to protect the finish. If the brass is plated to be used for rubber bonding, the thin (0.5–2.0 μm) coating is not chromated or lacquered. Control of the yellow color in the brass by that name is simplified by the use of ammonia to redissolve the zinc. The cyanide/zinc ratio plays a key role in the proportion of copper–zinc deposited. Other, more alkaline baths have been used with Rochelle salts or other complexing agents to keep all components in solution. Noncyanide brass plating baths have been suggested (106) but it never gained significant use.

Copper–Tin Alloys (Bronze). Electroplated bronze electrodeposits are being used for decorative applications as a final finish, with and without subsequent coloring or antiquing treatments. A clear lacquer helps preserve the deposit. In addition, though on a limited basis, bronze has also been used as an undercoat for nickel–chromium finishers on steel, zinc, and aluminum. In some functional applications, plated bronze is used as a stop-off material in the selective nitriding of steel parts. This system finds frequent use as a nongalling bearing material. A single process simultaneously hones and plates the

Table 16. **Typical Bronze-Plating Solutions**

Parameter	(1)	(2)	Speculum
CuCN, g/L	35	29	11
Cu metal, g/L	25	20	8
$Na_2SnO_3 \cdot 3H_2O$, g/L	38	35	90
Sn metal, g/L	17	14	40
NaCN, g/L			
total	54	64	27
free	15	22	16
NaOH, free g/L	7.5	10[a]	16
Rochelle salts, g/L		45	
pH	12.6		
temperature, °C	65	65	65
cathode current density, A/dm^2	3	2–10	3
Sn in deposit[b], %	10[c]	12	40[d]
anodes	Cu[e]	Cu	Cu or dual Cu and Sn

[a] Potassium salts, which permit higher currents and better efficiency, are used.

[b] To increase Sn in deposit, raise NaCN and decrease NaOH. New bath may need 0.2 g/L ammonia to obtain high Sn.

[c] Ductile.

[d] Brittle.

[e] If using bronze anodes, Sn should be <10% and anode current density <1A/dm^2.

inside diameters of bearing surfaces in a high speed operation. Speculum (tin rich) deposits, when polished to a high luster, resemble silver plate, have good hardness, and resist staining by most foods. These deposits have therefore found use on tableware and household fixtures; speculum plating is not recommended for outdoor use, however. Typical bath formulations for bronze plating baths are shown in Table 16. Bronze plating is done primarily in cyanide–stannate baths; noncyanide baths do appear in the literature (107), but are not in common use. The more common bronze contains ~10–15% tin; speculum bronze is 40–45% tin.

12. Patterned Electrodeposition for Microelectronics

Computers, microprocessors, and other microelectronic devices could not exist without the technology of depositing thin metal or alloy films with fine litographic patterns. There seem to be three trends propelling patterned electrodeposition into a phase of major expansion. First, high speed machines require the high conductivity of copper and acid copper plating is simple and capable of reaching high rates. Second, the pattern replication powers of electrodeposition are ideally suited to the level of miniaturization required for wiring structure. Third, demands for cost reduction have increased the importance of reducing ths capital and operating expenses asociated with metal deposition processes, and it is therefore likely that electroplated copper thin film, which is important today, will continue to play a central role in the future.

12.1. Gold.

The motives behind the use of electroplated gold changed dramatically in the mid-twentieth century when the emerging electronics industry required special purpose electrical connections. In the last analysis, it is used both for decorative and industrial or engineering purposes. The engineering use has grown rapidly since the 1950s, due to expanding usage in the electronics and computer industries. The important properties of industrial gold are corrosion resistance, low electrical contact resistance, and good solderability. The introduction of small amounts of other metals reduces one or more of these properties, often significantly, eg, as little as 1% iron increases the electrical resistance of gold >1000%. Common electronics applications include semiconductors, printed/etched circuits, and contacts/connectors. Engineering gold is classified into three types based on purity and hardness (108). Type 1, code A is used for semiconductor components, thermocompression bonding, and where ever high temperature resistance is needed. Type 2 is for general purposes, high reliability electrical contacts, solderability, and wire wrap connections. Type 3 is used for wear resistance, but does not stand high temperatures. Types 1 and 2 are preferred for solderability.

Plating of gold is usually over electroplated (or electroless) nickel-plated substrates. The smoothest substrate allows the thinnest gold deposits without porosity. For many substrates, the minimum gold thickness for pore-free deposits is ~2.5 μm (and even less). Gold plate thicknesses may vary from a flash or wash of 0.5 μm up to ~10 μm depending on application. In electronics applications, the range is more often 0.5–1.25 μm since, thicker gold deposits produce brittle solder joints. Decorative gold plate has to be a minimum of ~0.18 μm to be identified as electroplated gold on jewelry. If thickness is 2.54 μm, it can be classified as heavy gold electroplate. A small amount of gold is used in electroforming with substantial thicknesses. Aerospace applications for both thin and thick deposits are among the many newer uses for gold.

There are literally hundreds of gold-plating bath formulations; most of which are proprietary. Gold flash, gold strikes, soft golds, hard golds, bright golds, and golds of all purities and colors account for the wide selection (109). Formulations can be classified as alkaline, neutral, or acidic; typical baths are shown in Tables 17 and 18.

Gold baths, even acid gold, have always been primarily based on cyanide. Gold solutions and rinses are recovered for gold value. Of the noncyanide gold

Table 17. **Gold-Plating Bath Compositions**

Parameter	Alkaline[a]	Neutral[a]	Acid[a]	Strike
Au metal, g/L	2–12	4–16	2–16	0.5–2.0
$KAu(CN)_2$, g/L	3–18	6–24	3–24	0.75–3
KCN, g/L	15–48			15–90
K_2CO_3, g/L	0–45			
K_2HPO_4, g/L	0–45	0–90	0–100	15–45
KOH, g/L	1–30			
pH	11–13	6–8	3–6	8–13
temperature, °C	50–70	25–70	40–70	40–60
cathode current density[b], A/m^2	10–100	20–100	10–100	
anodes[c]	Pt, SS	Pt, SS	Pt	SS

[a] Proprietary brighteners and chelators are used.

[b] Higher currents require higher gold contents.

[c] SS = stainless steel; Pt may be platinized titanium or platinized niobium.

Table 18. **Typical Cyanide-Based Plating Baths (Concentrations in g/L)**

Bath operation	Alkaline cyanide		Buffered citrate		Buffered phosphate	
	Rack	Barrel	Rack	Barrel	Rack	Barrel
$KAu(CN)_2$	12	6	20	20	20	20
KCN	20	30				
K_2HPO_4	20	30			40	40
KH_2PO_4					10	10
K_2CO_3	20	30				
K_2H citrate			50	50		
T, °C	50–60	50–65	60–70	60–70	60–70	60–70
KmA/cm^2	1–5	1–5	1–2	4–6	0.7–2	4–6
pH	11–11.5	11–11.5	4–5.8[a]	4–5.8[a]	6–8	6–8

[a] pH may drift during use. Citric acid or KOH can be used to adjust pH.

systems, gold sulfite baths, which may contain phosphates, citrates, and chelating agents, have been growing in use. Claims are made for better ductility and throwing power, good alloy deposition, and more tolerance to impurities. Most baths are proprietary but Ref. 109 contains many useful details.

12.2. Indium. Indium compounds (In_2S_3, InP, InAs, and InSb) electrodeposition has been investigated and demonstrated as those materials are important semiconductors. A thorough discussion and source of references is found in Ref. 87. Indium in itself, diffuses readily into copper, silver, and lead, increasing hardness and imparting good antifriction properties. Indium plating of copper wire, used in joining aluminum wire to copper wire, has declined with decreased use and near elimination of aluminum wiering (as a potential fire hazard) in housing. Indium plating is used for bearing materials, and some is used in electronics for contact pads for flip chip bonding. Indium may be plated from cyanide, fluoborate, and sulfate baths, the standard bath recommended is based on sulfamate (110). A typical bath contains 105-g/L indium sulfamate to give ~30 g/L indium metal along with 150-g/L sodium sulfamate, 26-g/L sulfamic acid, 46-g/L sodium chloride, and 2.3-g/L triethanolamine. The bath is operated at pH 1.5–2.0 at room temperature with 100–200 A/m^2; anodes are indium metal. Higher indium content allows current up to 1000 A/m^2. The metal is expensive, and plating is not widely practiced.

12.3. Iron and Iron alloys. Practically all iron is plated from acidic solutions of iron(II) (ferrous) salts. The presence of iron in the iron(III) (ferric) state in these baths, in an appreciable concentration, is undesirable because it lowers the cathode efficiency for depositing the metal and it may cause the deposit to be brittle, stressed and be pitted. In practice, it is not difficult to maintain the concentration of iron(III) ion at harmless level. Copper alloy soldering iron tips are plated with thick (175–200 μm) iron layer to prevent solder from dissolving the copper. Iron has also been used to plate stereotype printing plants, and in plating of aluminum pistons and cylinders in automotive engine blocks. Mismachined and worn parts have been salvaged on a small scale with iron plating. Some sleeves used on larger engines have been iron plated. Printing plates for printing currency have been electroformed in iron plating baths. Iron has been plated from chloride, sulfate, mixed chloride–sulfate, fluoborate,

Table 19. **Composition and Operating Conditions for Iron Plating Baths**

Solution	Composition	Operating conditions
sulfate	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$: 250–300 g/L	Low pH 2.8–3.4 or High pH 4.0–5.5 2A/dm^2 25°C
	$FeSO_4 \cdot 7H_2O$:250 g/L $(NH_4)_2SO_4$:120 g/L	pH 2.1–2.4, 4–10 A/dm^2 60°C
(for production of strip)	$FeSO_4 \cdot 7H_2O$: 600 g/L	pH 1.4, 6.7 A/dm^2 47°C
chloride (Fischer-Langbein)	$FeCl_2 \cdot 4H_2O$: 300 g/L $CaCl_2$: 335 g/L	pH 0.8–1.5, 6.5 A/dm^2 90°C
	$FeCl_2 \cdot 4H_2O$; 300–450 g/L $CaCl_2 \cdot$150–190 g/L	pH 0.2–1.8, 2–9 A/dm^2 88–99°C
(for electrotype)	$FeCl_2 \cdot 4H_2O$: 240 g/L KCl: 180 g/L	pH 5–5.5, 2–5 A/dm^2 25–40°C
(for production of strip)	Ferrous chloride 120–150 g/L as Fe^{2+}	pH 0.5–4.7, 33–40 A/dm^2 98–106°C
sulfate-chloride (for electrotype)	$FeSO_4 \cdot 7H_2O$: 250 g/L $FeCl_2 \cdot 4H_2O$: 42 g/L NH_4Cl: 20 g/L	pH 3.5–5.5 5–10 A/dm^2 40–43°C
(for production of strip)	$FeSO_4 \cdot 7H_2O$: 500 g/L NaCl: 50 g/L	pH 2.5, 3–27.5 A/dm^2 80°C
sulfamate	Iron(II) sulfamate: 250 g/L Ammonium sulfamate: 30 g/L	pH 3.2–15 A/dm^2 50–70°C
fluoborate	$Fe(BF_4)_2$: 226 g/L NaCl: 10 g/L	pH 2–3, 2–10 A/dm^2 55–60°C

and sulfamate solutions; chloride is the most common. Composition and operating conditions for iron plating bath is given in Table 19. while in Table 20 bath compositions and operating conditions of iron alloy plating is given. Finally, the characteristics of iron deposits is delineated in Ref. 111.

12.4. Lead and Lead (Tin) Alloys. The preferred field of application of lead coating is the corrosion protection against sulfuric acid containing media. Historicaly, lead has been used in battery parts for its good resistance to sulfuric acid. Lead is plated from fluoborate solutions, as shown in Table 21. In additive free acidic electrolytes, lead will be deposited in dendritic form. A full list of additives for lead deposition in acidic electrolytes, can be found in Ref. 112. The deposition of tin lead alloys has the most technical importance among all tin or lead alloys. Alloy deposition is possible in all compositions. Low tin alloys of lead are used in bearings; 93% lead-7% tin was specified for bearings on piston aircraft engines. Lead–tin alloys of 3–15% tin are referred to, by some, as terne; for hot-dip coatings, terneplate can be 20% tin. Terneplate has been used to protect steel in gasoline tanks. Solder deposits are also plated. Lead–tin baths are similar to lead baths. Stannous fluoborate is added to supply the tin. Sulfamate solutions have been described for lead plating (108,109), but have found only limited industrial use. Requirements for lead and lead–tin deposits on steel have been specified (113). Lead–tin deposits on steel have outstanding resistance to atmospheric corrosion, especially with a 0.25-μm copper strike undercoat. Lead coatings (~20 μm) show an expected life of >9 years in an industrial atmosphere. Up to 15% tin does not decrease the corrosion resistance. Baths based on methane sulfonic acid are gaining in use both for lead and lead–alloy baths. Lead is under strict regulation in the environment and waste streams. Conse-

Table 20. **Bath Composition and Operating Conditions for Iron Alloy Plating**

Alloy	Purpose	Bath composition	Operating conditions	Characteristics
iron–nickel	decorative	$NiSO_4{\cdot}6H_2O$: 150 g/L $NiCl_2{\cdot}6H_2O$: 90 g/L $FiSO_4{\cdot}7H_2O$: 20 g/L H_3BO_3: 45 g/L stabilizer and brightener	60°C pH 3.5 4 A/dm^{-2}	Fe-50%Ni hardness: 508 Knoop
	magnetic	nickel sulfate: 16 g/L nickel chloride: 40 g/L ferrous sulfate: 1 g/L boric acid: 25 g/L sodium saccharin: 0.375–3 g/L sodium lauryl sulfate: 0.2 g/L	26°C pH 2.5 1.5 A/dm^2	Fe-80% Ni (705 nm thick) Coercive force: 0.25 Oe
	invar	nickel sulfamate: 0.75 mol/L ferrous chloride: 0.25 mol/L boric acid: 0.5 mol/L sodium dodecyl sulfate: 0.5 g/L ascorbic acid: 1 g/L saccharin: 2 g/L	50°C pH 2.5 10 A/dm^2	Fe-39% Ni: thermal expansion coefficient of $8.1 \times 10^{-6\circ}C^{-1}$ $4–5 \times 10^{-6\circ}C^{-1}$ (after annealing at 680°C)
iron–zinc	corrosion protection	$FeSO_4{\cdot}7H_2O + ZnSO_4{\cdot}7H_2O$: 500 g/L Na_2SO_4: 30 g/L $CH_3COONa{\cdot}3H_2O$: 20 g/L $C_6H_8O_7$: 5 g/L	50°C pH 2.5 3 A/dm^2	
iron–cobalt	antifriction	$FeCl_2$: 227 g/L $CoCl_2{\cdot}6H_2O$: 8 g/L H_3BO_3: 10 g/L NH_4Cl: 75 g/L NaCl: 75 g/L NH_4BF_4: 10 g/L	50°C pH 1 5–40 A/dm^{-2}	Fe-6% Co: hardness: 640 vickers
iron–chromium nickel	corrosion protection	$K_2Cr_2(SO_4)_4{\cdot}25H_2O$: 326 g/L nickel sulfate: 84 g/L ferrous sulfate: 56 g/L glycine: 150 g/L	20°C pH 2–2.2 8.5 A/dm^2	9.8–11% Ca7.3–6% Ni

Table 20 (*Continued*)

Alloy	Purpose	Bath composition	Operating conditions	Characteristics
iron−phosphorous	corrosion protection	$FeCl_2$-$4H_2O$: 240 g/L KCl: 180 g/L hypophosphorous acid	40°C pH 2 40 A/dm^2	Fe-0.4% P
	magnetic	$FeSO_4 \cdot 7H_2O$: 1.0 mol/L $(NH_4)_2SO_4$: 0.1 mol/L $C_6H_7O_6$: 0.1 mol/L $NaH_2PO_2H_2O$: 0.01 mol/L	25°C pH 2.5 1 A/dm^2	Fe-6% P coercive force: 2 Oe
iron−boron	magnetic	$FeSO_4 \cdot 7H_2O$: 0.07 mol/L KBH_4: 0.3 mol/L $KNaC_4H_4O_6 \cdot 4\ H_2O$: 0.6 mol/L $(NH_4)_2SO_4$: 0.08 mol/L NaOH: 0.4 mol/L	30°C pH 12.5 1 A/dm^2	Fe-8% B coercive force: 3.6 Oe saturation magneto atriction: 27×10^{-6}
iron−carbon	antifriction	$FeSO_4 \cdot 7H_2O$: 40 g/L L-aacorbic acid: 3.0 g/L citric acid: 1.2 g/L	50°C pH 2.5 3 A/dm^2	Fe-1% C hardness: 600 Vickers
iron−carbon−boron	antifriction	$FeCl_2$-$4H_2O$: 1.0 g/L malic acid: 5×10^{-3} mol/L boric acid: 40 g/L dimethylamineborane: 2.5 g/L	50°C PH 3.5 5 A/dm^{-2}	Fe-0.2% C-0.11% B hardness: 800 Vickers

Table 21. **Lead and Lead–Tin-Plating Baths**

Parameter	Lead	7% Sn–Pb	Solder, 60% Sn–Pb
lead metal, g/L	120	88	30
$Pb(BF_4)_2$,[a] g/L	220	160	53
HBF_4 free, g/L	30	100–200	100–200
H_3BO_3, free, g/L	13.3		30
Sn metal, g/L	6	52	
$Sn(BF_4)_2$,[a] g/L		15	130
peptone,[b] g/L	0.2–1.0[c]	0.5	5.0
temperature °C	25–40	15–38[d]	15–38
current density, A/m^2			
cathode	50–500[e]	300	300
anode	100–300	150	

[a] Available commercially as liquid concentrates.

[b] Used as brightener.

[c] Animal glue or gelatin has also been used, 0.2 g/L. Peptone is predissolved and stored warm for a few days before use.

[d] Higher temperatures decrease Sn in deposit.

[e] Doubling the concentration of the chemicals, except the brightener, permits higher currents, up to 700 A/m^2 for barrel plating and heavy buildup.

quently, in the future the use of lead plating will be reduced to a minimum. The application of low lead containing alloys will further increase, however.

12.5. Nickel. Nickel electroplating is a commercially important and versatile surface finishing process. The applications of nickel electroplating fall into three main categories: decorative, functional, and electroforming. A great variety of plating baths have been formulated, but most nickel plating is done in either Watts or sulfamate baths. Watts baths contain sulfate and chloride nickel salts along with boric acid, and were first proposed in 1916 (114). Nickel was first plated from sulfamate in 1938 (115) and patented in 1943 (116). The process was brought to market in 1950 (117). Typical bath compositions and conditions are shown in Table 22.

Other (nine)nickel plating solutions are delineated in Ref. 118. Watts and sulfamate baths, however, are both used for most applications. The difference in the deposits is in the much lower internal stress obtained, without additives, from the sulfamate solution. With the presence of additives tensile stress can be reduced through zero to a high compressive stress with the addition of proprietary sulfur-bearing organic chemicals that may also contain saccharin or the sodium salt of naphthalene-1,3,6-trisulfonic acid. These materials can be very effective in small amounts, and difficult to remove if over added. Thus, as an example, about 100 mg/L of saccharin reduced stress of a Watts bath from 240 MPa (34,800 psi) tensile to ~10 MPa (1450 psi) compressive. Internal stress value vary with many factors (72) and numbers should only be compared when derived under the very same conditions.

Common problems when additives are used in nickel-plating baths include codeposition of the sulfur compounds. Sulfur-bearing stress reducers can increase brightness, brittleness, strength, and hardness, and decrease corrosion resistance, heat resistance, and resistance to oxidation. For applications that

Table 22. **Nickel Electroplating Solutions**

	Electrolyte composition[a] (g/L)		
	Watts nickel	Nickel sulfamate	Basic semibright bath[bc]
nickel sulfate, $NiSO_4 \cdot 6H_2O$	225–400		300
nickel sulfamate, $Ni(SO_3NH_2)_2$		300–450	
nickel chloride, $NiCl_2 \cdot 6H_2O$	30–60	0–30	35
boric acid, H_3BO_3	30–45	30–45	45
	Operating conditions		
temperature, °C	44–66	32–60	54
agitation	air or mechanical	air or mechanical	air or mechanical
cathode current density (A/dm^2)	3–11	0.5–30	3–10
anodes	nickel	nickel	nickel
pH	2–4.5	3.5–5.0	3.5–4.5
	Mechanical properties		
tensile strength, MPa	345–485	415–610	
elongation, %	10–30	5–30	8–20
Vickers hardness, 100-g load	130–200	170–230	300–400
Internal stress, MPa	125–185 (tensile)	0–55 (tensile)	35–150 (tensile)

[a] antipitting agents formulated for nickel plating are added to control pitting.
[b] Organic additives available from plating supply houses are required for semibright nickel plating.
[c] Typical properties of *full-bright* nickel deposits are as follows: Elongation percentage—2–5; Vickers hardness, 100-g load—600–800; internal stress, MPa—12–25 compressive.

require low stress and pure deposits, sulfamate baths are used. In an often proposed, two-stage method of electroforming large nickel textile printing screens; Watts baths with a stress reducer in the first stage and a brightener/stress reducer in the second stage are used to make high quality screens in high volumes (119).

Sulfamate nickel bath has some other differences (comparred to, say Watts) in operation. First, under conditions of higher temperatures and lower pH, the sulfamate ion can hydrolyze to form sulfate and ammonium ion. High concentration ammonium ions increases stress and decreases ductility at higher currents. Ammonium ion cannot be removed practically from the plating bath. The second issue concerns a phenomenon whereby the sulfamate ion is oxidized at an anode surface that is not completely active. Higher chloride content is helpful in moderating this when nickel anodes having a slight passivity are employed. Completely inactive or insoluble anodes can oxidize the sulfamate rapidly. The oxidized sulfamate acts much like the sulfite or dithionite ion in that some sulfur ion is codeposited, and the deposit has properties (respecting stress) similar to those obtained using saccharin. The principle of using a portion of the tank current to go through an inactive, or <100% active, anode as a means of stress control is recommended. If conditions require the use of insoluble auxiliary anodes, higher chloride concentration seems to retard the oxidation. If the stress becomes too compressive, an electrolytic recovery process may be used. The use of active sulfur-containing nickel anodes may eliminate the anode oxidation problem, when required.

In general, nickel sulfamate is far more soluble than the sulfate salt, consequenly baths can be operated using higher nickel concentrations and higher currents. In addition, sulfamate baths have been found to have superior microthrowing power, the ability to deposit in small cracks or crevices. Using one nickel salt, only a hydrometer and pH paper are needed to control the bath. A small amount of chloride salt may be added as a proprietary. Highly purified nickel sulfamate concentrates are commercially available those can be used to make up new plating baths without further purification.

For Watts baths, nickel sulfate provides most of the nickel ion. Nickel chloride aids in anode corrosion, conductivity, and throwing power, but increases tensile stress. Boric acid is a buffer that works principally on the cathode film. It also reduces burning and pitting, and allows the use of higher current densities. It contributes to smoother, more ductile deposits. Common impurities that affect nickel baths include iron, copper, zinc, chromium, and lead. Treatments and some additives for removal or control of these have been developed over the years so that nickel plating baths can be used for many years with proper attention and care. When making up a new bath, it is often desirable and necessary to purify the solution before it can be used. Typically, high pH, (5.0–5.2) and activated carbon treatments are applied along with several hours of low current density (LCD) electrolysis. Iron is removed by high pH precipitation, or sometimes complexed with citrates or gluconates. Anode efficiency is higher than cathode efficiency, thus, using closed loop systems, nickel ion builds up and eventually solution has to be withdrawn. Several methods are available for recovery of nickel from waste streams, or it is easily precipitated as the hydroxide sludge. Cost considerations of nickel make it favorable to recover the metal.

Wetting agents such as sodium lauryl sulfate are usually necessary to reduce pitting in most nickel baths. Improved proprietary wetting agents are available with less foaming and better antipit properties. One nickel process that rarely needs wetting agent is barrel plating. Nickel plating in a barrel with the sulfamate bath often requires higher (5–6 g/L) chloride, temperatures of 60–63°C, and lower (3.3–3.6) pH, to avoid laminated plate.

In addition to the above, it is important to note that nickel strike solutions are used primarily to obtain good adhesion on nickel, stainless steels, and other passive substrates. The most common among those is called Woods strike. It is composed of nickel chloride and hydrochloric acid in various proportions. One specific common formula contains 240-g/L nickel chloride hexahydrate and 12% by volume hydrochloric acid. Nickel glycolate strikes have had limited use for plating directly on zinc-based die castings. All sulfate, sulfamate, and Watts nickel strikes have been used in plating on plastics (in addition to electroless nickel) (120). A low (1.5 or less) pH nickel sulfamate strike, operated at room temperature, has been used for many years for plating on multimetal composites and passive metal substrates. Electroplated nickel coatings for engineering uses are covered by ASTM B689-97, 2003 (31).

To sum, the physical and mechanical properties of electroplated nickel vary with the type of bath, impurities, and additives used, along with operating conditions such as pH, current density, temperature, and agitation. Plating thickness should always be included when expressing values for elongation and other mechanical properties. Generally, nickel deposits from sulfamate baths are a little harder and stronger, with less elongation than Watts deposits.

Bright Nickel. Electroplated from pure nickel salts, nickel is a dull gray, satin–like deposit. It has to be buffed to obtain a bright finish. Brighteners should be used to obtain bright deposits directly from the bath (121). The additives currently used fall into two classes/categories. They have variously been labeled (*1*) primary and secondary, (*2*) first class and second class, and (*3*) carrier and brightener. The last is more commonly used in plating plants, while the scientific/engineering literarure uses either the first or the second.

Specifically, the carrier portion of the system usually contains materials that have been found to produce some grain refinement, some brightness, and contribute to more compressively stressed deposits. The brightener portion, sometimes called brightener leveler, contains materials that in conjunction with the carrier produce high luster and leveling to build considerable brightness. These materials often contribute to high tensile stress. Impurities have to be kept low and plating solutions well-filtered. Wetting agents are usually required to control pitting. For best consistent results, bright nickel baths should be periodically purified using LCD electrolysis and activated carbon treatments.

Even after all these years of activities in electroplating, additives that go into the fairly common-place nickels bath are almost always proprietary; carrier portions may include the sodium salts of benzene disulfonic acid, naphthalene 1,5-disulfonic acid, saccharin, and allyl sulfonic acid. Generally, these compounds are characterized by a $=C-\ SO_2$ group. Brightener leveler portions include a large number of possible materials. A few are based on small amounts of zinc, cadmium, lead, selenium, or tellurium, etc, and many are based on organic compounds containing unsaturated groups such as $C{=}O$, $C{=}C$, $C{\equiv}C$, $C{=}N$, $C{\equiv}N$. In general, nickel brighnteners and the theories of the brightening processes are well covered in patents and other literature (122). When using carrier-brightener additives, portions of these materials are codeposited; as much as 0.06–0.10% sulfur, as sulfide, or higher is present. High sulfur content increases the activity of the nickel deposit. This is not always a desirable case. Bright nickel baths are usually based on Watts bath formulas, regular or high chloride. Sulfamate solutions have been used, but to a lesser extent.

Dual Nickel and More. Sulfur-free systems are referred to as semibright nickel. The more well known of these are based on coumarin. In the past, these soft, hazy deposits were buffed bright and a layer of bright nickel was deposited for appearance. It was later observed that better corrosion protection was obtained using this dual nickel system; not all of which could be attributed to the buffing. Rather, the improvement is ascribed to the sulfur-free nickel being much more noble than the more anodic top layer; pit penetration as it reaches the cathodic layer is reduced and directed more laterally. This potential difference is being used in specifications as the STEP test (123). The sulfur content in the semibright layer should be <0.005 mass% and >0.04 mass% in the bright nickel. Improvements in sulfur-free additives have resulted in much brighter deposits. As an extension to the dual nickel, a thin, higher sulfur-containing nickel strike is deposited between the sulfur-free and the bright nickel. The sulfur content of this minimumally 2.5-μm strike is 0.15–0.20 mass%. Triple nickel and dual nickel are covered by ASTM specification B456 (91). A fourth nickel deposit has shown improved protection by the effects it has on subsequent chromium deposits. Highly stressed, these nickel strikes have been used to aid in producing microcracked chromium.

Special Nickel Plating Baths. Nickel for nonreflective, decrative, or solar absorptive uses is plated from nickel solutions containing ammonium, zinc, and thiocyanate salts. These deposits are referred to as black nickel. Very low (5–20 A/m^2) currents are used for the deposition (118,124); coatings are thin and often waxed to protect the finish. Nickel composites containing hard particles for wear (eg, diamond dust), or abrasive particles (eg, very fine glass particles) for cutting and grinding tools, are plated from conventional Watts or sulfamate solutions to which the particles are added. Special techniques are required to obtain even particle deposition throughout the deposit. In the case of electroless deposition even distribution is 'automatic'. Other composites having plastic powders, fibers, or polytetrafluoroethylene (PTFE) for lubricity require additives to aid in wetting and particle dispersion.

12.6. Nickel Alloys. The electrodeposition of nickel alloys and other metal alloys is discussed in detail in Ref. 125.

Nickel–Iron. Nickel alloys containing 10–35% iron are useful in decorative applications as a cost-saving substitute for all-nickel deposits. One Watts-based variation contains about 45 g/L nickel, 3 g/L iron, and boric acid and additives such as citrates and gluconates. Hydroxy carboxylic acids act as stabilizers for the ferrous iron. The bath is run at 55–65°C at a pH of 2.8–3.6 and current densities of 300–400 A/m^2. Iron salts are added as ferrous sulfate or ferrous chloride. Bright nickel additives are used. Decorative nickel iron alloy plating processes were commercialized back in the late 1970s and nondecorative processes with ~20% iron, often called permalloy for their high permeability, are plated for their magnetic properties.

Nickel–Cobalt. Nickel–cobalt alloys (125) are used for engineering properties, especially in electroforming. Alloys over the entire range (0–100% cobalt) have been obtained from various baths containing simple salt solutions. Nickel–cobalt plating solutions are similar to those used for nickel deposits with cobalt salts substituted for some of the nickel salts. Sulfate, chloride, and sulfamate salts of cobalt are used. Cobalt adds strength and hardness to nickel deposits. Cobalt content of the deposit increases with bath agitation and with the ratio of cobalt to nickel in solution. Generally, the cobalt in the deposit decreases with current density.

Nickel–Phosphorus. Considerable interest in electrodeposited nickel–phosphorus was created with the realization of the benefits of the electroless nickel–plated alloy (126). The properties of those alloys appear to be the same from either process and are related to the phosphorus content (126,127). Deposits using 2–15% phosphorus and higher can be electroplated; lower phosphorus deposits are dull while higher phosphorus deposits are bright. Phosphite ion provides the phosphorus; the more expensive hypophosphite used in electroless nickel, as reducing agent, is not required. Low (2%) phosphorus deposits, can be obtained simply using phosphorus acid additions to a Watts bath and operating the bath at 0–2 pH with a temperature of 75–95°C and current of 500–4000 A/m^2. Higher phosphorus alloys require higher phosphite in solution. To obtain this without making the bath too acidic, part of the nickel content is added as the reaction product of nickel carbonate and phosphorus acid.

Nickel–Tungsten. These alloys may be deposited from acid Watts baths that contain sodium tungstate producing deposits with up to ~5% tungsten. Alkaline baths with ammonium salts in the nickel solution, along with Rochelle salts, citrates, or glycolates can deposit 10–20% tungsten. The properties of the alloy have been reported lately (125) and they are being considered as possible substitute for decorative chromium. Thin nickel–tungsten coatings having <4% tungsten have been found to solder very well even after aging. Nickel–tungsten alloys having codeposited silicon carbide particles have been proposed (128,129). The deposit contains 5–10% silicon carbide and 44–50% tungsten. They are considered as a possible replacement for hard chromium plating.

12.7. Platinum Group Metals.

Rhodium. In addition to its decorative uses, rhodium has useful properties for engineering applications. It has good corrosion resistance, stable electrical contact resistance, wear resistance, heat resistance, and good reflectivity. The use of rhodium for engineering purposes is covered by an ASTM specification (130). Typical formulae are shown in Table 23. The rhodium content is obtained from prepared solutions available from proprietary plating supply houses. Replenishment is required because anodes are not soluble. Rhodim for decorative use may be 0.05–0.15 μm thick; for industrial use, it may be 1.0–5.0 μm thick.

Platinum. Plating of this metal has found application, eg, in the production of platinized titanium, niobium, or tantalum anodes that are used as insoluble anodes in many other plating solutions. Plating solutions are often based on platinum "P" salt, which is diamminedinitroplatinum(II). Also, dinitroplatinite sulfate–sulfuric acid bath has been used to plate directly onto titanium. Specifically, this bath contains 5 g/L of the platinum salt, pH adjusted to 2.0 with sulfuric acid. The bath is operated at 40°C with current density 10–100 A/m^2. Baths based on chloroplatinic acid have been used in both acid and alkaline formulations: the acid bath uses 20 g/L of the platinum salt and 300 g/L hydrochloric acid at 65°C and current density 10–200 A/m^2. The alkaline bath uses 10 g/L of the platinum salt, 60 g/L of ammonium phosphate, and ammonium hydroxide to give a pH 2.5–9.0. The alkaline bath can be plated directly onto nickel-base alloys; acid baths require a gold strike, first, on most metals.

Table 23. **Rhodium-Plating Baths**[a]

Parameter	Decorative: Phosphate bath	Decorative: Sulfate bath	Industrial
rhodium, g/L[b]	2	1.3–2.0	5
phosphoric acid (85%), mL/L	40–80		
sulfuric acid (96%), mL/L		25–80	25–50
current density, A/m^2	200–1000	200–1000	100–300
temperature, °C	45–50	45–50	45–50

[a] Anodes can be platinum or platinum clad.

[b] Rhodium from commercial concentrate in appropriate acid, phosphoric or sulfuric.

Palladium and Palladium Alloys. Palladium is often used as catalyst. This application is rising rapidly in quantity among European and North American automotive manufacturers. It is also used in telephone equipment and in electronics applications as a substitute for gold in specific areas. Palladium is usually plated from ammoniacal and acid baths; available along with chelated variations as proprietary processes. One typical alkaline bath uses 8 g/L diammine-dinitropalladium, 100-g/L ammonium nitrate, and 10-g/L sodium nitrite. The pH is adjusted to 9–10 using ammonium hydroxide, and the bath is operated at current density 100 A/m^2 at 50°C. If ammonium sulfamate, 100 g/L, is used in some baths to replace the nitrate and sodium nitrite salts, the bath is run at lower temperature, 25–35°C, and a pH 7.5–8.5. A palladium–nickel alloy, 75% Pd, is plated from a bath having 6-g/L palladium from the same salt, 3-g/L nickel from nickel sulfamate concentrate, and 90-g/L ammonium hydroxide. The bath is operated at 20–40°C current density 50–100 A/m^2. A number of bath formulations is given in reference 131.

Other Metals. Ruthenium, the least expensive of the platinum group, is the second best electrical conductor (after silver), has the hardest deposit, and has a high melting point. A general purpose bath uses 5.3-g/L ruthenium as the sulfamate salt with 8-g/L sulfamic acid, and is operated at 25–60°C with a pH 1–2. Insoluble lead-based anodes have been replaced by catalytic dimensionally stable anodes for oxygen evolution. IrO_2-based catalytic layers appear to be favored on titanium substrates. Osmium has been plated from acid chloride solutions (132) and iridium (132) from bromide solutions. Osmium deposits are sometimes used as wear counterfaces for jewels in watch improvements.

12.8. Silver. Cyanide baths are the standard for silver plating. The baths are fairly stable and easy to maintain. Cathode and anode efficiencies are close to 100% and solutions can be kept in balance for long periods of operation. For this reason, the use of high quality of silver anodes (purity 99.98% or better) is desirable. Only minor modifications and improvements in brighteners have occurred since silver electroplating was first patented in 1840 (15). Typical plating baths are shown in Table 24. Silver strikes are necessary to obtain adhesion on most metals. A sample of those is given in Table 25 and 26. A large proportion of silver plating is used for decorative purposes, such as tableware, jewelry, art work, musical instruments and the like, a growing amount,

Table 24. **Typical Bath Composition (In g/L^1)**[a]

	Bright silver (conventional)	High speed (thick deposit)
silver (metal)	20–45	35–120
silver cyanide	31–55	45–150
potassium cyanide (total)	50–80	70–230
potassium cyanide (free)	35–50	45–160
potassium carbonate	15–90	15–90
potassium nitrate		40–60
potassium hydroxide		4–30
current density, A/dm^2	0.5–1.5	0.5–10.0
temperature, °C	20–28	35–50

[a] Note: Brighteners are added as required.

Table 25. **First Strike Bath for Steel**

silver cyanide	1.5–2.5 g/L
copper cyanide	10–15 g/L
potassium cyanide	75–90 g/L
temperature	22–30°C
current density	1.5–3.0 A/dm^2
volts	4–6

Table 26. **Strike for Nickel and Nonferrous Metals, and Second Bath for Steel**

silver cyanide	1.5–5 g/L
potassium cyanide	75–90 g/L
temperature	22°–30°C
current density	1.5–3.0 A/dm^{-2}

however, is found in industrial applications. These uses include bearings, reflective surfaces, contact areas on busbar and other electrical and electronic contacts, solderable surfaces, in thermocompression bonding, selective plating on semiconductor components to replace gold on many devices, and other applications where the high thermal and good electrical conductivity (best among metals) are useful. There is an ASTM specification covering silver plating for engineering uses (133). Chromate conversion coatings are sometimes specified as a posttreatment in engineering applications. A proprietary, noncyanide, slightly alkaline silver-plating bath based on succinimide is being marketed, although the system has some limitations in comparison with cyanide.

A phenomenon known as "silvermigration" has limited the use of silver plating in miniature circuit boards: Under a positive dc potential within a damp resin component silver will migrate across insulating paths. On drying, silver is found in the body of the insulation or media creating a low resistance leakage path.

12.9. Tin and Tin Alloys.

Tin may be plated from fluoborate, sulfuric acid/sulfate, or alkaline stannate, baths (Tables 27, 28 and 29.) The deposits are matte when plated without brighteners. One older method of brightening is termed reflowing or flow-brightening where the plated tin part is heated for a few seconds just above the melting point and then quenched. Brighteners for use in sulfate baths have been vastly improved, and very bright, decorative deposits can be obtained directly from the bath. The key to operation of the stannate bath is in proper control of the anode current density to ensure that tin dissolves in the stannate state. If the proper anode film is not formed, stannite tin is generated with immediate poor results. Tin anodes containing ∼1% aluminum increase the proper anode current density range.

Tin, as well as some other metals, can undergo a phenomenon where tiny metal filaments, called whiskers, form randomly on parts used in electrical applications. In low voltage, miniature circuitry, whiskers can cause short circuits. Alloys having 2% lead minimum or 0.5% bismuth or heat treatments are said

Table 27. **Typical Bath Composition and Operating Parameters of a Fluoborate Chemistry**

Parameters	Rack and barrel	Reel to reel
Sn $(BF_4)_2$, g/L	75–113	225–300
Sn (g/L)	30–45	45–60
HBF_4, g/L	188–263	225–300
H_3BO_3, g/L	22.5–37.5	22.5–37.5
anode current density (ASF)	20–25	do not exceed 25
cathode current density (ASF)	1–80	up to 300
temperature, °C	30–55	30–55
typical additives	peptone, β-naphthol, hydroquinone	
anode	pure tin, bagged with dynel or polypropylene	
agitation	mild, mechanical	
filtration	constant filtration using a nonsilicated filter aid is desirable, although not necessary; such treatment keeps the solution clean and affords agitation	

Table 28. **Typical Bath Composition and Operating Parameters for a Sulfate/Sulfuric Acid Based Electroplating Chemistry**

Parameters	Range
$SnSO_4$, g/L	15–45
Sn, g/L	7.5–22.5
sulfuric acid	135–210
additives (62)	alkylphenol, imidazoline, heterocyclic aldehydes
anodes	pure tin
anode current density (ASF)	25 max
cathode current density (ASF)	1–25
temperature	room temperature
agitation	mechanical, cathode rod

to overcome the problem. A specification for electroplated tin coatings is available (134).

Tin baths, tin–lead baths, and lead baths that have been entering the market, are based on methanesulfonates. The higher makeup cost of tin methanesulfonate baths, ~1.5 times the cost of fluoborate baths, may be justified since restrictions on fluoborates and boric acid in wastes exist in most places.

Table 29. **Typical Bath Formulations and Operating Conditions of Potassium Stannate Baths**

Parameters	Barrel	Rack
$K_2Sn(OH)_6$, g/L	95–110	390–450
KOH, g/L	13–19	15–30
cathode current density (ASF)	3–10	up to 40
temperature, °C	65–90	80–90

A special bath for high speed plating of strip steel using all halogens was introduced in 1942 (135).

Tin–Lead. A major application of these alloys is in the production of electronic components. Tin lead coatings are a prerequisite for reliable soldering when making interconnections on PCBs. They are plated from fluoborate baths and more recently methanesulfonate solutions. Solder, 60% tin plate, is the most often used one on contacts and as a solderable etch resist on printed circuit board (PCB)s. Higher (96–98% tin) alloys are used in semiconductor and other electronic applications. For 60% tin alloys, proprietary methane–sulfonate baths may contain 16-g/L tin, 10-g/L lead, 20% by volume methane–sulfonic acid, and brightener. Solution is operated at 25°C and current density 100–400 A/m^2. A fluoborate bath to produce 60% tin deposits contains ~60/65-g/L tin, 25–26-g/L lead, 40-g/L fluoboric acid, and 23–30-g/L boric acid along with a brightener; 6-g/L of glue has been used. This bath is operated at 20–25°C up to ~320 A/m^2. More acidic, dilute baths having 15-g/L tin, 10-g/L lead with 400-g/L fluoboric acid, and 30-g/L boric acid are used for high throw baths. Tin–lead alloys become considered lead–tin alloys when the tin present is <50%. Anode material for tin–lead plating baths should be of the same alloy as being plated, to maintain bath integrity.

Tin–Nickel. Tin–nickel alloy deposits having 65% tin have been commercially plated since back about 1951 (136). The 65% tin alloy exhibits good resistance to chemical attack, staining, and atmospheric corrosion, especially when plated copper or bronze undercoats are used. This alloy has a low coefficient of friction. Deposits are solderable, hard (650–710 HV_{50}), act as etch resists, and find use in printed circuit boards, electronics in general, watch parts, and as a substitute for chromium in some applications. The rose-pink color of 65% tin is considered attractive. In marine exposure, tin–nickel is about equal to nickel–chromium deposits, but has been found to be superior in some industrial exposure sites. Chromium topcoats increase the protection further. Tin–nickel deposits undergo a transformation upon heating. This phase change causes cracking and exfoliation and so should be kept at a temperature <250°C. It is also not recommended to be used as diffusion barrier.

The most common plating bath of tin–nickel alloys uses fluoride to complex the tin. A typical solution contains 45-g/L stannous chloride, 300-g/L nickel chloride hexahydrate, and 55-g/L ammonium bifluoride. It is operated at pH 2.0–2.5 using ammonium hydroxide; temperature is 65–75°C and current density ~200 A/m^2. The bath has excellent throwing power. Air agitation can be avoided. The deposit is bright without additives. Anodes are cast nickel, and the tin is replenished by additions of stannous chloride. Alloy anodes of 72% tin have been used to a much lesser extent. Tin–nickel deposits are covered by ASTM (137) and ISO (138) specifications.

Tin–Zinc. While tin–zinc alloys are deposited from acid, alkaline and neutral baths and all concentrations are possible, 80% tin-20% zinc gives the best combination of properties. This alloy has a low coefficient of friction, low electrical contact resistance, is solderable, slightly anodic to steel, and does not form voluminous corrosion products. In addition, the tin–zinc alloy has good paint adhesion qualities, good ductility, and is easily spotwelded. Due to the softness of the alloy they are susceptible to mechanical damage.

A typical bath is based on stannate and cyanide; for 80% tin, the solution is made using 120-g/L potassium stannate, 11.3-g/L zinc cyanide, and 30-g/L potassium cyanide. The bath is operated at 65°C with cathode current of 100–800 A/m^2 and anode current of 150–250 A/m^2. Anodes that exhibit the same efficiency as the cathode are to be the same composition as the alloy, and for best performance, have to be "filmed" properly as for stannate tin plating.

Accelerated tests, such as, salt spray tests, humidity tests and others, some using sulfur dioxide and carbon dioxide, have given favorable results for tin–zinc in comparison with either zinc, cadmium, or tin deposits. Chromating, naturally, improves the performance even further.

A low tin alloy, more specifically, 90% zinc–tin alloy, has been in use as an economical solderable substitute for cadmium. For this 10% tin deposit, the same type of plating bath, but using 40-g/L tin, 15-g/L zinc, 15-g/L potassium cyanide, and 45-g/L free potassium hydroxide is use.

Other Tin Alloys. The success of tin nickel deposition suggested the analogous tin–cobalt alloys and some publications have appeared (139,140). Proprietary tin–cobalt alloys having a third metal were used for a short time as a substitute for chromium in decorative applications. In spite of the higher cost, growing restrictions on chromium by enviromental authorities, brought renewed interest in tin–cobalt alloys.

12.10. Zinc and Zinc Alloys. Zinc has a standard reversible potential (−0.76 V/SHE) that is more negative than that of iron (Fe/Fe^{+2} −0.44 V/SHE). For this reason zinc is used for sacrificial cathodic protection of steel against corrosion. Bright decorative, chromium-like coatings can be obtained. Postplate treatments in chromate conversion coatings are used to extend corrosion protection and aid in paint adhesion. Chromate conversion coatings are available in several types, from the thinner blue-bright coatings, through the thicker yellow iridescent ones, to the thickest olive-drab coatings. Olive-drab chromates can extend salt spray protection of zinc coatings up to 400–500 h. Fresh chromate coatings can be dyed a variety of colors, and the process is used for part identification.

Zinc is plated on pipe, conduit, strip, sheet, and wire, as well as sheet metal stampings, all sorts of hardware, and fasteners. Zinc plating is used on electronic housings and cabinetry to reduce high frequency radiation interferences.

Plating solutions for continuous strip, called electrogalvanizing, sheet, and wire are usually simple zinc sulfate solutions, although chloride and mixed variations have found some use. A typical bath for strip may contain 350-g/L zinc sulfate heptahydrate and 30-g/L ammonium sulfate. Baths are operated at pH 3.0–4.5, 40–55°C, at currents of 1000–6000 A/m^2. Zinc thickness is often 0.3–4.3 μm. A wide variety of additives have been used to produce some grain refinement, eg, dextrin, licorice, glucose, and gelatin. Wire plating, which may have 13–130-μm zinc plate, has been plated in more acidic zinc sulfate solutions using insoluble silver–lead alloy anodes. Currents up to 30,000 A/m^2 are reported.

Commercial zinc plating is accomplished in cyanide baths, alkaline noncyanide baths and acide chloride baths. For general zinc plating in the United States, estimates of the zinc baths in use in 1970 showed cyanide at >90%, chloride at 3%, and noncyanide alkaline (zincate) baths at 4%. The strong

Table 30. **Composition and Operating Characteristics of Acid Chloride Zinc Plating (g/L)**

Constituent	All ammonium chloride	Low ammonium: Potassium chloride	Low ammonium: Sodium chloride	No Ammo potassium chloride
Zn	15–30	15–30	15–30	22–38
NH_4Cl	120–180	30–45	30–45	
KCl		120–150		185–225
NaCl			120	
H_3BO_3				22–38
carrier brightener	4 vol%	4 vol%	4 vol%	4 vol%
primary brightener	0.25%	0.25%	0.25%	0.25%

international effort to lower pollution emissions has changed it so that by 1990, cyanide zinc was 20%, chloride 50%, and zincate 30% (138). In 1992 the cyanide was 16%, chloride 48%, and zincate 36%. Moreover, the cyanide zinc baths of 1992 were more likely to be run at 15–30 g/L sodium cyanide in contrast to the 100 g/L normal in 1970. Proprietary brighteners are used by each of these three zinc systems.

Chloride Baths. Zinc deposits obtained from chloride baths are brighter, can plate directly on cast iron, and operate at high efficiency, but have poor throwing power, require acid-proof equipment, and as such, are more corrosive to surrounding steel materials. To be specific, a typical chloride zinc may contain ~35-g/L zinc, 135-g/L Cl^-, 30-g/L boric acid, proprietary brighteners and wetting agents. The chloride source in earlier baths was the ammonium salt, which did not require boric acid. Potassium chloride, which is less volatile, is now more common, although some sodiuchloride systems are used as well as mixtures with low ammonium salts. Higher current densities are possible with the ammonium chloride baths, followed by potassium and then sodium. Table 30 lists the composition and operating characteristics of acid chlorid zinc plating baths.

High purity zinc anodes, which are usually bagged to reduced roughness in rack plating, are used. Brighteners may be slightly soluble organic materials solubilized in the plating solution with mixtures of some wetting agents. Dilute baths with 15-g/L zinc or less have been used in barrel plating of small parts such as nails. Baths require regular peroxide additions to precipitate iron, often on a daily basis; the ferric iron is then to be filtered out. Baths are operated at pH 4.8–5.4, with current densities up to ~330 A/m^2, and at ambient temperatures. More recently, baths have been operated at warmer temps (44°C) to increase evaporation rate. This reduces tendency of zinc solution to increase in volume and flood the tanks. At low surface tension, drag-out is less than drag-in.

Zinc Baths. Zincates baths are simple, economical, noncorrosive to steel and have superior throwing power. Some recent systems are showing better tolerance to operating variables, with less tendency toward flaking or delayed blistering, and good brightness. Zincate baths, however, require good cleaning, frequent analysis, close chemical control, and have low cathode efficiency. Zinc plating is discussed in detail in the literature (141).

Alkaline zincate bath formulations vary according to the brighteners used. Zinc at 6–12 g/L (called low chemistry LC) is common; newer baths have zinc at

9–18 g/L (high chemistry HC). Sodium hydroxide is ~10 times the zinc, and is varied to control the rate of zinc dissolution. Sodium carbonate, ~30 g/L, is added to new baths for conductivity and to reduce impurity effects. Zinc anodes corrode when the bath is idle. To resolve this and anode-caused roughness, only steel anodes are used in the plating tank in many plants and plating houses. The zinc is replenished electrochemically through a separate generator tank where plating solution is recirculated through zinc balls or slab in steel baskets. Deposits from the zincate are powdery and noncoherent without (~1–3%) additives. Additives, needed for both adhesion and cohesion, are almost always proprietary, and contain mixtures of organic brightening compounds along with certain polyamines or other materials that perform the same functions as cyanide. Complexing agents are generally avoided because of possible effects on waste treatment and codeposition of metallic impurities. Zincate baths are operated at 27–40°C at current densities up to 300 A/m^2.

Cyanide Baths. Cyanide baths can be divided into four broad classifications based on their cyanide content (142). These baths produce zinc deposits that have excellent covering power and throwing power, good cleaning ability, deposit relatively pure zinc, are capable of thick deposits, and require little control. Also, zinc deposits from cyanide baths are purer than from the other baths, but still do contain traces of the metal contaminants, brightener components, sulfur, hydrogen, and other gases. Pure, sulfur-free zinc is resistant to hydrochloric acid.

Zinc coatings on iron and steel, eg, are covered by an ASTM specification (143). Because of the varying purity of zinc deposits from chloride and zincate baths, some thickness measuring methods can vary considerably. Methods based on physical measurement or magnetic methods (144,145) are used for best accuracy.

Other Baths and Methods. Other than the above discussed forms of zinc plating are also in use. Thus, eg, immersion zinc deposits are used as a preparatory step in electroless plating or electroplating of aluminum (146), magnesium (147), and beryllium (148) alloys. Formulations vary with the application; typical baths are listed in the references cited.

Finally, a mechanical plating method, often called peen plating, uses zinc dust, tumbling equipment, glass beads, or other impact media, along with some proprietary chemicals. No current is used. An advantage is that hydrogen embrittlement is avoided, and springs and other hardened steel parts can be plated safely (149).

Recent decades have seen considerable worldwide activity in the area of plating zinc alloys. This interest and activity result from efforts to improve the corrosion resistance of automobiles, automotive components, and components in the aerospace arena, without using, the rather toxic, cadmium (84). The use of zinc–alloy plated coils for automotive body steel originated in Japan, has spread through Europe, and eventually reached the United States. Three zinc alloys dominate the practical interest: zinc–nickel, zinc–iron, and zinc–cobalt. Europe produces predominantly zinc–nickel. In Japan, zinc–nickel and zinc–iron are more popular (150). The annual worldwide nickel consumption for zinc–nickel alloy plating has been conservatively estimated at 2700–3400 metric tons (151). In the United States, consumption is estimated at ~350 metric tons for this purpose. Alloys are generally 6–12% nickel. Usage is, if anything, expected to increase.

Zinc–nickel usually shows better results than zinc–cobalt in salt spray tests. The reverse is true when the Kesternich test is used. Tin–zinc performs well in both salt spray and Kesternich tests, but appears only to equal zinc plating and zinc–nickel in humidity tests.

Zinc–Nickel. These alloys can be plated from acid or alkaline noncyanide solutions. Corrosion protection of steel increases with increasing nickel content up to ~15%. Beyond that level the deposit becomes more nobel than the substrate, loosing it's sacrificial properties. Also, >10% the deposit becomes more passive and accordingly less receptive to form a good chromatic conversion coating. At those levels and above, corrosion resistance usually decreases and is dependent on a complete lack of porosity for protection of the steel. In efforts to replace cadmium and nickel–cadmium diffused coatings in the aircraft industry, zinc–nickel has insufficient wear properties for some application. Nevertheless, it may serve as an undercoat in a number of systems (152).

When zinc–nickel plate is to be painted, whether on strip or on component parts, plate thickness of 4 μm or more is effective in reducing corrosion creepage on scribed test panels. Minimum creep is at ~13 μm. Typical bath formulas for zinc–nickel and the other zinc alloys are given in Table 31. Acid zinc–nickel baths used on strip lines may not use additives. All other zinc–alloy baths use brighteners and other additives, almost always proprietary. The chloride or alkaline bath options behave similarly to all-zinc baths with regards to throwing power and efficiencies.

In general, deposits from acid zinc–nickel baths give deposits with higher nickel conten, but the alloy ratio and thickness varies considerably with current density among other variables. Deposits from alkaline baths are lower in nickel but are more consistent in both nickel content and plate thickness distribution. Anodes for acid zinc–nickel are usually to be made of zinc along with some

Table 31. **Plating Baths for Zinc Alloys**

	Zn–Co		Zn–Ni		
Parameter	Acidic[a]	Alkaline	Acidic[b,c]	Alkaline	Zn–Fe
zinc, g/L	25	8	30	8	8
cobalt, g/L	4	0.04			
nickel, g/L			25	1.6	
iron, g/L					0.05
total chloride, g/L	135		240		
boric acid, g/L	25				
sodium hydroxide, g/L		90		130	90
temperature, °C	29	25	40	22	22
cathode current density, A/m^2	215	320	320	320–850	320
deposit, %	0.3–0.8% Co		10–15% Ni	6–10% Ni	0.3–0.8% Fe
anodes	zinc	steel	zinc	Ni-plated steel	steel

[a] pH = 5.0.

[b] pH = 5.8.

[c] Also contains 4% NH_4OH by volume.

graphite anodes; the proportion is to be adjusted to prevent excessive zinc concentrations. Anodes for the alkaline system are usually made of steel and the zinc metal is supplied by dissolving zinc anodes in a separate generator tank. The alloying metal is added as the metal salt to maintain a set ratio. Zinc–nickel alloys, as well as the other zinc alloys, vary widely with changes in the system. The plating processes need good control of the chemical constituents including additives along with temperature, agitation, and current density, to produce consistent alloys. Corrosion resistance benefits for lower nickel contents have been reported on fasteners with 2–3% nickel, and in another process with nickel contents as low as 0.25–0.75% nickel. Corrosion protection of steel increases with increasing nickel content up to ~15%. Beyond that level, the deposit becomes more noble than the substrate loosing its sacrificial properties. High salt spray protection has also been claimed using a duplex coating with higher nickel undercoating with a lower nickel alloy topcoat.

Zinc–Cobalt. These alloys usually contain 0.3–0.8% cobalt. Alloys with higher cobalt content, from 4–8%, have shown better salt spray resistance (153), but the commonly plated alloy is still 0.3–0.8%. One automotive company specifies 0.3–1.0%. Cobalt is a relativelly expensive metal, and economics favor the lower alloys. Costs, have been quoted for (low cobalt content) zinc–cobalt at ~1.2 times the cost of chloride zinc, with zinc–nickel alloys at 1.5–1.6 times the chloride zinc. Deposits can be very bright, but the improved corrosion resistance advantage requires yellow or bronze chromates. Alkaline baths give fewer problems in plating components with lapped, spot-welded seams.

Zinc–Iron. These alloys are mainly used for their ability to produce a nonsilver black chromate. At iron concentration of 0.3–0.9% they proved to have a very good resistance to the new methanol fuel blend. The Zn–Fe alloy is plated from an alkaline bath (see Table 20). Deposits are 0.3–0.8% iron and, as stated, can be given attractive, resistant, black, silver-free chromate coatings. Corrosion protection requires the heavier, darker chromates. Zinc–iron baths are the most economical of the zinc alloys.

Posttreatment. Many posttreatments are being used over plated metals, chromate conversion coatings remain as one of the most popular. Chromates are used to improve corrosion resistance, provide good paint and adhesive base properties, and/or to produce brighter or colored finishes. Formulations are usually proprietary, and variations are marketed for use on zinc, zinc alloys, cadmium, copper and copper alloys, and silver. Chromates are also used on aluminum and magnesium alloys. More recently, chromate passivation has been used to extend salt spray resistance of autocatalytic (electroless) nickel plated parts.

For zinc deposits, various chromates can produce very thin, blue-bright coatings to get up to ~24-h salt spray protection before the zinc corrodes (white corrosion salts), thicker yellow iridescent films for up to ~100 h, and thickest, olive-drab coatings that may give upward of 300 h. A modification of the olive-drab chromate solution with a silver salt produces a black finish, but salt spray resistance drops back to 48–72 h. Topcoats of waxes are often used on such blacks. Higher salt spray resistance is being claimed for chromates on the zinc alloys; eg, 250 h for yellow chromate on zinc–cobalt, 1000 h for yellow on zinc–nickel, and 300 h on a black over zinc–iron electroplate. This black chromate does not contain silver. The higher nickel contents in zinc–nickel alloys are difficult to chromate; at this time no olive-drab or black coatings are marketed.

13. Electroforming and Electrofabrication

Electroforming with copper was first invented in 1838 by Jacobi in St. Petersburg. Electroformed nickel was done first in 1843 by Bottger. Electroforming is the production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit. The separated electrodeposit becomes the manufactured article. Of all the metals, to this day, copper and nickel are most widely used in electroforming with nickel being utilized in the largest number of applications. This is so because it is strong, tough, resistant to corrosion, erosion and wear and because its mechanical properties can be varied and controlled by changing bath composition, by alloying and by incorporating particles and fibers within the electroplated nickel matrix. Mandrels or molds are of two types: permanent or expendable. Permanent mandrels are treated in a variety of ways to passivate the surface so that the deposit has very little or no adhesion to the mandrel, and separation is easily accomplished without damaging the mandrel or the deposit. Expendable mandrels are used where the shape of the electroform would prohibit removal of the mandrel without damage to the deposit (or mandrel). Low melting alloys, metals that can be chemically dissolved without attack on the electroform, plastics that can be dissolved in solvents, are typical examples.

The surface of the mandrel is reproduced exactly down to submicroscopic detail on the electroform. This duplication of detail accounts for many applications for electroforming. The U.S. Bureau of Engraving uses ~45 t/year of nickel in electroforming printing plates for currency and stamps. One of the principal uses of copper in electroforming is in the continuous production of copper foil used in the printed circuit industry. Applications are more diverse for nickel. The largest nickel application is in the manufacture of textile printing screens, where mandrels are rolls coated with a developed photoresist pattern, or a mandrel prepared by etching and masking to produce a screen or mesh pattern. Printing screens can be 6 m long, over 30 cm in diameter, and 100–125 μm thick.

Nickel electroforms were used in the past making phonograph records, these are not in use anymore; however, one of the replacements, the compact (audio) disk (CD), utilizes a nickel electroform as a mold or stamper to produce these as well as video disks. Also, computer disks for data storage are being produced with an electroformed stamper. Applications are found from very thin filters of ~25 μm thick having microscopic holes, to large electroformed rocket motor components used in the U.S. space shuttle, which can be ~2-cm thick in some areas. Seamless cylinders, used in copying machines, have been produced in large volume on automatic plating machines. Many parts are manufactured by electroforming that would be difficult or impossible to make by other methods.

Plating solutions used in nickel electroforming are primarily the Watts bath and the nickel sulfamate bath. Watts baths exhibit higher stress and require additives for stress control, which may affect other properties. Sulfamate baths produce much lower stress and are preferred where purer nickel or nickel–cobalt deposits are needed. A detailed discussion covering this subject is available in Ref. 154.

Electrofabrication also involves processes that result in production of components and parts but that do not involve the use of traditional mandrels. In electrofabrication, the substrate often becomes an integral part of the component, and electrodeposition takes place selectively through masks or by means of spesially design cells. The distinction between electroforming and electrofabrication lies in the nature of the mandrel and the role of the substrate.

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