Source: Electronic Materials and Processes Handbook

Chapter

6

Electroplating and Deposited Metallic Coatings

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6.1 Electroplating for Electronic Applications

The electroplating industry is essential to many manufacturing operations. Electroplated coatings and related finishes are classified into three categories according to their main function, although these categories do overlap. Plated finishes may be used to

1. Improve the appearance of the part
2. Impart a protective surface on the part
3. Modify the chemical or physical properties of the part's surface

Without electroplating and surface finishing, our modern standard of living would be difficult to maintain.[1] Surface finishing plays a primary role in the electronics, communications, and aviation/aerospace industries. These industries drive product miniaturization and demand increased product reliability. Present-day surface coatings are applied to parts in a manner that meets the designers' requirements while using chemical solutions that are environmentally friendly in both production processes and waste treatment.

Of the numerous elements in the periodic system, only about 16 are available as electroplated finishes. Of course, the number of coating processes increases when you include all of the alloy formulations.

Electroplating is adaptable, because it is used on tiny semiconductor parts as well as large industrial components. When to use a single-layer coating or a

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multilayer composite is based on expert opinion and experience with the coatings and how they perform. Electroplate coatings are not adaptable to all substrates, although most materials can be electroplated if proper preplating procedures are used. If a part is to be electroplated, some restraints on the design of the product may be imposed so that a satisfactory coating will result. Electroplated coatings are subject to rigid specifications. Control documents are provided by ASTM International as well as other associations, government bodies, and by the internationally recognized International Organization for Standardization (ISO).[2]

6.2 The Plating Cell

The purpose of this document is not to provide detailed directions for application of metallic coatings, as that is the expertise of the plater. The purchaser or engineer will find material informative in providing an elementary background in surface finishing. He will then know what can be expected of the coating and what is impractical.

All the coatings we discuss are plated out of a water-based chemical solution. The electroplating cycle includes a series of stations or tanks that will vary according to the type of part and the complexities of the plating process. Rinsing stations are provided between each processing station and after the final plating station to remove electroplating solution from the parts. The final rinse is critical to ensure that chemical salts do not remain and dry on the parts or cause the coating to corrode.

The plating cell consists of these components:

1. The rectifier or power supply. In the external circuit, it moves or pumps the electrons from the anode to the cathode.
2. Charged atoms, called *ions*, that carry the current in solution.
3. The electrode that is the source of the metal ions for the solution, and that provides the electrons for the circuit, is called the *anode* and is connected to the positive side of the rectifier.
4. The other electrode (the workpiece) is called the *cathode*. It is connected to the negative side of the rectifier and completes the circuit.

6.2.1 Cathode reactions

The cathode is the negative electrode, and it represents the part being plated. The electrons on the surface of the part neutralize the positive charges on the metallic nickel ions in solution (Fig. 6.1). The net result is that metallic nickel is deposited on the surface of the part. At the same time, some of these electrons also neutralize the positive charges on hydrogen ions in the water solution. This forms hydrogen gas that is liberated at the surface of the part. This loss of hydrogen ions results in a higher concentration of hydroxide molecules and an increase in the pH of the solution at the workpiece–solution interface.[3] The more efficient the plating bath, the less hydrogen gas is formed. If the

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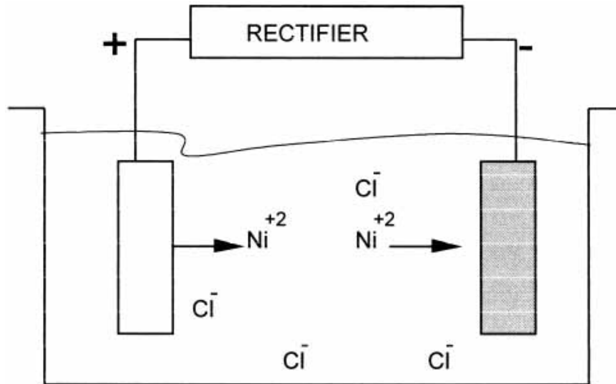

Figure 6.1 A galvanic (plating) cell.

concentration of metal ions in solution is low, or their movement to the cathode is impeded, the excess current can liberate additional hydrogen gas by splitting a water molecule.

6.2.2 Anode reactions

At the anode, electrons are removed from the metal electrode, and metallic ions are formed and released into the solution. This is the primary reaction with a soluble anode. Secondary reactions can also take place. One such reaction involves the generation and liberation of oxygen gas. This reaction also occurs when an insoluble anode is used as in precious metal plating. In this case, hydroxide ions in the aqueous solution supply electrons to the external circuit and produce water and oxygen gas.[4] It is important to avoid excessive anode current on soluble anodes, because the oxygen formed will react with the metal surface, forming oxides. These oxides interfere with proper anode dissolution. Like the cathode reaction, high current densities can split water but, in this case, it results in the release of oxygen gas and the production of hydrogen ions, which lowers the pH.

6.2.3 Cleaning

A typical processing cycle contains the steps of cleaning, rinsing, and activating the surface of the part prior to plating.[8] All the steps are important. Trying to take a shortcut in any of the processes can compromise the success of the operation.

The quality of the chemicals used in the various baths and the purity of the rinse water all work together to determine the overall quality of the product. Most mechanical processes, such as forming, machining and die casting, leave the substrate surface contaminated in some way.

Pretreatment cleaning is important to ensure good adhesion of the plating to the base metal. To remove contaminants from the surface of a part, in addition to chemical cleaners, physical work may also be incorporated. Grit or

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bead blasting, scrubbing, media tumbling, and sanding are some examples. Solvent cleaning or degreasing involves a liquid and/or vapor immersion to remove solvent-soluble oil, waxes, and greases. (*Note:* environmental concerns may limit availability of some solvents.) Following the degreasing step is alkaline cleaning in the form of either a soak or spray operation. In many cases, the alkaline cleaning process is substituted for the solvent cleaning.

All alkaline cleaners contain chemical compounds that promote solution "wetting" of the surface. This allows the chemical formulations to attack and remove the surface soil and hold it in suspension.

More than 80 percent of plating "problems" can be traced back to improper surface cleaning and preparation. In the cleaning process, several energy forms may be used individually or combined to assist in soil removal. The most common of these forms are mechanical, thermal, electrical, and chemical. An example of the mechanical assistance is ultrasonic cleaning, which often is the only way to loosen a contaminant. Most cleaning processes do not make the contaminant disappear. Solution filtration is necessary to extend the life of most cleaners.[5]

Typical alkaline cleaner ingredients are sodium hydroxide, sodium metasilicate, sodium carbonates, and sodium phosphates. Sodium hydroxide (caustic soda) provides alkalinity, conductivity, and saponification (converting animal fats to water-soluble soaps).[6]

After the soil is removed from the surface of the part, the cleaner must keep it from redepositing. Other chemical components in the cleaners are the sequestering agents, chelating agents, deflocculating agents, and peptizing agents that aid in solution soil retention.

The sodium metasilicate provides soil dispersion and prevents redeposition. It also acts as an inhibitor to reduce alkaline cleaner attack on the active metal surfaces. Surfactants are surface-active agents that promote solution wetting of the surface by lowering the surface tension of the aqueous solution. These may be ionic or nonionic in structure.

Sodium carbonate in the cleaner acts as a buffer to stabilize the pH of the solution.

Phosphates improve rinsing quality and provide water conditioning.[7] (Some localities prohibit phosphate use, because they promote algae growth in lakes and rivers.)

Electrocleaning is usually the last (but a very important) step in most cleaning cycles.[9] There are three common types of electrocleaning. The first is *forward (direct)* or *cathodic*. In this process, the part is made to be the cathode, as is typical in plating. The second is *reverse* or *anodic*, in which the part is made to be the anode. The third is *periodic reverse,* wherein the advantages of both types are employed. Some processes may avoid the use of electrocleaning for various reasons, e.g., attack on active or light metals such as aluminum, magnesium, or zinc.

The cathodic reaction releases hydrogen and has the greatest gas evolution, hence the greatest amount of cleaning through the scrubbing action of the liberated gas. It also reduces oxide films on the surface, which promotes adhesion of the plating. The drawback is that it deposits smut. Smut is a metallic

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contaminant from the solution that forms on the surface of the part as finely divided particles. The anodic reaction releases oxygen gas and does not produce this smut, but it will help remove any that has deposited on the surface. Thus, the anodic direction is more tolerant to metal contaminants that have accumulated in the cleaner. The downside of anodic cleaning is the generation of an oxide film on the part, which can passivate the surface (i.e., interfere with deposit adhesion).

Periodic reversal combines best features of both reactions.

All cleaners become contaminated with use. If you experience poor bonding between the plating and base metal, the cleaning step is suspect. Residual alkaline films remaining on the surface of the part after cleaning are difficult to remove by rinse alone. For this reason, an acid dip or *pickle* is used to neutralize this film.

The acid chosen will also remove any residual light surface oxides and microetch (lightly attack) the surface to improve bonding. Heat-treat scales or heavy oxides present on the surface are best removed in more concentrated or heated acids, away from normal production processes. All metals above hydrogen in the electromotive force (EMF) series (Table 6.1) react with the acid to form hydrogen gas. Caution should be observed when pickling high-strength alloy steels, because they are susceptible to absorption of hydrogen that can lead to hydrogen embrittlement of the steel.

TABLE 6.1 EMF Series

Anodic end	Standard potential volts at 25°C
Aluminum	–1.66
Zinc	–0.76
Iron +2	–0.45
Cadmium	–0.40
Nickel	–0.25
Tin	–0.137
Hydrogen	0.00
Copper +2	+0.34
Copper +1	+0.52
Silver	+0.80
Gold +1	+1.68
Cathodic end	

6.2.4 Current distribution

Figure 6.2 illustrates an important aspect of electroplating—the current distribution on the surface of a part.[1] In plating, you are concerned with the vari-

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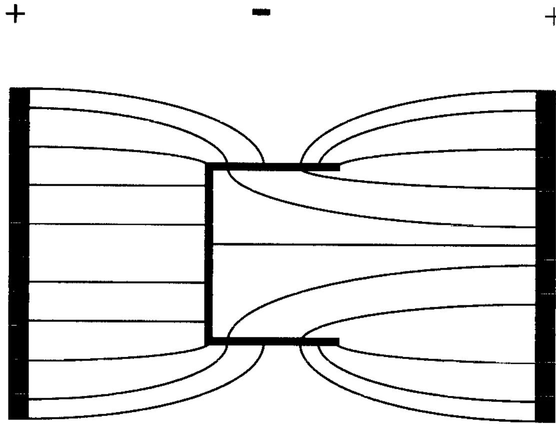

Figure 6.2 Current distribution box.

ations in thickness of the plated metal on a part. In almost all rack plating, some areas of the articles will be nearer to the anodes than others, and, with most plating solutions, these areas will receive a heavier deposit than those farther from the anodes.

The current flow lines depicted in the diagram flow from the anode (+) to the cathode (–) and are close together near the edges and on the outside corners of the part. Notice in the diagram that the current flow lines are farther apart in the bottom and at the inside corners of the part. These lines represent the current density or current concentration. Obtaining a uniform current distribution over the entire cathode surface is extremely difficult and seldom achieved in practical plating practices. The outside corners of the box may have as much as ten times the current density as the inside corners.

In many common plating baths, the metal deposit thickness can vary by this tenfold factor. Blind holes should be avoided on parts to be plated, as it is difficult to get any plating or coverage in these holes. The ability of a plating solution to produce deposits that are more uniform in thickness over a shaped cathode is known as the *throwing power* of the solution. An important factor influencing thickness distribution in some plating solutions is the decrease in plating efficiency with an increase in current density.

Current density is expressed in amperes per square foot (A/ft^2). Figure 6.3 depicts the relationship between current density and plating bath efficiency for an acid nickel bath and a cyanide zinc bath.

Nickel deposition (efficiency) is seen as relatively constant over the range of 10 to 50 A/ft^2. This means that nickel will plate about five times faster at 50 A/ft^2 than it will at 10 A/ft^2. This gives a thicker deposit at the higher-current-density areas of a part.[3]

The behavior of the cyanide zinc bath is quite different. As the current density increases, the plating efficiency drops. Increasing amounts of hydrogen gas are produced at the cathode. As a result, the zinc deposits thickness variation will be about 2.5 to 1, not 5 to 1 as in the nickel plating. In the cyanide

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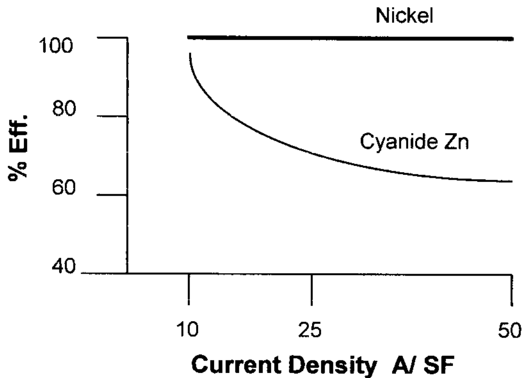

Figure 6.3 Plating efficiency vs. current density, nickel bath compared with a cyanide-zinc bath.

zinc bath, the metal distribution will be more uniform in thickness. Again, the term *throwing power* is used to describe this characteristic of deposit thickness uniformity. Because uniform deposit thickness over the surface of a part usually cannot be expected, it is important to specify those surfaces considered to be significant for proper operation or appearance of the part. These areas should then be specified as critical and an agreement reached beforehand between the purchaser and the plater as to ensure the minimum or maximum plating thickness required.[11]

Plating time is also a factor in controlling the deposit thickness, as is the total surface area of the part. The amount of metal deposited is controlled by the amount of current that flows in the circuit and the length of time the part spends in the plating bath. Although this is a very simplistic explanation, all plating processes follow this principle.

6.2.5 Deposit quality

Pinholes or porosity are common in all plated deposits. These openings through the plating will allow the underlying material to be attacked. Increasing the thickness of the coating reduces the amount of porosity at the expense of time and materials. In most cases, coatings of 1.5 to 2.0 mils in thickness have no pinholes. There are other ways of reducing the deposit porosity, such as pulse plating or the use of chemical additives in the plating bath. By using multiple plating layers, you minimize the effect of porosity and in effect improve substrate corrosion resistance. A deposit that is uniform in thickness, with no thin spots or skipped plating, provides good protection for the base metal.[12]

6.2.6 Brush plating

In the brush plating technique, the plating solution is carried to the part instead of the part being immersed in a plating bath. Most metals can be brush plated, and aluminum parts can also be anodized. This process can be used

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both in production and as a repair tool. The handle, called a *stylus*, has absorbent material wrapped around a carbon rod, which is connected to the positive side of the power supply. The negative pole of the power supply is connected to the part. The absorbent material is dipped into the plating solution and then swabbed or brushed along the area on the part that requires plating. Areas that are not intended to be plated are masked to protect them from the chemicals. Figure 6.4 details a typical brush-plating setup.[20]

6.2.7 Copper

Copper can be electroplated from acid, alkaline, and neutral bath formulations.[2] Each of these plating solutions has unique features to provide a very economical electrodeposition of copper on complex shapes. There are safety and environmental concerns associated with any plating process, and one always needs to address the chemical treatment and safe disposal of wastes to prevent pollution. Federal, state, and local regulations include restrictions for copper discharge. Copper is rarely used as the final finish, because its brightness is quickly lost in most atmospheres as a result of oxidation and surface corrosion. However, it performs a supportive role as an underplate for nickel, gold, tin, and other top coatings.

6.3 Acid Copper Plating

Copper coatings are popular because of copper's high electrical and thermal conductivity as well as its high melting point.[21] The electronics industry requires copper for properties such as solderability, corrosion resistance, high ductility, and low cost.

The acid copper sulfate baths are economical to prepare, operate, and waste treat. They are used in printed circuits, electronics, semiconductors, rotogravure, electroforming, and decorative and plating-on-plastics applications. In addition, the fine-grained structure of the deposit makes it ideal for producing sharp and well defined boundaries after machining or etching.[23]

The physical properties of the deposit, such as brightness, ductility, leveling, freedom from stress, and fine-grained deposits, are controlled through the

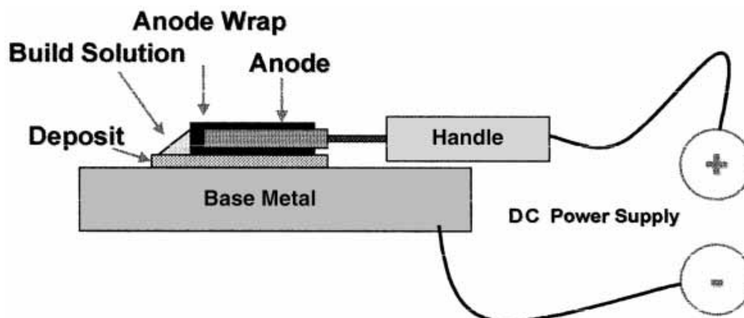

Figure 6.4 Typical brush-plating setup.

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use of chemical addition agents.[22] Acid copper is desirable as an undercoat to nickel and chromium on zinc-based die castings because of its very good *micro-throw* and excellent ductility (Fig. 6.5). Elongation of 15 to 25 percent is common. Micro-throw is the ability to fill surface defects such as microporosity and other basis metal flaws. Fine-grained crystal structure and low stress are inherent in the deposits while plating at very high speeds. The use of proprietary addition agents, along with various DC wave forms such as pulse, square wave, or periodic reverse, combine to produce copper surface smoothness that is better than that of the substrate over which it is plated. It also provides an ideal metallic undercoat for plating on plastics. Leveling is the ability of the deposit to fill in minor surface defects and present a smooth surface finish (Fig. 6.6). Acid copper levels well, and its ductility and freedom from stress assist in overcoming differences in coefficients of expansion and contraction between subsequent plates and the plastic base material. This provides a thermal cushion when the workpiece is subjected to acceptability tests such as thermal cycling or solder float testing.

The acid copper electrolyte is prepared by dissolving copper sulfate in water and adding sulfuric acid, a small amount of chloride, and the specified amount of addition agents. The ability of addition agents to provide brightness and

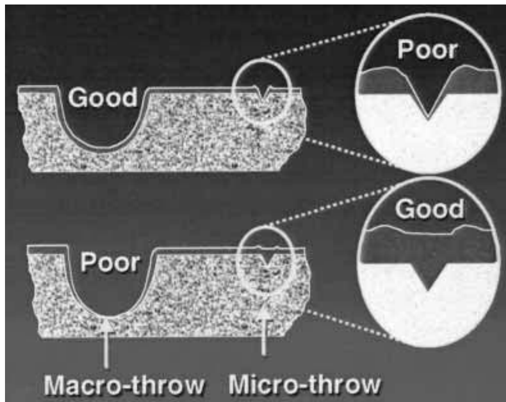

Figure 6.5 Depiction of macro-throwing and micro-throwing power. *(Optical photo courtesy of F. Altmayer, Scientific Control Laboratories.)*

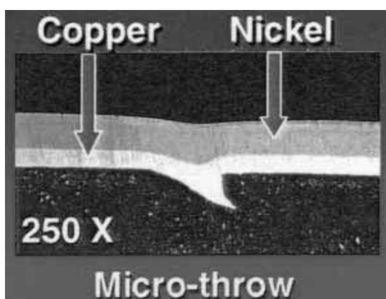

Figure 6.6 Leveling of acid copper over defect in zinc diecast.

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leveling is influenced adversely by elevations in operating temperature. Therefore the bath operates slightly above room temperature up to 90°F (32°C). Operation above this temperature consumes extra amounts of brighteners; while not a drawback, this does increase the cost of operation. Because the bath does contain sulfuric acid, it is corrosive (Fig. 6.7).

The acid sulfate plating solution can tolerate large quantities of zinc and iron contaminants with the plating speed being affected only slightly. Chromium contamination affects the deposit quality at concentrations above 100 parts per million (ppm). One part per million is equal to 1 mg of contaminant per liter of solution. Organics will cause the deposit to become pitted, dull, and/or coarse-grained, with some burning of the deposit in high-current-density areas. In addition, the deposit can also become striated and experience a loss of leveling. Both air agitation and constant bath filtration are required to produce good deposits. Air supplied for agitation must be from a low-pressure blower, not "shop air" from a compressor. Compressed air can introduce organics in the form of lubrication oil. The chloride ion concentration is carefully maintained at specified levels to enable the addition agent to perform its function of providing all the desirable physical properties previously discussed. The very low levels of chlorides present in the bath require that anodes containing small amounts of phosphorus are used for good anode corrosion and to produce optimal deposits. These anodes must be bagged to prevent particulate material from the anode getting into the bath and causing rough deposits.

When plating copper on steel or zinc die castings, they must first have an appropriate strike of copper from a copper-cyanide bath.[22] This is to prevent immersion copper deposition from the acid bath from forming on the substrate. Typically, immersion coatings are nonadherent and undesirable. The cyanide copper strike will also prevent attack on the zinc metal from the acid in the acid copper bath.

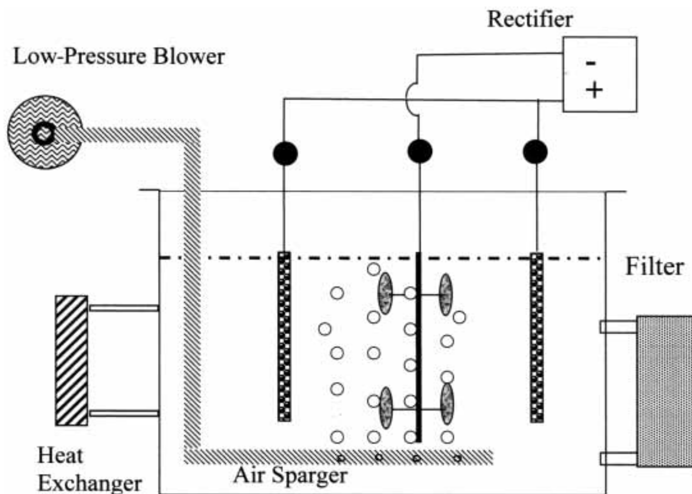

Figure 6.7 Example of an acid copper plating tank.

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6.4 Cyanide Copper Plating

Electroplated copper from cyanide-based plating solutions has long been used both as an engineering or decorative finish and as an undercoat for other plated metals. Cyanide copper solutions are used on a wide variety of base materials. An important property of copper deposited from cyanide-based systems is its ability to form strong adherent bonds to most base metal and alloy substrates. Because acid copper plating solutions attack most basis metals and/or produce immersion deposits with poor adhesion, cyanide copper plating is used as a thin undercoating or strike to produce good adhesion.[3] Following the strike, a high-speed acid copper plating formulation can be used to produce the desired film thickness.

Cyanide plating solutions are highly poisonous, and the rinses and spent bath solutions must undergo complete destruction before disposal. Allowable cyanide in wastewaters is very small, and waste treatment is required in all areas. However, it should be recognized that cyanide destruction technology is well established and proven effective.[16]

Because deposits from cyanide plating solutions exhibit good throwing power, more complicated shapes can be completely covered, with a uniform film thickness. This is a result of the relationship of efficiency and current density. As the current density increases, the bath efficiency decreases. There is a drawback that must be addressed. The drop in plating efficiency yields an increase in the formation of hydrogen gas. This evolved gas can be absorbed by the base metal. The result can be a reduction of the metal's fatigue strength by hydrogen embrittlement. To relieve hydrogen embrittlement when plating on hardened steel (Rockwell C35 or higher), the parts are baked within 4 hr after the final plating operation at 325 ± 25°F (162 ± 14°C) for up to 24 hr.[22,26,31] Periodic reverse plating cycles in cyanide copper baths have been used with some success in producing fine-grain deposits with good leveling.

Plating of parts with cyanide copper will continue with little change in total volume until a suitable and environmentally acceptable system can replace it. The ability to plate an initial coating with good adhesion to light metal base materials with good throwing power and coverage are the key features of cyanide copper systems. The associated cyanide destruction, disposal costs, and safety measures required in cyanide handling can be accomplished with proper education and training.[22]

6.5 Pyrophosphate Copper

Copper pyrophosphate plating baths require more control and maintenance than cyanide or acid copper baths. They are relatively nontoxic and primarily used in electroforming operations and on printed circuits.[23] The operational temperature range of 110 to 140°F (43 to 60°C) should not be exceeded; above these temperatures, the pyrophosphate complex is hydrolyzed to orthophosphate. The orthophosphate formed will degrade the solution. Copper pyrophosphate baths are sensitive to organic contamination, addition agent breakdown products, and lead, all of which can cause dull, nonuniform depos-

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its with a narrowing of the plating range. The bath produces deposits that exhibit high purity and ductility along with nearly 40 percent elongation.[25] This was especially useful in the printed circuit industry for plated-through holes on thick multilayer boards, which require strong deposits to withstand the z-axis expansion during soldering and thermal cycling operations. The deposit also has high tensile strength of 40,000 ± 2000 psi and low internal stress.[22] Improvements in substrate material and product design changes have reduced z-axis expansion, allowing the use of lower-cost nonpyrophosphate baths. The biggest drawback to the system, besides bath control, for the printed circuit industry was that the photoresists used in the pattern plating operation were dissolved by the bath's alkalinity. The bath is less corrosive to equipment than the acid copper and less toxic than the cyanide processes.[22] This bath can be used to deposit copper directly on zinc die-cast parts, steel, and zincate prepared aluminum.

6.5.1 Other copper plating processes

There is continuing development of a noncyanide alkaline copper bath. This type of bath would replace the cyanide bath for plating directly on zinc die-cast and steel. Presently, these formulations have found limited use in industry.

The fluoborate copper bath formulation allows very high current densities and increased plating speed. This is because the copper salt is highly soluble, and large amounts of it can be dissolved in water. The biggest drawback to fluoborate copper is the extreme corrosivity of the solution. Everything associated with the plating operation must be constructed of noncorrosive materials.[22] The bath operation is similar to the acid sulfate copper bath. Organic contaminants affect the deposit appearance and ductility. The other mechanical properties are only slightly affected by organics. Lead is the only metallic contaminant that is a problem in this bath.

6.6 Nickel Plating

The nickel plating processes are used extensively throughout the world for decorative, engineering, and electroforming purposes. Decorative electroplated nickel coatings are lustrous, smooth, and mirror bright. Engineering nickel coatings are smooth and matte in appearance and are most often applied to improve corrosion performance of industrial equipment. These pure nickel deposits can provide hardness and also can be used to control wear, surface erosion, and lubricity. Nickel is valued for its magnetic and electromagnetic characteristics and for optical properties such as reflectivity, emissivity, and absorptivity.[1] In electronics applications, nickel coatings are widely used as underlayers beneath precious metal deposits wherein the nickel acts as a barrier to prevent interdiffusion of substrate and coating. Additionally, this nickel barrier improves the reliability of electronic components. Nickel coatings thus enhance the value and expand the operating range and usefulness of industrial equipment and electronic components.[6]

Nickel coatings are most widely applied by electro-deposition from aqueous solutions. They can also be applied by electroless (autocatalytic) techniques,

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by chemical and physical vapor deposition processes, and by thermal spray methods.

The solutions for decorative nickel plating differ from those for engineering applications in that they contain multiple addition agents. Fully bright deposits, for example, contain significant amounts of codeposited sulfur. The most common nickel solution used is the Watts nickel bath, which is based on nickel sulfate as the source of nickel (Mil-Spec QQ-N-290).

Soluble nickel salts can be irritating to skin and eyes and, in some cases, physical contact with nickel or certain nickel compounds may cause allergic dermatitis. Engineering coatings using sulfamate nickel plating are controlled by MIL-P-27418. This is a pure nickel that is generally used for functional or engineering purposes rather than for decorative purposes, because it provides good corrosion resistance and high-temperature stability. For electroforming and most electronic applications, a bath using nickel sulfamate as the metallic salt is preferred, as this coating can be produced with compressive or low-tensile stress.[1]

The sulfamate bath uses soluble sulfur depolarized nickel anodes, whereas the Watts bath anodes do not contain sulfur. The anodes for both baths are bagged because, as the anodes corrode, they can release small nickel particles called *fines*. The bag helps to trap these fines and keeps them from coming in contact with the part; thus, it helps to prevent rough deposits. Continuous filtration of the bath is recommended with filter sizes ranging from 5 to 20 μm.

Good agitation and solution circulation are recommended to produce the best deposits. Keeping contaminants low is an important factor in maintaining low stress and good quality deposits from both Watts and sulfamate plating solutions. In addition to affecting deposit appearances, contaminants can cause other problems such as lower cathode efficiencies, reduced throwing power and covering power, excess pitting, and poor adhesion.[26] It should be noted that the effect of these impurities could be additive, and many impurity effects are more pronounced at certain current densities. For this reason, regular purification of the solution is necessary to control contaminants and minimize their effects.

Metallic contaminants such as copper, lead, and zinc can be removed from both nickel solutions by *dummy* (i.e., low-current) electrolysis using corrugated cathodes at a current density of 2 to 5 A/ft^2.[27]

Organic contamination may be removed from the nickel solution by treatment with activated carbon. Iron and chromium can be removed from the solution by precipitation. Their hydroxides become insoluble when you raise the pH of the bath to 5.0.

Generally, electrodeposits from a sulfamate nickel bath are used on electronic components as a barrier coating. Ultra-high-purity formulations are available that allow plated parts to be formed, bent, and crimped without damage to the deposit.[28] Most sulfamate bath formulations produce deposits that have good tensile strength and low deposit tensile stress. The baths can also produce compressively stressed deposits. This is useful in high-speed strip line or reel-to-reel plating (see Table 6.2).

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TABLE 6.2 Mechanical Properties of Electrodeposited Nickel*

Bath	Hardness, HV	Tensile strength, psi	Elongation, % in 2 in (51 mm)	Internal stress, psi
Watts	130–200	50–70 ($\times 10^{-3}$)	20–30	+25 to +65 ($\times 10^{-3}$)
Sulfamate	170–230	60–110 ($\times 10^{-3}$)	5–30	–5 to +15 ($\times 10^{-3}$)

*Without addition agents

Deposit characteristics can be varied as desired over a wide range. Chemical additives such as organic sulfonic acid salts and other sulfur-bearing compounds have been used as hardening agents and stress-reducing agents. These additives can reduce tensile stress or increase compressive stresses as well as increase deposit hardness, brittleness, and tensile strength. It is important to note that certain additives will incorporate sulfur compounds in the deposit. Removal of these compounds from the bath, once added, is difficult.[28]

Barrel plating with sulfamate nickel can lead to some problems if care is not taken in the process. Very pure nickel deposits passivate easily when current is interrupted, as happens in barrel plating. This results in a deposit that, when viewed under the microscope in cross section, appears as laminated layers.

The plating layers can separate at the laminations when stressed. A simple troubleshooting procedure to use when you have a plating defect wherein the gold plating over the nickel plate is peeling is to look at the bottom side of the gold blister for the appearance of nickel. If you see nickel, then the layers of nickel plating are separated because passivation of the nickel layer occurred during the plating. If nickel is not present on the bottom side of the peeled gold, then there was passivation of the surface between the nickel and gold plating steps that resulted in poor adhesion. If the substrate material is visible under the peeled layers, then the part was not properly cleaned and activated prior to plating.

6.7 Precious Metals

The precious metal group is also referred to as the *noble metals*. Both names are appropriate. They have high monetary value and show marked resistance to chemical reaction with inorganic acids. The plating application for these metals is determined by the metal's particular properties and characteristics.

Eight metals compose the precious metal group, as indicated in the bottom two rows of Table 6.3.

The following are some of the factors to consider in the selection of a precious metal for a particular application:[21]

- Contact characteristics
- Reflectivity
- Corrosion resistance

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TABLE 6.3 Position of the Precious Metals in the Periodic Table

	26 Fe	27 Co	28 Ni	29 Cu	← ←	Atomic number Chemical symbol
Light group	44 Ru	45 Rh	46 Pd	47 Ag		
Heavy group	76 Os	77 Ir	78 Pt	79 Au		

- Solderability
- Heat resistance
- Wear resistance
- Color
- Cost

Each of the precious metals has both advantages and disadvantages. The following information highlights this. Silver provides low cost, but it does tarnish when exposed to sulfur. Gold provides low electrical resistivity but, at 24-karat purity, it is a soft, easily smeared coating. Palladium does not cold weld, but material costs are high.

Although the cost must be considered, it is secondary to the required properties. As an example, the plated finish on a PWB tab or separable electronic connector should display certain characteristics. These could include high corrosion and oxidation resistance, low contact resistance, low stress or high ductility, and low porosity. A uniform appearance and smooth surface topography are aids in functionality for this type of part.

6.7.1 Silver

Silver is a low-cost metal, has excellent thermal properties, and is the best conductor of electricity. The penalty for silver is that a black, brown, or yellow tarnish forms on the surface when it is exposed to sulfur. The tarnish formed raises the surface contact resistance. The poor resistance of silver to corrosion, tarnishing, and ion migration must be considered if you are specifying a silver coating. As with copper, postplating surface treatments of silver can reduce or prevent the formation of tarnish.[4] Commonly used surface treatments include protective lacquers and acrylic or epoxy films. There are also chromate conversion coatings per MIL-S-365 and organic preservatives that protect and still allow for a solder joint to be formed with the silver.[30] The last and most expensive treatment is to overplate the silver with 0.1 to 0.3 μm of rhodium. This is generally not cost effective but works quite well. Typical silver thickness requirements for electronic contacts are 50 to 250 μin; this is generally applied over 150–300 μin of nickel.

Of major concern when specifying silver plating is ion migration.[2] Silver ions under the influence of a high DC potential can move across insulated surfaces. This is prevalent in areas of high humidity. The ions can be reduced

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back to silver metal atoms, and the tracks formed by this metal migration between two conductors can lead to electrical shorts. The methods employed to prevent this migration include wide spacing of adjacent tracks, the use of conformal coatings to prevent moisture intrusions, and overplating the silver surface with gold, rhodium, or platinum. Any discontinuities in the protective coating can expose the base silver, and ion migration can still occur.

A silver strike is always used before plating silver to avoid immersion deposition.[4] An immersion deposition, in many cases, is a nonadherent thin layer of the metal. This low- or nonadherent film would allow the functional plating to flake off under stress. With iron base material, a double strike is sometimes used. The first is a silver-copper cyanide alloy followed by silver. Always enter the silver strike bath "HOT," i.e., current on with the part as the cathode.[1]

The common practice for plating silver on nickel alloys is to use a Woods nickel strike, which precedes the silver strike for improved adhesion of the final plating. Compounds that contain sulfur, selenium, or tellurium are the most common chemical brighteners for silver baths and are called *addition agents*. They are used to improve the surface characteristics of the deposit.

The most widely used agents perform multifunctional duties that include brightening, hardening, and grain refinement. Most organic brighteners used for silver are unsaturated alcohols and long-chain polar molecules. They are essentially surface-active agents (surfactants).

Antimony is the most powerful brightener and is used at 2 to 3 percent by weight. It produces beautiful silver deposits that are quite hard.[4] A major problem using antimony as an addition agent is that the deposit produced has only 10 percent of the conductivity of pure silver; therefore, the antimony brightened bath should not be used when plating electrical contacts.

Silver anode purity is generally expressed in parts per thousand. The manufacturer processes it to have a fine grain structure. Some suppliers recommend bagging the anodes for silver plating. Sloughing of anode particles into the plating bath can cause grainy or nodular plating, because these particles find their way to the cathode. Another costly anode problem is an accelerated state of stress-assisted corrosion that occurs when a small piece of anode breaks off, loses electrical contact, and is of no further use as anode material. Continuous bath filtration is recommended, which will remove most of the sloughed anode particulate from the bath along with any other suspended contaminant.

6.7.2 Rhodium

Rhodium has been used extensively for electronic applications that require wear resistance and stability at high temperatures. The high metal costs have minimized the application of heavy deposits. Rhodium is plated from very strong acid solutions, and these baths operate at low current efficiencies, generating considerable amounts of hydrogen gas.[4] Thicker deposits from proprietary systems contain additives for stress control and are almost always applied over an underplate of gold, silver, or nickel to avoid immersion deposition and solution contamination.[16] Rhodium has high and stable reflectivity in

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the visible range, hence its appeal as a top coating in jewelry. The metallic color of rhodium is similar to that of stainless steel. This metal has excellent corrosion resistance and is almost as hard as chromium. In most cases, rhodium is plated directly over nickel, with the use of a nickel strike on most base metals to prevent immersion deposits. When plating rhodium on steel parts that exceed Rockwell C40 hardness, the parts must be baked within four hours of plating to reduce hydrogen embrittlement.[31]

6.7.3 Palladium

Palladium has been suggested as a replacement for gold, because it is harder than gold and does not cold weld. It has a low melting point and a density of 12.02 g/cm^3. When compared to gold of equal thickness, the palladium deposit weighs about half as much as gold. Because you buy precious metal plating salts in troy ounces but sell the deposit by thickness, this cost difference once was attractive. However, the increased cost of palladium salts in recent years has diminished the dollar savings. In the past, there were drawbacks to using palladium because of difficulty in obtaining low-stressed noncracked deposits. The baths presently in use are of the ammoniacal, chelated, or acid formulations. New palladium bath formulations are proprietary but allow for simplified chemical control and produce thicker deposits without cracking. They differ from the older-generation baths mainly in the use of additives for brightening and stress relief.[4] Palladium plated from these baths provides a deposit that is very low in surface porosity.

6.7.4 Gold

Gold is a relatively expensive coating, has low electrical resistivity, and provides low surface contact resistance, because it does not form surface oxides. Gold deposits of 99.99 percent purity (24 karat) smear under load and will easily bond (cold weld) to another gold surface, because it is such a soft metal. In separable connectors or contacts, the gold is alloyed with small amounts of other metals such as nickel, copper, or cobalt, to increase the deposit hardness.

For many years, the standard for electrical contacts has been an electrodeposited layering of nickel, at least 50 μin thick, followed by at least 30 μin of hard gold, then a 5- to 10-μin thick layer of soft gold. This combination is usually accepted as the nearly ideal surface.[30]

The double gold layer serves to reduce surface porosity, which improves corrosion resistance, and the soft gold topcoat provides lubrication to the mating surface. This plating combination can also be easily soldered and, in some applications, wire bonded. Table 6.4 indicates different applications and the preferred plated gold thickness.

The precious metals also have some special properties that make them attractive. Platinum resists corrosion and serves as an anode in plating paths that contain chlorides. Gold has high reflectivity in the infrared region.

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TABLE 6.4 Deposit Thickness Requirements for Gold Plating

Thickness, μin	Purpose
1–7	Flash color decorative coating
10–30	Minimum for solderability on contacts
30–50	Minimum for weldability on contacts
50–100	Etch resist and solderability
100–200	Engineering for abrasion resistance
200–300	Exceptional corrosion resistance
500–1500	Electron emission characteristics
≥1500	Electroforming applications

In the early and mid 1990s, a great deal of attention was paid to using palladium as a substitute for gold. Since that time, increases in the palladium metal cost have tipped the scales back toward favoring gold.

Iridium is ideal for protection of refractory metals at very high temperatures.

Thickness requirements for precious metal deposits are determined by the end use. Prime consideration in the choice of finish should be given to the physical properties of the deposit and the service requirements of the part.[21]

Generally, most gold electroplating baths are proprietary and covered by patents. The choice of which bath to use will depend on the functional requirements of the gold coating and the substrate upon which it is plated. Three types of cyanide gold plating baths are available for use today.[4] One is alkaline, at a pH of 9.0 to 13. The neutral-type baths operate at pH 6.0 to 8.0, and the acid type at pH 3.0 to 6.0. Potassium gold cyanide salts supply the metal necessary for deposition and will also increase the solution conductivity and improve the throwing power of the bath. In addition to forming the gold cyanide complex, the cyanide reduces the free gold ion concentration in solution, which retards the deposition of base metals and minimizes the formation of immersion deposits.

The bond between gold and cyanide is very strong, which accounts for the high stability of the gold cyanide complex even under acidic conditions. The alkaline bath provides good throwing power, and the deposit has reduced amounts of codeposited base metals. The neutral and acid baths do permit alloy formation through base metal codeposition but will cause little or no attack on delicate substrates. The acid bath solution does produce the purest commercial gold deposits. Along with conducting salts and pH buffers, baths producing bright deposits will contain brighteners that promote grain refinement. Many of these brighteners are metallic in nature and usually codeposit with the gold. The amount of codeposition depends on the type of brightener used. The metallic brighteners not only affect the appearance of the deposit, they also increase the hardness. Organic brighteners change the appearance of the deposit but do not necessarily alter the hardness. All brighteners tend to reduce the density and electrical conductivity of the gold electrodeposits.

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The gold concentration in the plating solution is kept relatively low with respect to other plating bath formulations to minimize gold metal loss due to chemical drag-out following plating. The neutral and acid baths do not contain any "free cyanide" like the alkaline baths, because the cyanide molecule would be unstable in the lower pH range. This absence of free cyanide in these baths allows for alloy deposits. Chelating agents are used in these baths to retard the deposition of metallic impurities that may be present. All nonadditive baths produce deposits that are matte in appearance but, if alloyed, the deposits are semibright to bright. The acid baths, when alloyed with various metals, can produce deposits with a wide range of colors from pale yellow to deep orange. Pure unalloyed matte-finish gold electrodeposits produced from the acid bath have been measured at 99.999+ percent purity.[30] A bright acid gold solution that does not use phosphates as pH buffers may contain small amounts of nickel or cobalt complexes as brighteners. The formation of an organic-cyanide polymer (Munier polymer) as an inclusion in the deposit appears to contribute to the good wear resistance of these coatings.[30] Other brightening additives such as arsenic or thallium may also be used. These refine the grain structure and increase the deposit hardness. Typical gold deposit requirements for semiconductor components and wire bonding are 99.99 percent purity with a 90 Knoop maximum hardness. For wirewrap connections, the deposit requirement is 99.7 percent minimum purity.

For solderability, the gold deposit should be 99.7 percent minimum purity, and the thickness should not exceed 50 μin. A minimum of codeposited metals is desirable to maintain good solderability.[28] If you are plating finger tabs for printed wiring boards, a deposit purity of 99.0 percent is acceptable with a hardness value of 91 Knoop and up. The deposit thickness should not be more than 100 μin. For plated separable connectors, many combinations of purity and hardness are acceptable, depending on the specific requirements for the part.

The military specification MIL-G-45204 is a good reference for gold plating. After proper cleaning and activation of the substrate, a gold strike is desirable. The strike bath prevents chemical contamination of the pure gold plating bath by drag-in from previous plating baths, and it promotes adhesion of the deposit by activating the surface. The gold strike also prevents immersion gold deposits from forming on most substrates. Poor adhesion of immersion deposits can jeopardize subsequent deposit adhesion.

Following the gold plating bath, recovery rinses are used to minimize gold plating bath loss through solution drag-out. The final rinse should be with high-quality deionized water. This is to eliminate any water residue drying on the gold surface. The final process step is drying the plated parts to leave the gold as clean as possible.

Gold deposit hardness should be specified for all plated parts. The hardness of the deposit affects the wearability of the deposit.[26] The wear resistance of the deposit increases with increased hardness. The most commonly used hardening agents are cobalt, nickel, and iron. Small amounts of these materials can have dramatic effects on the hardness of the deposit. A high-speed plating process for pure gold can give you a deposit that exceeds 90 Knoop hardness without using metallic alloying agents. This increase in hardness results from

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the plating process. Pulse plating and periodic reverse plating will also affect the deposit characteristics of gold. Depending on the selection of the duty cycle used in pulse plating, a gold deposit can be produced that will have a density equal to that of pure wrought gold at 19.3 g/cc.

6.7.5 Deposit hardness

Table 6.5 lists the typical hardness ranges encountered for electrodeposits employed as finishes in electronic applications.

TABLE 6.5 Comparisons of Metallurgical Properties of Deposits

	Hardness, Knoop, 25 g load	Tensile stress, psi
Raw acid copper	100–120	1400
Bright acid copper	145–160	2000–4000
Cyanide copper		5000
Semibright nickel	250–350	
Bright nickel	500–700	
Chromium	700–1000	

To measure the hardness of a coating, a carefully prepared cross section of the part is marked with an indenter. The impression made in the coating is then examined under a microscope using a calibrated eyepiece. Knoop and Vickers are the most common hardness types. The Vickers indenter is a symmetric diamond, and measurements are the average length of the two diagonals. In contrast, the Knoop indenter is nonsymmetrical, and measurements are made of the long diagonal (see Fig. 6.8). Both types use a fixed load whose value should be identified with the presented data. The measuring instrument must be vibration free with no relative horizontal movement between indenter and deposit. The Knoop indenter has included angles of 130 and 172.5°, whereas the Vickers included angle is 136°.[26]

The best results are obtained with a metallurgical mount on a polished cross section. If you try to measure directly on a plated surface, you run the risk of a false value because of the anvil effect. The deposit tested directly on the plated surface must be sufficiently thick to prevent the substrate or underplate from compromising the reading. Be aware that work hardening of the deposit from the grinding and polishing operations is possible while producing the mount.

6.8 Deposit Performance

Temperatures exceeding 257°F (125°C) can degrade many types of electroplated finishes. Diffusion through the deposit grain boundaries and deposit po-

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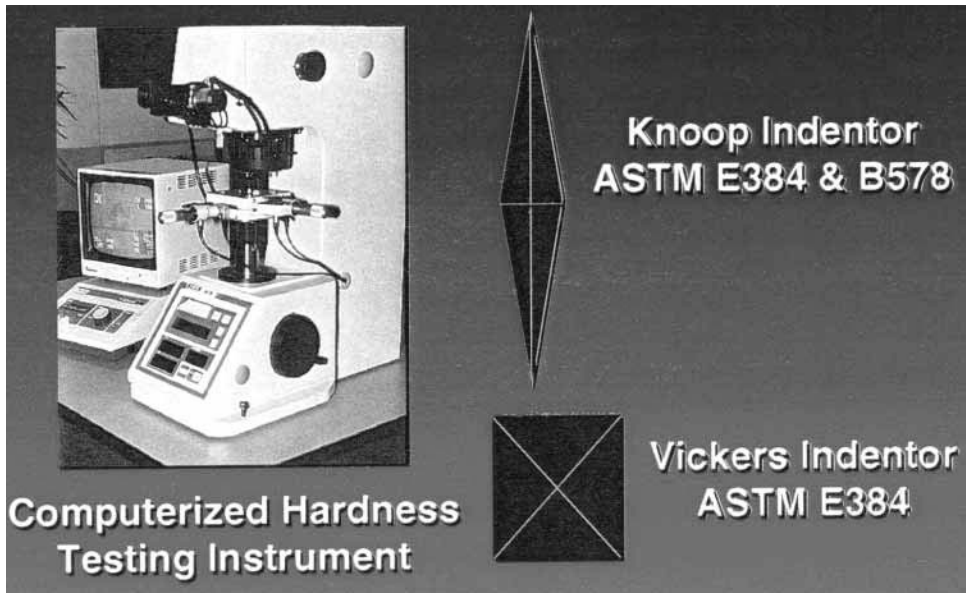

Figure 6.8 Knoop and Vickers impressions for deposit hardness testing.

rosity will allow the movement of base metal atoms to the surface of the deposit.[31] These diffused metals are now exposed and can oxidize. The oxidized metals will increase the contact resistance of the deposit, which can lead to device failure.

Occluded polymers in the hard gold plating can also contribute to increased contact resistance. Hard gold samples exhibit significant increases in contact resistance after exposure to 200°C for 2000 hr.[26] Variation in solution composition, current density, and temperature can also affect the concentration of impurities in a deposit.

It is very important to analyze the deposit as well as the plating solution. Plating solution analysis is necessary for proper bath maintenance and can warn of accumulating metallic impurities. Specific analysis for hardeners and alloy constituents is also done on the plating solutions to control the bath composition and make sure the bath is operating within the manufacturer's specifications.

In general, gold deposits require an underplate. In most cases, a gold strike is used on top of the underplate. Typical underplates are nickel deposits, which provide a diffusion barrier to copper and copper-based alloys at high temperatures.[31]

For low-temperature applications, you can use copper as a diffusion barrier over brass alloys to retard the movement of zinc to the surface of the gold. A tin-nickel alloy is also a good corrosion-resistant deposit that promotes solderability, but the deposit is brittle.

Silver has severe drawbacks for high-reliability applications. It has excessive ion migration and cannot be used as underplate on military hardware.

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Palladium-nickel alloys have bright, hard deposits that show little tendency to microcrack. The typical alloy composition range is 40 to 99 percent Pd. The various alloy compositions exhibit good chemical stability and are fairly wear-resistant. A typical hardness range for them is 450 to 600 Knoop. The alloys have a slight material cost savings over pure palladium. Table 6.6 provides a comparison of hard gold, palladium, and palladium-nickel films.

TABLE 6.6 Comparison of Film Properties of Hard Gold, Palladium, and Palladium-Nickel[4]

	Gold	Palladium	Palladium-nickel
Hardness (KHN 25)	140–200	450–600	450–550
Hardening agents	Co	Additives	Ni + additives
Grain size, Å	200–250	50–200	50–220
Density, g/cc	17.3	11.75	10.73
Ductility, % elongation	2.3–3.5	>9	>9
Volatile impurities, wt%	<1.5	<0.5	<0.1
Bulk thermal			
Stability, °C	150	>450	380
Porosity, pores/cm			
0.5 µm thick	60	80	20
1.0 µm thick	20	20	<10

6.9 Pulse Plating

In pulse plating, the metallic coating is deposited by pulsed electrolysis. Pulse plating can be defined as *current-interrupted electroplating*. Interrupted current consists of a direct current applied for a specific time period and then returned to ground (0 V) for another specific time period.

Pulse plating is useful in certain cases in which improved characteristics of electrodeposits are desired. It benefits the electronics industry by producing deposits with low porosity resulting from the higher deposit density. Pulse plating can produce a gold deposit with high purity and good ductility; it can control the deposit grain size and structure and produce a surface with low electrical resistance.[29]

For many years, the plating industry used current interruption (CI) to improve the performance of the deposit. The main difference between CI and pulse plating is length of time. The CI cycle is generally a matter of seconds, whereas pulse cycle is in milliseconds. The frequency of the pulse, the duty cycle used, and the waveform selected will determine the rate of electroplating within the parameters of any given electrolyte system. The duty cycle is de-

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fined as the current time on (T_{on}) divided by the current time on plus the current time off ($T_{on} + T_{off}$).[29] Because the duty cycle is expressed as a percentage, you need to multiply your answer by 100. Therefore, a sequence of 2 ms on followed by 8 ms off would be a 20 percent duty cycle. Because the peak current in pulse plating could be five times greater than that used in straight DC, the plating time would not necessarily be longer.

The square and periodic reverse square are generally accepted as the standard pulse waveforms. Figure 6.9 shows an example of these waveforms. Many other waveforms can be used to produce unique deposit characteristics.

6.9.1 Electroless plating

Electroless plating is a controlled electrochemical reduction of aqueous metal ions onto a catalytic surface. Electroless plating baths do not utilize anodes or power supplies. A chemical identified as a reducing agent, with the help of the catalytic surface, converts the metallic ions into deposited metal at the surface of the part. This chemical process requires close control of the plating solution composition and conditions. In the electroless nickel process, the nickel alloy deposited is the catalyst, and the electrochemical reduction reaction to produce additional nickel metal is sustained by that deposit.[14] The process is referred to as *autocatalytic*. In all electroless baths, the metal ions are complexed to provide solution stability in the presence of the reducing agents used. All baths contain the following components:

1. A source of metallic ions
2. A reducing agent
3. Complexing agents
4. Reaction inhibitors and stabilizers

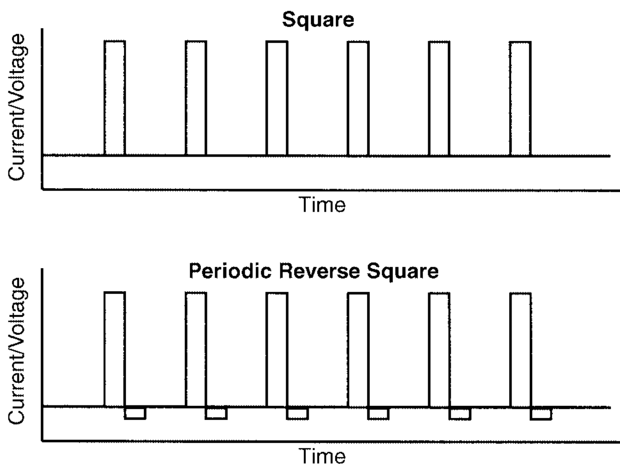

Figure 6.9 Pulse plating waveforms.

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Energy in the form of heat generally drives the reaction and, of course, the solution becomes contaminated with reaction by-products. Electroless nickel is the most familiar of the autocatalytic plating solutions. Nickel sulfate or nickel chloride salts are commonly used in the EN bath formulation as a source of nickel ions. There are four reducing agents used with electroless nickel. They are sodium borohydride, dimethylamine borane (DMAB), hydrazine, and the most common sodium hypophosphite. When sodium hypophosphite is used as a reducing agent the metallic deposit produced is an alloy of nickel and phosphorous. Only the hydrazine produces an almost pure nickel deposit. Several theories have been proposed for the mechanism of the electroless deposition process. All of them account for the reduction of metallic nickel at the catalytic surface and the release of hydrogen gas.

One theory is that the hypophosphite ion is catalytically oxidized (dehydrogenated) on the surface to be plated. This releases hydride ions (H^-) that are very reactive but are stabilized by the catalyst. The stable hydride ions are now available for the reduction of nickel ions at the surface of the part. The products of these multiple reactions are nickel, phosphorus, phosphite ions, hydrogen ions, and hydrogen gas. The phosphorus ion can also be reduced to a phosphorus atom. This phosphorus atom is codeposited with the nickel at 1 to 15 percent by weight. In reality, you have a nickel-phosphorus alloy deposit. If other reducing agents, such as borohydride or amineborane, are used in place of the hypophosphite, 0.2 to 6 percent by weight of boron is codeposited with the nickel. The selection of the reducing agent determines the metal alloy produced and influences the physical and chemical properties of the coating.

The primary function of the complexing agents is to control the activity of the "free" nickel ion concentration in the solution. The stabilizers control the reduction reaction so that deposition occurs only on the catalytic substrate. Good solution stability also affects the rate of deposition and may affect the character of the deposit.

Uncontrolled reactions or bath decomposition is usually preceded by the increased evolution of hydrogen gas and the appearance of finely divided black particles in the solution. If the stabilizing chemical is in excess in the bath, incomplete deposit coverage, skipped or missed plating, and deposit porosity are the most likely results.

The reaction during nickel deposition produces by-products that accumulate in the bath and have an effect on the process. The temperature control has a very important effect on the deposition reaction. In all electroless nickel systems, the plating rate increases with the increase in temperature. Below 150°F (66°C), the reaction rate is very slow. The typical bath operates in the temperature range from 190 to 200°F (88 to 93°C). Localized overheating of the solution must be avoided, or bath decomposition could result.

Some precious metals can also be deposited from electroless formulations. The common ones are silver, gold, palladium, and platinum. Gold and silver electroless formulations use a boron-type reducing agent.[17] Gold can also be deposited from a hypophosphite bath. All these solutions produce alloying deposits containing small amounts of either phosphorus or boron from the reducing agent. Electroless copper deposition is usually accomplished from

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alkaline solutions utilizing formaldehyde as the reducing agent. *Note that formaldehyde is considered a potential cancer-causing agent, and the exposure of production operators to this material must be limited.* Typical solutions contain copper sulfate as the source of copper, sodium hydroxide for alkalinity, and Rochelle salts as a complexing agent to keep the copper ions in solution. Additional chemical compounds are added in trace quantities to prevent spontaneous formation of finely divided copper particles and consequent solution decomposition. For each atom of copper deposited, at least two molecules of formaldehyde and four molecules of hydroxide ion are consumed, and one molecule of hydrogen gas is evolved. In practice, there is always additional consumption of formaldehyde and hydroxide by a disproportionate reaction.

Electroless palladium and platinum deposits exhibit microcracking as a result of the hydrogen produced in the reaction. This hydrogen is absorbed in the deposits, making thick deposits brittle. Electroless silver processes are rare; however, an alkaline dimethylamine borane is referenced.[47] Immersion silver coatings have been used as a substitute for nickel/gold on copper for wire bonding and soldering operations.[2]

Immersion-type gold plating has been around for years and is very successful in some applications. Because immersion deposition relies on a replacement reaction between the substrate metal and the metal ions in solution, the deposit thickness is limited. In summary, when selecting an electroless deposit, one must also identify the reducing agent utilized, because the properties of the deposit are affected by the alloying element incorporated in the coating.[18] Substrates are generally prepared for electroless plating in the same manner as for electroplating. However, special activation procedures are necessary to provide deposit initiation on noncatalytic metals or on nonconductors. Electroless plating is utilized where advantage can be taken of one or more of the unique characteristics provided by the deposit. These include exceptional deposit thickness uniformity; low porosity; solderability; the ability to deposit directly on nonconductors; and specific chemical, mechanical, or magnetic properties of the deposit (see Fig. 6.10).

6.10 Tin and Tin Alloy Plating

The most common nonprecious metal finishes on electronic components are pure tin and tin alloys. MIL-T-10727 and ASTM B22 provide useful information on the tin-lead alloys. The use of tin and tin alloy plating has increased largely because of applications in the electronics industry.[32] The deposited metal is inexpensive and has properties of solderability and performance that are well understood.

For improvement of base metal solderability, the part can be either tin or tin-lead plated or dipped in a molten solder that is an alloy of tin and lead in various compositions. There are also commercially available immersion tin coatings. These coatings work on copper and other "noble metal" substrates by the replacement reaction. When the tin has replaced all the available surface

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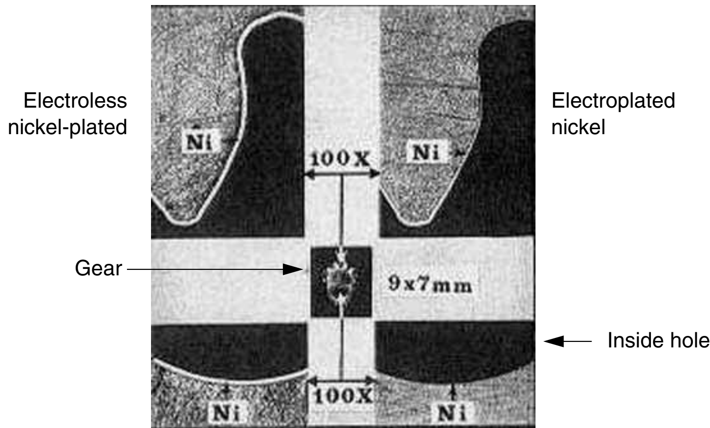

Figure 6.10 Uniformity of electroless nickel. *(Optical photo courtesy of Don Baudrand, Witco Corp.)*

ions of the substrate, the reaction stops. MIL-T-81955 covers thin immersion tin on copper and copper alloys. The solder mask over bare copper (SMOBC) process may use immersion tin to preserve solderability on printed wiring boards, although the process is more expensive than tin plating and reflow or hot air solder leveling (HASL). The immersion coatings are thin and porous, so they offer minimal protection in high-temperature or high-humidity environments.[2]

The solderability of a surface comprises the physical, metallurgical and chemical history of the finish before, during, and after manufacture. The solderability of assemblies with tin-based solder is directly dependent on a thin bonding layer between the surface metallization and the tin in the solder. Impurities such as sulfides, carbonates, and oxides degrade the quality of this bonding layer.

Similarly, solderability can be degraded if reactions result in an increase or segregation of impurities to the solderable surface.[33]

Solderability of a surface permits molten solder to readily wet that surface under the correct conditions of flux, time, and temperature. Proper wetting occurs when a metallurgical bond or intermetallic compound (IMC) is established between the tin and base metal surface. A definition of intermetallic compound (IMC) is the alloy formed between the solder and the metallization.[20]

Nonwetting of a surface by solder is defined as no metallurgical bond formation and the solder pulling back, exposing the base metal as it solidifies. Oxides, organic films, and/or nonmetallic occlusion on the substrate surface can cause nonwetting.

Dewetting is the result of less severe surface contamination, but it still is an interruption of the IMC growth near the surface. This is most likely caused by the presence of nonreacting material on or near the surface. In dewetting, the base metal is covered with a thin intermetallic solder layer while the bulk of the solder has pulled back away from the area.[35]

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There are three types of solderable coatings: fusible, soluble, and nonsoluble. Examples of each of them are as follows:

- *Fusible*—tin and tin-lead deposits melt into the solder, and the bond is formed with the base material.
- *Soluble*—examples of which are gold, silver, and to some extent copper.[33] The solder bond is to the substrate or underplating, because the top plating layer is dissolved into the molten solder.
- *Nonsoluble*—such as nickel, iron, iron-nickel alloys, and tin-nickel. The solder wetting occurs directly at the surface of the coating; i.e., the intermetallic compound forms with the coating.[35]

There are many sources of solderability problems in fusible coatings. Listed below are some of the most common:[23]

- Base metal contamination
- Base metal preparation
- Plating process
- Post-plate thermal excursions
- Environmental storage factors
- Component soldering (PWB)
- Intermetallic compounds

Base metals can gather heavy oxides during die or wire bonding, mold curing, or stabilization bakes. Copper and silver base materials can form intermetallic compounds that result in brittle unreliable solder joints. Too often, the blame is placed on the plating process as the only source of the problem.

IMC formation occurs by diffusion; thus, the IMC surface, along with any transferred contaminants, becomes the new metallization to which tin must bond during soldering.[35]

The segregation of lead adjacent to the IMC can retard the melting rate as a result of the relatively high melting point of the lead-rich layer. The IMC layer grows in a coherent manner sweeping impurities to the IMC–plating interface.[34]

Organic vapors from curing ovens can contaminate the plated surface during bake-out procedures.

If a barrier plating is used on the substrate, choose a plating process that contains a minimum of codeposited materials such as organics or sulfur.[3,27] These contaminants can oxidize at the tin–barrier interface and interfere with solderability.

Passive or contaminated base metal surfaces are a problem in plating as well as soldering. Tin or solder plating over passivated (surface oxides) or contaminated surfaces constitutes a fabrication problem. During soldering, the plating would melt, and the surface would have too low a surface energy to

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bond to the tin in the solder. Improper cleaning or surface preparation can furnish a surface that is good enough for mechanical bonding but not clean enough for soldering a fusible coating. The intermetallic bond cannot be established, and wetting will *not* occur.[36] There is also an incompatibility problem wherein migration of zinc atoms from brass moves toward the surface and into the solder. In the case of brass, you must remove the intermetallic and also prevent further migration of zinc into the tin or tin-lead coating. Copper and nickel are commonly used on substrates as the barrier plate.[40] If a plating process based on acid tin is used, then choose grain refiners that codeposit a minimum amount of organics. The trapped organics can outgas during reflow or soldering as shown in Fig. 6.11. Also occurring during the "burn-in" procedure are thermal excursions that may allow organics to degrade the solder–substrate interface resulting in dewetting or simply decreasing the final solder joint strength. A safe upper limit is for a deposit to contain no more than 0.05 wt% organic inclusions measured and recorded as carbon.

Some organics in a plating bath do not codeposit, but their breakdown products do. Routine carbon treatment of the plating bath is necessary to remove the breakdown products. The breakdown of the organic additives can be the result of elevated bath temperature, excessive agitation that brings oxygen into the bath, or electrochemical activity.

The most common inorganic found in tin and tin-lead systems is copper. The most likely source of this copper is drag-in from copper plating baths. A second source is copper-plated parts that drop into the plating tank and dissolve. A level of 20 ppm copper will darken deposits, and 140 ppm will cause a grainy appearance at reflow and promote dewetting due to excessive intermetallic formation.[33,34]

Poor rinsing can leave chemical films or plating salts on the deposit surface that can also cause dewetting.

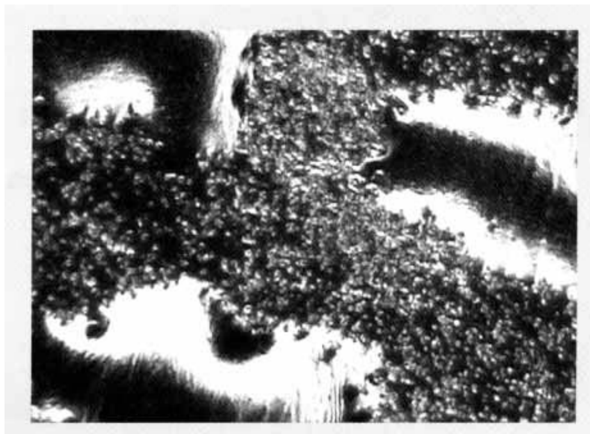

Figure 6.11 Blisters caused by organic contamination of solder bath. *(Optical photo courtesy of EC&S Analytical Solutions.)*

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Thin coatings resulting from poor solution throwing power will allow oxygen penetration to the substrate, or the total metal in a thin deposit can be consumed by intermetallic formation. High lead content can raise liquidus temperatures, which could result in microcracks at the solder joints. Flux reacts more slowly with surface oxide films, thus compromising the solder joint integrity.

Post-plate burn-in of components is the single largest contributor to solderability failures in the assembly process. When the coating is tin-lead, and a majority of the tin is consumed to form the intermetallic, this increases the lead concentration in the unreacted coating. The intermetallic compound formed, as well as the lead, will oxidize and interfere with the soldering operation.[35]

Organics can migrate to the surface during time–temperature excursions. During soldering, these organics can cause dewetting, or outgassing can occur that produces porosity in the coating or at the joint (Fig. 6.12).

6.11 Environmental Storage Factors

Surface oxidation and oxygen penetration to the substrate can interfere with the intermetallic formation. Contamination such as ink or fingerprints on the surface or plastizers from packaging can form on parts in storage and disrupt solderability. All halogens except fluorine react readily with tin at room temperatures. Lead will react with organic vapors. Oxygen penetration along grain boundaries is greater in humid conditions. This penetration will cause more rapid oxidation of any impurities that are present. Tin forms intermetallics with all base metals. Intermetallic growth rate at room temperature for tin plated copper is 1 to 1.5 µm per year as Cu_6Sn_5. Make sure that the solder problems are not the result of solder pot contamination.[35,36]

To increase the resistance of the coating to oxidation or to improve the chemical resistance of the deposit, tin can be reflowed or fused, which melts the coating and closes the pores in the deposit.

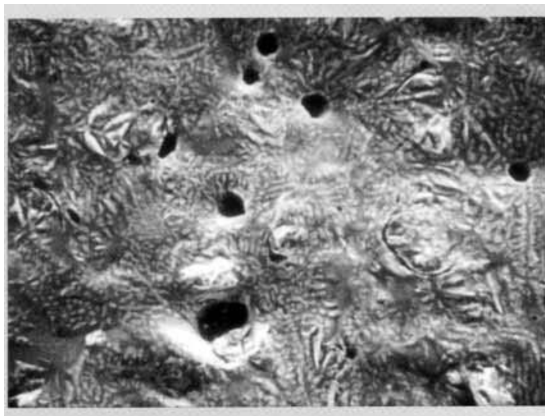

Figure 6.12 Pitting as a result of organic inclusions in tin-lead plating after fusing. *(SEM photo courtesy of EC&S Analytical Solutions.)*

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6.11.1 Tin whiskers

Tin whiskers are hair-like crystals that appear to grow spontaneously from a solid tin-plated surface. They can grow up to 1 μm in diameter and 5 mm long (Fig. 6.13).

Some studies have shown that a nickel base layer prevents whisker growth. As an additional precaution, an added stress relief heat treatment (i.e., fusing the tin coating) can be performed. Reflow or fusing reduces the risk of tin whisker growth.[37] The electroplated pure tin layer now has the same properties as a hot-dip coating of tin on nickel. This combination does not form whiskers. The whiskering reduction may be a result of alloying to the base metal or stress relief of the deposit.

Thin tin or tin-lead alloy plating provides a short diffusion path for metallic contaminants. Oxygen would have to travel only a short distance through the thin coating to oxidize the metallization. Metallic elements can migrate to the surface of the plating and oxidize. If oxidation of the metallization occurs, a compressive stress can form under the deposit, because the corrosion products produced occupy more volume than the metal they replace. The oxide layer formed on the metallization could impair the solderability, thereby resulting in a dewetting or nonwetting condition. Another method of minimizing the formation of tin whiskers in tin plating is to alloy the tin with 1 to 2 percent lead or bismuth.[38]

6.11.1.1 Solderability. The *finish* describes the metallization in addition to any coating such as tin or tin-lead plating that may be present. Analysis of a solder/copper base metal interface shows the formation of copper/tin intermetallics. Typically, Cu_3Sn and Cu_6Sn_5 are the primary alloys.

Tin reacts most readily with pure metal, less readily with either tarnished metal or pure IMC, and least of all with contaminated IMC.

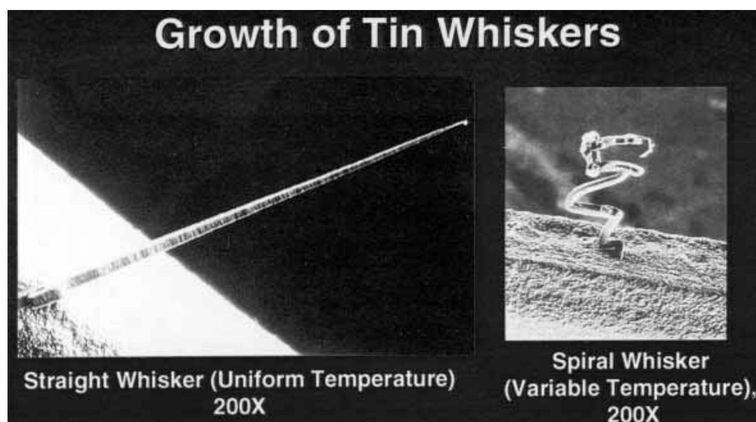

Figure 6.13 Tin whiskers. *(Photo courtesy of American Electroplaters & Surface Finishers Society, Inc.)*

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The following is a list of plating bath factors that affect solderability:

- High current density
- Organic contamination
- Suspended particulates
- Low metal concentration
- Thin deposits

The plater must be sure to keep the current density within the manufacturer's specified range, because high current density can result in burned coatings or improper alloy composition in some bath formulations.

A 0.05 percent epoxy contamination in sulfate-type electrolyte is enough to cause organic contamination of the tin coating. Suspended particles can be occluded in the deposit, causing localized stress. Low metal content in the bath can result in poor grain formation or incorrect alloy composition. If the plating is below 2 μm in thickness, the deposit is unable to distribute the stress that could result in whisker growth.[39]

Newer production processes, however, call for more aggressive manufacturing cycles, including higher soldering or molding temperatures, longer cure times, and several passes through a range of temperature profiles. The manufacturing processes and the storage practices of the manufacturer can affect components solderability.

Information regarding the degree of solderability degradation present in each phase of production can be combined with the knowledge of the original finish solderability to determine the primary influences on the product's overall solderability.[35]

Most base metals will have a nickel diffusion barrier layer that serves as the solderable metallization layer. This nickel layer generally has a protective coating of tin plating or gold plating.[31] If gold is used, the gold quickly dissolves into the molten solder during soldering, and the solder bonds to the nickel metallization. This bonding can be impeded if the solderable finish is contaminated. Gold must be sufficiently thick to be nonporous, and the nickel must be oxide free prior to the gold plating process.

Tin wets the nickel underplating and not the oxide film, because tin has a greater affinity for nickel than for nickel-oxide. To maintain good solderability, the nickel must remain oxide-free during the interval between plating and soldering.

Tin plated directly on nickel in a single operation has better solderability shelf life than tin plated on an activated nickel as would occur in an interrupted process.[33] Diffusion of impurities to the nickel layer increases when the time interval grows and includes the fabrication processes and thermal excursions. Examples of thermal cycles are when the connector leads undergo high-temperature exposure during the molding of component bodies, the deflashing operation, package sealing, epoxy curing, heat-shrink coating, stabilization bake, burn-in, and component marking.

Diffusion is the key mechanism for solderability degradation.[31] Atoms in the solid state diffuse, i.e., move toward one another and then react to form

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compounds. *Note: this solid state diffusion occurs below the melting point of the solder.* Nickel is superior as a diffusion barrier material in most environments. It is not sufficient to just specify "nickel" for optimal use. The nickel layer must be a fine-grain, high-purity (sulfur-free) deposit.

Proper design is not a guarantee of solderability. The entire fabrication history is critical in achieving this goal.[33]

The following are known good plating practices to achieve defect free surfaces:

1. Plate with sufficient thickness to provide a good diffusion barrier.
2. Maintain clean plating solutions and provide filtration to remove all particles from the bath.
3. Use good cleaning and activation preplate steps.
4. Monitor all plating solution constituents and operating conditions to produce a high-quality deposit.

These known good practices will minimize or help to eliminate plating problems in the majority of electronic devices. Why won't these good practices solve all the problems?

Some devices operate at elevated temperatures. The diffusion rate of metallic atoms is increased by the heat. Thicker plated deposits may be required to retard base metal diffusion to the surface. Pure nickel electroplate may not be the best diffusion barrier in some applications. Electroless nickel provides a somewhat better diffusion barrier, but at a little higher electrical resistance, and the plating cost may double. Diffusion of metals, and in some cases nonmetals, can lead to changes in surface resistivity.[31]

One of the requirements for tin and tin-lead coatings is that they have "long term" solderability and be reflowed or fused without dewetting. The organic film that has been used to preserve the solderability of copper is a solution of benzotriazole in IPA and/or water. Imidazole, the active agent in flux, will remove this film during the soldering operation.[35]

The organic inclusions, surface oxides, and intermetallic compounds all affect solderability and fusing of the electroplated tin and tin-lead electrodeposits. Organic inclusions are particularly significant, because most electroplating processes utilize "organic addition agents" to impart brightness to the deposits.

The organic content of a deposit can be assessed by a number of methods. Elemental gas fusion analysis for carbon remains the most direct and accurate and provides quantitative results. However it requires sophisticated analytical instrumentation.

An in-service problem with tin or tin-lead plating of connectors is fretting corrosion. *Fretting* refers to the repetitive sliding movements between mated surfaces that can result in open circuits.

Applications to be avoided are those involving low-frequency vibrations, a long wipe distance/cycle, and low contact force. Fretting corrosion is characterized by the presence of black spots at the point of motion. The spots indi-

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cate a buildup of tin-oxide debris that acts as an insulator in low-contact-force applications.[33] To circumvent the problem, a high contact force will reduce sliding and provide contact resistance stability, but be aware that the increase in contact force may accelerate wear.

Contact lubrication reduces wear by decreasing the coefficient of friction, floating debris away from the contact area, and preventing oxidation of the exposed metallurgy. A downside of lubrication, however, is attraction of dust and lint to the contact surfaces.

The electronics industry uses alloys with tin contents in the range of 30 to 98 wt% tin as well as pre-tin plating. In general, the higher the tin content of the alloy, the greater the ease of soldering.

There are electroless tin deposits that use titanium chloride as the reducing agent,[46] and electroless solder from fluoborate and sodium hypophosphite are cited in the literature.[47]

6.11.1.2 Get the lead out. For decades, the electronics industry has been utilizing tin-lead as both an electrodeposited finish and a solder joint material. There are environmental concerns about the amount of lead in electronic components. Pressure in the U.S. and foreign markets has forced manufacturers to turn to lead-free alternatives in both plating and solder material. Legislation has been adopted to require the elimination of lead by 2002 in Japan and by 2008 in Europe.[41] Lead is very toxic and can enter the groundwater through leaching. Investigations continue into finding nontoxic replacements for lead-containing finishes.

Listed below are the eutectic melting points of some tin alloy solders that do not use lead.

High-melting[33]	
221°C	SnAg 96.5/3.5
227°C	SnCu 99/1
236–240°C	SnSb 95/5
280°C	AuSn 80/20
Low-melting	
139°C	BiSn 57/43
117°C	InSn 52/48

In high- and low-melting point solder joints, half the metal comes from the solder used and the other half from the pretinning of the components. The lead alloy can dramatically change the melting point of the joint.

An example of this is a PbSnAg (88/10/2) solder with a melt temperature of 290°C. The melting point of this solder can be lowered to 179 to 200°C when

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soldered to a 60/40 SnPb coated component, resulting in a finished composition of SnPbAg of (53.2/45.1/1.7).[33]

Lead is a headache for the plater because of the need for environmentally safe disposal. Many shops are eliminating solder plating entirely so they do not have to deal with treatment of lead containing wastes. Other shops address the problem by segregation of the lead-containing waste stream and through waste treatment of the lead before it hits the sewer system.

6.11.2 Lead-free electrodeposits

The electronics industry is rapidly moving toward lead-free solders.[41] By alloying tin with lead, you produce many desirable deposit characteristics. Among them are a lower melting point, retarded whisker growth, and excellent solderability. There are many tin alloy deposits other than tin-lead for component finishes. The reported finishes are tin-zinc, tin-nickel, tin-cadmium, tin-cobalt, tin-bismuth, and tin-copper.[41] Electroplated pure tin may be the simplest process replacement for tin-lead. Tin is a nontoxic metal, and recycle-recovery procedures are well established. Precious metals are not a cost-effective replacement, and solder joint embrittlement can be a nagging problem.

Lead-free deposits such as tin-copper and tin-bismuth are two of the viable replacements for tin-lead. In any alloy plating system, the final composition of the deposit can be difficult to control. Special applications may warrant the use of tin-bismuth alloy coatings, but in general they have not been accepted for printed wiring board manufacturing. The tin-bismuth and other environmentally friendly alloys are being evaluated by the National Center for Sciences. They completed a study of more than 75 different alloys without finding an exact drop-in replacement.[41] Tests were designed to measure the solderability of these deposits and compare them to tin-lead and tin-silver-copper. The use of the wetting balance allowed for accurate measurements to be taken. The wetting balance measures and reports the wetting force versus time for a solder meniscus to wick up the surface of a test sample.

In "Factors Influencing the Solderability of Lead-Free Electrodeposits,"[42] the authors determined that the solderability performance of the pure tin, tin-copper, and tin-bismuth electrodeposits compared favorably with tin-lead when using tin-silver-copper or tin-lead solders. Aging of the deposits for 16 hr at 155°C followed by steam exposure for 4 hr had the biggest effect on solderability. An RMA or no-clean flux was needed to achieve maximum wetting force. When the deposits were tested after the 16-hr bake, the pure tin or tin-bismuth performed well. The authors concluded that, by choosing the correct soldering parameters, many of the lead-free deposits might be suitable replacements for tin-lead finishes.

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