Failure of Electroplated Deposits: Detection & Prevention

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To assure expected results from plated coatings, it is essential to select the correct metal or alloy and the proper thickness of deposit for the application. A number of different plated deposits are discussed, including gold, zinc, sulfamate nickel, bright nickel, electroless nickel, multiple layers and alloys. Causes of failure and prevention are discussed in general and for the specific coatings mentioned above.

When expected results are not realized from plated deposits, failure analysis should be done to determine causes. If corrections are to be effective, all of the possible causes of failure should be considered. Otherwise, the defects illustrated in the collection of photomicrographs throughout this article will be the result.

It is essential to select the correct coating and thickness for the particular application. It is important to know the properties and characteristics of plated deposits in order to properly select the best coating for the application. Corrosion protection (sacrificial or chemical resistance of the plated coating), electrical properties, including specific resistivity and magnetic characteristics, and mechanical characteristics such as tensile strength, ductility, smoothness, hardness and abrasion resistance, are important considerations. Environmental factors play a part in the selection. For example, cadmium plating, with a chromate conversion coating, provides excellent sacrificial corrosion protection for steel alloys. However, cadmium and hexavalent chromium are toxic. Exposure may be hazardous. Zinc and zinc/nickel, zinc/cobalt, and zinc/iron have been successful substitutes for specific applications.

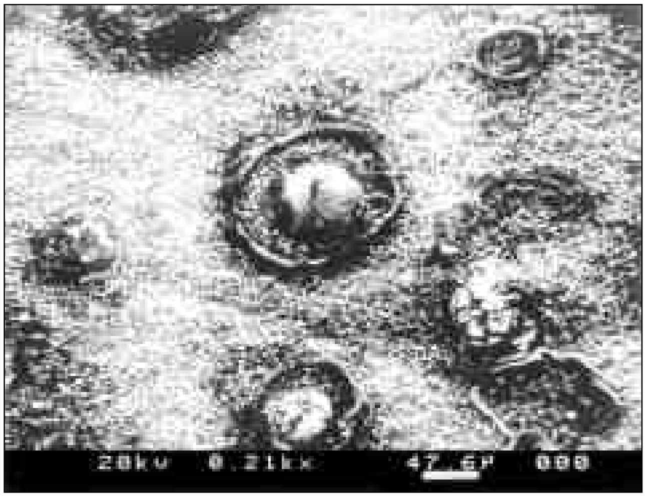

Fig. 1— Bleed-out on over-etched aluminum after lifting blister.

Fig. 2— Skip plate.

People are searching for substitutes for chromium plating because of the hazards of exposure to chromium compounds in plating shops.[1] Electroless nickel-phosphorus, heat-treated, will substitute for chromium for many applications. In some cases, improved performance is experienced.

Failure Modes

Poor Corrosion Protection/Resistance

Detection is usually by visual examination or by evaluation of specific accelerated tests. These include salt spray (ASTM-B117) CASS tests (ASTM B-368), humidity tests (ASTM G-60) and various porosity tests, such as the “ferroxyl test” (ASTM B-765).

Typical causes of poor corrosion resistance are 1) wrong selection of the plated coating for the application, 2) contaminated plating solution, 3) poor control of the plating bath, 4) rough or porous basis material, 5) insufficient plate thickness or 5) porosity.

In electroless nickel baths, poor corrosion protection may arise from low phosphorus content. Phosphorus content can be increased by running the bath at a lower pH and with a higher reducer concentration.

The selection of the proper plating deposit depends on the required performance.[2] For example, gold deposits differ in characteristics, depending on the type of gold solution. There are a number of different gold plating solutions from which to choose. Among these are acid gold alloyed with cobalt, nickel or iron, all based on citrate/potassium gold cyanide electrolytes. Sulfite gold solutions, which are usually 24 K (pure gold) or with alloying constituents added, vary in deposit properties. Cyanide golds can be alloyed with numerous materials to produce 14 K, 18 K or colored gold deposits or pure gold. Specific resistivity varies with the purity of the gold deposit. Acid/cobalt gold with “low” cobalt content has a resistivity of about 4 $\mu\Omega$-cm.

Gold and electroless nickel (particularly high phosphorus deposits) have extremely good resistance to most chemicals. However, the deposit must be pore-free to protect steel or aluminum. The basis metal must have a smooth surface free from pores, metal splinters, metal powder or heat-treat scale to achieve excellent corrosion protection.[3] One major advantage to electroless nickel is that a uniform deposit thickness is achieved over all surfaces. Electroless nickel deposit characteristics vary with the phosphorus or boron content. For example, a low boron alloy (0.5% B) has a resistivity of about 8-10 µΩ-cm. High phosphorus alloys (10.5-11% P) have resistivities of from 150 to 200 µΩ-cm. Electroplated deposit thickness depends on current distribution. If proper racking and current shielding are not exercised, low current density areas get little or no plating and therefore little protection.

Corrosion protection for steel substrates is achieved by a number of sacrificial coatings. Among them are zinc, cadmium and the zinc alloys, zinc-nickel, zinc-cobalt and zinc-iron.

Corrosion can be prevented by a number of approaches. One may choose a smooth pore-free basis material, or use a surface preparation treatment such as chemical- or electropolishing, mechanical polishing or closure of the pores by vacuum impregnation. A sacrificial or multilayered deposit is often chosen. For example, dual- or tri-nickel plus porous chromium provides a bright corrosion-resistant finish on a steel substrate. Pure zinc, or zinc-cobalt, -nickel or -iron alloys also protect steel surfaces. An electroless nickel deposit, with its inherent uniform thickness, will protect component areas having smooth surfaces that cannot be electroplated with sufficient protective thickness (*e.g.*, in recesses) (Figs. 1-12).

Dull or Dark Deposits

Dull or dark deposits that arise from solutions normally given to producing bright or semi-bright deposits result from many causes. The plating solution chemistry can be out of balance. Organic addition agents such as levelers or brighteners can be too low or too high, outside their recommended concentration range. Other common causes are impurities in the solution, and poor cleaning of the parts.

Sources of organic impurities are tank linings containing plasticizers, oils, colorants, fillers in the surface, biocides, impact modifiers, mold release aids and stearates. All of these potential contaminants must be leached from new linings prior to filling with plating solutions. All these substances are detrimental to plating solutions. Masking materials contain solvents and plasticizers, which can contaminate plating solutions. Proper curing can help prevent contamination. Drag-in from rinse waters, or from cracks in the rack coatings that entrap preparation solutions will introduce impurities. Removal of impurities is usually done by carbon-peroxide treatments, electrolytic purification (dummy plating at low current density) or high pH treatments.[4]

Adhesion

Adhesion of electroplated metals to the basis material has always been a concern to the electroplaters and their customers. The importance of good adhesion is increased with the trend toward engineering applications. Detection of adhesion failure is done visually, inspecting for peeling or blisters. Peelers and blisters can originate in a number of ways.[3] Detection can be augmented by microscopic observation.

Adhesion testing is done by various means. Formerly, impact or hammering tests were frequently used. The qualitative method of hammering the electroplated parts with a blunt instrument is primitive, effective and naturally drastic in that it combines the effect of deformation, shock, impact, local heating and fatigue. Among other qualitative tests are the ASTM bend tests, chisel tests, grinding wheel tests, saw-cut tests and the like.[5,6]

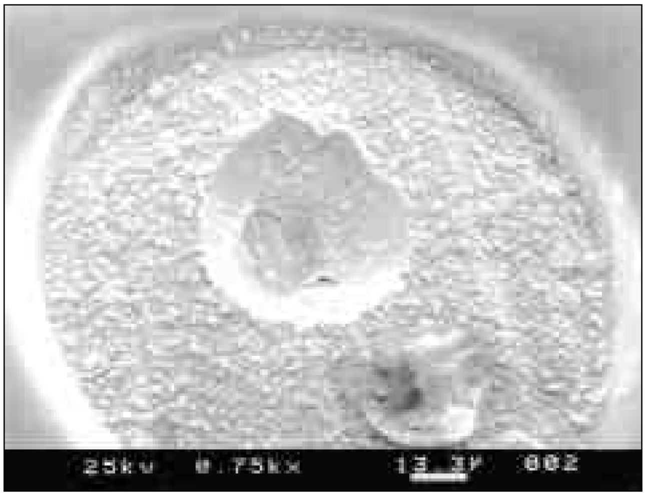

Fig. 3— Pit.

Fig. 4— Cross section of porous substrate.

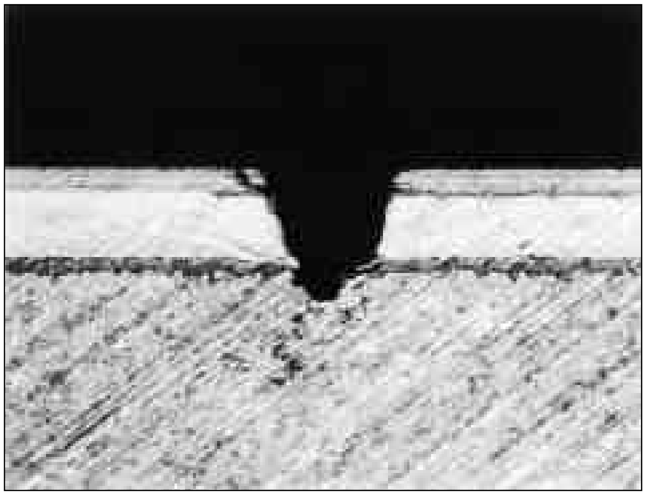
Fig. 5— Porous substrate and resulting pit in plated coating.

Quantitative adhesion tests are useful tools for the evaluation of mechanical properties of the electrodeposits and for the investigation of process parameters in the preparation of metals for plating that lead to improved adhesion. Among quantitative tests are the ring-shear test[7,8], the modified Ollard test[9] and the conical pull test.[9] Each, however, is characterized by practical considerations, which limit their application.

These considerations range from specimen preparation time and machining equipment to the use of specialized test equipment.

The most common causes of poor plate adhesion are related to poor cleaning or poor activation.[10,11] Hydrogen entrapment is also a common source of failure.

Proper preparation is the most important preventive measure. Surfaces to be plated must be "chemically clean," *i.e.*, free of all soil, contaminants and oxides. The use of the correct cleaning cycle and materials, acid treatments, and special strike solutions where applicable, combined with the correct use of these processes, will prevent adhesion failures (Fig. 11).

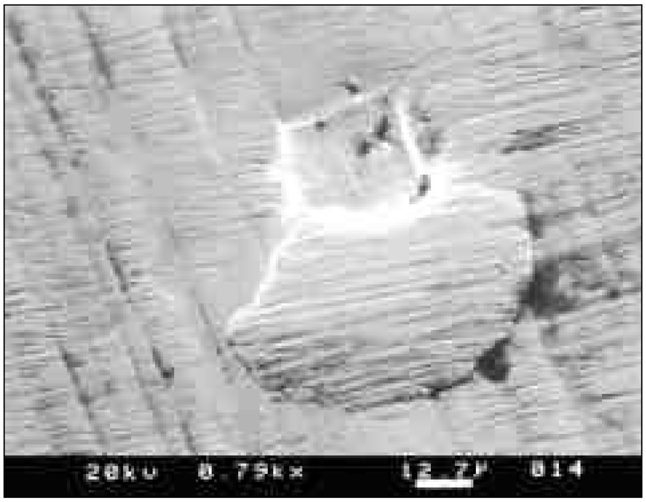

Fig. 6—Skip plate.

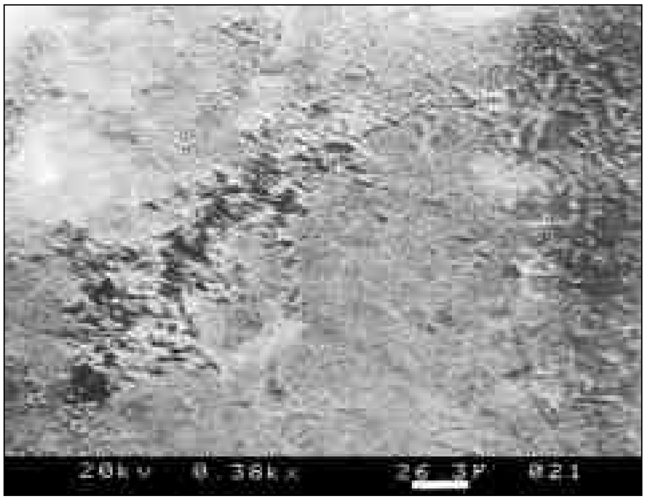

Fig. 7—Bleed-out of cleaner salts on porous plate.

Fig. 8—Roughness.

Roughness

Detection of plate roughness is done by visual means, with or without a microscope, and simply by feel. The causes of roughness include a need to filter the plating solution, magnetic particles on the basis material, poor cleaning and rough basis metal.

Plating roughness can be prevented by proper preparation of the basis material, as in the section of adhesion, above. If necessary, the basis material should be demagnetized (degaussed).[12] The plating solution should be filtered, using the proper solution flow distribution in the tank, and the correction micron-sized filter medium. If necessary, the preparation solutions should be filtered as well (Fig. 8).

Pitted Deposits

Pitting is detected visually, with or without a microscope. It can arise from a porous substrate surface on which plating takes place, inadequate cleaning prior to plating or from contaminated plating solutions.[3] In the case of electroless nickel plating, pitting can be caused by an over-stabilized plating solution, or by too much agitation.

Pitting can be avoided by using a high quality basis material. One should clean and prepare the component using the correct solutions and procedures. Silicone spray, used anywhere in the shop, carried by air, can contaminate the surface of the material to be plated in such a way that cleaning is difficult to impossible. Therefore, avoid using silicones or other similar materials if the component is to be plated (Figs. 3, 4, 5, 7, 9 and 12).

Skip Plating

Skip plating is usually detected visually. It can arise from contaminated surfaces, contaminated plating solutions, solutions out of balance, poor rinsing or oil on the rinse tank. For electroless nickel, excessive stabilizer or agitation can cause skip plating. Again, proper maintenance of all solutions and tanks is mandatory to combat this condition (Figs. 2 and 6).

Poor Coverage

Poor coverage is usually detected visually. In general, this is a result of a design flaw in which the part shape is not designed for plating. The current/thickness distribution is poor because of recessed areas, sharp edges or protrusions. It also may arise from inadequate current density, temperature, concentration or insufficient anode area.

Coverage can be improved by the use of insulating shields and/or "robbers" on the racks, where necessary. Suggested design criteria are available in shop guides[13] or handbooks.[14] Further, a different plating solution with better throwing power or coverage can be selected. Of course, selecting electroless nickel can provide uniform distribution of the deposit, if that finish meets the other requirements.

Tarnish

Tarnishing is also detected visually. Primary causes are poor rinsing, contaminated rinse water, bleed-out from porous basis materials and long transfer times. To avoid tarnishing, one should select a basis metal free from roughness and porosity. When rinsing, use clean deionized water and dry quickly (Figs. 7 and 9).

Functional Deposit Failures

There are several properties of the deposits themselves, which are often required to be maintained within certain parameters. These properties define the functionality of the coating. If they are out of range, this too constitutes a deposit failure. Among these functional properties are hardness, strength, elongation, wear resistance and thickness.

Hardness

Hardness is basically resistance to deformation. Hardness testing operates on the principle of converting deformation (caused by applying a load to a penetrator/indenter) to a numerical value. Hardness is measured by an indenter is not a single fundamental property but a combination of properties. The contribution of each property to the hardness number varies with the material and the type of test.[15]

According to ASTM B-178, the currently accepted test procedure for hardness measurement is the Knoop method. A 100g load is specified for hard deposits and lower loads are used for soft deposits. The Vickers method was formerly used, but currently, ASTM does not recommend the Vickers and Rockwell methods for plated deposits.

If the hardness is not in the desired range, possible corrections are 1) use of a harder basis metal, 2) change in temperature and/or concentration of the plating solution, 3) alloy plating, 4) selecting a different deposit entirely or 5) for electroless nickel, heat treatment.

Strength

Deposit strength is measured by a tensile test on an especially-prepared dog-bone-shaped specimen 25 µm (1.0 mil; 0.001 in.) thick.

Elongation

Elongation, or ductility, is a concept, rather than an ability that can be defined with precision. It is the capacity of the plated deposit to be flexed without flaking or cracking. By definition, ductility is not measured in its own units; it is merely indicated as a relative function of another measurable property, usually expressed as a percentage. Many factors can influence ductility, including stress, strain, reduction of area, elongation embrittlement temperature and the previous history of the part. The measured ductility also depends on the thickness of the part, structural imperfections, the direction in which it is measured and the care taken in specimen preparation.

Ductility can be measured by using tensile test procedures[16] by measuring the distance that a standardized specimen was stretched during the test. Commonly used is a simple bend test on a 25-µm thick deposit removed from the basis material as in tensile testing. The specimen is bent over a sharp edge by a specific number of degrees, usually 180°. This bending is repeated and the number of bends before cracking is related to ductility. Other tests used are the micrometer test,[17] the mandrel bend test, the spiral bend test, the tab bending test, the modified Erichsen bend test and the hydraulic bulge test.

Ductility is usually improved by purification of the plating solution, or by selecting a deposit with greater ductility characteristics. For example, nickel plated from a pure sulfamate solution is more ductile than copper.

Wear Resistance

The formal definition of the wear agreed upon by the OECD committee on Terms and Definitions in Tribology[18] is "the progressive loss of substance from the operating surface of a body as a result of relative motion of the surface". Behind this deceptively simple choice of words lie a whole range of complex phenomena associated with the production of wear debris. It is a dual reliance, as wear is dependent not only on material properties but also on externally-imposed conditions of sliding. Wear is not one intrinsic property of the metal, and even minor changes in the sliding conditions can induce very large changes in wear.

Poor wear resistance can be corrected by selection of another metal deposit or adjustment of the alloy in the deposit. The actual results will depend on the application. For example, electroless nickel will perform better than hard chromium on the blocks of the Falex tester. On the other hand, hard chromium will perform better than electroless nickel on a Taber wear tester. There are many types of wear, including fretting, sliding friction, rolling friction, abrasive wear, chemical attack and erosion. All are tested differently depending on the desired results for the application.

Wear resistance is detected by the Taber abrader or the Falex wear test. While these are the most common, other wear test methods include falling sand, abrasive blasting and grinding.

Thickness Testing

Since the earliest days of electroplating, the purchasers of plated objects have asked the question: "How thick is the plate?" The measurement of coating thickness is the most frequently performed test. The reason for its popularity is the belief that the protective value of the coating is nearly proportional to the thickness of the plated deposit

There are currently 19 methods for thickness testing listed in ASTM B-659, which lists both ASTM and ISO standards. The best methods so far for testing plated deposits are 1) microsectioning and microscope measurements and 2) X-ray fluorescence (XRF). There are numerous other methods, including: (1) magnetic thickness testers (limited to magnetic substrates plated with a non-magnetic deposit), (2) microbalances for on-line testing, (3) beta back-scattering, (4) coulometric dissolution, (5) surface profiling using laser scanning, (6) scanning electron microscopy (SEM) and (7) field-emission scanning microscopy (FESM). Each method has its limitations and possible errors. For example, when microsectioning is used, smearing of softer metals during polishing can lead to high results. The mounting of the specimen is critical. If it is placed at an angle off the vertical, an error can occur. X-ray fluorescence is best done on thicknesses less than 25 µm (0.001 in.). The deposit density must be known and correct standardization must be done.

Failure to meet thickness specifications is one of the most frequent causes for rejection. Accurate thickness measurements are important. Specifications are needed that identify critical areas where it is important to maintain thickness and areas that are not critical to performance or corrosion protection. Thickness variations are a fact of life for electroplated deposits because of the laws of current distribution. Shields and "robbers" and auxiliary anodes can be used to minimize thickness distribution variations, but at considerably higher cost. The possible exception is for gold electroplating. Shields and auxiliary anodes usually reduce the cost of gold plating by meeting thickness requirements in critical areas. Electroless nickel deposits are uniform in thickness wherever the solution can contact a catalyzed surface. If hydrogen bubbles are entrapped during plating, little or no deposition can occur.

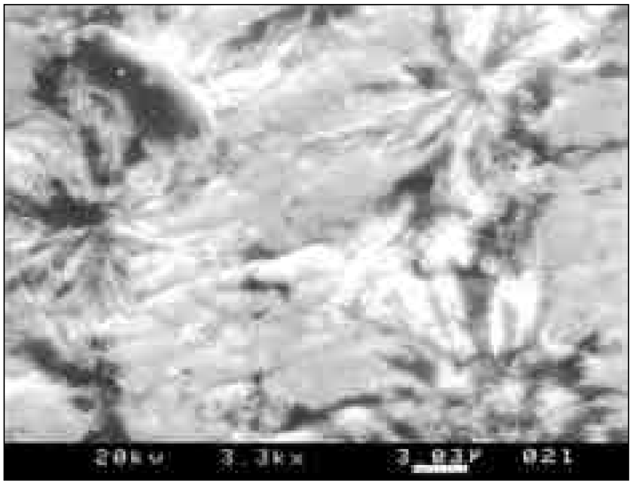

Fig. 9—Salts on substrates under blister.

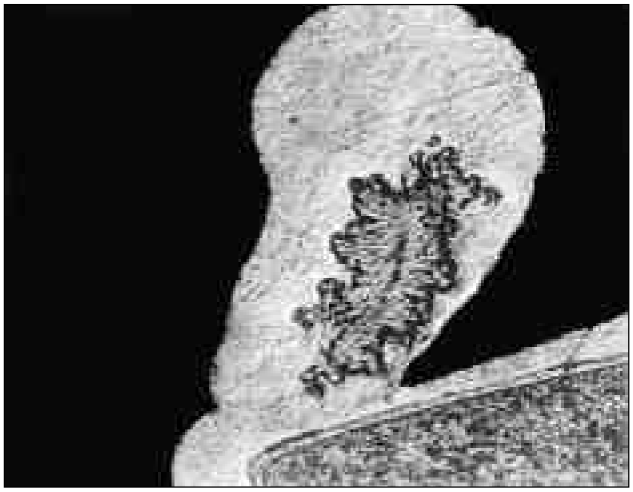

Fig. 10—Copper tree plated with nickel.

Fig. 11—Poor adhesion of nickel on steel (note dark stains where bleed-out and deactivation began).

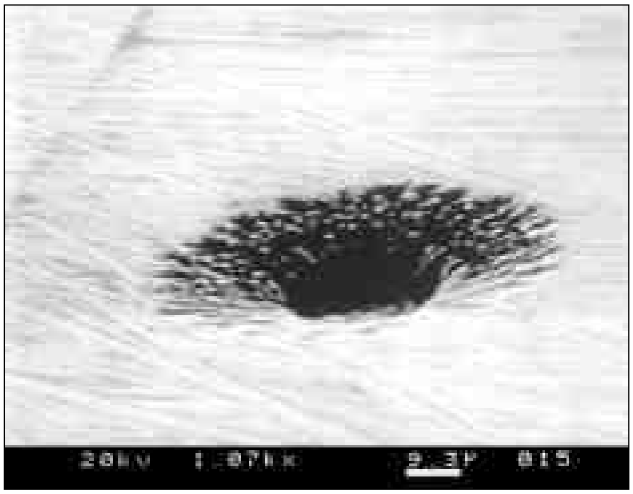

Fig. 12—Plating pit.

Thickness measurements should be adjusted for density differences, particularly for beta back-scattering measurements[19,20] that are compared to pure gold standards (ASTM B-567). For example, pure gold has a density of 19.3 gm/cm^3 while electrodeposited hard gold (containing cobalt or nickel) has a density of 17.5-19.0 gm/cm^3. Since only gold is measured, a low thickness reading may result if the density is not considered:

$$\text{Gold thickness} = \text{Beta back-scatter reading} \times \frac{\text{gold density (standard)}}{\text{gold density (deposit)}}$$

Surface thickness and roughness variations must be avoided to reduce their effects on gold thickness measurements.

Finally, measurements on electroless nickel deposits must take the alloying materials into consideration as for gold.

Summary

There are a number of different gold deposits. For electronic use, there are soft golds (high purity, 24 K) and hard golds (alloyed with cobalt or nickel in small quantities). These are plated from several different types of plating solutions. For decorative gold applications, alloys of copper, nickel or silver make different colors of gold deposits, such as 14 K, 18 K, rose, green, white and others.

If gold is to be soldered the deposit should be as thin as possible. Otherwise, gold in the solder will cause a weak, dull joint.

Nickel deposits of all types are barriers to corrosion. To protect a basis material however, the deposits must be pore free. Rough or porous basis materials most often cause porosity. Careful attention to the selection of basis materials for plating is very important if desired results are to be obtained.

Electroplated nickel, and most acid plating baths for that matter, do not have good throwing power, that is, the ability to plate sufficient thickness in recessed areas. The design of the component to be plated with nickel must compensate for this. The exception is electroless nickel, which covers all areas the solution can reach. However, blind holes, which entrap air or hydrogen gas, generated during plating, will not be plated. Care must be taken to be sure that such holes face upward in the plating solution so gas can escape.

Nickel deposits are also good diffusion barriers to prevent the migration of copper or gold into other coatings. Electroless nickel is a superior diffusion barrier for most applications.

Zinc and cadmium are sacrificial to iron alloys; that is, they corrode preferentially therefore protecting the basis metal. Tin, solder alloys, palladium, gold, copper and nickel are not sacrificial coatings, and like nickel must be pore free and remain so in order to provide effective protection.

Considering this entire discussion, notice how many times the problem of failure is traced to the basis material. Notice also that failure to select the correct plated deposit results in failure to achieve the expected results. And notice that thickness specifications are often incomplete. Critical areas are not identified. The design makes uniform thickness impossible or else the wrong thickness is specified. This is critical to successful results.

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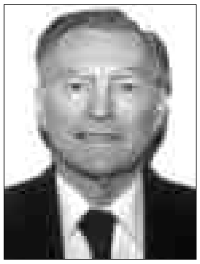
References

1. E.W. Brooman, *Metal Finishing*, **98**, 38 (July 2000); 98, 39 (August 2000).
2. G. Dibari, *Plating & Surface Finishing*, **85**, 12 (October 1998).
3. N.V. Mandich, *Plating & Surface Finishing*, **87**, 74 (December 2000).
4. L. Gianelos, *Plating & Surface Finishing*, **64**, 32 (August 1977); **64**, 32 (September 2000; **64**, 23 (October 1977).
5. A.L. Ferguson & E.L. Stephan, *AES Research Report, Serial No. 1, Project No. 3*, AESF, Orlando, FL (1945).
6. R.W. Polleys, *Proc. AES*, **50**, 54 (1963).
7. J.W. Dini & H.R. Johnson, *Metal Finishing*, **72**, 44 (August 1974).
8. J.W. Dini & H.R. Johnson, *Surface Technology*, **5**, 405 (1977).
9. J.W. Dini & H.R. Johnson, *Metal Finishing* **75**, 42 (March 1977).
10. N.V. Mandich, *Plating & Surface Finishing*, **85**, 91(December 1998).
11. W.M. Robertson & F. Mansfeld, *Plating & Surface Finishing*, **67**, 56 (June 1980).
12. R.S. Modjeska, *Products Finishing*, **29**, 44 (May 1965).
13. S. Heimke, *67th Metal Finishing GuideBook*, **95**, No. 1A, Elsevier Publishing, New York, NY, 1999.
14. J. Hyner, in L.J. Durney, ed., Electroplating Engineering Handbook," 4th ed., Van Nostrand, New York, NY, 1984.
15. J. Horner, *67th Metal Finishing GuideBook*, **95**, No. 1A, Elsevier Publishing, New York, NY, 1999.
16. G.C. Van Tilburg, *Proc. AES*, 50, 51 (1963).
17. C. Durbin, *Proc. AES*, 38, 119 (1951).
18. OECD, Glossary of Terms and Definitions in the Field of Friction, Lubrication and Wear, Paris, 1969.
19. J.M. Neve, *Metal Finishing*, **76**, 17 (November 1978).
20. A. Ott, *Plating & Surface Finishing*, **63**, 28 (November 1976).

About the Author



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