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Failure of Electroplated Deposits

Detection and Prevention

Introduction

This paper looks at failure from the view of the user of electroplated coating instead of from the plater’s point of view. The net result is often corrective action on the part of the plater. However, Corrections often need to be made in the basis material to be plated, the design, or Pre-plating treatments not necessarily revealed or known by the plater.

It is important to know the properties and characteristics of plated deposit 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, magnetic characteristics, mechanical characteristics such as tensile strength, ductility, smoothness, hardness, abrasion resistance, etc. 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.

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

Failure mode

Poor corrosion protection /resistance.

Detection is usually visual or specific accelerated tests. Salt spray, ASTM-B117, CASS tests, Humidity tests, various porosity tests, such as the "ferroxyl test, outdoor exposure, in service exposure, etc.

Causes:
Wrong selection of plated coating for the application. Contaminated plating solution. Poor control of plating bath. Rough or porous basis material. Insufficient plate thickness. Porosity.

Selection of the right plating deposit depends on required performance. For example for 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. Acid gold with cobalt alloy, or with 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 properties. Cyanide gold deposits can be alloyed with numerous materials to produce 14 Karat, 18 K, and various colors. Specific resistivity varies with the purity of the gold deposit. Acid/cobalt gold with "low" cobalt content has a resistivity of about 4 micro-ohm-cm.

Electroless nickel (particularly high phosphorus deposits) has extremely good resistance to most chemicals. However, the deposit must be pore free to protect steel or aluminum. A smooth surface free from pores or metal splinters metal powder, and scale is necessary to achieve excellent results. One major advantage to electroless nickel is that uniform deposit thickness over all surfaces is achieved. Electroless nickel deposit characteristics vary with the phosphorus or boron content. For example, a low B alloy (0.5% B) has a resistivity of about 8-10 micro-ohm-cm. High phosphorus alloys (10.5-11% P) have resistivities from 150 to 200 micro-ohm-cm.

Electroplated deposit thickness depends on current distribution. Low current density areas get little or no plating thus little protection. Sacrificial coatings for steel are zinc, cadmium, and the zinc alloys, zinc-nickel, zinc-cobalt and zinc-iron.

Dull deposits that are expected to be bright or semi-bright. Dark deposits

Causes:
Plating solution chemistry out of balance or lack of organic addition agents such as levelers or "brighteners", to much brightener, impurities in the solution or poor cleaning of the parts contribute to the problem.

Sources of organic impurities are: PVC tank linings contain plasticizers, oils, colorants, fillers in the, biocides, impact modifiers, mold release aids and stearates thus must be leached from new linings prior to filling with plating solutions. All these 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 by carbon-peroxide treatments, electrolytic purification (dummy plating at low current density), high pH treatments, Permanganate/carbon treatment, etc.

**Adhesion**

Detection is visual, peeling, blisters or by microscope.

Poor cleaning or poor activation, failure of specific adhesion tests or Hydrogen entrapment. Testing is done by various means: --ASTM Bend tests, Saw test, Smash, etc. Quantitative tests are "Ring-Shear test" and "Conical pull test."

**Roughness:**

Detection is visual, feel, or Microscope.

**Causes:**

Plating solution in need of filtering, magnetic particles on basis material, poor cleaning or rough basis metal or other substrate material.

**Pitted deposits.**

**Causes:**

Porous surface onto which plating takes place, inadequate cleaning prior to plating or contaminated plating solutions.

**Skip plating**

**Causes:**

Contaminated surface, contaminated plating solution, poor rinsing, oil on rinse tank for electroless nickel, too much stabilizer content too much agitation. Solution out of balance.

**Poor coverage**

**Causes:**

Item to be plated is not designed for plating. Current/thickness distribution poor because of recessed areas, sharp edges or protrusions. Insufficient anode area. Need for "current robbers or masks." See any MFSA shop guide for suggested design criteria.

**Tarnish**

**Causes:**

Poor rinsing, contaminated rinse water, or lead out from porous basis material.

**Deposit functional failures**

**Hardness**

Tested procedure by the Knoop method, ASTM. 100 gm load for hard deposits lower loads for soft deposits. Vickers was formerly used. ASTM does not recommend Vickers and Rockwell methods for plated deposits.

Correction: is alloy plating, selecting a different deposit, or for electroless nickel, heat treat.

**Strength:**

Tensile test on a dog bone 25 micrometers (one mil, 0.001") thick.

**Elongation:**

Elongation % using tensile test procedures. Bend test on a 1-mil thick deposit removed from the basis material as in tensile testing. Bend over sharp edge specific degrees usually 180 degrees. Count the number of bends before cracking.

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

**Wear resistance:**

Detection is by the Tabor Abrader, Phalanx Wear test are the most common, or other wear test methods including falling sand, abrasive blast, grinding, etc.

**Prevention:**

Selection of the deposit or adjustment of alloy in the deposit will provide correction. The actual results will depend on the application. For example, electroless nickel will perform better than hard chrome on blocks of the Phalanx tester; hard chrome will perform better than electroless nickel on a Tabor 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.

**Thickness testing**

Methods and specifications: ASTM B-659 lists more than 21 methods, referencing each ASTM method. The best method so far for testing plated deposits is the use of microsectioning and microscope measurements and X-ray fluorescence. (XRF) There are numerous other methods, including, Magnetic thickness testers (limited to magnetic substrates) plated with a non magnetic deposit), Micro balance for on line testing, Beta back scattering, Coulometric dissolution, Surface profiler using laser scanning, Scanning Electron Microscope (SEM), Field-emission Scanning Electron Microscope (FESM), etc. Each method has limitations and possible errors. For example, when microsectioning is used, smear of softer metals during polishing can lead to high results. The mounting of the specimen is critical. If it is placed at an angle from vertical, an error can occur. X-ray fluorescence is best done on thicknesses less than 0.001" (25 micrometers). 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 due to 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 where the solution can contact a catalytic surface. If hydrogen bubbles are entrapped during plating, little or no deposition can occur. Thickness measurements should be adjusted for density differences, particularly for beta back scattering measurements that are compared to pure gold standards. For example, pure gold has a density of 19.3 gm/cm³ while electrodeposited hard gold (containing cobalt or nickel) has a density of 17.5-19 gm/cm³. Since only gold is measured, a low thickness reading may result if density is not considered.

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\text{Gold thickness} = \frac{\text{Beta back scattering reading} \times \text{gold density} - \text{gold deposit density}}{\text{gold deposit density}}
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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: soft gold (high purity, 24 karat), hard gold (alloyed with cobalt or nickel in small quantities). These are plated from several different types of plating solutions. For decorative gold alloys of copper, nickel, silver etc. make different color gold deposits, 14 K, 18 k, rose, green, white etc. If gold is to be soldered the deposit should be as thin as possible. Gold dissolved in solder will cause a weak dull joint.

Nickel deposits of all types are barriers to corrosion. To protect a basis material the deposits must be pore free. Porosity is most often caused by rough or porous basis materials. Careful attention to selection of basis materials for plating is very important if desired results are to be obtained. Electroplated nickel does 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 that covers all areas the solution can reach. Blind holes, which trap air or the hydrogen gas, generated when plating, will not be plated. Care must be taken to be sure such holes face upward in the plating solution where gas can escape.

Nickel deposits are also good diffusion barriers to prevent 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 thus protecting the basis metal. Tin, solder alloys, palladium, gold, copper and nickel are not sacrificial coatings, and like nickel must be pore free to protect.

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. Notice that thickness specifications are often incomplete. Critical areas are not identified. The design makes uniform thickness impossible, or the wrong thickness is specified.