Electroless Processes

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Applications

Electroless plating processes deposit a uniform thickness of metal onto parts by chemical reduction (no electrical current is required). This allows complex parts to be plated evenly and completely, even over sharp edges and deep recesses. These would be difficult to plate with electrolytic processes because of current density variations across the surfaces. Electroless nickel alloys and electroless copper are the most widely used processes. These systems are "autocatalytic" (self-catalyzing), meaning that they will continue to plate onto their own deposits after the substrate has been completely covered. They can be plated to substantial thicknesses. Some electroless gold, silver and palladium processes are also considered autocatalytic. Autocatalytic processes can plate onto nonconductive materials such as plastics after treatment of the materials with suitable catalytic solutions. Immersion metal plating is sometimes referred to as electroless plating, but the mechanism is chemical displacement—the substrate metal acts as a reducing agent to displace metal ions from their solutions and coat the surface. Plating only occurs when the substrate metal has a lower oxidation potential than the metal in solution, and continues only as long as the substrate metal is exposed. For example, silver and gold plate onto copper, alkaline tin onto aluminum, acid tin onto copper. Plating can proceed through porosity in the deposit to build thickness, but at the same time dissolving the basis metal.

Electroless Nickel Alloys

The properties of electroless nickel alloy deposits make numerous applications possible. Electroless nickel alloy deposits, especially nickel-phosphorus alloys, exhibit excellent corrosion resistance. Since deposits are uniform in thickness over all surfaces, irregular shapes can be protected from corrosion in areas where electroplated deposits would be thin or totally lacking, due to current distribution limitations. Its hardness and low surface friction characteristics make electroless nickel-phosphorus deposits well suited for bearing surfaces, drills, taps, gears, sprockets and similar devices where sliding or rolling friction may cause wear. It is used for buildup of undersize or worn parts (including inside diameters).

Electroless nickel alloys are widely used for corrosion protection of aluminum and steel. Since no electrical contacts are necessary, small and large parts can often be basket or barrel plated.

Table 1
Electroless Processes

Metals	Reducing Agents
Copper	Formaldehyde, sometimes amine boranes, sodium hypophosphite
Cobalt	Sodium hypophosphite, amine boranes
Gold	Potassium or sodium borohydride
Nickel	Potassium or sodium borohydride
Palladium	Amine boranes, sometimes hydrazine
Silver	Amine boranes, sometimes hydrazine

Because of their electrical and magnetic properties, electroless nickel-phosphorus and electroless nickel-boron alloys are widely used by the electronics industry for a variety of functions, including resistors, conductors, magnetic and nonmagnetic functions, and for metallizing plastics and other nonconductors after suitable catalyst treatment. Electroless nickel-boron deposits can be successfully soldered (RMA flux), welded and brazed. In addition, silicon chips ("dice") can be bonded to these deposits and their associated connecting wires can be bonded to metal pads of electroless nickel-boron using ultrasonic and thermosonic techniques.

Electroless Copper

Electroless copper is used primarily in metallizing the holes in two-sided and multilayer printed wiring boards and for plating onto plastics for decorative and EMI shielding applications. The most frequently used processes are high-speed formulations providing thicker deposits, allowing elimination of an electrolytic copper strike on "pattern plated" printed wiring boards, and to build entire circuit patterns for printed wiring boards made by the "additive" process. Electroless copper solutions with lower deposition rates are used to provide a conductive surface for "through-hole" printed wiring boards and for plastics in preparation for electroplating. These solutions typically use formaldehyde as a reducing agent. Other electroless copper solutions utilize sodium hypophosphite, or dimethylamine borane as reducing agents.

Processes

In electroless (autocatalytic) processes, electrons are supplied by "reducing agents" in the plating solution, not from external sources such as batteries or rectifiers (see Table 1).

Table 2
Typical Electroless Nickel Alloy Formulations*

Nickel Sulfate	25 to 40 g/L	Alternatives—nickel chloride, nickel sulfate, nickel acetate
Complexing agent	30 to 50 g/L	Selected from a combination of lactate, citrate, glycolic, malic acids or salts
Reducing Agent	25 to 38 g/L	Sodium hypophosphite, dimethylamine borane
Stabilizer	0.5 to 1 ppm	Lead or cadmium or thiourea or thio organic compounds, oxy anions, etc.
pH-acid solutions	4 to 4.6	
pH-alkaline	8 to 10	
Temperature	90 °C	
mil/hr	0.3 to 0.8	
µm/hr	7 to 20	

*There are numerous proprietary solutions available. The selection depends on the deposit characteristic desired.

Table 3
Electroless Copper Formulations[1]

Component	Solution A	Solution B
Copper Sulfate $\cdot$ 5H_2	13.8 g/L	5 g/L
Sodium potassium tartrate $\cdot$ 4$H_2$0	69.2 g/L	25 g/L
Sodium Hydroxide	20.0 gL	7 g/L
2-mercaptobenzothiozole	0.12 g/L	—
Formaldehyde 37%	39 mL/L	10 mL/L
Temperature, °C	25	25 to 30

Post-plating

Electroless nickel alloy deposits can be heat treated to increase their hardness. Heating to approximately 400 °C for 1 hr will raise the hardness significantly. Depending on phosphorus content, the hardness can change from 500 Knoop to 950 Knoop and, in some cases, 1000 Knoop at a 100-gm loading. Hardness number variations can be expected due to phosphorus content, deposit stress, temperature of heat treatment, gram loading of the test instrument and the test method. Chromate treatments after plating can improve salt spray resistance.

Electroless copper is rarely used as a final finish. Electroplated copper, nickel, or electroless nickel is most often plated over electroless copper deposits.

Gold and palladium deposits do not use post-plating treatments. Silver deposits are sometimes chromate treated to prevent tarnish and oxidation.

Table 4
Electroless Gold Formulations[1]

Component	Solution
Potassium gold cyanide	5.8 g/L
Potassium cyanide	13.0 g/L
Potassium borohydride	11.2 g/L
Temperature, °C	75

Health Impact

Electroless nickel plating solutions that are heated range in temperature from 130 °F (55 °C) to 195 °F (90 °C). Care must be exercised in placing parts into and out of tanks to avoid burns. OSHA requires proper ventilation. Nickel can cause severe allergic reactions in some people. Protective clothing, including rubber gloves, apron, boots, and a suitable face mask are required.

Electroless copper contains several toxic components; copper salts and formaldehyde are very toxic. Care should be taken to avoid contact with the solutions. Proper ventilation is required.

All electroless process solutions should be considered hazardous. Care should be taken to avoid contact. It is important that all federal, state, and local regulations in health and safety are met.

Environmental Status

Soluble nickel discharge to air is limited to 0.1 mg/m^3 (NIOSH recommends 0.15 mg/m^3. Disposal of nickel-bear-

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The AESF supports a government relations office in Washington, DC. Through this office, technical, scientific data are offered to legislators and governmental agencies.

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ing sludges must be in an EPA-approved facility for hazardous wastes.

Discharge of treated wastewater is regulated both by federal standards and state requirements. Each of the metals discussed, with the possible exception of palladium, is considered hazardous by EPA definition and must be treated in accordance with the latest regulations.

Trends

Because of the unique properties of electroless nickel alloy and electroless copper deposits, new uses appear regularly. Continued growth is expected in engineering and electronic applications for all the electroless processes. P&SF

Reference

1. Fred Pearlstein, "Electroless Deposition of Metals," *AESF Illustrated Lecture Series.*

Table 5
Electroless palladium Formulation[1]

Component	Solution A	Solution B
Palladium chloride	2 g/L	3.9 g/L
Ammonium hydroxide	160 mL/L	350 mL/L
Ammonium chloride	26 g/L	—
Tetra sodium ethylenediamine tetraacetate	—	33.6 g/L
Sodium hypophosphite · H_2O	10	—
Temperature, °C	50	80

Table 6
Electroless Silver Formulation[1]

Component	Solution
Sodium silver cyanide	1.83 g/L*
Sodium cyanide	1.00 g/L
Sodium hydroxide	0.75 g/L
Dimethylamine borane	2.00 g/L
Thiourea	0.0003 g/L
Temperature, °C	55

*Made from 1.34 g/L silver cyanide and 0.49 g/L sodium cyanide.

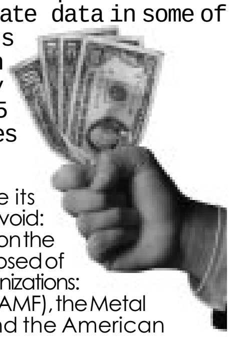
Table 7
Electroless Cobalt Formulation[1]

Component	Solution
Cobalt as sulfonate or citrate	18-19 g/L
Sodium citrate	120-130 g/L
Ammonium chloride	70-80 g/L
Succinic acid	10-20 g/L
Sodium hypophosphite	25-35 g/L
pH	9-11, with ammonium hydroxide or KOH
Temperature, °C	85-95

SURFACE FINISHING MARKET RESEARCH BOARD RELEASES LATEST REPORT:

"Purchasing Practices & Technology Trends"

The fifth report prepared by the Surface Finishing Market Research Board (SFMRB) is the most comprehensive to date. Not only does it confirm and update data in some of the previous reports, it provides important new information on purchasing practices, technology trends and sludge disposal. Report #5 is 82 pages in length, with 125 tables and figures.



The work undertaken by the SFMRB since its establishment in 1993 attempts to fill a previous void: the lack of accessible marketing information on the surface finishing industry. The SFMRB is composed of representatives of the following sponsoring organizations: the National Association of Metal Finishers (NAMF), the Metal Finishing Suppliers Association (MFSA) and the American Electroplaters and Surface Finishers Society (AESF). The level of cooperation among these three organizations as well as the support of trade publications (*Products Finishing, Metal Finishing, Finishers' Management*, and *Plating and Surface Finishing*) on SFMRB projects has steadily increased, and the size and scope of the surveys reflect that effort. The SFMRB surveys the surface finishing industry annually in accordance with mutually agreed-on directives from the sponsors.

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Some key findings, supported by text, tables and figures, are:

- QUALITY
  Quality is more important than price when selecting a supplier.
- TECHNICAL SERVICE
  The most important criterion in supplier selection.
- HIGH USE OF PROPRIETARY CHEMICALS
  The majority of finishers use proprietary chemicals in preference to "home brews."
- PROCESSES WITH HIGHEST EXPECTATIONS FOR GROWTH IN JOBSHOPS
  Electroless copper and electroless nickel plating are expected to show the highest growth.
- PROCESS WITH HIGHEST EXPECTATION FOR GROWTH IN CAPTIVE SHOPS
  Tin-lead plating is expected to show the highest growth over the next two years.
- TOP SUBSTRATES
  Carbon steel and stainless steel substrates, followed by aluminum and aluminum alloys.
- F006 DISPOSAL
  The average finishing shop disposes of 23.2 tons/yr of F006 characteristic waste sludge.
- F006 RECYCLING
  Approximately 40 percent of finishing shops send their F006 sludge out for recycling.

The cost of Report #5 is $125 for members of the sponsoring organizations and $250 for non-members. Computer disk (includes report) $495 for member/non-member.
The report is available from:

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