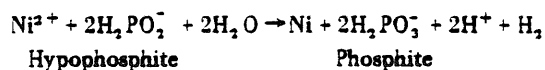


SERFILCO[®]

TECHNICAL BULLETIN

Operation and Filtration of Electroless Plating Systems

Electroless plating, (sometimes also called autocatalytic or chemical plating) is used to deposit metal by chemical reduction and without electric current. At present, the most widely used electroless process is hot, acid, electroless nickel on metal surfaces, while alkaline electroless nickel and electroless copper baths are primarily used for the deposition of a thin conductive coating on plastic surfaces prior to electroplating. Electroless nickel is primarily used in engineering applications because of its unique combination of thickness uniformity, corrosion resistance and hardness. Sodium hypophosphite, the most widely used reducing agent for nickel, reacts as follows:



Operating Hints

Electroless nickel can be deposited on most clean metal and plastic surfaces after suitable pretreatment. Once deposition has begun, plating will continue if the operating temperature and pH are maintained within the specified range, and the depleted chemicals are replenished periodically. Chemical control of the bath is more critical than in electroplating. The bath should always be checked before starting to plate any parts. With tank loadings of 1/3 ft²/gal or higher, hourly analysis for pH and metal content is necessary to maintain a constant plating rate. Analysis for hypophosphite content should be performed at least twice each shift to assure sufficient reducing agent concentration for optimum plating.

The required amount of each replenishing solution is measured out in separate, graduated, plastic containers, which are identified for each solution in order to avoid mixing of chemicals. Additions directly into the plating tank must be done slowly, with fast stirring to avoid local over-concentration, especially of alkali, since this will precipitate nickel hydroxide. In larger systems positive-displacement metering pumps feed the replenishers intermittently from containers into a separate tank, where they are mixed with the hot plating bath

and recirculated via the filter back to the plating tank.

Solutions containing sodium hypophosphite as the nickel reducing agent gradually increase in phosphite concentration. Approximately 100 grams of phosphite are produced as by-product for each mil-square foot of nickel deposited. Unfortunately, nickel phosphite is only sparingly soluble and its solubility decreases with increasing solution temperature. After replenishing the original nickel content four times (four turnovers) most electroless baths will have a phosphite content of about one mole/liter (1 lb/gal) and may turn cloudy even with continuous filtration. Clarity can be restored by decreasing the pH and/or plating temperature. Also, the addition of a nickel complexing agent will clear up the bath during plating. Eventually, there comes a time when the plating rate becomes too slow for efficient production, and the bath will have to be discarded. It is good practice to save 25% of the old bath and mix it with fresh make-up solution. This reduces the break-in time and chemical cost of the new bath. A new bath is always very "active" (fast plating) and relatively unstable. It is safest to reduce the bath temperature by about 5°F and/or the pH by 0.1-0.2 unit for the first few days of operation.

Another problem in electroless nickel plating is the formation of small, shiny nickel flakes, which float around the system. Unless they are removed by filtration, they may become incorporated into the deposit, causing plated parts to be rejected. These nickel flakes continue to plate and increase in size. Since this so-called random nickel wastes expensive chemicals, it should be removed from the tank and filter. After plating, the bath is cooled below 160°F and pumped to a storage tank. The nickel metal in the system is then dissolved in nitric acid, which must be flushed out thoroughly with water before refilling the tank with plating solution. The installation of two plating tanks allows uninterrupted plating while stripping one tank.

Thickness of deposit on large pieces or racks of parts should be checked by simultaneously plating 2 or 3 coupons. These coupons are stamped or cut from steel

(OVER)

and aluminum shim stock, are numbered for reference, and micrometer thickness measurements are recorded. Estimate the plating time from the known plating rate, and remove one coupon about 10 minutes before the desired plating thickness is reached. The exact plating time required for the parts can then be determined accurately (smoothen the coupon surfaces with crocus cloth before measuring). Thicker or close-tolerance coatings require periodic checking of more than one coupon. It is good practice to retain the coupon having the same plating time and heat treatment as the parts, should anyone question plating thickness, adhesion or hardness. For the most accurate measurement, the coupon is weighed before and after plating, and the plating rate (R) and thickness (T), for time (t) in minutes are calculated as follows:

$$R = \frac{\text{Wt. gain (grams)} \times 470}{\text{Area (in}^2\text{)} \times t} = \text{mils per hour}$$

$$T (\text{mils}) = \frac{R \times t}{60} = \frac{\text{Wt. gain} \times 8}{\text{Area (in}^2\text{)}}$$

A calibrated magnetic gauge can also provide fairly accurate thickness measurements of nonmagnetic deposits containing more than 8% phosphorus on steel coupons, but all measurements must be made before heat treatment or aging, as this induces magnetism in the deposit.

Since plating rate is affected by agitation, parts should not be positioned too close to a mechanical agitator or in front of the solution inlet from a circulating pump. Flow patterns will sometimes show on thick deposits if the part remains in the same position without moving. So-called shelf roughness on horizontal surfaces can be minimized by positioning the critical surfaces vertically during plating. Also remember that the hydrogen gas evolved on all plating surfaces must be allowed to escape. With some parts it may be advisable to occasionally shift their position during plating in order to prevent hydrogen entrapment in blind cavities and holes. All contact of parts with the tank walls and bottom must be avoided, since it will initiate plating on contacting tank surfaces.

ALKALINE SOLUTIONS:

To maintain clarity, alkaline electroless nickel and copper baths should be filtered continuously. However, once-a-day batch filtration by transfer pumping the cold solution to and from a storage tank is often sufficient if only light loads are plated or the solution is periodically recirculated through the filter. Due to their high activity, plate-out is a problem, and necessitates frequent cleaning and/or stripping of the plating tank and filter. If plastic liners are used in the tank, these should be changed before they collect too much nickel or copper on the bottom. Before plating, all parts must be rinsed thoroughly to prevent drag-in and contamination with activator and/or catalyst. Depth filter tubes (3-15 microns) should be changed periodically before they

become too loaded and overplate. With some care and proper maintenance these baths can have a long life.

Filtration and Purification

Since electroless deposition of nickel depends on a catalytic reaction, generating hydrogen, it is very susceptible to poisoning by organic and inorganic impurities introduced into the plating bath by drag-in or make-up chemicals. As little as 2 ppm of antimony, bismuth, cadmium and lead may produce misplating or streaking, while larger amounts will completely inhibit plating. Generally, small amounts can be removed by carbon treatment (as discussed below) and larger amounts by electrolyzing (dumming) the bath until the impurities are plated out.

The frequent drag-in of zinc from zincating of aluminum parts will impair deposit appearance and plating rate; thorough rinsing will minimize this. When plating quantities of brass and copper parts, copper contamination can also cause misplating. If feasible, plate only one rack of these parts along with steel parts. This will prevent the buildup of copper in the bath. All water used for makeup and additions should be "soft" or deionized, and filtered if necessary to remove suspended solids.

As in other types of plating, pitting is also encountered in electroless plating. This is often due to contamination by organic impurities, such as surfactants, oil and grease, and the first remedy to try is activated carbon treatment. This purification is easy to carry out with either carbon cartridges in a separate filter chamber or with canisters containing granular carbon. For batch treatment, about one pound of carbon is necessary per 100 gallons of solution, which should be slowly recirculated cold through the carbon for 30 to 60 minutes. To assure maximum carbon adsorbency, the contaminated bath should be filtered first. Since any loose carbon particles in the hot bath may trigger decomposition, powdered carbon can only be used with a precoat, and a filter trap is recommended with granular carbon. During the carbon treatment, sulfur compounds and/or trace amounts of heavy metals, present as stabilizers in all proprietary baths, will be depleted. These must be replenished before the bath is heated. Any wetting agents in the solution will also be removed. The supplier's technical representative should be consulted on how to restore stability.

FILTRATION:

Electroless plating requires efficient filtration in order to obtain not only sound, smooth deposits, but also to maintain the stability of the plating bath. This is particularly true for the electroless nickel solution. Dirt or insoluble particles can act as nuclei, on which random plating initiates the fallout of colloidal black nickel, leading to spontaneous decomposition of the plating solution. Once this reaction has started, the bath must be dumped and the whole plating system completely cleaned of the black particles. Continuous filtration is the best way to avoid this costly decomposition and

time-consuming cleanup. Also, the occlusion of particulate matter in the deposit can cause "cratering" and "pimpling", which are detrimental to the appearance and corrosion resistance of the coating.

Efficient filtration of electroless plating solution is most easily accomplished with either cotton or polypropylene cartridges. Suitable plastic filter chambers are available for 1 to 60 cartridges (10"); stainless steel or chemically-resistant, rubber-lined chambers are used in larger installations. Generally, one 10" cartridge is required for each 50 gallons of solution. They can be arranged in a variety of configurations to accommodate most space limitations. Each 10" depth cartridge has an effective filter area equal to 3.5 square feet of precoat surface filtration, with dirt-holding capacity of 6 to 8 ounces (15-30 micron retention). All synthetic fiber cartridges should be flushed first with hot water to remove all traces of organic sizing agents and lubricants. Filter tubes with polypropylene fibers and cores are most economical to use; if desired, they can be stripped with 50% nitric acid to remove nickel.

The optimum filter porosity depends to some extent on the type of parts being plated. For most applications, a 15 micron cartridge will provide sufficient filtration. However, for plating electronic or optical parts, a 3 micron cartridge may be necessary in order to minimize roughness on critical surfaces. These should be changed as often as necessary to maintain adequate flow through the system. Bear in mind that the coarser the cartridge the lower the pressure drop and, if centrifugal pumps are used, the higher the flow rate. Thus, the solids are removed more quickly from the solution. For untreated filtration, the filter capacity must be sufficiently large to hold all the dirt and particles introduced or generated for the desired time period (1 week, month, etc.). If preferred, excellent filtration can be obtained with pleated, stainless steel wire screens elements pre-coated with diatomaceous earth filter aid from a slurry tank. When loaded, these are cleaned by pressure release and backwashing. However, cartridge filtration reduces downtime, cleanup labor and solution loss.

System Engineering

All components of the plating system must be constructed of either suitable plastics, titanium, or stainless steel, the last requiring frequent passivation to prevent plating-out. Depending on operating temperature, polyethylene or polypropylene tanks are used for up to 500 gallon capacity. Tank walls and welds must be smooth to reduce plate-out. Either polypropylene or stainless steel are satisfactory materials for barrel plating.

The filter system should be adequately sized to maintain adequate flow as the filter becomes loaded. A flow rate sufficient to give two or more passes of the bath through the filter per hour is recommended. A flowmeter installed in-line after the filter will monitor the flow rate and indicate any pump or filter problems. A by-pass on the filter will permit cartridge replacement during plating without stopping solution circulation. With high flow rates, mechanical agitation in the plating

tank is not necessary. However, workpiece agitation by work rod or rotation is advisable to promote release of hydrogen bubbles from the surface and to minimize shelf roughness. Air agitation should not be used, as it increases the hypophosphite consumption.

In small systems, sealless, magnetic-coupled pumps have given good service with all types of electroless solutions. Fluorocarbon, polysulfone, or polyphenylene sulfide plastic are preferred pump housing materials for high temperatures, and polypropylene for low temperature plating. Plate-out in the pump can be reduced with a fluorocarbon encapsulated impeller. Magnetic particles must be kept out of these pumps, since they will damage the impeller and housing. When higher flow rates are required, centrifugal CPVC or stainless steel pumps with double mechanical seals, have been found best. The seals are water-flushed for lubrication and to prevent the crystallization of nickel salts during shutdown. If there is sufficient space in the tank or weir, vertical CPVC sump pumps can be used, with the filter chamber mounted either above or next to the tank. These pumps are economical and provide good tank agitation, but are not suitable for transfer pumping the solution.

With plating solutions heated by means of external stainless or titanium heat exchangers, the same pump can be used for filtration as well as circulation through the heat exchanger, which is located down stream from the filter. Remember, however, that the flow rate and heat transfer will decrease as the filter becomes loaded. The solution inlet should be situated near the bottom of the tank to provide uniform flow and temperature. In small installations, the bath may be heated directly by non-metallic immersion heaters, or by means of a jacketed tank using oil, low pressure steam, or hot water heat. To obtain good heat transfer and uniform plating temperature, a mechanical agitator in the tank is then mandatory. By piping the heat exchanger with water, it can also be used to speed up the cooling of the bath after plating and prior to storage.

The pump filter and tank can be connected with nylon or steel-reinforced PVC tubing, using CPVC, polypropylene or stainless fittings. *Do not strip PVC with concentrated nitric acid.* Larger installations generally use either CPVC, or stainless steel pipe, valves and fittings, which must be stripped periodically and passivated by circulating nitric acid through the system. After prolonged contact with plating solution, even the plastic components will eventually form deposits on rough spots and in corners which should be stripped before they build up. Priming of centrifugal pumps is facilitated with a slurry tank. A valve between the pump and filter, when closed, will keep the pump primed during shutdown. To prevent back siphoning of solution, the filter chamber should be slightly higher than the solution level in the tank.

Remember that electroless plating is a chemical process. For efficient operation and sound coatings it requires careful pre-treatment and close control of plating conditions. Good filtration and cleanliness are most important to avoid operating problems.