TECHNICALLY speaking

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Troubleshooting Electroless Nickel Baths

Electroless nickel plating is an autocatalytic process involving chemical reduction of nickel ions plated on activated substrate. The process differs from immersion plating, which is self limiting, whereas the autocatalytic process is continuous. An electroless nickel bath comprises nickel salts, hypophosphite as reducing agent, complexing salts and proprietary stabilizers.

Electroless nickel baths generally consist of two types:

- Acid EN, nickel-phosphorous
- Alkaline EN, nickel-phosphorus

We will discuss only the acid EN system in this article.

Every plating process requires a robust process control; in order to achieve this, an accurate analysis of key parameters is required at given intervals. A rigorous protocol must be observed in order to obtain consistent and reproducible results for electroless nickel (EN) process.

For achieving desired deposit properties, a proper EN system should be chosen, and its correct operation dictates the final deposit quality. All EN systems are similar in this respect. The chemistry, operating parameters, substrate surface preparation and equipment considerations are the primary variables that influence deposition rate, coverage, adhesion, smoothness, uniformity and brightness.

In order to maintain an EN solution, a thorough understanding of its chemical and physical process variables is extremely important, as these govern the final deposit quality and properties. The three primary areas include: the chemical balance, the interaction of rate and loading ratio, and the influence of the process equipment.

Initial make-up an EN solution is the easy part, but acceptable plating only occurs if the bath is properly balanced. The proprietary systems available today are conveniently made up and maintained. Standard homemade generic formulations can be perfected to produce acceptable deposits though with limited bath life. The key to a successful EN system is timely analysis and proper replenishment of components to maintain its chemical balance. Neglecting replenishment schedules or maintenance of solution levels can cause non-uniform deposits, premature bath decomposition, slow deposition rates, poor adhesion, poor brightness, pitting or roughness. Usually, the effects of poor bath control are noticed immediately after the parts have been plated or shipped to end user. The main ingredients of an electroless nickel bath are:

a) Nickel salts such as sulfates, sulfamates or chlorides for nickel source
b) Sodium hypophosphite as chemical reducing agent for converting nickel ions to nickel metal. The reducing agent may be termed as a “chemical rectifier” in EN baths
c) Complexing agents such as lactates, citrates, malates which facilitate controlled release of nickel ions
d) Buffering agents such as borates, acetates, succinates for pH control
e) pH regulators such as ammonium hydroxide, potassium carbonate for pH maintenance
f) Bath stabilizers such as Pb, Cd, Sn, Mo, and organic sulfur bearing proprietary compounds which control plating rates and inhibit plate out
g) Wetting agents used to regulate solution surface tension and help to dislodge hydrogen bubbles from workpiece

The balance and control of bath constituents is extremely important for a successful operation of an EN bath.

In this article, we will only deal with EN baths comprising sodium hypophosphite as the reducing agent. The EN baths are graded on the basis of percentage phosphorus in nickel deposit such as:

a) Low P content 1– 4 %
b) Mid-level P content 5-9 %
c) High-level P content 10-14 %

ANALYSIS OF ELECTROLESS NICKEL BATHS:

For a balanced EN bath nickel, hypophosphite and pH should be maintained within the specified range. The chemical concentration of Ni is determined by EDTA titration, and hypophosphite are conveniently determined by iodometry. The solution pH should be monitored using a calibrated pH meter with a reliable glass electrode with temperature compensation.

Additives in commercial EN baths are proprietary, comprising organics and inorganic moieties at low levels. Their analyses by conventional methods are not feasible. For example, systems containing lead may be analyzed by pulse polarography or by inductively couple plasma (ICP), which is not done routinely in all labs.

Proprietary systems are usually balanced to maintain the proper chemical ratios if replenishment schedules are diligently followed. EN systems contain proprietary stabilizers and brighteners in mg/liter range that play a key role in regulating the plating rate while also preventing the solution from spontaneous plate-out. This will affect the deposition rate, deposit coverage, brightness and solution stability. The key parameters include:

a) *Nickel*: With the decrease in nickel concentration, nickel deposition rate decreases; coverage, brightness and uniformity of the deposit are also affected. In proprietary systems, the nickel analysis is used for estimation of the reducing agent, stabilizer, complexor and brightener concentrations.

b) *Hypophosphite* : The reducing agent is consumed for nickel deposit and also in side reactions. The reducing agent influences plating efficiency. During plating, the sodium hypophosphite is consumed in a given ratio to the nickel metal. The solution should be periodically analyzed and hypophosphite concentration adjusted. A reaction by-product formed during plating is orthophosphite, which builds up in aged baths. This build-up increases the density of the solution, which decreases the solubility of other components and reduces the plating rate. As the orthophosphite level increases, the deposit smoothness, brightness, plating rate and adhesion can be affected. Oftentimes, deposit roughness, pitting or porosity may occur.

Role of Contamination: The concentration of trace metals and other contaminants within the plating solution will affect deposit quality and appearance. Some metals may also tend to act as stabilizers and/or catalytic poisons that inhibit plating. Elements that act as stabilizers include sulfur, cadmium, bismuth, antimony, mercury, lead, zinc and iron. Sources of organic contamination include masking agents, oils, plasticizers from hoses and liners, airborne organic materials and silicates. Nitric acid contamination from stripping the EN tank slows the plating rate, increases deposit porosity, poor adhesion, and may cause black-streaked deposits.

c) *Operating pH:* The solution's operating pH influences plating rates and phosphorus content in deposit. Higher pH values favor lower phosphorus in the deposit while increasing the plating rate. Higher pH values may lead to precipitation of metal hydroxides or orthophosphates resulting in porous deposits with decreased corrosion resistance.

   Lower operational pH levels increase the phosphorus content in the deposit while decreasing the plating deposition rate. Slower plating rates due to operation at reduced pH produce less porous, more corrosion resistant deposits. The pH should be monitored electrometrically using a calibrated glass electrode.

d) *Operating temperature*: The deposition is influenced by bath temperature of an EN plating solution. The deposition rate increases as the operating temperature increases. It is important to have the proper heating system to avoid localized overheating, which can result in bath decomposition or deposit roughness.

e) *Bath loading and agitation*: For EN solutions, the plating tank size should be custom designed to meet production needs. Bath loading and agitation govern the deposit quality due to interactions with stabilizer concentrations.

Agitation also helps to maintain uniform heating and mixing of the solution. A bath with optimum loading and normal stabilizer concentration can produce poor quality deposits at high solution agitation.

f) *Equipment:* The equipment used in plating affects deposit consistency and quality. Steady maintenance of the tanks, heating, filtration equipment and racks is critical to success. Equipment materials should be resistant to the EN plating solution and the elevated temperatures used in plating.

The air used to provide solution agitation must be clean and supplied from a non-oil-containing air compressor or blower. Disposable, flexible PVC liners can be used in EN applications. Caution should be used when choosing flexible liners to avoid organic contamination

The heating systems should be designed to avoid localized overheating of the plating solution, which may lead to decomposition of the chemistry resulting in pitted, rough or porous deposits. External steam