Chapter 3
Troubleshooting Electroless Nickel Plating Solutions

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The chemical reduction potential of the electroless nickel plating reaction can be affected by many factors; hence, troubleshooting these solutions can be difficult and time-consuming. A working knowledge of the chemistry of the electroless process, coupled with the selection of the proper pretreatment techniques, is necessary to insure reliable, consistent results.

In order quickly and effectively to solve the technical problems that may arise, it is first necessary to outline the typical problems that can arise. These problems can be categorized into four basic groups:

- Bath chemistry imbalance
- Improper substrate preparation/activation
- Equipment/mechanical problems
- Solution contamination

By taking a logical approach to these four categories, troubleshooting can be accomplished effectively and efficiently.

BATH CHEMISTRY

Components of the electroless bath include an aqueous solution of nickel ions, reducing agent(s) (NaH_2PO_2, DMAB, etc.), complexing agent(s), buffer(s), and stabilizer(s). These components work in concert with each other and operate in specific concentration, temperature and pH ranges. Optimizing these parameters can be different from solution to solution. Maintaining the optimum metal content, reducer concentration, pH and temperature of the solution can minimize many of the technical problems that can arise. Analytical techniques to determine these parameters can be obtained from text books or from suppliers.

One of the first and easiest bath parameters to be checked is pH. The pH is determined by pH meter or pH paper. Caution should be used here because some pH papers may differ from the electrometric readings by as much as 0.5 pH units. In some electroless processes, pH papers can give erroneous values because of the "salt-ion" effect of the solution. As an electroless bath ages, there is a buildup of ions such as NH_4^+, Na^+, K^+, $SO_4^=$, Cl^-, etc., and all can contribute to the change in ionic strength of the solution. Consequently, pH paper may act differently in new solutions than in old solutions. Electrometric pH readings are preferred.

Calibration of the pH meter is mandatory for reliable information. Electrometric pH meters require standardization between two units of the pH scale (e.g., 4 and 7). One buffer solution should be above the expected pH of the sample to be measured, while the second buffer should be below. Once the meter is standardized to both of these standards, the solution pH can be measured. A common error in reading pH accurately is temperature variations between the bath sample and the two buffers. The proper procedure is to have identical temperatures for both the buffers and the sample. Thus, a hot bath sample should be cooled to room temperature or the buffer solutions should be heated to the same temperature as the sample. A high pH value of the plating solution can cause abnormally high plating rates that may lead to roughness, pitting, and/or cloudy deposits. Too low of a pH will cause slow deposition rates and matte/dull finishes.

The temperature of the solution should also be closely monitored for consistent high quality deposits. Accurate temperature controllers are necessary. Checking temperature controllers with certified thermometers provides further assurance that temperatures are maintained at proper levels. Unchecked temperatures can lead to decomposition of the plating bath (temperature too high) or no plating at all (temperature too low).

Finally, solution imbalance as a result of poor maintenance of the nickel and/or reducing agent concentrations can give slow plating rates, poor coverage, and dull deposits. Maintaining the nickel and reducing agent concentrations within 10 to 15 percent will usually provide consistency in terms of rate, color, and stability. Periodic analysis of these constituents is required, with the frequency of analysis proportional to the workload being processed. Excessively large replenishments can lead to overstabilization or suppressed rates, as many of the components used for replenishment often contain high concentrations of stabilizers and/or brighteners, which may act as catalytic poisons.

In "home-brew" situations, where commodities such as pH adjusters, metal salts, and reducing agents are added to the plating solutions, only high-purity chemicals from an approved source should be used. Low cost chemicals have often been found to contain impurities that may lead to pitting, dullness, or suppressed plating rates. Insoluble materials can also be present, which will cause roughness or act as nuclei for the spontaneous decomposition of the bath.

Keeping records of replenishment additions, pH adjustments, and temperature readings provides valuable information for maintaining the chemistry balance of the solution. Automatic controllers have proven useful if they themselves are closely monitored. The use of controllers avoids large additions to the plating bath and eliminates the possibility of bath overstabilization. When bath parameters are found to fall within the given ranges and problems still exist, then such circumstances as inadequate surface preparation and/or contamination of the bath should be examined.

SUBSTRATE ACTIVATION

Proper preparation of the substrate to be plated is vital for quality results. Poor surface preparation can cause lack of adhesion, deposit porosity, roughness, non-uniform coatings and/or dark deposits.

A properly prepared substrate is one whereby surface contamination is removed, which leaves a clean, nominally oxide-free surface. Typical surface contaminants that must be removed (or replaced) prior to plating usually include one or more of the following:

- Oils, lubricants
- Buffing compounds
- Oxide films (replaced on Al)
- Weld scale
- Fluxes

Depending on the type of soils present, different pretreatments are needed. Pretreatment choice should be the best available for the specific substrate and should be closely monitored. Cleaners and pickling solutions should be changed at predetermined intervals to eliminate the possibility of ineffective cleaners and descalers, which will cause poor adhesion, streaky deposits, or blistering.

The quality of the substrate itself also must be checked carefully as a potential problem source. Often plating problems resulting from inferior substrates are wrongfully diagnosed as pretreatment or bath chemistry problems; for example, intermetallic compounds at aluminum substrate surfaces can manifest themselves as nodules or pits in the final plate. In other cases, porous castings or powdered metal substrates can entrap solutions, which result in bleedout or voids.

The way in which a part is stamped, cast, drilled, or machined can have a great impact on the final plated product. Improperly stamped parts can imbed difficult-to-remove oils or compounds into the surface of the part. This will lead to dull and often non-adherent coatings. Improper temperature control while casting aluminum or zinc die cast parts can cause lamination of the substrate, which will lead to uneven appearance in the end plate. Obviously then, much attention must be focused upon the raw part itself. By noticing imperfections early, problems can be avoided later in the plating process itself. Pretreatment of various substrates is covered extensively in another section of this book.

EQUIPMENT/MECHANICAL NEEDS

When bath parameters appear to be satisfactory and pretreatment processes are in order, the next area of concern is the type of equipment and the mechanical techniques that are being used. Electroless nickel solutions should have constant filtration to eliminate any particulate bath impurities such as dust, sand, or loose maskant material. With proper filtration ($\geqslant$10 turnovers/hr at 5 μm or less), roughness of the final deposit can be greatly reduced or even eliminated. Replacement of these filters on a regular basis is recommended so that retention of pore size of these filters is maintained. Since electroless plating is an autocatalytic process, it is vital to remove all foreign particulates so that plate-out will be virtually eliminated. Plate-out, if allowed to occur, can lead to roughness of the deposit, bath decomposition, and excessive plating costs.

The type of heating that is used in the plating process is also of great concern. Electroless nickel plating tanks can be heated internally or externally. Excessive localized overheating can cause plate-out, roughness, or even bath decomposition.

Lack of agitation of the plating solution can also cause problems. Solution stratification can occur, resulting in gas pitting, patterns, and/or streaking of the deposit. Proper agitation allows uniform distribution of plating chemicals and helps to eliminate localized overheating. Work-rod agitation or clean, filtered air is suitable for most electroless nickel solutions. Agitation of the solution or parts is necessary to provide a fresh supply of solution to the parts, and to enhance the removal of hydrogen gas produced during deposition.

In most cases, high-temperature, stress-relieved polypropylene is the material of tank construction. Etched tanks can become more active towards electroless processes and should be replaced to minimize plate-out on the tank walls. Stainless steel may also be used as an alternative for tank construction. A small anodic charge will minimize plate-out on these tank walls. Caution must be used when plating in stainless steel tanks (even anodically charged tanks), because the walls may become catalyzed and plate, accompanied by an excessive usage of metal. Plastic drop-in liners are convenient to use, provided all sizing materials are leached out prior to use. This is usually accomplished by soaking the liners in hot deionized water or dilute sulfuric acid and then neutralizing them with acid or alkali. Retained sizing materials in the liner can cause pitting and roughness, besides creating a foam on the surface of the solution.

CONTAMINATION OF THE SOLUTION

When all other parameters appear to be in order, extraneous solution contamination can be a reality. The electroless nickel plating reaction is affected by many impurities. Trace impurities can be organic in nature, such as oils or solvents, or inorganic, such as silicates or nitrates. Metallic contaminants such as lead, copper, cadmium, bismuth, etc., can cause severe problems if they are introduced into the bath in excessive quantities. Most metallic ions will plate out and have little effect on the electroless nickel process if they are introduced into the plating solution in small quantities.

The organic contaminants can come from degreasing solvents, oil residues, mold releases, drag-in of cleaners or acid inhibitors, and unleached equipment or filters. These contaminants will manifest themselves in cloudy, streaked deposits, along with poor adhesion.

Inorganic ions, such as nitrates, can be introduced from improperly neutralizing tanks after stripping with nitric acid. High levels of nitrates can reduce the plating rate or even stop deposition entirely. Silicates are equally detrimental. Drag-in of these ions, usually from preplate cleaners, can form gelatinous films on the work, which is manifested by cloudy deposits or pitting. Improved rinsing will decrease this occurrence.

Metallic impurities can have a profound effect on electroless nickel plating and can be introduced by drag-in from previous tanks, dissolution of base metal of the substrate (i.e., leaded alloys), poorly cleaned or exposed plating racks, or the water itself. Heavy metals that are of special concern include, but are not limited to, lead, cadmium, copper, bismuth, arsenic, and palladium.

Lead can be built up in an electroless bath by dissolution of leaded alloy substrates and by the improper use of lead as a masking material. Lead concentrations of greater than 5 ppm can cause dark deposits, skip plating, pitting, short bath life, and even cessation of plating.

Copper contamination of electroless nickel baths can be equally detrimental. Copper concentrations of $\geqslant$100 ppm will cause immersion-deposit on ferrous alloy parts, which in turn causes adhesion problems of the electroless nickel plate. Poor pretreatment, which leads to poor initiation on copper, may allow excessive amounts of copper to dissolve in electroless nickel baths. Checking preplate cycles, where acid pickles leave an immersion copper deposit on ferrous substrates, may also be the source of copper ions.

Cadmium is usually introduced by the use of plating racks that had been previously used in cadmium plating. Contaminated cleaners may also contain cadmium from stripping operations. Cadmium and lead can also build up in the bath when either or both are used as brightener and stabilizer, respectively. Cadmium concentrations of $>$3 ppm can cause dark deposits, feathering around the holes, and skip plating.

Calcium and magnesium are introduced from the water supply system. If allowed to build up through evaporation, these contaminants will cause rough, hazy, pitted deposits. Precipitation of insoluble compounds may even lead to spontaneous decomposition of the plating solutions. The proper corrective action is to check the deionized water system, or if using tap water, to change to deionized water.

Palladium is used in the activation of non-catalytic substrates. If not rinsed properly, palladium ions or particles may be introduced into the electroless bath, which form nuclei and cause spontaneous decomposition of the plating bath.

Most of the kinds of contamination described above can be reduced by carbon treatment (for organic contaminants) or dummy plating (for heavy metals). The effectiveness of these techniques depends on the type and quantity of the contaminant and the age of the plating solution. Carbon treatment can leave residual carbon, which could lead to considerable roughness or dullness. Some contamination can even be leached from the carbon itself. Carbon treatment can lead to destabilization of some electroless nickel baths because of its ability to remove the stabilizers and brighteners necessary to the bath chemistry itself. Excessive dummying of the solution may lead to severe reduction of other bath constituents, such as nickel, hypophosphite, and stabilizers. Maintaining optimum ratios of these constituents is imperative to successful operation.

CONCLUSION

In addition to the aforementioned observations, a list of the most common problems found in electroless nickel plating is included at the end of this section. Sources of these problems and their remedies are also listed.

When electroless nickel-coated parts are rejected because of roughness, lack of adhesion, poor coverage or lack of uniformity, stripping and replating is feasible. The stripping should be done with as much care and planning as required in the original plating process.

To choose wisely from the many strippers available, it is important to take into consideration the nature of the substrate the deposit is to be stripped from, time, thickness of the final plate, and overall cost. Stripping from steel usually can be accomplished with nitric acid solutions, cyanide/nitroaromatic/caustic solutions or amine-based strippers. In situations where concentrated nitric acid solutions are used, parts to be stripped should be dry prior to stripping, and rinsed immediately after stripping. Close attention to this process is required to minimize water drag-in. Severe etching can occur if the stripping solution does become diluted with water. Copper and its alloys can also be stripped with inhibited strippers, which tend to contain some type of sulfur inhibitor. These strippers may also contain amines or other complexors along with oxidizing nitroaromatic compounds. Aluminum alloys are easily stripped in concentrated nitric acid solutions. Minimum immersion times are preferred here to minimize any possible attack of the aluminum surface itself.

What is evident throughout this chapter is that troubleshooting is not an easy task. First, classifying the problem into one of the four categories, then identifying the cause of the problem are the two most important steps to a viable troubleshooting strategy. When the problem is identified, the economics of remedying the solution should be addressed. Depending on the nature of the problem, the difficulty or cost to remedy the solution, and the downtime required to cure the problem will determine whether the bath should be discarded or if it should be "troubleshooted".

Troubleshooting Guide Electroless Nickel

Problem	**Probable Causes**	**Suggested Remedy**
Poor adhesion and/or blistering	1) Improper surface conditioning	1) Improve cleaning and pickling cycle
	2) Poor rinsing	2) Improve rinse and transfer time
	3) On aluminum, poor zincating	3) Analyze and correct zincating solution
	4) Metallic contamination	4) Dilute or dummy plate solution
	5) Organic contamination	5) Carbon treat solution
	6) Reoxidation	6) Reduce transfer times
	7) Improper heat treatment	7) Correct time and/or temperature of heat treatment
Roughness	1) Suspended solids	1) Filter solution and locate source of solids
	2) Improper cleaning	2) Improve cleaning and rinsing
	3) Too high pH	3) Lower pH
	4) Drag-in of solids	4) Improve rinsing, clean rinse tanks
	5) Contaminated liner or filter cartridges	5) Leach tanks and filters prior to use
	6) Inadequate nickel chelation	6) Reduce drag-out, check replenishment cycles
	7) Contaminated water supply	7) Use deionized or distilled water
Pitting	1) Suspended solids	1) Improve filtration
	2) Excess loading	2) Reduce workload, lower pH
	3) Organic contamination	3) Carbon treat solution
	4) Metallic contamination	4) Dummy plate
	5) Poor agitation	5) Improve agitation, work rod preferred
Dullness	1) Too low temperature	1) Raise temperature
	2) Too low pH	2) Raise pH
	3) Low nickel or hypo concentration	3) Check and correct
	4) Metallic contamination	4) Dummy plate
	5) Organic contamination	5) Carbon treat
	6) Aged bath	6) Replace with new bath
Patterns/streaking	1) Poor agitation	1) Improve agitation
	2) Poor surface preparation	2) Improve and correct cleaning cycle
	3) Metallic contamination	3) Dummy plate

	4) Surface residue	4) Improve rinsing, minimize silicate drag-in
	5) Gas patterns	5) Reposition work, increase agitation
Step/skip plating	1) Metallic contamination	1) Dummy plate
	2) Substrate effect (i.e., leaded alloy	2) Copper or nickel strike prior to plating
	3) Bath overstabilized	3) Dummy plate or dilute bath
Low deposition rate	1) Low temperature	1) Increase operating bath temperature
	2) Low pH	2) Raise pH
	3) Low nickel or hypo content	3) Analyze and correct
	4) High orthophosphite content	4) Discard all or part of bath
	5) Too small a workload	5) Increase workload or reduce agitation
	6) Overstabilization	6) Dilute or dummy bath
Instability	1) Bath temperature too high	1) Lower temperature
	2) Too high pH	2) Lower pH
	3) Localized overheating	3) Locate and correct
	4) Improper passivation of tank	4) Improve passivation solutions and times
	5) Airborne contamination	5) Clean area of dust and loose dirt
	6) Drag-in of catalytic metals	6) Improve rinsing
	7) Large additions made of replenishers	7) Use more frequent additions to maintain consistent stabilizer concentration
No deposition	1) Overstabilization	1) Dilute bath, avoid large additions of replenishers
	2) Improper substrate surface	2) Substrate may not be autocatalytic and require a nickel or copper strike, i.e., stainless steel, copper
	3) Too low temperature or pH	3) Analyze and correct
	4) Metallic contamination	4) Electrolytically dummy solution
Dark deposits	1) Contaminated rinse after EN	1) Improve rinsing
	2) Improper surface preparation	2) Improve pretreatment
	3) Too low pH and/or temperature	3) Check and correct
	4) Low bath activity	4) Analyze bath constituents and correct
	5) Organic contamination	5) Carbon treat
Rapid pH changes	1) Drag-in of pretreatment	1) Improve rinsing
	2) Excessive workload	2) Reduce workload and check plate-out on tank and heaters

	3) Bath not at proper pH range	3) Check pH and adjust to optimum buffered range
High nickel usage	1) High drag-out	1) Reduce drag-out with replacement of stagnant rinse after plating tank
	2) Bath decomposition	2) Cool and filter solution
	3) Plating on tank and equipment	3) Filter solution and strip tank and heaters
	4) High surface area	4) Reduce workload size
Cloudy plating solution	1) pH too high	1) Lower pH with dilute sulfuric acid or hydroxyacetic acid
	2) Drag-out losses excessive	2) Reduce sources of drag-out losses. Add more make-up additive
	3) Under-complexed solution	3) Add more make-up additive