

## Effectively Problem Solving an Electroless Nickel Plating Operation

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Electroless deposition has been commercially viable and successfully utilized since the 1950's. The deposits have effectively met many engineering requirements in a variety of market applications. In any metal finishing operation, the potential for problems will exist. In order to achieve the maximum benefits of these deposits, the nuts and bolts of the solutions utilized must be fully understood to properly overcome problems when they occur. Specific problems, with their resolutions, will be reviewed through customer experiences and case studies.

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## **Introduction:**

This paper is actually the culmination of input from many colleagues who have spent much of their career working with and understanding electroless nickel technology. This experience and interaction is the underlying basis for effectively troubleshooting Electroless Nickel systems. Over my career this author has had the opportunity to work with these colleagues at MacDermid. As such, I consider this paper to be written by all of us and include Boules Morcos, Mike Barnstead, Carl Steinecker, Mike Malik, David Crotty, Bob Laughton, Franck Robin and Duncan Beckett. I am sure there are also other individuals, but these gentlemen are the ones who in my mind have contributed the most to the accumulation of this information being presented in this document.

## **Troubleshooting 101**

Troubleshooting any process is an art form with the basis of science if properly executed. It involves the identification of key variables and the ultimate acceptance or elimination of those variables with a successful outcome. Troubleshooting is by no means a perfect process in every case but the process itself allows some expressiveness with the input of those individuals charged with properly resolving the problem(s). Not everyone sees a problem in the same manner. Some people have a knack for troubleshooting while others do not. I am not sure what differentiates them exactly but I do know that the two requirements every successful troubleshooter has to solve problems are an open mind and open eyes & ears. Being able to see change and listening to what those have to say who are involved in the problem are important attributes for successful troubleshooting of any process. Also, the patience not to jump to conclusions is important for overall success in the troubleshooting discipline. Additionally, the successful troubleshooting for any process, particular for Electroless deposition processes, can be accomplished by breaking down the troubleshooting process into 5 basic components. We refer to these as the “5 P’s” of the troubleshooting process. These critical “P’s” include 1)the true identification of the problem, 2)inspection of the parts, 3)the process of the plating, 4) the people involved in all these processes and 5)the plating line. Once all the key attributes in each category are identified properly, even the most complex problems can be solved. This procedure or technique of troubleshooting is often more important than expert knowledge of a particular product. Sometimes too much expert knowledge will incorrectly influence one’s perception of a problem without identifying the real causes for the defect. I admit to falling into this trap at times but have learned to temper my initial thoughts and conclusions through experience. It’s far easier to ask more questions in this situation than to immediately exert your opinion with limited information. By applying ones knowledge of general plating practices, one can usually determine the cause of most problems, even with an unfamiliar product. Understanding of this simple fact will be the creation of a successful troubleshooting experience.

## **The problem?**

One has to accurately determine the exact problem or identify the root cause of the problem in

order to solve the problem. How is this done? Simply asking a few key questions will help in this regard.

- √ Define what exactly is wrong.
- √ What could cause this problem?

The real challenge to accurately determine any problem is to separate the problem from the symptoms that occur. We easily see the symptoms of the problem which occurs in the form of the defect. By making selective modifications to different portions of the plating process, we often end up curing the symptoms and not correcting the actual problem. The problem will eventually always come back in this case.

Defining the problem accurately can be the tricky part of the troubleshooting because of the number of variables to identify and maintain can be overwhelming at times. This is why a systematic approach is important. Here are some thoughts for consideration when identifying the problem.

- √ Know the common problems, causes, and cures for EN technology. For this, you can review the attached troubleshooting guide to assist with narrowing down the potential causes and where to look.
- √ Consider the effect that each process step could have on the defect. This is a difficult concept for many to grasp since the tendency is to change many items at once to affect a positive change. That's not a very systematic approach. Normally it is the combination of many variables that will contribute to any given problem. For example, any EN process relies on successful cleaning, rinsing, activation & plating which includes all of the process equipment. Changing some aspect with each variable at the same time may yield some resolution but without knowing the root cause, the problem will likely reoccur in the future.
- √ Sometimes simply the elimination of variables through tests on the line or in the laboratory will provide an advantage in the troubleshooting process. In other words it can sometimes be beneficial to know something does not affect the defect as opposed to having a direct affect on the defect.
- √ Look for patterns that exist with the particular problem. For rack plating, does the defect problem occur on the same location on the rack? Is it random? Maybe there is no pattern? These are all important aspects to identify.
- √ Locate potential problem areas because every process line has some inherent weakness that will contribute to problems. It may not be the root cause of the problem you are trying to troubleshoot but will affect something else that impacts the problem more directly. For example, did someone forget to empty (maintain) the oil trap and change the filter on the air compressor that provides air agitation to the process line? It is known that compressed air is a weakness and not recommended for providing air to the process

line but by not maintaining the oil filter will yield the potential for oil contamination not only in the EN but also in the water rinses. Air provided from a blower is preferred to provide our air-agitation to the process.

- √ Look at your records as this will help identify patterns with the defect. Does the defect occur at the same time during any given shift or with a particular type of part? Have some SEM work performed to correctly identify the attributes of the defect. The source of pitting and roughness sometimes look alike until a more thorough study is completed.

### **The Parts Never Lie?**

Electroless deposition reproduces the topography of surface to which it is applied. The smoother the surface finish (Ra) of the particular substrate being plated, the smoother and less nodular will be the resulting EN deposit. In these conditions, lower EN thickness' can be tolerated to provide the necessary deposit performance whether that result is corrosion performance, wear resistance or other attribute. Performance problems arise when substrate surface topography is a rough surface finish as in the case of most castings and where as few as 5 microns of EN is applied with the expectation that hundreds of hours of corrosion performance will be the result. This is an unrealistic expectation. The substrate conditions tell much about the ability to process and also the potential for defects to occur. Here are some additional thoughts for consideration with the parts.

- √ Look at the problem parts, do all the problem parts have the same defect or is the defect in the same position on the parts?
- √ Compare rejected parts to acceptable work - what else is different? What else is the same?
- √ Look at some raw pieces, and compare different lots of material. Were parts machined by the same machine shop or on different machines within the shop? Determine when the problem really started.
- √ Has anything changed? Really the better question is "What has changed?" because the correct answer is always "yes" to this question. Simply put, there would not be a problem if something had not changed. This is true unless of course the problem always did exist and now due to higher quality standards being executed, the problem is now being seen by the new quality standards system. Look for any difference in the parts, and the interaction with the process or the people. Is this really a new problem, or just another symptom of an old problem? Find the root cause, not just effect. You must design the troubleshooting process to find the root cause in this case.

### **The Process:**

The process includes the processing of the substrate (machining, grinding) and also the post plating processing which can include machining, polishing, and heat treatment just to name a few. This is the most difficult to troubleshoot especially for a job shop because they can receive the same type part from several different sources. This adds a lot of variability into the troubleshooting process. One advantage for a captive shop is the fact they own both the responsibility for the manufacture of the part as well as the finishing responsibility. Technically this should make it easier but this is not true in every case for all situations.

- √ Know what each step is supposed to do in the entire process sequence. In other words, know how each step can affect the others from the parts machining or casting to the final polishing or subsequent finishing after EN plating.
- √ Look at parts being processed; before the plating line, during the processing in the plating line, and after the plating (post plating). Heat treatment scales produced on some types of parts become a large variable for the plating process to effectively remove consistently. Is all the heat treatment scale the same color before processing in the plating line and after the acid pickle?
- √ Look for variations between different runs (or lots) of parts and if any the effects they have on the final quality.
- √ Record the data that is collected and then review the data as it is collected. Sometimes data can give different insights and should be examined from differing perspectives. Looking at the same data more than once is not a bad practice.
- √ Has anything changed with the process?

### **The People:**

Even with automatic plating lines, the people responsible or those working around any line will have some type of potential impact on the quality produced from the line. After all, the people are the ones looking after the maintenance of the equipment and those who maintain the chemistry on these lines. People make honest, sometimes un-avoidable mistakes and additionally in many shops today people are overloaded with many different responsibilities so the potential for more mistakes will be possible. It is hoped people are empowered to own the process but equally important we must ensure that all personnel associated with any line are properly trained to know the affect of their actions on the quality and performance of any given line. When there are problems don't over-look the following inputs.

- √ Do different line operators get the same results?
- √ Have there been any changes to/with line personnel?
- √ Any changes in the laboratory personnel?
- √ Any changes in the inspection personnel?

- √ Any changes at your customer with personnel? Is there a new quality manager or inspector? Maybe this defect always existed but was not a problem until the personnel change?

### **The Plating Line:**

Of course, the plating line is the responsibility of the metal finisher and usually the part of the entire process where blame is focused. After all the metal finisher is the last stage of the process before the part gets assembled into something larger. Also the plating deposit has the distinct disadvantage to emphasize defects by its nature of producing bright deposits. A bright deposit over a defective substrate exaggerates the defect. It seems like it's just easier to blame the last stage of the cycle in any given process. For this reason, our troubleshooting skills must be honed to the best possible; if for nothing else, to protect your company reputation and protection from potential liability and added cost. If the other "P" variables examined have yielded a negative result, then the focus to the plating line will likely produce insight regarding the root cause of the problem. At this point, the following items should be carried out.

- √ Inspect the entire line; look for anything out of the ordinary or unusual.
- √ Verify everything yourself because those who live with the line everyday often will not consider even the smallest change significant to the source of the problem.
- √ Consider the effect of each product not working correctly. The old standard for troubleshooting is the verification of time, temperature and concentration for all the stages of the plating process. Confirm all operating conditions and make sure equipment controls for temperatures and water flow control devices are working properly.
- √ Know the operating conditions for all the steps in the plating process and verify they are correct.
- √ Know the common problems of the line. Talk to the operators. Compare "now" to "then".
- √ Know the common causes of the defects. Is the problem related to chemistry imbalance or poor operating conditions? Is the problem related to equipment such as racks, barrels, tank filtration, heating, etc., in the shop?
- √ Know the common cures for the problem and not just the cures for the symptoms, assuming you have identified properly the defect.
- √ Has anything changed on the line? (Again, assuming you have narrowed down the troubleshooting process to this part of the process, the better question to ask is "What has changed?")

### **Chemistry problems versus Deposit problems:**

How does one determine the difference between chemistry problems and deposit problems? The obvious answer of course is troubleshooting. But, more importantly does this identification

of a chemistry problem versus a deposit problem really matter? At the end of the day, a defect still remains a defect regardless of the origin. Right? Well, it does matter whether a problem occurs from the chemistry or from the deposit as there are many different mechanisms even though many of these are inter-related. For example, poor corrosion performance of the Ni-P alloy is obviously a deposit problem on the surface but there can be many EN chemistry interactions that directly impact or can be the root cause of the poor corrosion performance. The following troubleshooting guide, finding fault with EN, a guide to what went wrong and why examines both deposit problems and EN chemistry problems and their respective impacts on the overall Ni-P quality. Also because troubleshooting 101 begins on the line and can end up in the laboratory, also included is a section on guidelines for beaker testing of the EN solution.

Defects in electroless nickel plating can be divided into two main categories; chemistry problems and deposit problems. Chemistry problems are problems seen in the plating solution, such as slow plating rate and white out. Deposit problems are problems seen on the parts, like poor adhesion and roughness. Here are more examples of each type.

<b>Deposit Problems</b>	<b>Chemistry Problems</b>
<b>Poor adhesion</b>	<b>Slow plating rate</b>
Roughness	<b>Excessively high plating rate</b>
<b>Pitting</b>	<b>White out (lime out, milking out)</b>
<b>Dull deposits</b>	<b>Plate out on tanks, equipment</b>
<b>Patterns and streaking</b>	<b>Excessive chemical usage</b>
<b>Dark deposits and staining</b>	<b>Rapid pH changes</b>
<b>Step plating and edge pullback</b>	<b>No deposition</b>
<b>Poor corrosion protection</b>	<b>Bath decomposition</b>

## SECTION I – DEPOSIT PROBLEMS

**Table 1**  
**DEPOSIT POOR ADHESION**

COMMON CAUSES	MECHANISM
Inadequate surface preparation	Using inadequate or incorrect cycles will not properly clean and activate the parts. Check the alloy of the part
Dirty rinses, or hard water rinses	<ol style="list-style-type: none"> <li>1) Can introduce foreign material onto the surface of the work.</li> <li>2) Can passivate an active surface, especially in situations where high air agitation is used</li> <li>3) Silicates in the pre-plate cycle in hard water areas may cause problems by forming a tenacious film of gel-like calcium silicate</li> <li>4) Rinsing is especially critical in aluminum processing and when plating castings.</li> </ol>
Long transfer time between tanks	Allows the work to form oxide films, and increases the chance of dry-down
Contaminated bath, including nitrates	<ol style="list-style-type: none"> <li>1) At 100 mg/L (PPM) nitrate poor adherence may occur from attack of substrate and passivation of deposited nickel. Use nitrate test strips to verify the purity of the water in the plating tank prior to making up the bath</li> <li>2) Excessive copper contamination in an electroless nickel bath can lead to immersion copper on ferrous alloys</li> </ol>
Drastic changes in bath chemistry can cause nickel to nickel adhesion failures	Operating pH has a major effect on phosphorous content and deposit stress. By drastically changing the pH during plating you get two dissimilar nickel layers

### Poor adhesion and pretreatment

The majority of the causes for poor adhesion can be traced directly back to deficiencies in the pretreatment. Be aware of the following indications of inadequate pretreatment:

- 1) Look for “smut” on the parts after acid activation. A smut from aggressive acid activation will give poor adhesion. Use a shorter or weaker activation or, if possible, remove the smut using anodic electrocleaning. Also, the formation of smut on an ID surface can be different than the formation of smut on an OD surface.



*Adhesion failure ID surface*



- 2) Look for water breaks on the parts after the acid activation rinse tank. This is a good indication of soils on the parts. Improve the cleaning cycle.
- 3) Look for the formation of flash rust on the parts after acid activation. This loosely adherent oxide layer may cause bad adhesion. Flash rusting may also occur during alkaline electrocleaning. When this occurs, it is an indication of low caustic in the cleaner.

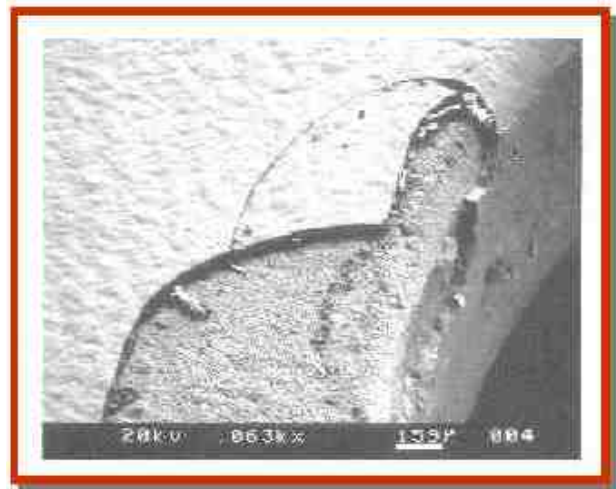
Poor Adhesion ID surface.

- 4) Look for dry down of the cleaners on the work. This frequently happens with large, massive parts, but it can also occur in situations where very hot cleaners are used, or long transfer times between tanks exist.
- 5) Look for *uniform* gassing over the surface during acid activation. This is a general rule, not always accurate. In situations where the activating acid does not attack the substrate, there will be no gassing. Activating acids typically perform three functions:
  - A) Neutralize alkaline cleaner films.
  - B) Remove oxide films.
  - C) Microetch the substrate.

During the neutralization and oxide removal steps, hydrogen gas is not produced. Only when microetching the part does gassing occur. If the part is not gassing *uniformly*, then it may not be uniformly active.

### **Silicates and poor adhesion**

Silicates are a common ingredient in many industrial cleaners. If a silicated cleaner is used in conjunction with hard water rinses, there is a strong possibility of forming a tenacious film on the surface of the parts. This film is a combination of the metals present in hard water (such as calcium) and the silicate from the cleaners, and is a common cause of poor adhesion and patterned plate. Thorough rinsing after cleaning is critical to avoid forming this film. A small amount of fluoride in the acid activation step will remove the film.



*Adhesion failure on aluminum ring*

### **Poor adhesion and aluminum**

- 1) Aluminum will blister in an older electroless nickel bath due to decreased bath activity, increased attack on the zincate coating, and increased deposit stress.

- 2) A very rough guide is to avoid plating aluminum in a bath over 4 metal turnovers unless an alkaline EN strike is utilized.
- 3) The use of an alkaline electroless nickel strike eliminates this 4 MTO restriction.
- 4) Be aware that using stainless steel racks, wire, or bolts in contact with the aluminum will set up a galvanic interaction. This “battery” on the work often will cause blisters on areas immediately surrounding the area of contact.
- 5) Immersion deposits form readily on aluminum. Processing large amounts of copper containing alloys may introduce copper into acid based desmuts and activators. This may lead to immersion copper on the part, and subsequently result in poor adhesion.

**Table 2**  
**DEPOSIT ROUGHNESS**

COMMON CAUSES	MECHANISM
Suspended solids in solution	1) Particles in the plating bath are the leading cause of roughness. This is usually evident on shelf areas. 2) Filtration will remove the particles, but the source should be isolated and eliminated
Magnetic parts	1) Magnetic parts will attract any magnetic particles in the bath, causing roughness on the magnetic areas of the part 2) Degaussing magnetic parts is recommended
Nickel flakes from the racks	1) The flakes can settle on the parts 2) Strip the racks often
Plate out on tank	Deposited electroless nickel on the tank can break loose and settle on the parts
Improper surface preparation	Foreign material may be introduced with the parts due to poor pretreatment
High pH High temperature “Hot Spots” in the tank	1) Increases the bath activity, which can cause plate out and “seed out” 2) Several impurities, such as iron, are less soluble at higher pH ranges, and may precipitate
White out	Nickel phosphite is insoluble. In extreme cases this may lead to roughness
Drag in of pretreatment chemistry	Drag in of phosphated cleaners can produce metal-phosphate particles in the bath
Low stabilizer	Increases bath activity, increasing plate out on the tank and “seed out”

**Roughness and Particles: Where do they come from?**

- 1) Nickel flakes from the racks can dislodge during plating and settle on the work.
- 2) Foreign material introduced with the parts due to poor pretreatment, such as sand from blasting operations, can cause roughness.



*Roughness due to nickel nodule*

- 3) Is there a source of airborne particles nearby? Check for blasting operations, buffing wheels, airborne dust from outside, etc. Was the bath treated with powdered carbon?
- 4) Hot spots, high temperature, low stabilizers, or high pH in the tank can cause the formation of nickel particles. Make sure the bath temperature does not exceed 205°F in the heat exchanger.

#### **How to reduce or eliminate roughness**

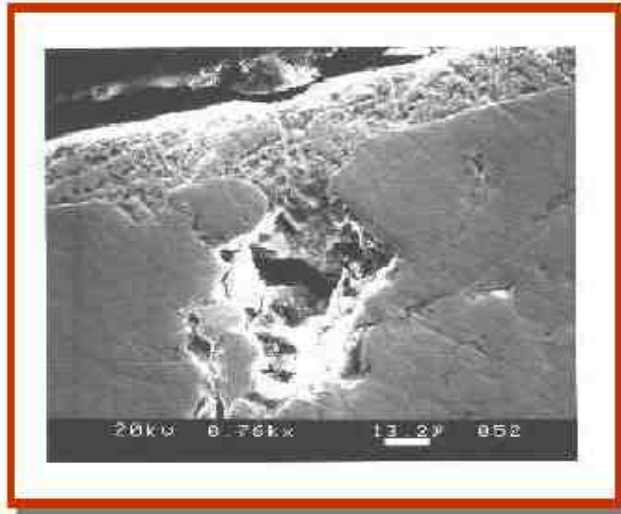
- 1) Improve EN solution filtration – at least 10 to 15 solution turns/hour through a 1 micron filter media.
- 2) Change the filter frequently, leach new filter media to remove sizing
- 3) Maintain good housekeeping on the line.
- 4) Maintain good chemical control of the bath.
- 5) Pay attention to the pretreatment. Check the parts prior to plating for cleanliness and verify whether parts are magnetic.
- 6) Use additives in the plating bath, such as a dispersing agent or wetting agent to reduce surface tension.

**Table 3  
DEPOSIT PITTING**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Suspended solids	1) Particles in the bath are a common cause of pitting. If the particles stay on the work, they cause roughness. If they fall off, they cause pitting 2) This pitting is usually seen on shelf areas
Contaminated bath	1) Organic contamination is a leading cause of pitting. This type of pitting looks unique - usually a spherical dimple in the plate, usually on the underside of the parts 2) Filter bags and cartridges are a common source of organic contamination. Leach filters in dilute sulfuric acid prior to use 3) Low sulfur stabilizers can lead to pitting. Copper and nitric acid consume sulfur stabilizers
Porous or pitted substrate	Electroless nickel will not typically fill in voids in the substrate, resulting in a pitted deposit
Poor pretreatment	Poor pretreatment cycles that leave oils and organics on the work can cause pitting
Gas pitting	1) On thick deposits gas pitting is a major problem 2) Reducing the surface tension usually helps 3) On the sides of the work it causes "fish eye" pits
Low complexors	Low complexor allows the formation of nickel phosphite and nickel hydroxide
Additions made directly on top of parts Make-up or replenishment chemistry mixed together prior to adding to the bath	Chemical additions made directly on top of parts or mixing the replenishment chemistry together prior to adding to tank can form nickel hydroxide particles, which will eventually dissolve and leave a pit behind

**How to reduce or eliminate pitting**

- 1) Improve filtration - 10 to 15 solution turns/hour through a 1 micron filter.
- 2) Change the filters frequently, and leach the filters prior to use in dilute (0.5 to 3% by volume) sulfuric acid to remove tramp organics.
- 3) Maintain good housekeeping on the line.
- 4) Maintain good chemical control of the bath. Look for oil on the bath and on the tank walls. Look for foaming in the electroless nickel bath. These are signs of organic contamination.
- 5) Pay attention to the pretreatment. Check the parts prior to plating.
- 6) Use additives in the plating bath, such as a wetter or a dispersing agent.



*Cross Section Pitting due to porous substrate*

#### **Avoiding pits on thick deposits**

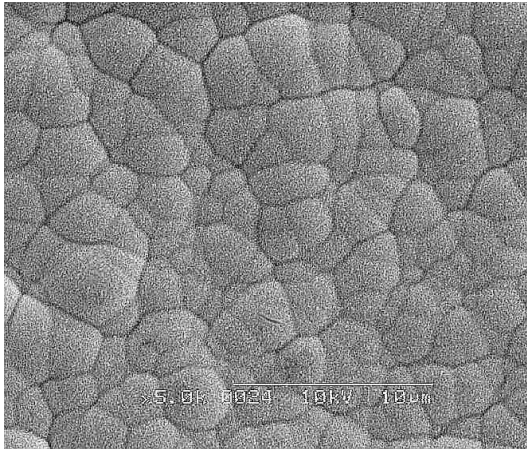
- 1) Slow down the plating rate - lower the solution pH and the temperature.
- 2) Increase the complexors in the bath; add 1 to 2% by volume of the make-up “B” component.
- 3) Maintain good filtration, solution agitation, and solution sparging.
- 4) Use mechanical agitation - i.e. cathode rod instead of air agitation
- 5) Never make chemistry replenishments over the parts.
- 6) Use surfactants. Wetting agents reduce the surface tension and aid in releasing hydrogen gas, while dispersing agents keep particles away from the work.

**Table 4  
DULL DEPOSITS**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Old bath	The buildup of by-products cause dullness
Low hypophosphite Low nickel Low pH Low temperature	Low activity in the plating bath can cause dull deposits by producing a more nodular deposit
Poor pretreatment	1) Oils and soils left on the work can cause dullness after plating 2) Manually cleaning the parts before plating is a good test for this
Contaminated bath, including nitrates	1) Nitric acid contamination can cause dark, dull deposits 2) Several metallic and organic contaminants will cause dull deposits
Parts over-etched in acid or electrocleaner	1) Aggressive pretreatment cycles generally give a rougher part 2) Use minimum electrocleaning and acid activation if this is a problem

#### **How to reduce dullness**

- 1) Maintain the bath chemistry, pH, and temperature, and adjust as necessary.
- 2) Track bath solution age.
- 3) Pay attention to the pretreatment. Look at the parts prior to entering the electroless nickel bath.



*Example of dull deposit caused by nodular plate*

A) Look for “smut” on the parts after acid activation. A smut from aggressive acid activation cause dull plate. Use a shorter or weaker activation.

B) Look for water breaks on the parts after the acid activation rinse tank. This is a good indication of soils on the parts. Improve the cleaning cycle.

C) Look for the formation of flash rust after activation.

D) Look for dry down of the cleaners on the work. This frequently happens with large, massive parts, but it can also occur in situations where very hot cleaners are used, or long transfer times between tanks exist.

4) Check the bath for contamination, including nitrates. Look for an oil slick on the bath, or a dark, oily ring on the walls of the plating tank. Look for foaming in the electroless nickel bath. These are signs of organic contamination.

5) Add brightener as a last resort.

**Table 5  
PATTERNS AND STREAKING**

COMMON CAUSES	MECHANISM
Improper surface preparation	1) Finger prints, cleaner dry down, acid etching, and oil stains can all cause patterned plate 2) Be aware that silicates in the pre-plate cycle in hard water areas may cause problems by forming a gel-like silicate film on the parts 3) Rust etch will cause patterns in the part
Contaminated bath	1) Metallic and organic contamination can result in streaky, patterned deposits 2) Nitric acid contamination can cause dark, dull, streaky deposits
Stabilizer imbalance	1) In cases of high metallics “tiger stripes” may result 2) In cases of low metallics, white streaks may result 3) Nitrates and copper consume sulfur stabilizers, causing high ratios of metallic stabilizers
Low loading Over-stabilization	Over-stabilization or low loading can lead to edge defects
Gas patterns	Gas bubbles taking the same path on the part can cause a different appearance in the plate
Poor agitation	Depleted chemistry can cause the appearance of the plate to be different in areas of poor agitation

### **Pretreatment and patterned plate**

The majority of the causes for patterned plate can be traced to deficiencies in the pretreatment. Be aware of the following indications of inadequate pretreatment:

- 1) Look for “smut” on the parts after acid activation. A smut from aggressive acid activation can give patterned plate. Use a shorter or weaker activation.
- 2) Look for water breaks on the parts after the acid activation rinse tank. This is a good indication of soils on the parts. Improve the cleaning cycle.
- 3) Look for the formation of flash rust on the part after activation. Flash rusting may also occur during alkaline electrocleaning. When this occurs, it is an indication of low caustic in the cleaner.
- 4) Look for dry down of the cleaners on the work. This frequently happens with large, massive parts, but it can also occur in situations where very hot cleaners are used, or long transfer times between tanks exist.
- 5) Often, existing patterns in the substrate will become highlighted after plating. In addition, patterns left on the part from pretreatment operations will be visible after electroless nickel plating. An etch pattern on the parts from the removal of rust is a common example.



*Patterned EN deposit due to pretreatment issues*

### **Silicates and patterned plate**

Silicates are a common ingredient in many industrial cleaners. If a silicated cleaner is used in conjunction with hard water rinses, there is a strong possibility of forming a tenacious film on the surface of the parts. This film is a combination of the metals present in hard water (such as calcium) and the silicate from the cleaners, and is a common cause of patterned plate and poor adhesion. Thorough rinsing after cleaning is critical to avoid forming this film. A small amount of fluoride in the acid activation step will remove the film.

### **How to correct a stabilizer imbalance**

- 1) Use current to dummy plate out excess metallic stabilizers.
- 2) Hang a passive copper panel in the bath to consume excess sulfur stabilizers.



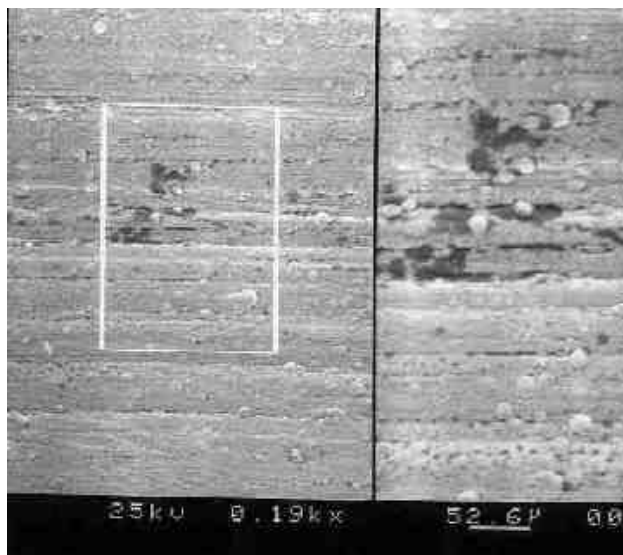
3) Dilute the bath. Portions of the excess bath removed can be added back to the bath during plating. If the bath is diluted, adjust the hypophosphite level with the make-up “B” component.

**Table 6**  
**DARK OR STAINED DEPOSITS**

COMMON CAUSES	MECHANISM
Poor final rinsing	1) Using dirty rinses after plating can discolor the nickel deposit 2) Look for brown or gray water streaks as a sign of this type of staining 3) Hot DI rinses (over 150 F) can tarnish more active electroless deposits
High nickel High hypophosphite High pH High temperature	High nickel, hypophosphite, pH or temperature makes the deposit more active, and increases its tendency to stain
Improper surface preparation	Improper surface preparation can lead to a more porous deposit
Contaminated bath	1) Some common contaminants can make a deposit more likely to stain. Iron is an example. 2) Nitric acid contamination gives dark deposits
Additions made too late in cycle	Additions made too late in cycle can make the deposit more active. Avoid making additions during last few minutes of plating.

**Why is my bath staining now?**

- 1) Some baths inherently stain more than others. Lower phosphorous baths tend to stain more.
- 2) Deposits containing more sulfur tend to stain more.



*Photomicrograph of staining due to surface contamination*

- 3) Deposits from old baths stain more, since the deposit is more porous.
- 4) Dull deposits tend to stain more.
- 5) More active deposits stain more. Reducing the temperature and pH in the plating bath may help.
- 6) Post plate rinsing is critical. 10 to 15 megaohm DI is water recommended. Avoid using DI water over 150° F on low-mid phosphorous and low phosphorous deposits, since it can tarnish the deposit. If hot DI water (over 150° F) is used, avoid using air agitation, since it increases the chance of deposit tarnishing.



### Sometimes cleaning the stain will remove it

- 1) Soak cleaning has been known to work.
- 2) In some cases, using a dilute acid dip removes stains. Take care to avoid darkening the deposit in strong acid solutions.
- 3) Wiping the stain with acetone works very well. Take care to use proper safety precautions.
- 4) After baking, stains are generally much harder to remove.
- 5) Replating the stained part with a thin layer of EN usually covers the stains. Be aware that proper pretreatment of the nickel is necessary to avoid adhesion failures.

**Table 7**  
**STEP PLATING AND EDGE PULLBACK**

COMMON CAUSES	MECHANISM
High stabilizers	1) Stabilizers are adsorbed onto edges first 2) The first sign of over-stabilization is normally on the edges of the work
Stabilizer imbalance	1) A bath can become over-stabilized by a chemical imbalance 2) High metallic stabilizer or low sulfur stabilizer can cause edge pullback 3) Adding sulfur stabilizer back to the bath often cures the problem, especially in Teflon baths
Contaminated bath, including nitrates	1) Several bath contaminants, notably metallics, will poison the bath. Chrome and tin are common examples 2) Contamination with nitrates or copper can cause skip plating by consuming the sulfur stabilizers, leading to a stabilizer imbalance
Low workload	Low loading situations will make a perfectly balanced bath act over-stabilized
Excessive agitation	Extremely high agitation can make a perfectly balanced bath act over-stabilized
Low pH Low temperature	Low operating temperatures or pH ranges may make the bath act over-stabilized by significantly reducing its activity

### How to correct a stabilizer imbalance

- 1) Use current to dummy plate out excess metallic stabilizers.
- 2) Hang a passive copper panel in the bath to consume excess sulfur stabilizers.
- 3) Dilute the bath. Portions of the excess bath removed can be added back to the bath during plating. If the bath is diluted, adjust the hypophosphite level with the make-up "B" component.



*Edge pullback on OD area of part*

Do not use the replenishment “C”, as this may add an excess of stabilizers back to the bath.

**Operational control and edge pullback**

1) Verify the loading in the bath is sufficient. If low loading is encountered, add more work to the tank and check the effect on the deposit. A beaker test is often very helpful to see the effects of loading on edge pullback. A standard hull cell panel in one liter of bath is equivalent to a workload of 0.56 square feet/gallon; half a panel is 0.28 sq. ft./gal; a quarter panel is 0.14 sq. ft./gal.

2) Check the agitation. If solution sparging is the only source of agitation, 10 to 15 tank volume turnovers per hour is recommended. If air agitation is used you want the solution surface to appear to “simmer”, not look like a rolling boil. Try reducing the agitation and check the effect on the deposit. A beaker test can often be used to see the effect of agitation on edge pullback.

3) Check the bath for nitrates if nitric acid is used to strip/passivate the tank.

**Table 8  
POOR CORROSION PROTECTION**

COMMON CAUSES	MECHANISM
Porous deposit White out Old bath	1) Electroless nickel is a barrier, or cathodic, coating. Any holes in the coating will lead to poor corrosion protection 2) An older bath contains more nickel phosphite, as well as other reaction by-products, which increase the deposit porosity. 3) White out is due to nickel phosphite in the bath. Nickel phosphite and will act as a particle in the bath, causing porosity
Substrate condition Aggressive pretreatment	The condition of the part has a dramatic impact on the corrosion protection. Smoother, less porous surfaces give maximum protection, while rough, porous parts give worse results.
High pH	Higher pH ranges reduce the phosphorous level
Contamination	1) Some contaminants, such as iron, co-deposit with the electroless nickel and lower the corrosion protection. 2) Insoluble particles in the bath will increase deposit porosity.

Wrong bath type	1) High phosphorous baths (>10% P) generally have the best corrosion protection. 2) Low phosphorous baths (<3 %P) usually perform better than high phosphorous baths in highly alkaline environments.
Thin deposit	Thinner deposits are generally more porous.
Divalent sulfur dragged into high phosphorous baths	Drag in of low, low-mid, and mid phosphorous chemistries that contain sulfur stabilizers into high phosphorous tanks can introduce sulfur into the deposit, as well as lower the %P of the deposit.
Heat treatment for hardness	1) Heat treatment at high temperatures (> 500° F) increases the porosity of the deposit. 2) Heat treatment can precipitate out phosphorous from the deposit. 3) Avoid heat treating at temperatures >500° F.



*Void in EN coating due to improper pretreatment*

#### **How to maximize corrosion protection**

- 1) Make the part as smooth as you can. Buffing is one option. Avoid abrasive blasting if possible.
- 2) Use the least aggressive pretreatment possible to avoid attacking the substrate.
- 3) Use the correct electroless nickel plating bath. As a general rule, use high phosphorous baths for every application EXCEPT where service in a highly alkaline environment is expected. In highly alkaline environments, low phosphorous deposits may be superior.
- 4) Run the bath at lower pH to increase the phosphorous in the deposit, and produce a less porous deposit.
- 5) Run the bath at a lower temperature to reduce the plating rate and give a less porous deposit.
- 6) Plate to the maximum thickness allowed to provide a thicker, less porous corrosion barrier.
- 7) Avoid using older baths to reduce deposit porosity.
- 8) Use thorough rinsing after plating. A rinse cycle of cold-hot-cold rinsing may be beneficial. The use of rinse aids and water shedders may help.
- 9) Use a post dip if possible. Chromates, chromic acid, oils, and waxes have all been used successfully to improve corrosion protection.
- 10) Avoid post-plate heat treatments over 500°F.

**NOTE:** Several of the problems that cause pitting and staining will also give poor corrosion protection.

**What's the difference between corrosion protection and corrosion resistance?**

Corrosion resistance is the ability of the electroless nickel coating to resist chemical attack.

This is usually measured by measuring weight loss of the coating in the corrosive media.

Corrosion protection is the ability of the coating to protect the substrate. The most common test for corrosion protection is salt spray testing. This test actually measures the porosity of the coating, and so is used as a measure of corrosion protection. Corrosion protection is an easy attribute to measure, yet is often difficult to predict. There will be drastic effects on the corrosion protection values of a coating due to several factors, such as substrate condition, substrate alloy, metalworking operations performed on the part, pretreatment process used, and several other factors. Since several variables beyond the metal finisher's control are thrown into the corrosion equation, it may be a good idea to test the performance of your coating on critical work on a random sample of the actual plated parts.

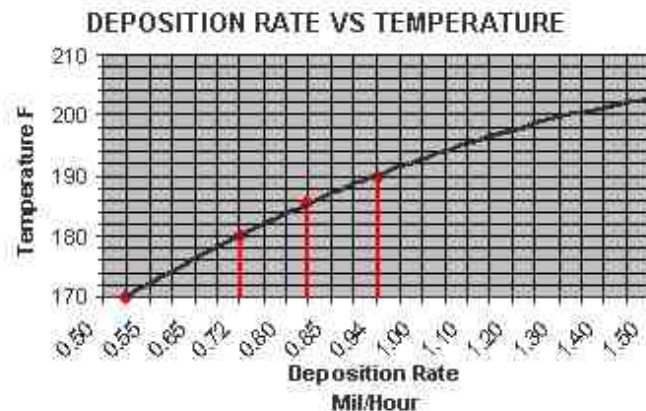
## SECTION II – SOLUTION PROBLEMS

**Table 9**  
**SLOW PLATING RATE**

COMMON CAUSES	MECHANISM
Low temperature Low pH Low nickel Low hypophosphite	Decreases the speed of the chemical reaction
Low workload	Creates a higher stabilizer to workload ratio
High stabilizers Low stabilizers Stabilizer imbalance	1) High stabilizer levels, especially metallics, can “poison” the reaction 2) Some sulfur stabilizers increase the efficiency of the reaction. The reaction slows with low levels of these stabilizers
High agitation	Allows a higher amount of stabilizer to be available to be adsorbed onto the part
Contaminated bath	1) Several contaminants, particularly metallics, will interfere with the deposition reaction 2) Nitrates lower the hypophosphite efficiency
Inaccurate thickness readings	1) Several methods commonly used to determine plating thickness are not suited to electroless nickel deposits. Use ASTM B 733 as a guide for selecting the proper method. 2) Make sure that standards used to calibrate instruments are of the same type as the deposit tested (high phosphorous standards for high phosphorous deposits, low phosphorous standards for low phosphorous deposits), and the base material of the standards is the same as the parts.
Old bath	The by-products formed by the plating reaction will interfere with the reaction

### What can I do if my bath is plating slowly?

- 1) Check the temperature. Double check readings from automatic temperature controllers using an accurate thermometer.
- 2) Check the pH. If pH papers are used, verify the reading with a pH meter.
- 3) Check the bath chemistry. Run a nickel and hypophosphite titration.
- 4) Verify the loading in the bath is sufficient. If low loading is encountered, add more work to the tank and check the



effect on the rate. A beaker test is often very helpful to see the effects of loading on the plating rate. A standard hull cell panel in one liter of bath is equivalent to a workload of 0.56 square feet/gallon; half a panel is 0.28 sq. ft./gal; a quarter panel is 0.14 sq. ft./gal.

5) Check the agitation. If solution sparging is the only source of agitation, 10 to 15 tank volume turnovers per hour is recommended. If air agitation is used you want the surface to appear to “simmer”, not look like a rolling boil. Try reducing the agitation and check the effect on the rate. A beaker test can often be used to see the effect of agitation on the plating rate.

6) Double check the thickness readings with an alternate method, such as cross section.

7) Verify the bath age by an orthophosphite titration, specific gravity, or by checking the total replenishment additions made to the tank.

8) Check the bath for nitrates if nitric acid is used to strip/passivate the tank.

### **Stabilizers and their effect on the plating rate**

Stabilizers work by being adsorbed onto the surface of the work being plated at scattered sites. These adsorption sites actually increase the nickel deposition reaction rate in these areas. However, if the stabilizer concentration gets too high, the deposition reaction is poisoned, causing slow plating rates or no deposition.

The amount of agitation affects the degree of adsorption of the stabilizers onto the work. As the bath passes over the part faster, more stabilizer is introduced to the surface, and so more stabilizer can be adsorbed onto the part. Even if the stabilizer concentration in the plating bath is ideal, high agitation may result in too much stabilizer being adsorbed onto the substrate. Edges are the first locations effected.

Loading also has an affect on the adsorption of stabilizers. Lower loading increases the relative ratio of stabilizers to surface area in the bath, causing “artificial over stabilization” to occur. Again, the first sign of this is seen at the edges of the work.

In electroless nickel systems that use sulfur stabilizers, the ratio of the sulfur to the metallic stabilizers is important. The divalent sulfur compounds used form a mild complex with the metallic stabilizers, and if the ratio of sulfur to metal becomes imbalanced, slow plating rates can result. Two main reasons that sulfur stabilizers are lost are copper contamination and nitrate contamination in the plating bath.

### **How much abuse can my bath take?**

Appendix A gives a list of common contaminants and the levels at which they may begin to interfere with the plating bath.

**Table 10**  
**HIGH PLATING RATE**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
High temperature High pH High nickel High hypophosphite	Increases the speed of the chemical reaction.
Inaccurate thickness readings	1) Several methods commonly used to determine plating thickness are not suited to electroless nickel deposits. Use ASTM B 733 as a guide for selecting the proper method. 2) Make sure that standards used to calibrate instruments are of the same type as the deposit tested (high phosphorous standards for high phosphorous deposits, low phosphorous standards for low phosphorous deposits), and the base material of the standards is the same as the parts.
Divalent sulfur dragged into high phosphorous baths	Drag in of low, low-mid, and mid phosphorous chemistries that contain sulfur stabilizers into a high phosphorous bath will depress the phosphorous content of the deposit, and can increase the plating rate.

**I wanted fast, but this is plating too fast**

- 1) Check the temperature. Double check readings from automatic temperature controllers using an accurate thermometer.
- 2) Check the pH. If pH papers are used, verify the reading with a properly calibrated pH meter.
- 3) Check the bath chemistry. Run a nickel and hypophosphite titration.
- 4) If a high phosphorous system is used, verify that other electroless nickel chemistries containing sulfur stabilizers are not being dragged into the bath.
- 5) Double check the thickness readings with an alternate method, such as cross section. Is the XRF properly calibrated with known Ni-P standards?

**Table 11**  
**SOLUTION WHITE OUT**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Low complexor from solution losses	1) The lack of chelates to complex the nickel allows the formation of nickel phosphite and nickel hydroxide. 2) Since chelates are added mostly on make-up, solution losses will result in a lack of chelates. 3) Check for drag out losses, solution transfer losses, and tank leaks. 4) If the solution losses are unavoidable, add the make-up chelate component (the "B") back to the bath on a periodic basis.
High pH	At higher pH values nickel phosphite is less soluble

Excessive iron, calcium, or other metallic impurities	1) Iron, calcium, and other metals may combine with the chelates, which reduces the amount of chelates available for the nickel. 2) Iron phosphite, calcium phosphite, and other metal-phosphite complexes may form
Drag in of phosphated cleaners	Metal-phosphates are usually much less soluble in the plating bath than metal-phosphites. They require a lower bath pH to make them soluble.
Low grade hypophosphite used	Some common impurities in lower quality hypophosphite include calcium and phosphate.
Drag in of strong oxidizers	Strong oxidizers might destroy chelates

### How to cure a white out

Baths that have experienced white out due to solution losses can usually be repaired with no lasting detrimental effects on the plating bath or deposit.

- 1) If possible, cool the solution.
- 2) Lower the pH of the bath with dilute sulfuric acid until the bath is clear - usually around 3.2 to 4.2. Steps (1) and (2) are done because nickel phosphite is more soluble in cooler, more acidic solutions.
- 3) Add the chelate containing make-up material (typically the "B") back to the bath at 0.5% to 3% by volume.
- 4) Perform a beaker test for chelation (below).

### Beaker test for chelation

- 1) Fill a 1 liter beaker half full of the electroless nickel bath to be tested.
- 2) Raise the pH of the bath to the highest recommended operating pH value.
- 3) Heat the bath to boiling, and keep it boiling for 10-15 minutes.
- 4) After boiling, the solution should be clear.
- 5) If the bath turns cloudy, get a new sample, add 1% by volume of the chelate containing make-up component (typically the "B"), and repeat the test. Continue adding additional "B" in 1% by volume increments to fresh samples until the bath passes the beaker test.

**Note:** Often, the beaker will start to plate out, causing gassing. It often helps when evaluating the bath clarity to transfer the bath to a clean beaker and allow the gassing to subside before checking for solution clarity.



**Table 12**  
**PLATE OUT ON EQUIPMENT**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Equipment not passive	1) Weak nitric acid or too short of a passivation time will not properly passivate the tank and equipment 2) For optimum results, maintain nickel content in the acid below 45 g/L (6 oz/gal) at 50% by volume nitric acid, 30 g/L (4 oz/gal) at 30% by volume
High temperature High pH “Hot Spots” in the tank	Makes the bath overactive
Work touching the tank walls	Plating work in contact with the tank can initiate plating on the tank.
Active sites in tank and equipment	Scratches and scores in the tank walls can provide active sites to initiate electroless nickel plating. Often these areas are not totally passivated using nitric acid.
Active metal in the bath	1) Nickel flakes from improperly stripped racks are a common cause of plate out. These flakes will plate, and if they settle on the tank can initiate plating. 2) Burrs, parting line flash, and other loose metal on parts can break off and introduce small, active particles into the bath, which can settle on the tank and initiate plating. This frequently occurs with screw machine parts plated in a barrel.
Bath contamination	1) Copper and nitrate contamination will consume sulfur type stabilizers 2) Excessive particles in the bath will adsorb stabilizers, reducing the effective amount in solution
Improper anodic passivation	Using too much current or using the unit while the bath is cool can consume metallic stabilizers
Excessive drag in of catalyst (palladium)	Will cause the bath to spontaneously plate out

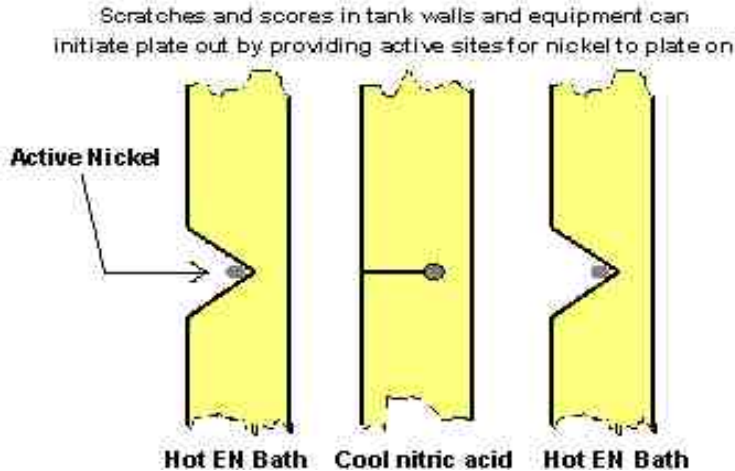
### **Plate out and passivation**

The strip/passivate step is an important aspect of electroless nickel plating. Using too short of a strip time or using weak acid can result in the incomplete stripping and/or passivation of the equipment.

### **Plate out and active sites**

Electroless nickel solutions typically operate at around 190°F. At this temperature, the tanks used in electroless nickel plating will expand. When the bath is removed and the tank rinsed with cold water, and during stripping/passivation with nitric acid, the tank will contract. Any

nickel in scratches and scores in the tank walls may not be removed, as illustrated below.



### Plate out and current

The most common stabilizer used in electroless nickel systems is lead. Other metals used as stabilizers include tin and antimony. These metals can be electrolytically plated out of the bath if a current is applied. If anodic passivation of stainless steel tanks is used, be aware of the following:

- 1) Always shut off anodic passivation when the bath is below plating temperature (normally 150°F or less). Running the unit while the bath is cool can dummy out the stabilizers. The stabilizers are usually present in the bath at milligram per liter concentrations, so they can be rapidly depleted from the bath. Proprietary anodic passivation systems have safeguards built in to minimize the effects of the applied current.
- 2) Avoid using too high of a current. Typical systems operate at about 0.75 volts, which should give a current of 10 to 20 mA/ft<sup>2</sup> of plating tank. Increasing the current past this level, even when the bath is working, can have detrimental effects. Higher current can dummy plate out the stabilizers, as well as etch the stainless steel tank. If the tank becomes etched, it can introduce iron and chrome into the plating bath. It also increases the surface area of the tank.
- 3) Check the cathode rods. If the rods are dark gray or black, it is a strong indication that the stabilizers are plating onto the cathodes.
- 4) Check the tank for gassing while the bath is cool. Gassing may indicate plating, which in turn indicates stray current. If anodic passivation is used, make sure it is turned off when the bath is cool.

### Plate out and heat exchangers

If the bath gets too hot in the heat exchanger, plate out, roughness, and bath decomposition can result. The temperature the bath reaches in the exchanger is a function of the flow rate of the

bath through the exchanger, and the temperature of the steam used. Follow your heat exchanger manufacturer's recommendations for maximum steam pressure to avoid overheating the bath. Typically, saturated steam pressure should not exceed 12 PSI. Always set up filter system between the external steam or hot water exchanger and the tank.

**Table 13  
EXCESSIVE CHEMICAL USAGE**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Plate out on tank	If the tank is plating, more chemistry will be consumed than is plated on the work.
High workload	If the workload is larger than what is normally run, more chemistry will be required
High temperature High pH High hypophosphite	The bath may be plating faster than you think
Incorrect thickness measurements	Thicker deposits will use more chemistry
Bath decomposition	The bath chemistry is being consumed without plating parts
Long idle periods at operating temperature High air agitation	1) Long idle periods at operating temperature can break down the hypophosphite. 2) Excessive air agitation will introduce air into the tank, which can oxidize the hypophosphite.
Bath contamination	1) Several contaminants, such as nitrates, lower the hypophosphite efficiency, causing more hypophosphite to be used to plate a given area 2) Copper will also lower the hypophosphite efficiency by consuming sulfur stabilizers. Some sulfur stabilizers increase the hypophosphite efficiency.
Low workload	Creates a higher stabilizer to area ratio, making the reaction less efficient, requiring more hypophosphite to plate a given amount of nickel

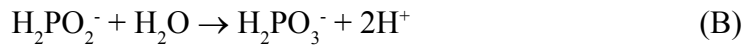
Why am I using so much chemistry?

- 1) Verify the operating conditions of the tank. Check the temperature, pH, and chemistry of the bath.
- 2) Check the tank for plate out. A quick check for this is to briefly turn off the agitation while the tank is hot and empty and look for gassing.
- 3) Measure the area of the work being plated, and determine your square foot per gallon loading. How does this compare to the loading factor recommended for your electroless nickel bath? Typically, 0.5 square feet per gallon is optimum.

4) Verify your thickness measurements with an alternate method, such as cross section.

**The missing hypophosphite syndrome: Where does it go?**

1) Sodium hypophosphite undergoes several side reactions in the bath:



Reactions (B) and (C), the conversion of hypophosphite to orthophosphite, proceed faster with heat. If the bath sits idle at operating temperature for long periods, hypophosphite can be converted to orthophosphite.

2) Air agitation introduces oxygen into the bath, increasing the potential for reaction (C) above to occur. This is especially true in cases of long idle periods at operating temperature.

3) Low loading in the tank increases the relative amount of stabilizers per workload area. This increase in the effective level of stabilizers decreases the efficiency of the hypophosphite, causing more of it to be used to plate a given amount of nickel. Conversely, higher loading makes the system more efficient.

4) High stabilizer levels in the bath will lower the efficiency of the deposition reaction, causing more hypophosphite to be used plating a given amount of nickel.

5) Low levels of certain sulfur stabilizers will lower the efficiency of the reaction, causing increased hypophosphite usage. Both nitrate and copper contamination will consume sulfur stabilizers.

6) Aside from nitrates and copper, several other contaminants in the plating bath will reduce the efficiency of the reaction, increasing the hypophosphite usage.

**How much surface area will my EN bath plate?**

A comparison of the actual amount of work processed through your plating tank to the theoretical yield of the bath can often point to processing problems, such as plate out. One good method of comparing electroless nickel yields is to calculate the amount of work you can produce from one gallon of plating solution, and express the yield as mil-square feet per gallon. The formula is as below:

$$\text{Mil-ft}^2/\text{gal yield} = (160.417) \times \frac{\text{g/L of Ni in plating bath}}{(\text{deposit density in g/cm}^3)(\% \text{ Ni in deposit})}$$

**NOTE: For the “%Ni in deposit” use whole numbers. For example, use 94, not 0.94.**

1) 160.417 is a factor that converts cm<sup>3</sup>/liter yield to mil-ft<sup>2</sup>/gallon yield:  
**(cm<sup>3</sup>/L) X (3.78541 L/gal) X (1 in<sup>3</sup>/16.387 cm<sup>3</sup>) X (1000 mils/inch) X (1 ft<sup>2</sup>/144 in<sup>2</sup>) = 1.60417**

2) Since the formula given above uses a whole number for “%Ni in deposit” in the denominator, we need to account for it in the numerator:

$$(1.60417) \times (100\%) = 160.417$$

3) To calculate the total yield from a bath over its life, the following calculation is used:  
**(Mil-ft<sup>2</sup>/gal yield) X (Tank volume in gallons) X (Number of metal turnovers)**

In order to determine the deposit density and the %Ni in deposit, the % phosphorous of the deposit must be known. Consult the technical data sheet or contact your vendor if you need this information. Once the %P is known, use the chart provided in **APPENDIX B** to obtain the deposit density. The percent nickel in the deposit is equal to (100 - %P).

**Table 14**  
**RAPID pH CHANGES**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Drag in of acid or alkali	Will cause the pH to change depending upon what is dragged in
High workload	More hydrogen gas will be evolved faster
High temperature Excessive air agitation	Will allow the ammonia in ammoniated systems to volatilize faster, resulting in lower pH

**How to determine the cause of pH changes**

Track the bath pH. Determining when the pH changes will be a strong indication of why it changes. If it changes when the rack is introduced into the plating tank, drag in is the likely source. If the pH drops over the course of the run, but remains stable while the tank is empty, more pH adjust chemistry is necessary during plating. If the pH raises during the run, too much pH adjust chemistry is being added. If the pH changes while the tank is idle, you may be blowing off ammonia from the bath.

**Table 15**  
**NO DEPOSITION**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
High stabilizers	Stabilizers present beyond a critical concentration will stop the plating reaction
Contaminated bath	Certain contaminants, especially metallics, will poison the reaction.
Low temperature Low pH Low hypophosphite	1) Temperature and pH ranges below a critical point will stop the reaction. 2) If the level of hypophosphite is too low, the reaction may not occur.
Low workload	Lower loading will give a higher stabilizer to work ratio. In extreme cases this will result in an overabundance of stabilizers per workload
Non-catalytic part	Not all metals will act as a catalyst to start the plating reaction

### **No deposition and non-catalytic parts**

An example of a non-catalytic metal is copper. To initiate a non-catalytic part, several methods are possible:

- 1) Use an electrolytic nickel strike prior to electroless nickel plating to make the surface catalytic.
- 2) “Touch off” the reaction using a plating part. The contact between the non-catalytic part and the plating part results in an electron transfer that will start the plating reaction. This method is not recommended for new lead free stabilized EN technologies
- 3) Use DC current to “jump start” the reaction. A few amps per square foot cathodic (direct) current will start the plating reaction.
- 4) Use a catalytic pre-dip, such as palladium.
- 5) Use a specially formulated electroless strike based upon DMAB or similar which would have some advantages in many niche applications.

### **How to rescue an over-stabilized bath**

Several methods exist to salvage an over-stabilized bath.

- 1) Use current to dummy plate out excess metallic stabilizers.
- 2) Hang a passive copper panel in the bath to consume excess sulfur stabilizers.
- 3) Initiate plating by using current to start the reaction, and then letting the parts plate normally. This may lead to edge defects from over-stabilization on the work.
- 4) Dilute the bath. Portions of the excess bath removed can be added back to the bath during plating. If the bath is diluted, adjust the hypophosphite level with the make-up “B” component. Do not use the replenishment “C”, as this may add an excess of stabilizers back to the bath.

**Table 16**  
**BATH DECOMPOSITION**

<b>COMMON CAUSES</b>	<b>MECHANISM</b>
Excessively high temperature or pH	Makes the bath over-active.
Poor bath maintenance	If the chemistry strays too far outside operating parameters, the stabilizers may drop below a critical level
Excessive particles, such as dust, sand, iron filings, zinc dust, carbon, etc.	Stabilizers work by being adsorbed onto the surface of the parts. If the stabilizers adsorb onto particles, they will not control the reaction
Improper anodic passivation	1) The metallic stabilizers present in electroless nickel systems are present in very low concentrations. Using too much current for anodic passivation or using anodic passivation while the bath is cool can electrolytically plate the metallic stabilizers 2) Check the cathode rods. A dark gray or black coating indicates the stabilizers are being dummied out onto the rods
Stray current on tank or equipment	Any stray current in the system can “dummy plate” the metallic stabilizers out of the bath
Bath contamination	1) Copper and nitrates consume sulfur stabilizers 2) Excessive drag in of catalyst (e.g. palladium) can cause the bath to spontaneously decompose

**Finding the cause of decomposition**

- 1) Check the tank for gassing while the bath is cool. Gassing may indicate plating, which in turn indicates stray current. If anodic passivation is used, is it shut off when the bath is cool?
- 2) Verify the operating temperature with an accurate thermometer.
- 3) Verify the operating pH with a properly calibrated pH meter.
- 4) Check the chemical additions and the bath analysis records. Make sure the bath chemistry was kept within operating ranges.
- 5) Is a heat exchanger being used? If so, is the steam pressure correct? How hot does the bath get while in the heat exchanger?
- 6) Is excessive pretreatment chemistry being dragged into the plating bath?
- 7) Is there a source of airborne particles nearby? Check for blasting operations, buffing wheels, airborne dust from outside, etc. Was the bath treated with powdered carbon?
- 8) Was the tank plating out excessively before the decomposition? How often is the tank passivated? How long does the bath last in the tank before plate out occurs?
- 9) Check the make-up and replenishment chemicals, and the amount used. Do they appear normal?

### **Heat exchangers and decomposition**

If the bath gets too hot in the heat exchanger, plate out, roughness, and bath decomposition can result. The temperature the bath reaches in the exchanger is a function of the flow rate of the bath through the exchanger, and the temperature of the steam used. Follow your heat exchanger manufacturer's recommendations for maximum steam pressure to avoid overheating the bath. Typically, saturated steam pressure should not exceed 12 PSI.

### **Recovery of a decomposed bath**

- 1) If the bath is decomposing, immediately transfer it to a holding tank. You must filter the bath during the transfer.
- 2) Cool the bath as quickly as possible to below plating temperatures to stop the reaction. It might be possible to stop the reaction by using dilute (10%) sulfuric acid to lower the pH below 4.0.
- 3) Once the reaction is stopped and the bath is filtered, analyze the chemistry and replenish. For any hypophosphite add over 20%, use the make-up "B."

## **EN CHEMICAL BALANCE AND SOLUTION CONTROL**

Sometimes it is prudent to perform a thorough troubleshooting study in the lab on the EN solution. This allows one to segregate the interaction of the EN solution and equipment on the line with just the EN solution. For troubleshooting the EN solution, the general approach involves a thorough analysis of the solution is first required to enable the diagnosis & proposal for corrective action to resolve the problem. This includes:

- Nickel (g/L) concentration
- Hypophosphite (g/L) concentration
- Solution pH @ Room Temperature
- Solution Density (g/mL)
- Sodium Orthophosphite (g/L) concentration
- Stabilizers concentration (mg/L) if applicable
- Contaminants including, Iron, Copper, Calcium, Zinc, Nitrates
- Complexor Tests

Once these basic analyses are completed, the performance test can be carried out. Generally, it is not advisable to "correct the chemistry" before performance testing so the problem can be seen in the beaker. If you are trying to see the best rate performance from the solution, the chemistry should be balanced before proceeding with the beaker testing. Depending upon the outcome of the performance test result will determine the type of adjustments required before continuing with production.



When working on a problem, try to always plate to the same thickness that the customer or application is attempting to target. Often, the same problems are not seen visually until that thickness range is obtained.

Beaker testing for EN solutions can be a useful technique for troubleshooting and evaluating from the tank, the performance of these EN systems in the laboratory. Great care is required to keep the conditions constant and under control so that valid observations and comparisons to the tank side conditions can be made.

### **Performance Testing Electroless Nickel Solutions:**

Beaker testing of Electroless nickel solutions can accomplish much to identify and correct problems that may exist in the tank. These techniques can be utilized to determine the plating rate, visualize stabilizer problems or verify solution life. It is important to standardize these techniques to provide reproducible results. However, the parameters can be changed to accomplish specific goals toward identifying a problem. A one liter “fleaker” beaker works well for this application because the narrow neck reduces the evaporation but these are not required. If a fleaker beaker is not available, a tall, 1 liter beaker will work well. A magnetic stirrer hot plate is utilized to provide agitation for the solution.



The test panels chosen can be steel or brass hull cell panels (267mL size). Steel panels are normally utilized to calculate plating rate and verify stabilizer effects. The brass panels are good to utilize for identifying pitting especially for thick deposits. The preparation of these test panels is critical and the results obtained can be misleading if the panels are not properly cleaned and activated. Nickel wire, stainless steel wire, glass hooks or nickel plated copper wire is used to suspend the panels in the beaker. With this technique the loading of the beaker can be varied by cutting the size of the hull cell panel. Panels can also be bent 90 degrees to verify the effects of upper and lower shelf areas of the panel.

Once the loading (area per unit volume in square feet/gallon or square decimeter/liter) is chosen, the amount of agitation is determined depending upon the purpose for performing the beaker test. Some form of agitation should always be used and lab work has shown agitation to have an effect on the deposit rate and other important deposit characteristics such as phosphorus content.

For illustrating the effects of stabilizers, choosing a low load of 0.25 square feet per gallon with moderate to high agitation is a good beginning point. For plating rate determinations, 0.5 square

feet per gallon with moderate agitation is a good starting point for beaker testing. It is important to maintain the operating temperature within 2 degrees to ensure consistency and reproducibility of the beaker testing. There can be many variations with these tests however they can be very useful to determine the quality of the Electroless nickel deposit.

It is important to standardize the technique so consistency is obtained in viewing the problems. Sometimes very small differences in procedures or the controls can have a significant impact in the results, which can be misleading, especially if the causes and effects are not recognized.

One needs to use the following set up for the evaluation:

- Beaker: 1-L fleaker (narrow necked beaker which reduces evaporation) or Tall 1-L beaker
- Heat source: Magnetic-stirrer Hot plate with 1" stir bar
- Test panels: Zinc coated steel Hull Cell panels (267mL size) or brass panels (267mL size)
- Wire: Suspend panels in beaker

All plating rates should be determined by utilizing the weight gain method, plating for 20 minutes each. For examining pitting or step plating, panels should be plated for 60 minutes minimum. A 90 degree bent panel is advisable to assist showing these defects.

**While panels are plating it is important to control the total system:**

- Temperature: Keep within +/- 2 degrees F
- Water Level: Evaporation makes room for replenishment additions; fleakers will sometimes "flood" with faster plating systems due to large additions required.
- Operating pH: Check frequently and keep within +/- 0.1 pH unit with pH papers.
- Chemistry-Activity: Check and add frequently enough to keep 90-100%.

After the first analysis, an estimate can be made for consumption and adds made on this estimate without having to analyze ever hour. Faster chemistries and baths at higher loading may require additions every 15 minutes. Estimates can be based on the weight of nickel plated out. For a 120 g/L replenisher, for every 0.12 grams of nickel plated from solution, the addition of 1 mL of this 120 g/L replenisher is required. For a 100 g/L Nickel metal content, each 1 mL will provide 0.10 grams of nickel plated.

- Loading: For normal plating rate determinations, use a full 2.75" X 3.88" hull cell (20.67 in<sup>2</sup> area) to provide 0.54 ft<sup>2</sup>/gal (0.14 in<sup>2</sup>/Liter) loading. For determining stabilizer effects, using a 1/2 panel (10.34 in<sup>2</sup>) provides 0.27 ft<sup>2</sup>/gal.

**Conclusions:**

Effective troubleshooting of Electroless technologies requires a systematic approach to understanding all the variables. These variables include the problem, the parts, the process, the people and the plating.

**APPENDIX A**  
**COMMON CONTAMINANTS IN A CONVENTIONAL EN BATH**

<b>CONTAMINANT</b>	<b>MAXIMUM LEVEL</b>	<b>EFFECT</b>
Antimony	5 PPM	Slow plating rate or no deposition. Edge pullback or step plating. Dark stripes in deposit (Tiger or zebra stripes).
Bismuth	7 PPM	Slow plating rate or no deposition. Edge pullback or step plating. Dark stripes in deposit (Tiger or zebra stripes).
Cadmium	4 PPM	Slow plating rate or no deposition. Dark stripes in deposit (Tiger or zebra stripes). Edge pullback or step plating. Brittle, unusually bright deposit.
Calcium	250 PPM	Roughness, white out, dull, milky deposits, depressed plating rate, poor corrosion protection, poor adherence. May interfere with nickel titration.
Chrome	4 PPM	Slow plating rate or no deposition. Edge pullback or step plating.
Copper	100 PPM	Immersion copper on parts. Poor adhesion.
Iron	200 PPM	Dull, rough, porous deposit. Poor corrosion resistance.
Lead	2 PPM	Slow plating rate or no deposition. Edge pullback or step plating. Dark stripes in deposit (Tiger or zebra stripes).
Mercury	4 PPM	Slow plating rate or no deposition. Edge pullback or step plating. Dark stripes in deposit (Tiger or zebra stripes). Deposit may become very bright.
Nitrates	50 PPM	Dark, streaky deposits. Poor corrosion resistance. Slow plating rate. Poor adhesion.
Nitrites	2 PPM	Edge pullback or step plating. Dark, streaky deposits. Dark stripes in deposit (Tiger or zebra stripes). Slow plating rate or no deposition.
Organics (oils)	VARIABLES	Dull deposit. Pitting. Poor corrosion protection. Slow plating rate. Poor adhesion.
Palladium	4 PPM	Plate out. Bath decomposition.
Phosphate	VARIABLES	White out. Rough or dull deposits. Poor corrosion resistance.
Sulfur, divalent	5 PPM	White, streaky deposit. Slow plating rate or no deposition. Will make high phosphorous baths fail nitric acid test. Reduces %P in high phosphorous deposits
Tin	5 PPM	Slow plating rate or no deposition. Edge pullback or step plating. Dark stripes in deposit (Tiger or zebra stripes).
Zinc	250 PPM	Dull deposits. Roughness. Slow plating rate. Poor corrosion resistance.

Determining critical numbers for contamination levels is difficult, since different baths tolerate different levels of contamination. Use the preceding chart as a guideline to the approximate concentration at which the effect of the contamination may become evident.

**APPENDIX B  
DENSITY OF EN DEPOSITS**

<b>% Phosphorous in deposit</b>	<b>% Nickel in deposit</b>	<b>Deposit density (g/cm<sup>3</sup>)</b>
0	100	8.9
1	99	8.8
2	98	8.7
3	97	8.6
4	96	8.5
5	95	8.4
6	94	8.3
7	93	8.2
8	92	8.1
9	91	8.0
10	90	7.9
11	89	7.8
12	88	7.7
13	87	7.6