

Advancing Electroless Nickel Technology: Benefits to an EN Plater

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Abstract

Use of electroless nickel continues to grow and new applications are beginning to emerge that will likely challenge existing EN technology. Enhanced deposit properties will be required to meet the needs of these applications. The following is a status report for recent technology advancements in electroless nickel and the practical benefits for EN applicators.

Technology Overview

Electroless Nickel (EN) deposits are classified as a "Functional Class" of coatings used primarily to enhance the surface performance properties of a variety of substrates. The majority of applications require that the coating provide maximum protection against corrosion and abrasive wear resulting in an extension in the useful life of the component. Because of unique deposit properties and uniformity of the resultant film, many other engineered uses have emerged over a diverse application spectrum.

The majority of EN films used commercially are deposited from solutions formulated with sodium hypophosphite as the reducing agent and therefore will be the focus of our attention. This yields nickel films that are alloyed with phosphorous in ranges between 1-12 weight percent.

The mechanical properties of NiP (ENP) deposits can be further enhanced by the codeposition of inert particles such as Teflon[®], silicon carbide, synthetic diamond or boron nitride. Ternary Ni-P-X alloys, where X can be copper, tin, tungsten or many other metals also shows great promise.

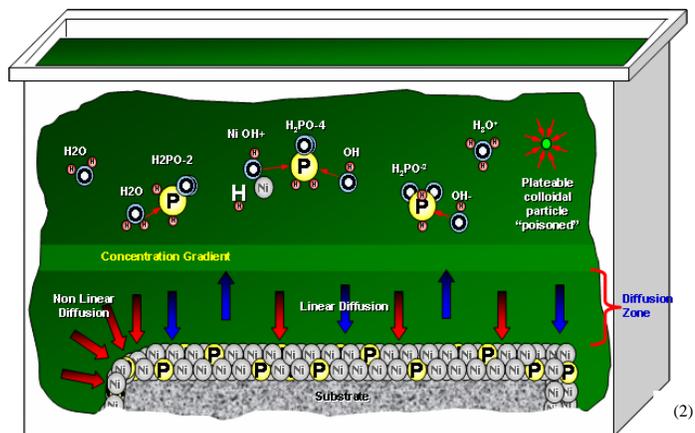
Optimum performance of the mechanical and physical properties of the EN films will result only if the coating is free of defects. It is well documented that deposit phosphorus content plays an important role in determining the performance of an EN deposit. Equally important is the absence of pores, nodules and pits as well as optimized ductility and intrinsic stress. It has been found that EN film defects can be directly correlated to the deposition mechanism itself and EN film growth during the plating process. Critical reactants, additives and reaction by-products move in various directions within the diffusion zone and play a vital role in determining the microstructure and performance of the resultant coating.

The Autocatalytic Deposition Process ^{(1) (2)}

The continuous deposition process for chemical reduction of nickel ions in an aqueous solution, utilizing a reducing agent, is termed autocatalytic. The plating process is heterogeneous since the reactants, namely nickel ions and sodium hypophosphite are evenly distributed throughout the plating solution. Since the reaction does not occur in the bulk of the plating solution but rather at the interface of the solution and the catalytic surface, two conditions must be fulfilled for the reaction to occur:

First, the interface must be a catalytically active site for the oxidation of hypophosphite to occur, readily adsorbing the hydrogen produced and secondly, the reactants must easily migrate to this site for the reaction to continue and self propagate.

The requisite migration of the dissolved ions to the catalytic surface can occur either by diffusion or solution agitation (convection). Ions are charged species that are constantly moving throughout the plating solution to maintain an even distribution. However, because charged species tend to adhere to stationary solid surfaces and there is depletion of ions at the plating interface a concentration gradient is established and diffusion will take over.



This part of the solution is called the diffusion zone and involves the following :⁽³⁾

1. Diffusion of reactants to the catalytic surface.
2. Adsorption of the reactants onto the catalytic surface.
3. Reaction on the catalytic surface.
4. Desorption of by-products from the catalytic surface.
5. Diffusion of by-products away from the catalytic surface.

An important point to note is that all species do not diffuse linearly to the catalytic surface.⁽¹⁴⁾ Additives such as heavy metal stabilizers, brighteners and divalent sulfur compounds diffuse non-linearly to the catalytic surface. Controlling both the concentration and type of additive used in the formulation of the chemistry is a critical component in optimizing the performance of the plated EN-P film.

Key Physical and Mechanical Properties

The Microstructure and Composition of ENP Films

One of the distinct advantages of the electroless nickel deposition process is the ability to produce an alloy of nickel and phosphorous in varying composition. Depending on the formulation and operation of the chemistry, the film compositions can vary from 2 to 13 weight percent phosphorous. This variation in alloy content has a significant effect on the deposit microstructure and performance characteristics, offering flexibility to well informed platers and engineers that can take full advantage of these differences.

Electrodeposited nickel has a purity of greater than 99% and is highly crystalline. On the other hand, electroless nickel deposits that contain more than 10.5% phosphorous appear to be amorphous, i.e., lacking crystal structure. It has been well documented that amorphous deposits have improved mechanical and physical properties.² **The degree of amorphous character can be altered for a given high phosphorous formulation by using certain additives that affect the growth process of the EN-P film.**

Deposit Uniformity

A significant advantage of the electroless nickel process is the ability to produce deposits with uniform thickness on parts with complex geometries and shapes. Surprisingly, the degree of uniformity can vary on edges, threads, small holes or deep recesses where exchange of fresh solution may be difficult. This may also occur under conditions with excessive bath agitation, especially in the presence of heavy metals and when the EN solution is relatively new. **Our studies have found new EN solutions lack the ability to “block” access of stabilizers to the plating interface thus promoting their co-deposition at “high current density” areas such as threads and edges. Pitting, porosity and/or suppressed plating thickness are all likely results.** One can overcome these phenomena by optimizing solution dynamics and/or by controlling the concentration of certain additives formulated into the EN plating bath.

Corrosion Resistance

An important deposit characteristic of electroless nickel is the superior corrosion protection in a multitude of corrosive environments. Since the ENP coating is more noble than steel and aluminum, it protects the substrate by providing a pore free barrier coating against the corrosive media.

The nature of the corrosive environment and the deposits resistance to chemical attack are also important criteria when selecting a particular EN coating for optimum performance. High phosphorous coatings (10-12%) are more readily attacked in strongly alkaline media than low phosphorous deposits (1-3%); however they perform significantly better in acidic media.⁴ This is illustrated in figure 2

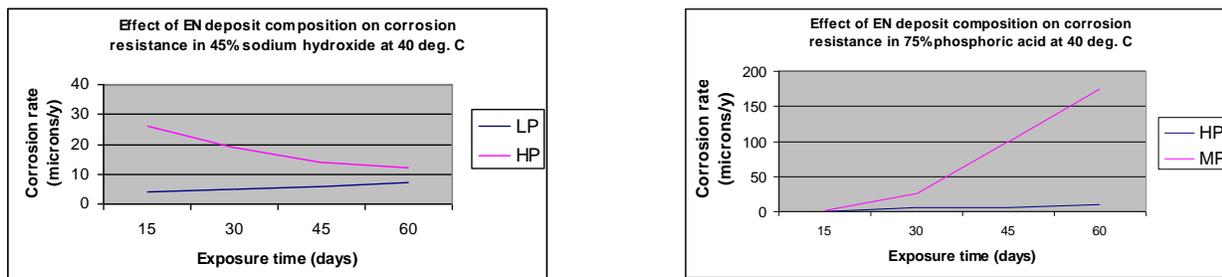


Figure 2 ⁽⁴⁾

Optimizing the performance of EN coatings for maximum corrosion protection not only requires that the coating be of optimum alloy content but that it be continuous and free of any defects. This would include porosity, nodules, pits, occluded particles and/or non-homogenous microstructure. It was stated earlier that high phosphorus EN deposits are considered amorphous. The lack of crystalline structure and phase boundaries reduces the possibility of inter-granular corrosion and enhances the ability to form a passive film on its surface. These deposit qualities provide the basis for an excellent barrier to both substrate and surface attack in corrosive environments.

The phosphorous content alone however is not enough to ensure maximum corrosion resistance in a given environment. Other factors that affect the corrosion performance of ENP films are:

1. Co-deposited impurities from poor quality raw materials, reaction by-products and contaminants.
2. Deposit thickness
3. Post plate operations such as heat treatment and rinsing
4. Condition of the substrate
5. Substrate preparation
6. Operation and maintenance of the EN solution during the plating process.

It is important to note the condition of the substrate prior to plating in order to determine the optimum pretreatment cycle and required deposit thickness. For example, machined substrates alloyed with sulfur and/or lead are particularly vulnerable to a high degree of porosity, since these alloying constituents are catalytic poisons to the deposition process. Porous and/or rough substrates typically require thicker deposits to provide adequate corrosion protection. This is primarily due to the formation of nodules on the roughened surface during the initial stages of deposition, resulting in microporosity of the ENP film. ⁽¹³⁾⁽¹¹⁾

Increasing the deposit thickness can minimize this affect but must be based on surface condition and application environment. Smooth substrates may only require a thickness of 25 microns (1.0 mil) to obtain a film with minimal porosity whereas roughened surfaces, cast iron for example, may require up to three times the thickness to provide similar corrosion protection. ⁽¹²⁾

Neutral salt spray testing, in accordance with the ASTM B 117 specification, is an accelerated measurement of the corrosion protection afforded by a specific coating. It is well documented in the literature and continues to be the most widely accepted method for coating evaluation. The results of neutral salt spray exposure, phosphorous content and deposit thickness are summarized in the following table:

Corrosion Resistance per ASTM B-117 Neutral Salt Spray Test ⁽¹⁰⁾

Coating Thickness	Coating 1	Coating 2	Coating 3	Coating 4
12 microns (0.4 mils)	24	24	24	250
22 microns (0.8 mils)	96	96	96	1,000
38 microns (1.4 mils)	96	96	96	1,000
50 microns (2.0 mils)	96	96	96	1,000

Coating 1- (4-5% ENP)

Coating 2-(7-8% ENP)

Coating 3- (6.5-8% ENP)

Coating 4-(10.5-12.0% ENP)

Intrinsic Deposit Stress

Electroless nickel deposits are subjected to two (2) types of deposit stress. Extrinsic stress which develops via an interrelationship with the substrate most notably through differences in coefficient of thermal expansion. ⁽³⁾ Intrinsic stress which is independent of the substrate and is dictated by the chemistry, operating conditions and the resultant electroless nickel film. In most applications, compressive intrinsic stress is desired for several reasons. For EN plated components under severe wear or strain applications, compressive stress does not reduce the fatigue strength appreciably, therefore extending the parts useful life. It has also been found that highly tensile EN deposits tend to exhibit poor adhesion on difficult to treat or improperly treated substrates. These deposits will also tend to crack when applied in excess of 50 microns (2.0 mils).

The graph below illustrates how intrinsic deposit stress increases over the life of a high phosphorus EN process. It is important to monitor stress over bath age since this property clearly degrades at or near 5 metal turnovers typically requiring the bath to be discarded. **A recent advancement in EN technology utilizes an additive, that when made to the high phosphorus system, maintains the compressive stress for an additional 3-5 metal turnovers.** This is also highlighted in figure 3.

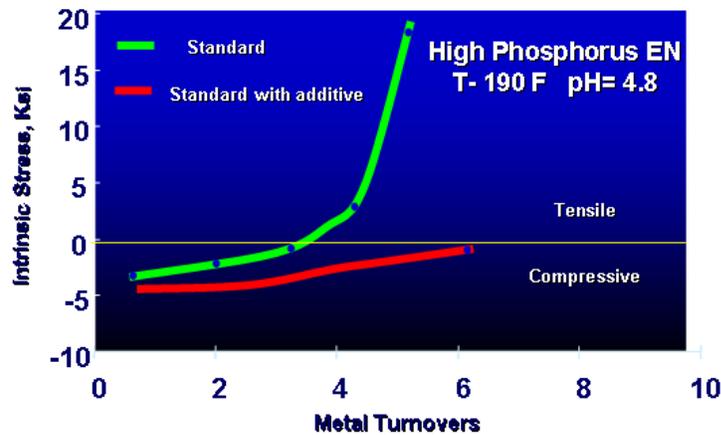


Figure 3

Ductility

Relatively speaking, electroless nickel is hard and brittle. High phosphorus deposits typically exhibit 1-2.5% elongation to fracture while in comparison, electrolytic nickel sulfamate deposits are at 10-25%.³ There have been numerous applications where EN has failed due to severe deposit cracking when subjected to various bend tests. **Recent advancements in EN additive technology has been shown to enhance ductility** as illustrated in Figure 4.⁽²⁾

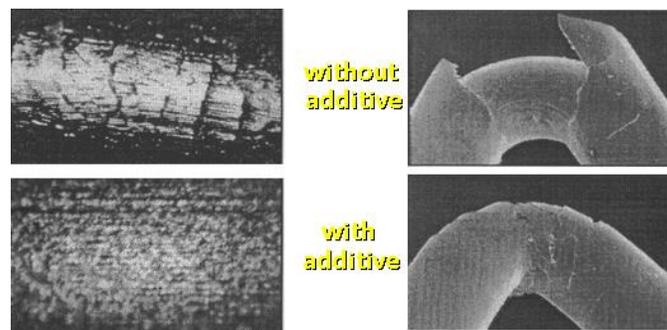


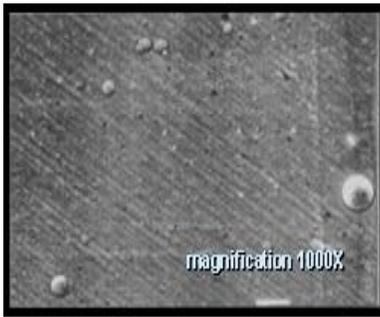
Figure 4⁽²⁾

Surface Roughness

A smooth, bright electroless nickel deposit offers more than a good appearance. Uniform, nodule and pit free EN coatings provide superior protection to the base material from corrosive attack. As EN baths age, reaction by-products accumulate and begin to co-deposit. In addition to reduced corrosion protection and an increase in stress, the deposit becomes more nodular. Nodular deposits trap rather than reflect light and therefore appear dull. Nodular deposits will also trap micro-volumes of EN plating solution. This combined with an increase in EN solution viscosity of an aged bath leads to more staining.

In certain applications, wear resistance is enhanced by smoother finishes. One automotive OEM subjects plated components to surface profilometry and has correlated "smoothness" to better wear resistance. Although the correlation is subjective, deposit brightness has been quantified by measuring the Rz values of the plated

surface. Rz value is the average absolute value of the heights of 5 peak/depth profiles over a specified sample length. **The effect of new grain refining additives is illustrated by the 1000 x photomicrographs in Figures 5.⁽¹⁾ and 6.⁽¹⁾ while the graph in figure 7 quantifies the improved “smoothness” differences between bare substrate and EN with and without new additives.**



Without additive

Figure 5

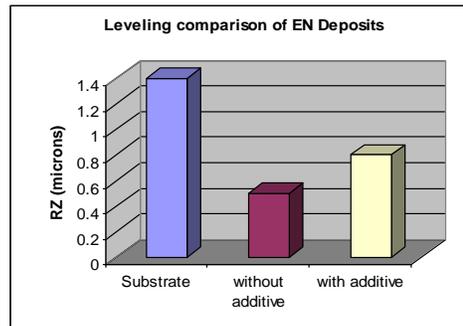
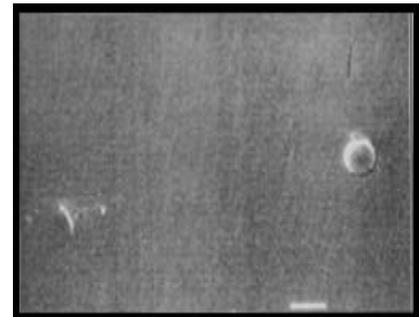


Figure 7



With additive

Figure 6

Deposit Pitting.⁽⁶⁾

Although surface condition and substrate pretreatment play a role in pitting of EN deposits, it is one of the most notable defects to emanate from the plating solution itself.⁽¹⁵⁾ Pitting is very common in low and medium phosphorus deposits and in thick deposits of all EN types. High phosphorus processes are less susceptible to pitting for a number of reasons. Lower stabilizer levels, heavy metal and sulfur-organic type, result in less co-deposition of impurities and a more homogenous deposit. The high phosphorus chemistry also plates slower. The significance of this is that it is believed that the most common cause of pitting is the attachment of hydrogen gas bubbles at the substrate-solution interface during plating. As the gas bubbles form on the plating surface they inhibit deposition until the gas bubble releases into the surrounding solution. The pit grows larger in size as the deposition process continues.

The hydrogen gas attachment process and subsequent formation of pit pre-cursors can be brought on by a number of factors.⁽¹²⁾ Substrate morphology and adsorption of microparticles are both considered suspects.⁽²⁾ High-speed EN processes are very susceptible to pitting because the plating continues to grow rapidly while the hydrogen gas bubble adheres to the trouble spot. Slower plating speeds, like those found in high phosphorus processes allows time for the hydrogen gas bubble to release before a significant amount of nickel can be deposited in the surrounding area. Wetting agents that lower surface tension and promote a quicker gas bubble release help to an extent, however the pits remain and the source is not eliminated.⁶

Better understanding of the pit formation mechanism detailed in figure 8 has led to the development of additives that impart specific charges to pit producing particles, repelling them from the plating interface and removing them from the diffusion zone.⁽¹²⁾ **Additives such as these now allow EN deposits to be plated to thicknesses in excess of 20 mils without pits or other related defects.**

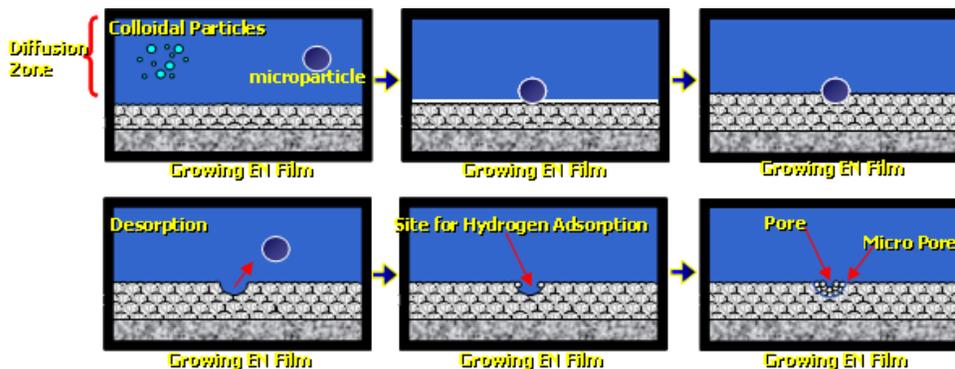


Figure 8⁽²⁾

Summary

Electroless nickel offers the engineering community a technology that is as reliable as it is diverse in meeting today's challenging applications. We must remain aware that current EN technology has limitations and maximizing deposit performance requires a cooperative effort between supplier, applicator and the end user. Success of electroless nickel in the future will require a strong commitment from these partners to advance the technology and the continued evolution of the EN family tree.

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