# ELECTROLESS DEPOSITION

## 1. Introduction

The term "electroless processes" are used to describe methods of depositing metals by means of chemical reduction. These systems are termed "autocatalytic" or self-catalyzing which refers to their ability to plate onto their own deposits to build metallization thickness. This mechanism is a result of the chemical reduction based upon the reducing agent used in the process solution. Electroless plating dates back to 1835 with the reduction of silver salts by reducing aldehydes. Progress in the field remained slow until 1944, modern electroless plating began with the rediscovery by Brenner and Riddell that hypophosphite could deposit nickel (1).

The growth of electroless plating is traceable to: (A) the discovery that some alloys produced by electroless deposition, notably nickel phosphorus, have unique properties; (B) the growth of the electronics industry, especially the development of printed circuits; and (C) the large-scale introduction of plastics and other types of substrates benefiting from electroless coatings to meet many types of engineering requirements. Electroless copper solutions underwent similar development during the same period (2).

Unlike electrolytically plated coatings, electroless coatings are produced onto catalytic metallic or catalyzed nonmetallic substrates without an externally applied electric current. In contrast to electrolytically deposited coatings, electroless coatings produced provide uniform coverage especially over complex shapes, complex geometries and over various size components. The deposit uniformity

**Fig. 1.** Parts plated with electroless nickel.

advantage allows the precise metallization to any coating thickness range on any section of a substrate surface exposed to fresh plating process solution. Figure 1 shows parts plated with electroless nickel phosphorus. For example, grooves, slots, blind holes, threads, and even the inside diameters of tubing can have the same thickness of coating. As a result of this deposit uniformity, many post-plate finishing processes, such as machining, can be eliminated.

Electroless copper (ECu) and electroless nickel (EN) alloys are the most common systems commercialized today. However, there are other metals and combinations that can be deposited by an electroless deposition mechanism.

Electroless deposition technologies are utilized to deposit metals on conductive metallic or nonconductive articles without the use of an externally applied electric current. Instead, the specific coating is deposited by an electro-chemical reduction mechanism utilizing various types of reducing agents to supply the necessary electrons. Depending upon the nature of the reducing agent, alloy deposits of metal−phosphorus (eg, Ni-P) when sodium hypophosphite or metal-boron (eg, Ni-B) when amine boranes, or sodium borohydride is utilized, or pure copper deposits are produced when formaldehyde is utilized. Metals common to commercial autocatalytic deposition processes (and their reducing agents) include (3–12): Nickel sodium hypophosphite, amine boranes, borohydride; copper formaldehyde, sodium hypophosphite, dimethylamine borane (DMAB); cobalt sodium hypophosphite, amine boranes, borohydride; Gold sodium hypophosphite, amine boranes; silver amine boranes (11), hydrazine (12), rochelle salt (12).

There have been laboratory studies of the electroless plating of the platinum group metals including, palladium, palladium phosphorus, palladium boron, platinum, ruthenium and rhodium alloys (13). While these may have some interest for specific applications, they will not be discussed in any detail here.

Electroless systems with the most commercial success today include copper and nickel in forms as binary, ternary or quaternary alloys. More common

electroless deposited alloys today include Ni-P, Ni-B, Cu, Cu-P, Co-P, Ni-P-Sn, and Ni-P-Cu.

Another form of chemical plating often confused with electroless plating is immersion plating. Immersion plating is the chemical replacement of one metal with another metal. A metal will displace from solution another metal ion that is more electropositive, at a lower position on the electromotive series table. The electrochemical series predicts the course of a reaction when two redox systems with different standard redox potential values ($E^0$) are brought into contact (14). For example, copper will plate by immersion on a steel substrate by the following reaction: $Fe^0 + Cu^{+2} \rightarrow Cu^0 + Fe^{+2}$. The electrons for the reaction are provided by the dissolution of the metallic substrate. For immersion plating, the mechanism is chemical displacement where the substrate metal functions as the reducing agent to displace metal ions from solution to coat the surface with metal. This plating only occurs when the substrate metal has a lower oxidation state potential than the metal in solution and continues only as long as the substrate metal is exposed (15). When the basis metal is completely covered by the metal deposited from this solution, the reaction stops. This is the major difference between immersion plating and electroless plating where the reaction continues even after the basis metal is completely covered.

## 2. Theory of Electroless Plating

The theory and practice of electroless plating parallels that of electrolytic plating. The actual metal reduction and film development occurs at the interface of the solution and the item being plated in both electrolytic and electroless processes. The main difference is that the electrons in electroless plating are supplied by a chemical reducing agent present in solution. In electroplating, these electrons are supplied by an external source such as a battery or generator. This means that electroless solutions are not inherently thermodynamically stable, because the reducing agent and the metal ions are always present and ready to react.
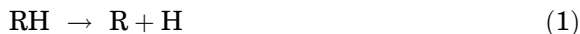
The reason certain reducing agents are useful is based on their kinetic behavior (16). The most effective reducers need a minimum amount of activation energy before they will react and they will then react slowly enough that the reaction can be controlled. This is especially true for industrially useful processes to produce functional coatings. For a classical silvering type solution, immediate reaction between metal ion and reducer is expected and necessary but is also wasteful.

The simplest electroplating baths consist of a solution of a soluble metal salt: the active species being a hydrated metal ion. Electrons are supplied to the conductive metal surface where electron transfer to and reduction of the dissolved metal ion occurs. Such basic electroplating baths are rarely satisfactory and additives are required to control conductivity, pH, crystal structure, throwing power, internal stress and other properties.

Electroless solutions contain a metal salt, a reducing agent, a pH adjuster, a buffer, one or more complexing agents and one or more additives to control solution stability, film properties, deposition rate, etc.
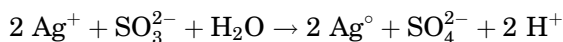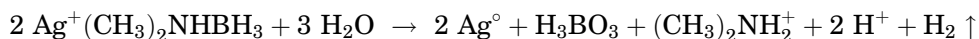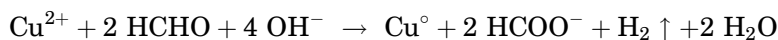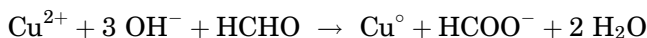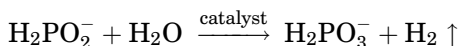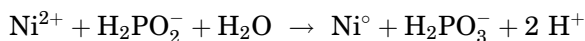
Of the large number of potential reducing agents, the principal commercial materials are formaldehyde for copper and silver, hypophosphite for nickel and palladium (17), and organoborane compounds for gold, nickel, palladium, silver and copper. Borohydride and hydrazine may be also used for nickel and formate for palladium (18). Most reducers also contribute to the composition of the deposit to some degree by introducing phosphorus, boron or carbon into the corresponding film. Likewise the stabilizing materials used in a process typically codeposit with the metal into the deposit. They are significant in that, although the concentration is relatively small, they may have a large influence on the physical, chemical and mechanical properties of the alloy. For example, phosphorus codeposited with nickel will increase the hardness of the coating but also reduce the melting point and the conductivity. The detailed theory of electroless plating has been discussed in a number of works (2,19–28).

One theory proposed by Van der Meerakker (24) generalizes the mechanism in the following equations where RH represents the reducer. Equations 3 and 4 represent the recombination and ionization of adsorbed atomic hydrogen which can occur in parallel.

$$RH \; \rightarrow \; R + H \tag{1}$$

$$R + OH^- \; \rightarrow \; ROH + e^- \tag{2}$$

$$H + H \; \rightarrow \; H_2 \tag{3}$$

$$H + OH^- \; \rightarrow \; H_2O + e^- \tag{4}$$

$$M^{n+} + ne^- \; \rightarrow \; M \tag{5}$$

Deposition reactions for some reducing agents are shown where hydrogen is a principal byproduct of each reduction. Gawrilov (23) shows how elemental phosphorus or boron is codeposited with the reduced metal from hypophosphite, borohydride, or organoborane baths. Courdeuvelis and Sutcliffe show minor reactions can also occur (29). Van Den Meerakker (24) and others (30–32) explain how these reductions can be viewed as dehydrogenation reactions.

*Deposition Reactions*

$$Ni^{2+} + H_2PO_2^- + H_2O \; \rightarrow \; Ni^\circ + H_2PO_3^- + 2\ H^+$$

$$H_2PO_2^- + H_2O \xrightarrow{\text{catalyst}} H_2PO_3^- + H_2 \uparrow$$

$$Cu^{2+} + 3\ OH^- + HCHO \; \rightarrow \; Cu^\circ + HCOO^- + 2\ H_2O$$

$$Cu^{2+} + 2\ HCHO + 4\ OH^- \; \rightarrow \; Cu^\circ + 2\ HCOO^- + H_2 \uparrow + 2\ H_2O$$

$$2\ Ag^+(CH_3)_2NHBH_3 + 3\ H_2O \; \rightarrow \; 2\ Ag^\circ + H_3BO_3 + (CH_3)_2NH_2^+ + 2\ H^+ + H_2 \uparrow$$

$$2\ Ag^+ + SO_3^{2-} + H_2O \rightarrow 2\ Ag^\circ + SO_4^{2-} + 2\ H^+$$

Most reducing agents are too slow, giving insufficient plating rates, or too fast, resulting in bulk decomposition. Each combination of metal and reducing agent requires a specific pH range and bath formulation. The metal ion and reducer are consumed in the reaction and so must be replenished at periodic intervals. Any components lost through spillage or drag-out also must be replenished along with adequate additional complexer to compensate for the build-up of salts and reaction byproducts. Stabilizers are used to prevent spontaneous decomposition and are typically used at a few to a few tens part per million (ppm). They may affect deposition rate, deposit color or reflectivity, ductility, hardness and internal stress. Other additives may be introduced specifically to improve the smoothness or reflectivity of the coating.

The ideal electroless solution deposits the coating only on an immersed article, never on the sides of the tank or as a fine powder. State-of-the-art compositions can approach this ideal but the plating reaction and side reactions never allow coating with a very high efficiency. In particular, the Cannizaro side reaction between alkali and formaldehyde can destroy all of the reducer without any copper deposition. Frequently a byproduct of electroless reaction is hydrogen gas which can cause foaming of the solution or gas pits in the deposit. The primary industrial metals that are plated include nickel, copper, gold, palladium and silver. Ternary alloys are also possible and have shown great potential but to date have not been successfully introduced into significant, commercial applications (33).

Electrolytic plating depends on current flow from the anode to the substrate surface to supply the electrons. Plating rates are controlled by the current density at the metal-solution interface. This results in a coating that will have great variations in thickness and coverage. Electroless plating has the ability to uniformly coat articles, especially in recesses or blind holes, since the reducing potential is equal all over the part surface. Film thicknesses range from <0.1 mm, where only conductivity or reflectivity is desired to 1 mm or more for functional applications.

A primary advantage of electroless solutions is the ability to produce conductive metallic films on properly prepared nonconductors. Electroless reactions for build-up must be autocatalytic. Some metals are autocatalytic, such as iron with electroless nickel. A first layer of the electroless metal being laid by a displacement reaction can also initiate the reaction: eg, nickel on zincated aluminum (26). Initial deposition on other surfaces needs a catalyst, usually palladium, which is a good dehydrogenation catalyst, on noncatalytic metals or a palladium-tin mixture on dielectrics (34,35). The catalyst develops a very high reduction potential to quickly cover the surface with a very thin film of electroless metal which then becomes the catalyst for further reaction. As long as the surface remains active and is not poisoned by excessive stabilizer or solution contaminants, more metal will be deposited indefinitely. Silver is a borderline material, being so weakly catalytic that only very thin films form unless the surface is repeatedly catalyzed; newly developed baths are truly autocatalytic (36). In every case there is a necessary balance between the reducing potential produced by the reducing agent and the potential at which the metal ion can be reduced to metal. Metals that require a high potential will not be reduced by a weak reducing agent. It is possible to predict to some extent which metals and reducers can

be used together. This is done by measuring the reducing potential of a reducing agent (usually done at various pH values) and comparing it to the standard half reaction potential for a metal or by measuring what is called the mixed potential of the system (37). The potential at which the metal is actually reduced incorporates the half reaction potential as well as an over potential to compensate for hydrogen generation as well as hindrance by complexers and physical phenomena. Copper and silver are examples of metals that are extremely easy to reduce by the relatively weak formaldehyde reducer. Nickel and cobalt cannot be reduced by formaldehyde but need the stronger hypophosphite or an organoborane reducer. Copper can be reduced by hypophosphite, but the reaction is not autocatalytic because copper is not a catalyst for hypophosphite. In one case palladium is used with hypophosphite to initiate deposition of copper onto nonconductors to provide a conductive layer whereupon more copper is subsequently electroplated in the same solution (38). The initial reaction is self-limiting and stops when all of the palladium is covered with copper.

Electroless plating rates are affected by the rate of reduction of the dissolved reducing agent and the dissolved metal ion which diffuse to the catalytic surface of the object being plated. When an initial continuous metal film is deposited, the whole surface is at one potential determined by the mixed potential. The current density is the same everywhere on the surface as long as flow and diffusion are unrestricted so the metal deposited is uniform in thickness over the whole surface. However, maximum plating rates are lower for electroless plating than those possible for electrolytic plating. Extremely thin films of electroless coatings are not uniform because the initial deposition is confined to discrete nucleation sites that grow and coalesce into a film.

**2.1. Electroless Process Controls and Chemistry Balance.** As every electroplating process requires and benefits from proper process controls, so do electroless systems. These controls are especially critical for electroless systems in particular since chemistry balance and operating conditions impact the quality, and performance of the both the process and the resulting deposit. Deposit performance and solution performance rely on the precise control of key parameters to maintain the proper equilibrium and balance to achieve optimum results. Critical control conditions for electroless systems include operating pH, operating temperature, solution loading (surface area of articles in tank per liter of plating solution), solution agitation, and control of contamination. Engineering of an electroless deposition plant and process including the equipment that is utilized for these processes become very important considerations to achieve adequate quality and performance. For example, selection of the proper solution, filtration, heating system, whether chemical or anodic passivation of the equipment, and the manner in which production is introduced to the process are significant control parameters for consideration. Good sources of review for electroless equipment can be found in many references (39,40).

## 3. Electroless Technologies Commercially Available

As electrolytic plating is often employed as an ideal means to provide a thin surface coating which has some property (or properties) superior to that of the

substrate, electroless deposited coatings offer a multitude of advantages that make them the preferred finish for a wide range of applications.

**3.1. Nickel Phosphorus Alloys.** Commercial nickel phosphorus alloy systems are available and formulated to co-deposit from 1 to 13% (w/w) phosphorus in the deposit. These deposits exhibit many desirable engineering characteristics. Their deposits have a low coefficient of friction and are antigalling. These systems offer the ability to provide metallization over nonconductors and are applied for improving the ease of soldering. They have a good "as plated" deposit hardness compared to other types of plated coatings, and the hardness can be further increased by subsequent heat treatment. By their nature of being cathodic coatings, these deposits provide excellent corrosion protection in most environments. They can also provide a range of corrosion resistance depending upon the exposure environments. The corrosion resistance data of these types are well documented (41–45).

All electroless nickel alloys exhibit good corrosion protection, especially over steel and aluminum substrates. Figure 2 shows 25 micrometers of high phosphorus deposit over aluminum connectors. Because these deposits provide a uniformity of coverage and thickness over all surfaces, irregular components and shapes can be protected from corrosion in areas where typical electroplated deposits would be thin or absent because of current density distribution limitations. Electroless processes provide the ability for small parts to be metallized in mass quantities utilizing a basket or barrel. Large articles that are the size of automobiles can also be processed with electroless technology given proper strategies (46). These types of technologies offer surface finishers the ability for high production throughput with flexibility. The resulting deposit hardness and low surface friction of Ni-P alloys provide additional resistance to wear and erosion for plated component bearing surfaces. This would include gears, sprockets, and applications where similar service conditions of sliding or rolling friction may cause wear.

For many applications, softer parts or components that have poor abrasion resistance can be given a hard wear resistant electroless nickel deposit. In some cases, EN plated components can be substituted for expensive more difficult to machine materials such as stainless steel. In other applications, nonconductors



**Fig. 2.** Twenty-five micrometers of high phosphorus nickel deposit over aluminum connectors.

can be plated with electroless nickel and copper to provide EMF shielding or a base metallization for subsequent decorative copper, nickel and chromium electrolytic plating. More recently developed lower phosphorus technologies of the early 1990s have been shown to replace electrolytically produced hard chromium deposits in some applications (47–49).

The suitability for choosing any type electroless process for specific applications is driven by the desired property. For Ni-P systems, the resulting properties are related to the phosphorus content of the deposit. The same can be said for Ni-B deposits. One type of Ni-P or Ni-B deposit may not meet all the requirements for any given application. The phosphorus or boron ranges are designed to optimize deposit properties for a wider application of engineering functions. Selecting the electroless process that will produce the optimum phosphorus content for any given application can sometimes be a difficult task due to a lack of understanding the relationship between phosphorus content versus the key properties provided by the deposits.

American Society for Testing and Materials (ASTM) recognized the importance of the relationships between the phosphorus content, their properties and the performance they provide. In 1997, ASTM B-733 specification document for electroless nickel deposits was revised to establish new ranges of phosphorus to more precisely define the relationship of phosphorus to performance. Table 1 summarizes these relationships as related to different types (50).

Each type helps to focus on the primary properties and the resulting best application that each range of phosphorus provides. Type 1 provides for any range of phosphorus that can be used. The other types and their primary properties are type 2 and 3 (alkali, brine, strong caustics), type 4 (alkali, brine, caustic solutions) and type 5 alkali, brine, mildly acidic solutions, marine environments (51).

Other, more common metal finishing industry nomenclature classification categories for nickel phosphorus ranges include the following: $1-3\% =$ low phosphorus; 4 to $6\% =$ medium-low phosphorus; $7-9\% =$ medium phosphorus; and 10 or higher $=$ high phosphorus.

Table 1. **ASTM B-733 Types of Nickel Phosphorus Deposits**[a]

| Type[b] | P, wt% | Significant applications |
|---|---|---|
| Type 2 | 1–3 | solderability, electrical conductivity, wire bonding, hardness and wear applications |
| Type 3 | 2–4 | high as plated and as heat treated deposit hardness, for high wear applications on aluminum, copper, beryllium copper and other substrates that have heat treatment limitations or restrictions; thickness ranges typical 3 to 30 μm |
| Type 4 | 5–9 | general wear and corrosion protection applications in industrial interior and exterior or non-marine environments; thickness ranges from 1 to over 200 μm |
| Type 5 | 10 | wear and corrosion resistance applications in marine and corrosive industrial environments; oil and gas environments, nonmagnetic applications |

[a] Refs. 50,51.
[b] Type 1 has no requirement for phosphorus.

Regardless of the range, knowing how the phosphorus content relates to specific deposit properties is the single most important aspect of understanding electroless nickel systems.

High phosphorus deposits provide the greatest corrosion protection and corrosion resistance in the widest variety and types of environments to which they are exposed. These deposits are nonmagnetic as plated and some formulations will maintain their deposit nonmagnetic characteristics up to temperatures of 300°C for 1 hour. High phosphorus deposits are particularly suited for heavy build up depositions (100 microns or more in some applications) or salvage rework applications. Typical high phosphorus systems produce low internal stress deposits and provide the best ductility or elongation.

Medium phosphorus deposits are typically used and suited for many types of applications. The deposits provide good corrosion protection and offer good as plated and as heat-treated hardness and wear resistance. These deposits can range in brightness (high reflectivity) from very bright, bright, semibright, and matte in their appearance. The chemistries used to produce these deposits operate under a variety of conditions and provide the most versatile processing capabilities.

Medium-low phosphorus alloy deposits are produced from the newest technology formulations for Ni-P systems. Earlier systems developed in this range were alkaline chemistries and were more difficult to operate and control compared to newer formulations based upon acid chemistry. The successful commercialization of these deposits in the early 1990s helped to grow the market for EN, especially in more varieties of applications. The deposits are characterized by providing high hardness and excellent wear resistance both in the as plated and as heat-treated condition. They offer engineers new opportunities for utilization while the metal finishers who use these technologies recognize improved operation, deposition rates and throughput, and as a result, they continue to become more versatile.

Low phosphorus alloy deposits, those ranging from 1.5 to 3.0% by weight phosphorus, are primarily utilized in specialized wear or electronic applications. These were originally developed and commercialized before the newer formulation 4%P systems of the early 1990s, but have yet to achieve similar industry success except in some specific niche applications. They are ideal for soldering or brazing and can be welded. The deposits are compressively stressed, have good elongation (ductility), and provide excellent hardness and wear resistance, as plated or heat-treated. In alkaline corrosive environments they out-perform high phosphorus deposits.

**3.2. Nickel–Boron Deposits.**   The investigation of alternative reducing agents to sodium hypophosphite led to the use of borohydrides and amine boranes to provide alloys of nickel–boron. The chemistry of boron reduced electroless nickel processes has been discussed in detail (52–55). Nickel–Boron alloys are deposited from formulations utilizing dimethylamine borane (DMAB) as the reducing agent and usually contain from 0.2 to 3.0% by weight boron in the deposits. Higher boron deposits, up to 5% by weight, are obtained using sodium borohydride as the reducing agent. Some of the earlier patents discuss the use of sodium borohydride or dimethylamine borane as reductants (56). Deposits from these systems exhibit many of the same characteristics as nickel phosphorus

**Fig. 3.** Various electronic components plated with various types of electroless depositions.

deposits, but the lower boron alloys are especially suited for use in the electronics industry because of their electrical and physical qualities. Figure 3 illustrates various types of electronic components plated with various types of electroless depositions. They are sometimes used in industrial wear applications because of their high hardness levels. Deposits can also be plated from acid to alkaline chemistries. Significant applications for boron alloy, <1% include electronic applications, replacement for gold in microelectronic equipment and printed circuit boards. Applications for boron alloy 2 to 5%, include wear applications, aircraft engines, landing gear components, valves, pumps, resistance to erosion and galling (51).

The lower concentration boron deposits (<1% by weight) provide high electrical conductivity, exhibit low contact resistance and show good "as plated" hardness and wear resistance. They are easily soldered or brazed and exhibit good shelf life solderability properties, that is, they maintain their ability to remain solderable and wire bondable for extended periods. EN boron deposits have found many applications to reduce or eliminate the usage of gold in some electronics industry applications (57). The deposits offer good diode bonding with ultrasonic methods and provide excellent wetting of brazing alloys. Higher concentration boron containing alloys (>3% by weight) are very hard and wear resistant coatings and tend to further retard the formation of oxides on their surfaces. Nickel boron deposits also provide an excellent strike coating for aluminum or plastics.

Traditionally, silicon chips have been bonded to Ni-B deposits and their associated connecting wires can be bonded to metal pads of electroless nickel-boron using ultrasonic and thermosonic bonding techniques. Wire bonding attachment techniques are important for chip-on-board and surface mount applications (58). Nickel boron deposits have shown excellent wire bonding characteristics when an ultrasonic or thermosonic bonding method was employed as
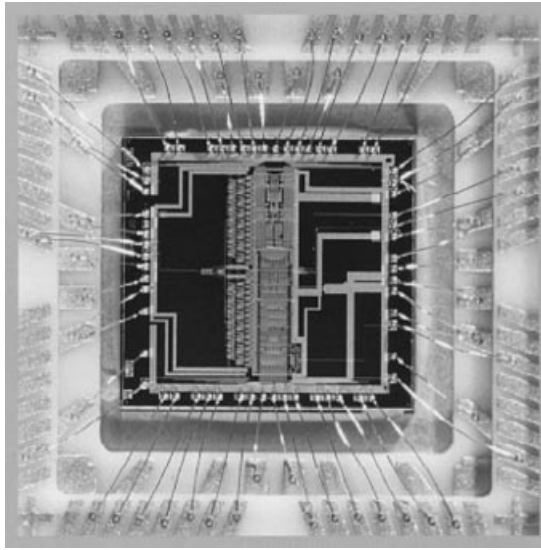
**Fig. 4.**   Nickel boron deposits used in wire bonding.

shown in Fig. 4. The ultrasonic bonding of aluminum wire to pads and header pins plated with Ni-B has proved economical and reliable by some manufacturers (59). Ni-B plated surfaces as a base for bonding of aluminum wire has been more reliable than aluminum–silver and aluminum gold bonding (60). The advantage of using Ni-B alloy deposits is such that gold plating on the pads and the header pins can be eliminated and the gold wire could be replaced by aluminum wire while Kirkendall voiding defects, caused by wire bonding to gold, can be eliminated.

Electroless nickel boron deposits when applied over metallized patterns and interconnects of ceramic substrates have been used in the production of sturdy, high-circuit-density electronic packages with increased reliability (61). In hermetic seals, a layer of Ni-B on the ceramic's metallized bonding areas provides a sturdy seal. In high-circuit-density, multilayer ceramic (MCL) modules, which are characterized by narrow line width and spacing, a Ni-B deposit enhances the circuit characteristics while avoiding the potential for bridging between circuit patterns. In hybrid circuitry designs, Ni-B deposits assure continuous and dense conducting patterns and pads while improving solderability, brazeability and wire bonding.

Molybdenum–manganese and other metallizing substrate materials are subject to moisture where corrosion and loss of adhesion can occur. The electroless layer will protect these substrates from corrosive attack.

Gold is frequently used to provide a solderable surface despite the fact it is known to dissolve in the solder. As gold contamination increases in the solder, the result is a weak, dull solder joint (62). Nickel is not readily soluble in liquid solder, so it will not erode in a dip or wave soldering operation, or easily contaminate the solder. Ni-B and high phosphorus Ni-P alloys are readily wetted by liquid solder, with proper flux, to provide excellent solderability (63).

**3.3. Electroless Copper.**    Electroless copper metallization is an important technology throughout the electronics and plastics industry (64). The chemistries typically use formaldehyde as a reducing agent. Other solutions utilize sodium hypophosphite, or dimethylamine borane as the reducing agents (65–68).

The processes have been used for metallization of holes in two-sided and multilayer printed circuit or printed wiring boards in order to provide copper on nonconductive plastics surfaces exposed after drilling through-holes (PTH) for maintaining internal electrical paths (69). Printed wiring boards (PWB) are manufactured from an epoxy glass laminate that is clad with an electrolytic copper foil. During board manufacture, the substrate is drilled, followed by a thin electroless copper deposit plated over the drilled copper foil to make the hole-path conductive allowing further build up with electrodeposited copper metal. Other PTH purposes include holding a component lead wire and to interconnect circuitry or printed wires. In the case of multilayer board designs, making the path conductive to those internal layers of copper that are adjacent to the just formed hole is critical. Electroless copper deposits are ideally suited for providing a uniform thickness when electrically discontinuous surfaces, or very high aspect ratio holes require plating. In another application fabrication of multi-chip modules require an electroless copper to define and build up conductive traces on the board surfaces (70).

As electronics components continue to shrink with the corresponding increasing complexity requirement of circuit boards, there will be reductions in conductor and hole dimensions; electroless copper technologies will continue to be favored for many applications.

Electroless copper deposits provide an initial strike layer for plating onto plastics (POP) for decorative purposes. For POP applications, electroless nickel or electroless copper metallization may be used to produce an electrically conductive deposit. Following either an electroless copper or electroless nickel strike layer, an electrolytic copper or nickel is used to build deposit thickness. The primary purpose of the 2.5 micrometer strike layer in this application is to prevent a condition called "burn off". Burn off is the loss of contact between the part and the rack tips which results in a poor quality deposit. The copper metallization develops a secure bond between the plastic and the electroplated layer. Automotive industry studies have shown that utilizing an electroless copper layer for exterior applications produces better durability in various humid and corrosive environments (71,72).

Attenuation of electromagnetic signals generated either internally or externally to a packaged component requires Electromagnetic Interference (EMI) Shielding for the component (73). EMI is electrical noise generated by electronic equipment that interferes with the operation of other electronic equipment. Plastic enclosures do not reduce EMI signals appreciably so electroless copper and electroless nickel deposits have been used to address the requirements. EMI Shielding is accomplished using 0.5 to 2.0 micrometers of copper to provide an effective shield. Electroless nickel deposits of 0.1 to 1.0 micrometer can be applied over the copper to protect the copper from corrosion.

There are also some unique niche applications where electroless copper deposits have recently been utilized to encapsulate particles or oxide layers

with a pure copper deposit. After encapsulation, the coated particles can be mixed with resins to be formed into components where they provide electromagnetic shielding instead of utilizing more traditional shielding techniques.

**3.4. Electroless Silver.** Silver has been used over the years to produce mirrors for optical and decorative applications (74). Other important functions for electroless silver deposits is to provide electrical conductivity or as a strike undercoating for other plating. In one example, the silver deposit was applied to the substrate prior to electroless gold plating (75). Additionally, electroless silver deposits have been used as an initial metallization step over aluminum oxide ceramics to improve the adhesion and texture of copper (76).

**3.5. Electroless Gold.** Electroless gold deposits are applied mostly in the electronics industry. The metallization of components for printed circuit boards is a primary use of this technology, on flex circuits, ceramics, three-dimensional circuits, and metals (77). Since these gold deposits are 99.9% pure, they have excellent electrical, soldering, and bonding properties and can be used successfully for metallization of isolated tracks and bonding pads that require a uniform deposit thickness. This is a benefit over existing electrolytic gold processes. Gold has also been used in the fabrication of multilayer ceramic packages to improve their brazing, soldering and wire bonding properties (78).

**3.6. Composite Coatings.** The excellent wear resistance of EN deposits can be further improved by the co-deposition of particulate matter, called composite coatings. These systems represent specialty types of deposits for specific applications and enhanced wear and abrasion resistance. Composites consist of particles dispersed throughout the electroless deposit. The particles can be either hard particles (eg, ceramic, silicon carbide, diamonds, or boron nitride) or soft particles.

Polytetrafluoroethane (PTFE) Teflon, a trademark of DuPont, fluorocarbon particles are more commonly used as the soft particles. Compared to non-particle EN deposits, composite coatings have improved frictional and release properties, and overall improved wear resistance in many applications. There are a few good sources of reference for these types of niche deposits (43,79).

PTFE deposits provide low frictional coatings utilized in some specialized, or sliding wear applications. These classes of deposits have excellent lubricity and release characteristics which is greater than for Ni-P alloys without PTFE co-deposition. They provide dry lubrication in some applications.

The normal, excellent wear resistance of Ni-P alloy deposits can also be improved by the inclusion of hard particles. Co-deposition of silicon carbide particles (4,500 HV), synthetic diamonds (10,000 HV) or other hard particulate matter will function to provide a deposit alloy which exhibits exceptional wear resistance under heavy loading conditions or in aggressive wear applications. Silicon carbide particles in a Ni-P alloy matrix are the most common coating systems utilized. The wear characteristics of these types of coatings approach that of the particle materials (80). For hard particles, they typically range in size from 0.25 to 4.0 μm in diameter. These passive particles deposit primarily by gravity and can become occluded into the deposit matrix ranging from 1 to 15% by weight. Application examples include some specialized mold and die applications, internal combustion engines, textile and cutting tool applications where improved abrasion resistance is required.

**3.7. Ternary Alloy Coatings.**   Also called poly alloys, these are electroless nickel deposits, which contain more than two elements. An example is nickel boron thallium (5% boron and 1% thallium) which is very hard as deposited and provides excellent wear resistance in specialized wear environments including the aircraft industry. Each type of ternary alloy is designed to maximize a given deposit property such as corrosion resistance, high hardness, high temperature resistance, electrical properties, and ferromagnetism or brightness characteristics. There are other commercial systems that have been available in the past but today more common systems are based upon Ni-P-Cu, Ni-P-Sn, and Ni-B-Tl alloy deposits. It has been shown that it is possible to include a number of different alloy constituents into systems which have many different deposit characteristics (33). However, many of these have not found commercial viability in application. Many of these alloys possess superior corrosion resistance, superior hardness, high-temperature resistance and interesting electrical characteristics. In 1963, Perlstein, Weightman and Wick (81) reported autocatalytic nickel-tungsten-phosphorus alloys. Others (82) have reported nickel–rhenium–phosphorus and nickel–copper-phosphorus. Mallory introduced ternary and quaternary alloys of nickel with boron, phosphorus, molybdenum, tungsten, tin, copper, iron and cobalt in many combinations (83).

**3.8. Encapsulation of Particles.**   Today, iron powders, ceramic powders, diamond powders, and other types of particles are being plated with nickel phosphorus and copper deposits. Often, these particles are plated so they can be molded or pressed with other polymers into complex shaped grinding wheels, dicing blades or to provide a more corrosion resistant part when pressed into parts utilizing powder metal metallurgy. The more common reason to plate the particle is to enhance the particles' ability to "bond" to other materials in the matrix where they are applied. Figure 5 shows synthetic industrial diamonds coated with a 56% by weight Ni-P deposit. Electroless nickel is well suited for this application. Utilizing specialized equipment, procedures and techniques, many types of particles can be plated up to 60% by weight of electroless nickel phosphorus or copper deposits.
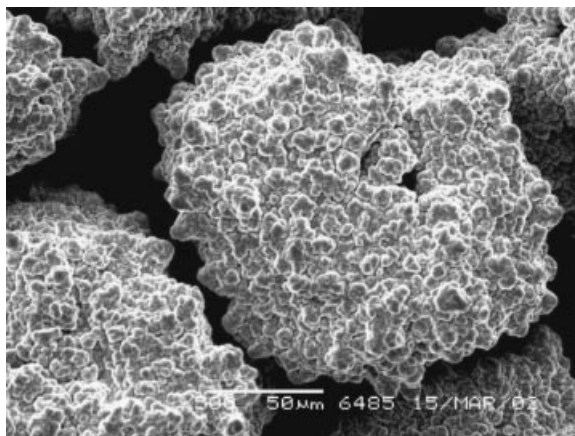


**Fig. 5.**   Industrial diamonds coated with a 56 wt% Ni-P deposit.

## 4. Standards For EN Deposition

Specifications are an important resource to understand and review the primary properties that are significant to electroless deposition. Consequently, standard specifications have been utilized for many years as guidelines to assist with the application of electroless nickel coatings. It was not until the late 1980s and through the mid-1990s that many of the traditional specifications dealing with EN deposition were recognized as being insufficient or inadequate. They were deficient in providing enough information for individuals and engineers trying to properly specify EN coatings. It was recognized that electroless nickel was much more than a single coating or type (89). Today, many of the older documents have been revised to reflect changes with EN deposits. There is more information regarding tests, methods and other reference information that make the documents more useful for finishers and those specifying EN.

Several industry documents exist for electroless plating and include the following for reference.

*ASTM B-733: Standard Specification for Autocatalytic Nickel-Phosphorus Coatings on Metals*.

*AMS 26074 (formerly Mil-C-26074): Coating, Electroless Nickel, Requirements for* (85).

*AMS 2404: Electroless Nickel Plating* (85).

*AMS 2405: Electroless Nickel Plating, Low Phosphorus* (85).

*AMS 2399: Electroless Nickel-Boron Plating* (85).

*ISO 4527: Autocatalytic Nickel-Phosphorus Coatings, Specification and Test Methods* (86).

*ASTM B-607: Standard Specification for Autocatalytic Nickel Boron Coatings for Engineering Use*.

This is by no means an all inclusive list. There are likely many others that would provide useful information for an EN process, but these are specific to EN plating applications. Many related references to other documents can be found in these specifications or guides. The key to using any specification would be to understand what deposit characteristic or performance is expected from the final product.

## 5. Industries and Applications for Electroless Deposition

There have been many industry applications for Ni-P deposits. Good sources of references include those listed in (43,87–89).

**5.1. Petroleum and Chemical Industries.** The petroleum and chemical process industries are the largest users of high phosphorus EN for corrosion protection. Coating thickness' from 25 to 75 micrometers are commonly used to retard corrosion and erosion in aggressive brines, acids and gases. Common applications include valves, chokes, blowout preventors, mud pumps, submergible pumps, pipe, heat exchangers and separators, packers, safety valves,

**Fig. 6.**   Chemical process ball valves plated with 25 μm of high phosphorus electroless nickel.

production tubing and all types of down-hole tools (90). Figure 6 shows chemical process ball valves plated with 25 micrometers of high phosphorus electroless nickel.

**5.2. Medical, Dental and Pharmaceutical Industries.**   High phosphorus EN is used because of the superior corrosion and wear resistance. The equipment is often subject to severe abuse but must remain completely reliable. The high phosphorus provides almost complete resistance to these environments and frequently allows steel or aluminum substrates to be substituted for more expensive stainless steel.

**5.3. Aerospace Industry.**   High phosphorus (HP) is favored in a number of applications to protect the surface of light metals, such as aluminum, from corrosion and wear. The relatively high strength and low compressive stress of these deposits are to reduce important fatigue on many other types of substrates. The HP enhances the appearance of some aircraft metals with a polished stainless steel look. The coating is used on a variety of aircraft parts, including engine components, structural air frame and landing gear pieces, refueling systems, compressor blades and servo valves. The uniform thickness, and ability to coat the inside of holes and recesses, makes it ideal for plating complex shaped hydraulic valves and manifold systems.

**5.4. Mining Industry.**   Mining environments are both very corrosive and abrasive. Mine waters are typically acidic and can cause a high rate of attack of unprotected steel. In addition, the dust produced during mining can result in severe erosion. High phosphorus EN coatings have been found to withstand these conditions with minimal attack. Common applications include hydraulic components, cylinder heads for jetting pumps, pipeline connections and tubing, and mine engine components. In some very severe environments, combinations of EN layers are utilized to provide high corrosion protection.

**5.5. Electronics Industry.**   In electronic devices, corrosion protection, diffusion barriers, conductive circuit elements, via-hole filling for semiconductor integrated circuits, through-hole connections for printed wiring boards and flexible circuits all benefit from electroless deposition technologies. All around, high

phosphorus EN and nickel−boron alloy deposits are widely used in many electronic applications. Coaxial connectors utilize high phosphorus for the lubricity, wear and corrosion properties. Headers, housings and cases, heat sinks, diode cans, interlocks and aluminum memory disks are only a few of the electronic applications. For electronic components, these coatings are used for their combination of superior corrosion resistance and their ability to enhance component solderability.

Electroless plating is used to fabricate passive devices on dielectric surfaces such as resistors, capacitors and to improve conductivity of metallized circuits that use thick-film conductors or frits on ceramic molybdenum and tungsten substrates. High phosphorus EN is used as a base layer for gold plating in some specific applications. The predictable electrical, thermal and physical properties are important reasons why high phosphorus EN coatings are utilized. Copper traces of printed wiring boards often require additional metallization to provide for reliable assembly of components on the boards by wire bonding and soldering.

Gold cannot be plated directly on copper due to the tendency for diffusion of the two metals. Ni-P, Ni-B and Co-P alloys provide good diffusion barriers. Also, some corrosion protection of the copper is required. EN-P deposits are chosen as the initial layer to provide a barrier coating and corrosion protection for gold.

**5.6. Salvage and Repair Applications.**   Electroless nickel deposits are very cost effective for salvage and repair applications. Because of its superior adhesion, low porosity, excellent wear and corrosion resistance, these coatings are often used to selectively build up worn or mis-machined parts. Thickness' of 125 to 250 micrometers are common for the high phosphorus EN deposits, although repairs up to 1000 micrometers have been made. The total cost savings from using EN can be substantial, since it allows mis-machined parts to be used. This avoids their remanufacture.

**5.7. Automotive Industry.**   Except for plated plastics, many components for the automotive industry historically have provided only a limited market potential for electroless nickel. With the greater reliability required for automobiles, their components need to have improved wear and corrosion performance and the growth of electroless in the automotive sector has grown. Important applications today for EN include, brake anchor bolts, differential pinion shafts, slip yokes, printed wiring boards, heat sinks, power steering forks, transmission thrust washers, brake pistons and fuel rail/carburetor parts.

**5.8. Molds and Dies.**   The ability of electroless nickel coatings to provide a uniform deposit, even into deep recesses, helps to ensure that the finish on a mold will duplicate the original surface. The natural lubricity of the coating provides smooth flow during injection and the quick and easy release of the part. Because of its high hardness at elevated temperatures, the EN minimizes erosion and abrasion of molds and dies and helps to extend their service life. The coating also provides excellent protection against the corrosive fumes produced during molding of such plastics as ABS, PVC, polycarbonate, acrylics and materials with thermoplastic additives. Similarly, electroless nickel has been found to provide a superior coating for zinc die cast dies and glass molds.

**5.9. Printing and Textile Industries.**   The use of EN for the cylinders and rolls has shown many advantages. The ability of the coating to deposit uniformly allows the cylinder to be machined to size, balanced, and plated without

subsequent finishing or grinding. With the typical coating thickness of 25 to 50 micrometers, the life of this equipment is greatly extended by the lubricity and wear resistance of the EN. Other common textile applications include thread guides, fiber feeds, fabric knives, heddles, bobbins, shuttles, ratchets, knitting needles and picks.


## 6. Key Properties

The key properties for Electroless nickel-phosphorus and nickel-boron deposits are summarized in Table 2.

A clear understanding of the inter-relationships concerning the properties for any of these coatings is important for the control of the overall performance characteristics for both the process and the resulting coating. Mechanical properties of electroless nickel–phosphorus alloys are dependent upon the amount of phosphorus in the deposit (94). Other electroless systems follow similar trends.

For Ni-P alloy deposits, the phosphorus content of the alloy is the most significant parameter to control. An understanding of operational factors that affect the phosphorus level is an important consideration as a result of this relationship to the property. Different formulations exist to provide each classification or range of phosphorus alloy. Although, there can be some overlap in the phosphorus content for each range. The operating conditions such as pH, temperature, solution loading (part surface area per liter of plating solution) and chemistry balance affects the phosphorus content for a particular system. The phosphorus in the alloy does not fall outside the expected range for that system unless contamination exists. Choosing the process that will produce the optimum phosphorus content for any given application can sometimes be difficult because of the variables mentioned. As an example, plating with air agitation in one system produces a 4% phosphorus deposit versus a 6% deposit being produced with no agitation from the same chemistry system.

Table 3 summarizes the trends associated with the properties as related to deposit phosphorus.

It is also important to understand that many of the properties of the EN deposits and the EN coating processes used to deposit them are interrelated (95). Changing one property will often change a different property. For example, maximizing deposit hardness through a post plating heat treatment will reduce the corrosion resistance of the deposit.

Sometimes a different property is evaluated for the actual one desired. This is done because there is a relationship between the two properties and a more practical test method exists for the substitute. For example, in some wear applications, hardness tests are often used as a substitute test method. Typically, deposit hardness has some relationship to wear resistance and deposit hardness testing may be considered a more practical test.

**6.1. Ni-P Deposits.**    *Structure.*    EN deposits may be amorphous, crystalline or a mixture of both based upon the phosphorus level in the deposit (91). When the phosphorus content exceeds 11%, EN coatings are considered totally amorphous without any distinct crystal structure. The distinction between a crystalline and an amorphous material is best made in terms of

Table 2. **Typical Physical Properties of Electroless Nickel Deposits**[a]

| Property | High phos | Mid phos | Low-Mid phos | Low phos | Nickel-Boron | |
|---|---|---|---|---|---|---|
| phosphorous or boron, % | 10–13 | 7–9 | 4–6 | 1–3 | 0.2–1 | 3–5 |
| deposit density range g/cm$^3$ | 7.6–7.9 | 8.0–8.2 | 8.3–8.5 | 8.6–8.8 | 8.8 | 8.25 |
| plating deposition rate m/hr | 7.5–15 | 15–25 | 18–30 | 11–19 | 5–10 | 5–18 |
| hardness as plated $HK_{100}$ | 450–525 | 500–600 | 625–750 | 725–800 | 600–700 | 650–750 |
| Rockwell C (Rc) hardness conversion as plated[b] | 41–46 | 45–51 | 53–59 | 57–61 | 51–56 | 54–59 |
| hardness heat treatment, $HK_{100}$ | 850–950 | 850–1000 | 850–1100 | 900–1100 | 500–600 | 1100–1200 |
| Rockwell C (Rc) hardness conversion at heat treatment[b] | 64–67 | 64–71 | 64–74 | 66–74 | 45–51 | 74–76 |
| Taber wear index as plated mg/1000 cycles–CS-10 wheel, 100 g load | 22–24 | 16–20 | 10–14 | 7–12 | 7–9 | 8–15 |
| Taber wear index after heat treatment mg/1000 cycles - CS-10 wheel, 100 g load | 10–14 | 10–12 | 7–10 | 6–10 | 7–9 | 3–10 |
| coefficient of thermal expansion mm/°C | 8–10 | 10–15 | 11–14 | 12–15 | no data | 11–13[c] |
| electricial resistivity mΩ-cm | 75–110 | 40–70 | 15–45 | 10–30 | 5–20[d] | 40–90 |
| thermal conductivity Cal/cm/sec/°C | 0.010 | 0.012 | 0.016 | 0.015 | no data | no data |
| tensile strength MPa | 650–900 | 800–1000 | 350–600 | 200–400 | no data | 110 |
| deposit internal stress as plated (tensile or compressive) | neutral to comp | slightly tensile | slightly tensile | slightly comp | tensile | tensile |
| elongation % | 1–2.5 | 0.5–1 | 0.5–1 | 0.5–1.5 | no data | 0.2 |
| modulus of elasticity, GPa | 55–70 | 50–65 | 45–65 | 55–65 | no data | 120 |
| melting range °C | 880–900 | 880–980 | 1100–1300 | 1250–1360 | 1350–1390 | 1100–1140 |
| coercivity Oe | 0 | 1–8 | 10–15 | 15–80 | 10–70 | no data |
| magnetic properties as plated | non-magnetic | slightly magnetic to magnetic | magnetic | magnetic | magnetic | magnetic |

[a] Refs. 23,42,43,89,91–93.
[b] Deposit Knoop to Rc hardnesss conversion are at best an approximation due to many factors.
[c] Ref. 56.
[d] Ref. 11.

Table 3. **Properties and Phosphorus Trends**

| Nickel phosphorus deposit property | Property trend |
|---|---|
| hardness performance | deposits become harder with decreasing phosphorus content |
| wear performance | better wear resistance with decreasing phosphorus content |
| electrical resistivity | more resistance with increasing phosphorus content |
| melting point | higher melting point with decreasing phosphorus content |
| corrosion resistance | less corrosion resistance with decreasing phosphorus content |
| corrosion protection | all ranges of Ni-P provide substrate protection |
| deposit elongation | lowest in the low and mid phosphorus range |
| internal (intrinsic stress) | more compressive with increasing phosphorus content |
| magnetic tendency | less magnetic with increasing phosphorus content |
| solderability | improved with lower phosphorus deposits |

X-ray diffraction analysis (96). The lack of structure of high phosphorus deposits has been confirmed by using electron diffraction at 150,000 magnifications (97). Amorphous deposits are also referred to as being a metallic glass. When in this state, Duncan points out that this transition deposit is said to be primarily in a gamma phase, which tends to favor the amorphous characteristics (91). Phase diagrams for EN deposits help explain these transitions and transformations (98).

As deposited, Duncan shows that as the phosphorus levels decrease from this 11% point, the transition to a mixed crystalline beta and amorphous gamma phase occurs and results in changing properties.

Between 4.5% and 11% phosphorus, the coatings consist of a mixture of both crystalline and amorphous phases. Below 4.5% phosphorus, the deposit is primarily defined as being microcrystalline (91). A noncrystalline structure provides an important basis for the many significant properties offered by high phosphorus deposits.

As nickel phosphorus deposits are heated to temperatures above 220 to 260°C, structural changes begin to take place. First, the amorphous nature of the deposit begins to change. The deposit begins to crystallize as a result of distinct particles of nickel phosphide ($Ni_3P$) being formed through precipitation. At temperatures between 330 and 360°C, the crystallization process is more complete as the amorphous character is completely lost. The formation of $Ni_3P$ particles cause the deposit to shrink by 0.3% or more and can cause deposit cracking (99). The result, from the formation of these intermetallic nickel phosphide particles, is an increase in the coating's hardness, wear resistance and

brittleness while the corrosion resistance is dramatically reduced in most cases. When heat treatment occurs at higher temperatures (>250°C), a reducing atmosphere is recommended to keep the deposit from surface oxide formation with resulting discoloration.

*Ni-P Density.* The density of pure metallurgical nickel is 8.91 g/cm$^3$. As shown in Table 2, the densities of Ni-P alloys vary with the amount of phosphorus and are lower than for pure metallurgical nickel.

*Ni-P Adhesion.* The adhesion of EN to most types of substrates is excellent. For example, bond strengths of EN deposits to copper and mild steel alloys have been reported to be 200 to 400 MPa (100). Bond strengths on aluminum or light metal substrates have been reported to range from 60 to 250 MPa (100). This range results from the many variations in alloys and the options for surface treatment. Stainless steel alloys are more difficult to provide good adhesion. An electrolytic nickel strike is necessary to provide bond strengths in the range of 160 to 200 MPa (100). Baking is often used to improve the adhesion to most types of substrates.

*Baking EN Plated Parts.* Post baking processes (after plating) are recognized to assist with providing improved adhesion to the substrate. Additionally, prebaking alloy steel parts in many cases will provide a stress "relaxation" and is essential to maximize adhesion. Heat treatment of electroless nickel plated parts is used for different purposes, and can be divided into several categories depending upon the purpose, according to the temperature range. Hydrogen embrittlement relief is also an important function of baking. The obtained results are a function of temperature and time, so that both independent variables can be controlled according to circumstances. There are many sources of information for pre-baking and post baking parts for metal finishing. ASTM B849 and ASTM B850 documents are good references for baking and heat treatment for reducing the risk of hydrogen embrittlement (101,102).

Ferrous alloys over 38 Rockwell C in hardness benefit from a stress relief bake ranging from 95 to 200°C prior to plating to improve their deposit adhesion. It is important not to exceed the temperature at which the steel can become tempered. Therefore, it becomes important to know the physical characteristics and annealing properties of these alloys so that the adhesion-baking temperature can be maintained just under that which would cause a lowering of tensile strength (increasing the time accordingly). The usual baking time is one hour for a coating thickness of 25 microns or less and 4 hours for a thickness up to 125 microns.

Mechanical finishing or shot peening of these substrates is sometimes carried out before plating which has the effect to reduce the residual stress in the alloy. This step often assists to improve the adhesion of the EN to the substrate especially for alloy steels.

The embrittlement relief for hydrogen for many steel alloys (Alloy Steels) is a requirement often specified. Appreciable quantities of hydrogen are absorbed by the base metal primarily during the surface preparation acid activation. The effect of absorbed or dissolved hydrogen will seriously affect certain mechanical properties of the alloy. Hydrogen in excess of two parts per million, and especially in the range of ten parts per million, greatly reduces the tensile ductility of steel alloys (103).

The rate of evolution of absorbed hydrogen is primarily governed by the diffusion rate of the gas through the steel and the coating, and is a direct function of temperature, time and other variables. Many have studied hydrogen embrittlement topics as related to metal finishing (104).

Post baking at 185 to 200°C, (or higher, if justified by other requirements) for a minimum of 4 hours based upon the tensile strength of the material is generally sufficient to alleviate concerns. Some specifications call for much longer baking periods (up to 24 hours). It is always prescribed to follow the post baking recommendations of the substrate supplier.

*Ni-P Electrical Resistivity.*   The electrical resistivity of pure metallurgical nickel has a value of 6.05 mΩ-cm (97). Once EN deposits are heat treated, their electrical resistivity decreases as a result of the precipitation of $NiP_3$ (nickel phosphide). The resistivity of a 7% Phosphorus deposit heat treated to 600°C was reported to be reduced from 72 to 20 mΩ-cm (100).

*Ni-P Ferromagnetic Properties.*   Deposits with more than 10 wt% Phosphorus are non-magnetic as plated (97). Actually, the magnetic tendencies of Ni-P deposits depend upon whether they are crystalline or amorphous. Crystalline deposits are ferromagnetic, while those having an amorphous structure are considered essentially non-magnetic (105). For this reason high phosphorus alloys have been traditionally used as a base coating under the magnetic media layers on aluminum memory disks. If a nonmagnetic Ni-P coating has been heat treated at 275°C up to 320°C, the coating becomes weakly ferromagnetic because of crystallization occurring in the deposit. Ternary alloys with copper or tin have higher resistance to ferromagnetism temperatures, ranging up to 310°C for 1 hour (106).

*Ni-P Mechanical Properties.*   Electroless nickel coatings have high strength but limited ductility. The ultimate tensile strength varies with phosphorus content (91,107–109). For 1 to 5% by weight deposits, the tensile strength ranges from 175 to near 600 MPa. As the phosphorus content increases to 8% by weight P, the tensile strength range of 800 to 1100 MPa is achieved. Higher than 8% P deposits have reported tensile strength ranges of 700 to 900 MPa. Except for the 1 to 5% lower phosphorus deposits, these deposit values are equal to those for many hardened steel substrates. The ductility of high phosphorus EN deposits range between 1 and 2% while deposits with less than 2% P by weight have been reported to have elongation values above 2%. The elongation for the 3% to 9%P by weight deposits is typically less than 1%. Although EN deposits are less ductile than most engineering materials, they are adequate for most coating applications. Thin films (<6 microns) can be bent completely around themselves without fracture. The post plating heat treatment of EN deposits above 250°C reduces the strength and ductility by up to 50% as the deposit hardens by $Ni_3P$ precipitation while the deposit shrinks.

*Internal Stress.*   Electroplated or electroless deposits where a substantial thickness is formed have an important property in common. The macro-internal stress in either can determine whether the coating formed can fulfill its ultimate function. The total stress in the deposit is composed of thermal and intrinsic stresses. Thermal stress results from deposition that occurs at elevated temperatures when the coefficient of thermal expansion (CTE) is different for the substrate and the plated coating. As the plated piece cools, the materials

shrink at different rates and develop either a tensile or compressive force in the plated layer (110). An example would be Ni-P on aluminum where the CTE is greater for the aluminum and induces a compressive component to the total stress.

It is possible to alter the deposit stress in electroplated deposits to a greater extent than in electroless deposits since electroplating solutions are more static in their operation and are more readily influenced by organic additives. Electroless solutions for heavy coatings are dynamic in that the composition is constantly changing from the build up of reaction by-products that can have a strong negative influence on the intrinsic stress. When the total stress in the coating is greater than the adhesive strength on the substrate, the layer will blister and peel. If the total stress is tensile and exceeds the tensile strength of the coating, the deposit will spontaneously crack. Generally it is accepted that a low compressive stress is ideal since it improves the fatigue life of the substrate and is somewhat beneficial to adhesion. High tensile stress, on the other hand, will yield reduced fatigue life and poor corrosion resistance.

Tensile intrinsic stress is caused by distortions in the crystal lattice that result from extraneous ions or hydrogen in the film. In every case where hydrogen is present, the deposit from an electroless solution will shrink when it is heated. Sudden shrinkage typically causes cracking of the coating but slow annealing may actually cause diffusion of the plate into the substrate. Regardless, the stresses inevitably relieve themselves quickly or slowly. For this reason many plating specifications require a period of annealing shortly after the parts are plated.

Macro-stress measurements may be determined with more or less accuracy by using equipment specially designed for this task. A thin strip of copper or brass may be masked on one side such that the plated coating builds stress as it is plated. The strip will bow out away from the deposit if the stress is compressive or curl in on itself if the stress is tensile. To provide accurate determinations, a device developed by Brenner and Senderoff using a coated stainless steel helix is employed where the helix transmits the force through a set of gears to a pointer. The measurements are made under standard conditions and to a standard coating thickness (111).

The internal stress of electroless nickel deposits are related to the substrate being plated, the formulation of the EN and the resulting phosphorus in the deposit. Low and high phosphorus deposits are compressively stressed, due in part to their structural phases from compressively 30 MPa (91). Medium phosphorus coatings range in stress to 50 MPa tensile.

*Solderability.*   The ability to be soldered is the property of a surface which permits molten solder to readily wet that surface. Wetting takes place when a continuous film on the substrate allows molten solder to obtain a permanent, metallurgical bond to the substrate (112). The metals that will be joined dictate the conditions including the proper flux, time and solder temperature. Electroless deposits are solderable given they have minimal oxide formation on their surfaces and that the proper flux is utilized. Fluxes remove the oxides of the base metal while they prevent reoxidation at the surface to allow wetting to take place. Electroless Ni-P alloys, Ni-B alloys and gold deposits are known for their ability to be soldered. Although copper is a very solderable surface, heat

during package assembly can create heavy oxide layers making the copper substrate unsolderable (113). Unlike copper, electroless nickel coatings also dissolve very slowly in molten solder which results in less potential for joint brittleness. Common lead-frame materials such as Kovar and Alloy 42 form tenacious oxide layers which are difficult to be removed by fluxes. However, these types of materials can be plated with EN for use in glass to metal seals. Nickel Boron deposits have very good solderability characteristics. For Ni-P alloys, the lower the phosphorus, the better is the solderability (114). With proper activation and flux, most Ni-P deposits are solderable (115). Higher tin content in the solder improves the soldering of EN deposits. Post-plating heat treatments in air or an oxidizing atmosphere compared to a reducing atmosphere will reduce solderability. Shelf-life solder stability is also a potential issue of concern with electroless deposits. Plated materials should be stored in areas where temperature and humidity are low and constant. Packaging plated materials in sealed plastic bags with a desiccant and corrosion inhibiting media is recommended.

**6.2. Nickel-Boron Deposits.**    The typical properties for the deposits are summarized in Table 2 (116,117,123).

The boron content of deposits can vary from 0.1% up to 5% by weight as a function of the reducing agent. Structurally, unlike nickel phosphorous coatings in the as-deposited condition, electroless nickel boron deposits are comprised of crystalline nickel mixed with $Ni_2B$ glass, thus their coatings are not completely homogeneous and consist of phases of different composition (118). The structure of coatings containing between 2 and 5% boron are also a mixture of microcrystalline and amorphous phases (119). During post plating heat treatments, nickel boron deposits harden in the same manner as nickel phosphorus alloys, forming particles of nickel boride ($Ni_3B$)from temperatures of $250°C$ to $380°C$. The melting range for nickel boron deposits is similar to that for Ni-P alloys but higher for the eutectic at $1018°C$. Electrical resistivity for Ni-B deposits decrease with heat treatment.

**6.3. Electroless Copper.**    Electroless copper deposits have a different physical structure than electrolytic plated copper. Comparing to electrolytic plated copper, the density of electroless copper is 2 to 5% less. An acid copper electrolytic deposit has been shown to be 99.9% pure, with a density of 8.92 $g/cm^3$ and a 1.72 mΩ-cm resistivity at $20°C$ (120). The standard for electroless copper in printed wiring board applications calls for a minimum purity of 99.2%, a density of 8.8+/− 0.1 $g/cm^3$ and a maximum 1.90 mΩ-cm resistivity at $20°C$ (120). In printed circuit applications, adequate tensile strength and ductility are crucial properties needed to ensure film performance and reliability since these deposits are subjected to hot solder during the manufacturing process. Tensile strength values up to 490 MPa and deposit elongation values of up to 15% have been reported (121). Generally, the ductility of electroless copper deposits has been reported in the range of 4 to 7 percent elongation and tensile strength in the range of 200 to 550 MPa (122). In some tests, an as deposited electroless copper ductility of 2.1% was improved to 6.5% when annealed at $150°C$ for 24 hours (123).

**6.4. Composite Coatings.**    The wear characteristics of these specialty coatings approach that of the particle material that is co-deposited. The electroless deposit has a primary function to support the particles so many of these

deposit properties will be similar to the EN deposit. The utilization of very hard particles provide exceptional wear resistance in a variety of conditions. This fact is related to the particles protruding from the surface of the relatively softer EN deposit matrix. The result is protection of the Ni-P surface from excessive abrasion and wear. The particles utilized in these deposits range in size from 1 to 10 mm in diameter. In most applications they are co-deposited from 10 to 40% of the total volume for the coating. EN-PTFE deposits tend to have their particles more uniformly dispersed through out the deposit matrix because these chemistries rely less on gravity and solution agitation to occlude the particle in contrast to a hard particle inclusion. Deposit hardness is difficult to analyze because of the particles' interference on the test. The actual wear resistance is more crucial to the success of the composite and representative of the performance than the deposit hardness by itself. Composite coatings have limited corrosion protection due to extreme porosity of their deposits. Normally a duplex layer system with an initial layer of high phosphorus Ni-P followed by the composite layer is recommended to provide improved corrosion performance.

**6.5. Corrosion Protection.** Electroless nickel like electrodeposited nickel deposits are barrier coatings and are commonly referred to as cathodic coatings. Cathodic coatings protect substrates by a mechanism of encapsulation from the environment to which they are exposed. Once this barrier is penetrated, the protective value of the deposit is lost with the resulting development of corrosion to the substrate. As a contrast, the mechanism for anodic coatings, such as zinc plating over steel, provide protection to the substrate by sacrificially corroding relative to the substrate.

Aluminum substrates are especially susceptible to galvanic attack due to the high electro-potential difference. Corrosion of the aluminum will occur if the substrate is exposed to corrosive elements through any pores of nickel deposit. For this reason, especially high phosphorus deposits provide good protection to aluminum substrates.

The two inherent properties of nickel phosphorus deposits are their low porosity (corrosion protection) and resistance to chemical attack (corrosion resistance). High phosphorus deposits have less porosity compared to lower ranges of phosphorus. Despite this, all ranges of nickel phosphorus deposits provide some level of corrosion protection to substrates given that their porosity is minimal. In various test environments, the phosphorus content has been shown to have a significant effect on the coating's protective value. High phosphorus EN has shown to provide the greatest protection in the widest exposure situations because of the lowest porosity and the highest deposit passivity compared to other phosphorus deposits. The overall high corrosion protective nature for high phosphorus deposits is related to the amorphous deposit structure (124).

Many have studied the factors that influence porosity (125,126). Increased nickel thickness improves the corrosion protection of the deposit. For a given thickness, however, the degree of protection to the substrate is influenced by several variables. The key drivers to affect porosity include the formulation of the chemistry, the porosity of the substrate itself and the degree of surface roughness. The coating performance therefore is impacted by the variables of the surface preparation process (127). Because the presence or degree of porosity in the EN deposit will affect the corrosion performance, documents like ASTM

Table 4. **Corrosion Resistance of 12% w/w Ni-P Alloy in Various Media**[a]

| Medium exposure | Concentration wt. % | Temperature, °C | Corrosion resistance, mm/yr |
|---|---|---|---|
| chlorine, wet | 100 | 25 | < 12.5 |
| chlorine, dry gas | 100 | 25 | < 2.5 |
| exhaust gases | reducing | 260 | > 25 |
| exhaust gases | oxidizing | 540 | < 2.5 |
| carbon dioxide | 100 | 25 | < 12.5 |
| crude oil | 100 | 25 | < 2.5 |

[a] Ref. 129.

B733 provide a good source of information for EN deposits for minimum coating thickness requirements related to various service conditions (128).

**6.6. Corrosion Resistance.** Electroless nickel deposits provide corrosion protection due to their cathodic nature but their degree of corrosion resistance is determined by many factors including the environment to which they are exposed. The exposure temperature, concentration of media, whether wet or dry, whether an oxidizing or reducing environment impacts the performance. For this reason, it's good to use reference material as a guide. Actual exposure tests to the environments where the phosphorus EN will be used are more meaningful. Table 4 illustrates how similar environments with varying exposure conditions will impact the corrosion performance for a 12% nickel phosphorus deposit (129).

The chemical corrosion resistance data is well documented in many additional sources (41,43,130). Reference (45) contains exposure performance data for high phosphorus deposits in various corrosive environments. Since the chemical corrosion resistance actually refers to the resistance of attack by chemical reaction, there are many tests that can be utilized to evaluate Ni-P deposits. For example, the resistance of deposits to blackening in nitric acid is a common test used mostly in the electronics industry. The higher phosphorus deposit provides better resistance to nitric acid exposure compared to other EN deposits. High phosphorus alloys provide the best overall corrosion resistance in the widest variety of environments. Electrochemical corrosion testing provides indications of performance of Ni-P alloys compared to other materials. Some results are shown in Table 5 (131).

Corrosion performance of high phosphorus alloys can be best explained by the homogeneous-amorphous nature of these deposits resulting in low deposit porosity and the ability of these deposits to form passive films on their surfaces (132). These deposits form a film that mimics the characteristics of glass that helps passivate them against attack. Since amorphous deposits lack grain boundaries, there are limited sites for the initiation of corrosion. In severe corrosion service environments, duplex or double-layer EN coatings are used to further enhance the corrosion resistance.

Not all high phosphorus EN deposits perform alike in all corrosion environments. For example, the codeposition of impurities or tramp constituents that may be present in an electroless nickel bath are even more important to its corrosion resistance than its phosphorus content. Most nickel phosphorus solutions

Table 5. **Electrochemical Corrosion Comparisons Engineering Metals vs High Phosphorus EN**[a]

| Alloy | Corrosion rate (0.001 inches/year) vs conditions | |
|---|---|---|
| | < 1% NaCl, 200 ppm $H_2S$, saturated $CO_2$ | > 1% NaCl, saturated $CO_2$ |
| high phosphorus 12.8%P | 1.90 | 0.945 |
| high phosphorus 11.2%P | 2.80 | 1.5 |
| high phosphorus 10.4%P | 2.83 | 1.045 |
| 316 stainless steel | 1.95 | 1.27 |
| Nickel 200 | 1.97 | 3.69 |
| Hastelloy | 1.67 | 0.44 |
| 410 stainless steel | 5.58 | 4.47 |
| Inconel 600 | 4.77 | 1.91 |
| Monel | 5.2 | 3.29 |

[a] Ref. 131.

are stabilized with lead, tin, cadmium, molybdenum or sulfur bearing materials. The codeposition of these elements in more than trace amounts causes a severe reduction in the coating's passivity and corrosion resistance. This is illustrated in Table 6, which shows the results of corrosion tests with four different high phosphorus deposits in a $CO_2$ saturated, 3.5% salt brine at 95°C medium (44).

The potential for corrosion is very high in petroleum production facilities. This is a result of several types of corrosive media being present with further complications from the effects of temperature, pressure and velocity. The most common corrosive materials are salt water, carbon dioxide and hydrogen sulfide. The presence of oxygen and other acid mediums will further exacerbate the conditions. High phosphorus deposits have been used extensively in oil field environments to retard corrosion (133–136).

Table 7 relates the performance of high phosphorous EN deposits in chemical process environments compared to other commonly used materials for substrates (137).

An important consideration when discussing corrosion resistance is whether post plate heat treatment will be required. Heat treatment can be required to improve adhesion, reduce the risk of hydrogen embrittlement and

Table 6. **Effect of Composition on Corrosion Resistance of Electroless Nickel in $CO_2$ Saturated, 3.5% Salt Brine at 95°C**[a]

| Deposit | Phosphorus content, % w/w | Other elements (stabilizers), % w/w | Corrosion rate | |
|---|---|---|---|---|
| | | | mm/yr | in/yr |
| A | 10.2 | trace | 5 | 0.0002 |
| B | 11.8 | 0.04 Sn | 7 | 0.0003 |
| C | 10.3 | 0.12 Pb | 15 | 0.0006 |
| D | 10.4 | 0.05 Pb and 0.08 Cd | 11 | 0.0004 |

[a] Ref. 44.

Table 7. **Comparison of the Corrosion Rates of EN Coatings vs Materials in Chemical Process Environments**[a]

| Corrodent[b] | Corrosion rates mm/yr, 60 days exposure at $40° ± 2°C$[c] | | | |
|---|---|---|---|---|
| | Nickel 200 | Ni-P11%P | Mild steel | AISI 315 SS |
| thionyl chloride (FP) | 7.0 | 2.5 | 200.0 | 5.1 |
| orthochlorobenzyl chloride (crude) | 12.7 | 7.1 | na | 25.0 |
| orthochlorobenzyl acid (FP) | 12.7 | 9.4 | na | 2.5 |
| phosphorous acid (FP) | 10.0 | 19.3 | 1270.0 | 2.5 |
| phosphorous oxchloride (FP) | 10.0 | 2.5 | 100.0 | 18.8 |
| benzotrichloride (FP) | 5.1 | 6.1 | 9.0 | 5.1 |
| benzoyl chloride (FP) | 5.1 | 0.5 | 8.6 | 5.1 |
| seawater | 30 | 1.5 | 125 | 75 |
| sulfuryl chloride | 7.5 | 1.8 | 200 | |

[a] Ref. 137.
[b] FP = final product.
[c] na = no data available, product polymerizes when exposed to mild steel.

increase the microhardness and wear resistance of the deposit. Heat treatment processes are carried out at different temperatures under different atmospheres. A reducing atmosphere is recommended to keep the EN deposit from discoloring at higher temperatures ($>250°C$). When EN phosphorus deposits are heated above the $250°C$ threshold, the structural changes that occur within the deposit significantly reduce the corrosion resistance of the coating. The formation of $Ni_3P$ particles creates small corrosion cells that accelerate the corrosion. Heat treatment temperatures that propagate deposit hardening induce cracks due to shrinkage of the deposit. This cracking exposes the substrate to attack. However, not all heat treatments are bad. Studies have also shown improved corrosion resistance when heat-treating EN deposits at temperatures ranging from 600 to $700°C$ (138). Primarily, this improvement is seen from diffusion bonding into steel substrates and some improved integrity of the coating. Conventional heat treatment to maximize hardness negatively affects the resistance to corrosion in various media (45).

Except in a few cases, heat treatment steps at lower temperatures ranging from 150 to $200°C$ are typically referred to as baking. This has been shown to have little negative effect on corrosion resistance of the deposit. These baking temperatures are often utilized for hydrogen embrittlement relief and for improving the EN coating adhesion especially on copper alloy substrates and light metal substrates such as aluminum. Baking is primarily useful when the pretreatment has been inadequate and the adhesion is marginal. During the baking, some co-diffusion may occur between the deposit and the substrate. It is generally felt that any residual traces of soils remaining on the interface surface between the EN and the substrate may also be diffused.

**6.7. Microhardness.** As shown in Table 8, deposit microhardness varies with Ni-P and Ni-B alloy content and also heat treatment temperature (93). Average knoop microhardness for other engineering types of deposits compared to electroless nickel can be found in Ref. (139).

Table 8. **Average Microhardness Knoop (HK$_{100}$) Value for Electroless Deposits**[a]

| Nickel deposit alloy type | Average as deposited | Heat treatment temperature, °C | | | | |
|---|---|---|---|---|---|---|
| | | 250 | 300 | 350 | 400 | 450 |
| 0.14% boron | 593 | 618 | 609 | 531 | 519 | 475 |
| 2.0% boron | 783 | 1146 | 1101 | 1008 | 939 | 853 |
| 4.4% phosphorus | 765 | 810 | 836 | 982 | 957 | 857 |
| 9.1% phosphorus | 519 | 628 | 891 | 902 | 865 | 867 |
| 11.2% phosphorus | 525 | 567 | 890 | 910 | 916 | 854 |

[a] Ref. 93.

**6.8. Wear Resistance.** The resistance to friction and wear is often cited as one of the features and a primary reason to use electroless coatings in many applications. For nickel phosphorus alloys, wear resistance is primarily a function of the deposit hardness which is related to phosphorus alloy content. However, the deposit hardness and wear resistance are not always synonymous and some data can show that a softer coating can provide longer wear life. With metal to metal contact, the condition and hardness of the contacting surface must be taken into account especially when the deposit is heat treated. Parker's wear resistance work shows that for rotating parts such as plated shafts, the hardness should be higher than that of the mated surface because the deposit will withstand higher loads (138). Often replacing a softer deposit with a harder deposit in a wear scenario will result in more wear to occur on the mated surface. Adhesive wear test methods show this relationship the best. Because these types of deposits possess a natural lubricity, all EN coatings have excellent resistance to many types of wear.

It has been pointed out by many that a persistent problem in engineering wear testing procedures involves the correlation of lab bench testing to actual wear behavior in field service conditions (140). In many actual field wear situations the precise loads, temperatures, contact geometries and corrosive environments are difficult to know or predict. In many cases, more than one mode of wear may be operating and the contact conditions could change with time. However, the ultimate success or failure of any EN coating is best determined by testing the deposit in the specific application. The wear test data presented here and in other publications provide indications of the characteristics of EN plated deposits ideally in a comparative environment. There are many combinations and conditions that can be tested. Without direct correlations to a specific test, it may be difficult to accurately compare wear and friction data from different sources.

There have been four wear methods utilized to comparison test EN coatings. The most common being the Taber abrasion wear tester (abrasion wear), followed by the Falex wear tester (adhesive wear, pin and V block), the Alpha LFW-1 ring/block and cross cylinder test for determination of the adhesive wear and coefficients of friction.

The Taber abraser wear test is used to measure wear under conditions of dry abrasion and is described in ASTM B607 (141). It measures the weight

loss of a rotating plated specimen panel by two dressed rubber-bonded abrasive wheels, usually under a 1000-gram load. The wear of the specimen is reported as the Taber Wear Index (TWI) in average weight loss in milligrams per 1000 cycles.

The Falex wear test is described in ASTM D2670 (142) and has been used to measure adhesive wear under lubricated and non-lubricated conditions. Variations on this test type are the Alpha LFW-1 block on ring (143) and a crossed cylinder test (144) designed to provide both friction wear and adhesive wear data. In the crossed cylinder test, the resistance of deposits to metal-to-metal wear is produced. This helps to show the compatibility of different metal couples. In the block-on-ring tests, the resistance of a deposit to sliding wear is evaluated under different conditions. These two types are more complex test methods because they allow the ability to test the adhesive wear characteristics in numerous ways. The loads utilized for these tests can also be varied. The performance of the EN varies depending upon which scenario is utilized. Parker has tested all possible combinations; plated pins and blocks, plated pin with unplated block and unplated pin and plated block (145).

The abrasion wear resistance of electroless deposits in Table 9 is shown to be improved through post plating heat treatment process steps. Also, the incorporation of particles to create a co-deposit alloy, for example Ni-P-Silicon Carbide, shows improvement with the wear of the deposit. Many different deposit combinations are reviewed in Table 9 (93,146–148). Table 10 (93) shows adhesive wear data using the Falex wear test. Adhesive wear data for

Table 9. **Comparison of Taber Wear (Abrasive Wear) for Different Deposit Combinations**[a]

| Electroless deposit type | Average Taber wear index (TWI)[b] (mg loss) | |
|---|---|---|
| | No heat treatment | Heat treatment |
| 11.2% P EN | 24.5 | 14.2[c] |
| 9.1% P EN | 20.1 | 10.0[c] |
| 4.4% P EN | 8.6 | 7.1[d] |
| 0.2% boron | 8.0 | 7.5[d] |
| 2.0% boron | 22.3 | 12.7[d] |
| 5.0% boron | 9.0 | 3.0[e] |
| sulfamate nickel | 16.7 | 18.4[d] |
| *Co-deposits* | | |
| EN-18% PTFE | 5.8 | not tested |
| EN-28% PTFE | 4.5 | not tested |
| EN + aluminum oxide | 10 | 5[e] |
| EN + silicon carbide | 3 | 2[e] |
| EN + boron carbide | 2 | 1[e] |
| EN + diamonds | 2 | 2[e] |
| hard chromium | 3 | not tested |
| aluminum hardcoat | 2 | not tested |

[a] Refs. 93,146–148.
[b] TWI: Average weight loss in mg/1000 cycles with CS-10 wheel and 1000 gram load.
[c] Heat treatment 1 hour 400°C.
[d] Heat treatment 1 hour 350°C.
[e] Heat treatment 10 to 16 hours at 290°C.

Table 10. **Falex Wear Test Results (Adhesive Wear)**[a,b]

| Deposit type | Deposit condition | Total Weight Loss (mg) | |
| --- | --- | --- | --- |
| | | Plated steel (SAE 3135) pin | Unplated AISI 1137 steel blocks |
| 4.4% phosphorus | as deposited | 8.0 | 4.8 |
| | best hardness (350°C) | 3.4 | 1.6 |
| 9.1% phosphorus | as deposited | failed on break in | |
| | best hardness (350°C) | 0.3 | 0.1 |
| 11.2% phosphorus | as deposited | failed on break in | |
| | best hardness (400°C) | 0.6 | 0.7 |
| 2.0% boron | as deposited | 0.5 | 5.9 |
| | best hardness (300°C) | 0.3 | 8.3 |
| 0.2% boron | as deposited | 0.7 | 2.5[c] |
| | best hardness (300°C) | 6.6 | 9.7[c] |

[a] Ref. 93.
[b] Test conditions: 60 min at 90 kg, 40 min 180 kg, white mineral oil lubricant, 290 rpm.
[c] Failed at high load.

rotating pins in V-Blocks with various combinations of nickel phosphorus, Ni-P composite coatings, chromium, versus different types of steel can be found in Refs. 149–151.

Low values for coefficient of friction correspond to low rates of wear in most applications. As shown in Table 11, the coefficient of friction for EN composite alloys with occluded particles tend to be lower compared to particle-free Ni-P deposits (99,147,151–153). Friction wear values are also dependent upon the mating material (154–157). Table 12 represents coefficient of friction data with pin on plate (158).

Much of the data attempts to characterize how Ni-P deposits and variations compare to other EN deposits including hard chromium (49,159). For wear

Table 11. **Coefficient of Friction Data Various Combinations Electroless Deposits**[a,b]

| Coating on block | Coating on ring | Coefficient of friction |
| --- | --- | --- |
| EN 9%P | Cr steel | 0.6–0.7 |
| EN + PTFE | Cr steel | 0.2–0.3 |
| EN + PTFE | EN + PTFE | 0.1–0.2 |
| EN + PTFE, heat treat 4 h 400°C | Cr steel | 0.2–0.5 |
| EN + PTFE, heat treat 4 h 400°C | EN + PTFE | 0.1–0.7 |
| EN | none | 0.12–0.14 |
| EN heat treat 400°C/1 h | none | 0.12–0.16 |
| EN + $B_4C$ | none | 0.10–0.11 |
| EN + SiC | none | 0.12–0.13 |
| EN + WC | none | 0.13 |
| EN Teflon | none | 0.11–0.16 |

[a] Refs. 99,147,151–153.
[b] Friction coefficients calculated from friction forces measured on friction and wear machine consisting of a steel ring rotating at 72 rpm on a line contact against coated block.

Table 12. **Coefficient of Friction Pin on Plate**[a]

| Pin material | Plate material | Friction (sliding)[b] | Total Wear loss (TWI) (mg/1000 cycles)[c] |
|---|---|---|---|
| chrome | chrome | 0.47 | 6.72 |
| EN | chrome | 0.27 | no data |
| EN + aluminum oxide particles codeposit | EN + aluminum oxide particles codeposit | 0.32 | 0.14 |
| EN | EN | 0.36 | 0.74[d] |
| EN + SiC particles codeposit | EN + SiC particles codeposit | 0.46 | 0.10 |
| EN + PTFE particles codeposit | EN + PTFE codeposit | no data | 33.5 |
| 1018 Steel | EN | 0.39 | 4.40[e] |
| 1018 Steel | EN + SiC codeposit | 0.42 | 0.48 |
| 1018 Steel | chrome | 0.51 | 4.9 |
| 1018 Steel | 1018 Steel | 0.60 | 402 |

[a] Ref. 158.
[b] Derived from pin on plate, dry friction tests 70-kg load pin.
[c] Total weight loss for coated cylinder rotated 100 rpm under 33 kg load against stationary cross cylinder.
[d] Heat treatment 343°C.
[e] Heat treatment 650°C.

comparisons to hard chromium, Ni-P alloys require heat-treatment to their maximum microhardness values. In adhesive wear tests, the chromium plated pin survives with the least amount of weight loss, but when the mated surface is not plated, it is badly damaged. It is known that galling occurs when both the pins and blocks are plated with chromium. An advantage of lower phosphorus EN deposits is their similar wear characteristics in this test. Some data has shown that chromium deposits do not provide the best wear under some conditions, while the high phosphorus EN deposits perform better on the mated surface than the chromium deposit. Additionally, EN coatings tend to produce less damage to the mating surface than do hard chromium coatings.

## 7. Surface Preparation For Electroless Deposition

For the successful application of electroless deposition, the process cycle has a significant impact on the final quality of the deposit. Matching the substrate to the proper cycle insures success with any electroless application. Inadequate surface preparation can result in lack of adhesion, deposit roughness, excessive coating porosity and premature failure of the coating. The methods used to prepare surfaces for electroless deposits are similar to those used prior to conventional electroplating.

A North American survey of electroless nickel job shops conducted in 1993 was completed to estimate the types of metals being plated (160). It showed that, excluding coatings used for aluminum memory disks, steel and high alloy steel

made up 60% of the total substrates being processed. This was followed by non-disk aluminum applications at 17%, other miscellaneous metals including ceramics, plastics, magnesium, zinc die castings, and sintered metals at 15% and copper alloys at 7%. For steel, this percentage represents a reduction of one quarter from that reported in 1979 Although much of the EN market growth today is shown to be in areas where non-ferrous alloys are processed, steel and alloy steel continue to be important substrate staples for application of the technology.

ASTM Specifications can be a good source of information for finishing operations processing many types of alloys. Information on cycle strategies can be found within the ASTM B08 Committee. The ASTM Annual Book of Standards, Volume 02.05, "Metallic and Inorganic Coatings; Metal Powders, Sintered P/M Structural Parts" is a necessity for review regarding process cycle sequences. Process guides and specifications can be found for many types of substrates. The following ASTM B08 Specification documents are good references with regard to surface preparation many substrates B-322, cleaning various metals B-253, aluminum alloys B-281, copper alloys B-320, iron castings B-319, leaded alloys B-343, Nickel and Nickel Alloys B-254, stainless steels B-183, steels, low carbon B-242, steels, high carbon B-252, zinc alloys.

For ferrous steel, aluminum and plastic, the typical process sequence would include those steps as shown in Table 13. There can be many factors and variables that will modify this basic type of sequence process cycle for any type substrate. There are general guidelines that should be followed for any substrate alloy to realize success (127,161).

Substrate strategies for more common alloys plated with electroless deposition include the following.

**7.1. Common Alloys.**   *Ferrous Alloys: High Carbon Steels, Alloy Steels, Stainless Steels or Monels.*   The surfaces of tool quality steels must be prepared carefully to avoid over cleaning or under activation of the surface. Periodic reverse or direct electrocleaning is recommended to minimize the formation of

Table 13. **Typical Substrate Process Sequence**[a]

| Carbon steel | Aluminum | Plastic |
|---|---|---|
| preclean (optional) | preclean (optional) | preclean (optional) |
| soak clean | soak clean | predip |
| electroclean | etch | etch |
| acid pickle/activate | deoxidize/desmut | neutralize |
| electroclean | zincate | preactivate |
| predip or strike | zincate strip | activate |
| electroless | zincate | accelerate |
| post treatment (optional)[b] | predip or strike | electroless |
| | electroless | post treatment (optional)[b] |
| | post treatment (optional)[b] | |

[a] Water rinses required between process steps.
[b] Many options exist for postplating depending upon final application requirement.

passive oxide films on the surfaces. Electrolytic acid activation process steps and electrolytic nickel strikes are recommended to activate the surface of the work to maximize adhesion to alloy and stainless steels.

*Castings Including Steel, Aluminum and Zinc.*    Electroless plating of castings is difficult because of the inherent porosity in these types of materials. The method of casting and type of mechanical finishing will affect the porosity in the substrate. Plating of castings require special precautions during the cleaning and rinsing process steps. Weaker alkaline or acid surface preparation steps are recommended because casting surfaces tend to easily form smut. If not properly processed, cast alloys can experience premature corrosion failures and poor adhesion.

*Leaded alloys.*    Lead is added to many substrates to improve the machinability. Lead can cause a problem with the electroless nickel plating process so the surface preparation process needs to consider this interaction. Special acid activators and electrolytic strike chemistries help to overcome the potential problems associated with leaded alloys.

*Copper Alloys.*    Copper alloys will not catalytically initiate plating in electroless nickel phosphorus systems without an additional activation process after normal preparation. There are several options for catalyzing copper surfaces including: (*1*) Electrolytic nickel strike the surface; (*2*) electrolytic initiation of plating in the EN bath with a rectifier or electrochemical activation by touching work with a piece of steel or aluminum wire; (*3*) utilize DMAB reduced electroless nickel strike; and (*4*) catalyze the surface with a palladium solution.

*Aluminum Alloys.*    The surface preparation of aluminum is especially critical due to the rapid formation of oxides that occurs on the surface. The basic process cycle steps are similar to those used on other substrates without electrocleaning. All acid chemistries can be used or a combination of an alkaline-acid cycle is effective.

Deoxidization (smut removal) of the surface is necessary to improve adhesion. There are many types of deoxidizers and the proper selection depends on the aluminum alloy being processed. High silicon containing aluminum alloys require fluoride to adequately deoxidize the surface. A combination of nitric acid and fluoride salts is effective for deoxidizing most alloys. Chromated deoxidizers are not recommended on EN lines since chromium is a poison to EN solutions and can be the cause of adhesion problems.

The zinc immersion displacement commonly referred to as a zincate coating is applied after deoxidation to protect the surface of the aluminum from reoxidizing until it reaches the electroless plating solution. Some of the zincate coating is dissolved in the EN as deposition begins. Double zincate cycles are utilized to maximize deposit adhesion while minimizing the amount of zinc being dissolved in the electroless solution. Alkaline electroless nickel strikes are used prior to the acid EN type chemistries to minimize this zincate dissolution and extend EN solution life.

**7.2. Plastics.**    In addition to ferrous and aluminum alloys, plastics and other nonconductors are substrates commonly plated by electroless deposition, primarily to provide a conductive base for subsequent electroplating processes for both decorative and functional processes. Typical processes are alkaline formulations and deposit from 0.25 to 0.50 mm of thickness. Occasionally

electroless deposition is used over plastics by itself for applications that require wear resistance or shielding. In order to initiate electroless deposition on plastics, the surfaces must be etched and then catalyzed with activators based upon tin and palladium to provide palladium nucleation sites on the surface. A typical pretreatment sequence for plastics includes, degreasing/cleaning, etching, neutralization, catalyzation, acceleration followed by the electroless deposition (162).

**7.3. Electrolytic Strikes.** Strikes are employed prior to electroless deposition to improve the adhesion on many high strength, high carbon, and stainless or other nickel–chromium type alloys. They are necessary activators for these more difficult to plate substrates. Most common are strikes based on nickel formulations which include Woods' formulations, Watts' formulations, and sulfamate formulations. Copper cyanide formulations can also be used but are not favored primarily because copper is not catalytic in electroless nickel and additional activation steps are required. However, copper has been primarily utilized over zinc or magnesium die castings.

# 8. Environmental Concerns

**8.1. Waste Management.** Electroplating or electroless processes require a large number of wet process steps that will involve waste handling and/or treatment consideration. In addition to the plating chemistries, the process rinses require waste management to meet federal, state and local regulations. The solution life of most electrolytic plating baths is indefinite if the proper care is taken to maintain the chemistry balance and limit the introduction of contamination. Also, purification methods can be carried out to help maintain the life of these systems. As a result, the waste produced by most electrolytic processes comes from rinse waters and surface preparation processes. By contrast, electroless plating baths have a short life, are not purified in most cases and must be discarded after plating as little as 24 g/L and up to 60 g/L of metal. As a result, facilities with high production will generate high volumes of waste solution.

A spent electroless Ni-P bath typically contains from 4,000 to 5000 mg/L of nickel metal which must be reduced to less than 3 mg/L to meet many local regulations. In addition to the nickel or other metal ions, complexors, and sodium hypophosphite, the solution also contains large amounts of ammonium, sodium, sulfate, orthophosphite and trace amounts of metallic stabilizers, (eg, cadmium, lead and other metals) that must be regarded during the waste treatment process. More common methods of waste management for electroless solutions include the plate out of the metal, haul away of the spent solutions to recycle for reclaiming the metal, autocatalytic precipitation, ion exchange and combinations of these as well as other methods. There are many good industry resources to find technologies and strategies for waste treatment of spent electroless solutions (163–166).

In efforts to minimize waste, there are fundamental approaches to extend the useful life of electroless nickel baths. Since the formation of byproducts is the

major reason a bath has a limited life, limiting their formation or removing them adds to the useful life of the bath. Strategies include the following:

1. Reduce or eliminate the formation of reaction byproducts by changing the basic formulation of the plating chemistry. This is accomplished primarily through the utilization of alternative nickel sources, for example, nickel hypophosphite. Extended life formulations are being used successfully with benefits of reduced production down-time, reduced waste volumes as a result of less solution renewal, and up to three times longer operating life on many types of substrates including aluminum.

2. Develop methods to purify the used plating baths. One method is referred to as precipitation regeneration while the other is electrodialysis. For both, the primary objective is to remove the byproducts that form and eventually cause a change in the deposit properties and solution performance. The precipitation regeneration method selectively removes orthophosphite, having a minor effect on the hypophosphite and almost no effect on the nickel metal. When used in conjunction with extended life formulations, a solution life over 30 metal turnovers can be attainable. The necessary capital equipment investment is much less than for other regeneration equipment such as electrodialysis units. Despite the expense of the equipment, electrodialysis (ED) is a technology for purifying electroless nickel plating baths by using a semi-permeable membrane in conjunction with an electromotive force to selectively remove by microfiltration reaction byproducts from the plating bath. ED technology has several benefits, including the ability to extend the electroless solution life over hundreds of metal turnovers. More importantly, the technology creates a "steady state" condition where predictable deposit properties and plating rates are desired, and this is perhaps the best feature of the process. The use of ED does not eliminate waste generation but may change the characterization of waste to be considered less hazardous in some regions.

More detail information on these waste minimization technologies can be found in the literature (167–170).

Additional strategies for the management of electroless waste today include reformulation to make the solutions easier for treatment. Some of the modifications to avoid waste issues include the following: elimination of strong chelating agents like EDTA, avoiding the use of ammonium hydroxide for the manufacture of components and control of process pH regulation. Low metal EN formulations operating at 3 to 4 g/L of nickel versus the conventional 6 g/L will also help to minimize waste. There are likely other options commercially viable but these approaches are ones with commercial success today.

**8.2. Legislative Restrictions.**   As environmental and legislative pressures continue to evolve and impact the metal finishing industry, the implementation of new regulations will motivate those who supply and use these technologies to focus on improving their strategies to meet environmental compliance demands.

Newer regulations of concern today to the industry are the *End of Life Vehicle* (ELV) ELV Directive 2000/53/EC Annex II June 2002 and Waste

Electrical and Electronic Equipment (WEEE) WEEE Directive 2002/96/EC initiatives. ELV and WEEE directives seek to eliminate materials, chemistries or deposits that do not allow easy recycling in the automotive and electronics industries.

For electroless technologies these directives prohibit the deliberate addition of certain inorganic metals such as cadmium and lead into their chemistries which subsequently co-deposit. Lead and cadmium is added to electroless solutions to promote process solution stability, speed of deposition and deposit brightness. As a solution stabilizer, lead has been critically important. Cadmium acts as a brightener for EN deposits but there are now many commercial bright systems that are cadmium free.

For conventional formulations, many electroless concentrates can contain from 100 to 150 mg/L of lead and/or cadmium. Spent electroless solutions and process rinse waters also contain these materials and are subject to regulation. From an electroless process solution perspective, the lead and cadmium is co-deposited. As a result, up to 0.05% by weight lead and up to 0.1% by weight cadmium become part of the nickel and phosphorus alloy. Because these elements are intentionally added into the chemistry, they become restricted according to ELV directives and current regulations. More challenging for the industry as a whole is that lead and cadmium have traditionally been very effective stabilizers and brighteners for EN systems. Finding replacements that provide the same functionality is challenging. Over the next many years, the birth of these new categories of electroless systems will evolve to meet current and future demands.

Electroless deposited coatings offer an alternative to many types of electrolytic plating processes to meet stringent engineering demands for numerous applications.

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