ELECTROLESS NICKEL PLATING

A GUIDE

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WHAT IS ELECTROLESS NICKEL?

This guide is concerned with autocatalytic nickel plating, commonly referred to as electroless nickel plating. In contrast with electroplating, electroless nickel (EN) does not require rectifiers, electrical current or anodes. Deposition occurs in an aqueous solution containing metal ions, a reducing agent, complexing and buffering agents and stabilizers. Chemical reactions on the surface of the part being plated cause deposition of a nickel alloy.

Since all surfaces wetted by the electroless nickel solution have the same plating rate, the deposit thickness is quite uniform. This unique property of EN makes it possible to coat internal surfaces of pipes, valves and other parts. Such uniformity of deposit thickness is difficult, if not impossible, to achieve by any other metal finishing method.

The discovery of electroless plating is credited to Brenner & Riddell in the 1940’s. Today EN has grown into a very substantial segment of the metal products finishing industry.

Compared with plating of other metals, electroless nickel (EN) plating is relatively young-being commercially available for less than 50 years; however, in the past decade the usage of the coating has grown to such proportions that electroless nickel plated parts are found underground, in outer space, and in a myriad of areas in between.

BASIC CHEMICAL REACTIONS

The chemical reactions that occur when using sodium hypophosphite as the reducing agent in electroless nickel plating are as follows:

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + H_2$$

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

$$H_2PO_2^- + H+ \longrightarrow P + OH^- + H_2O$$

GENERAL OVERVIEW

An electroless nickel coating is a dense alloy of nickel and phosphorus. The amount of phosphorus codeposited can range from less than 2% to more than 12%, depending upon bath formulation, operating pH and bath age. The deposition process is auto-catalytic; i.e., once a primary layer of nickel has formed on the substrate, that layer and each subsequent layer becomes the catalyst that causes the above reaction to continue. Thus, very thick coatings can be applied, provided that the ingredients in the plating bath are replenished in an orderly manner. In general commercial practice, thickness range from 0.1 mil to 5 mils, but in some salvage operations 30 mil deposits are not uncommon.

Electroless nickel deposits are functional coatings and are rarely used for decorative purposes only. The primary criteria for using electroless nickel generally falls within the following categories:

1) Corrosion resistance.
2) Wear resistance.
3) Hardness.
4) Lubricity.
5) Solderability and bondability.
6) Uniformity of deposit regardless of geometries.
7) Nonmagnetic properties of high-phosphorus nickel alloy.

In the early years, platers encountered many problems with electroless nickel because of poor formulations, inferior equipment, misapplications and a general misunderstanding of the process and the deposit. In the first decade and a half of its existence, electroless nickel plating had an aura of “black magic” attached to it. Modern bath formulations, however, use only the purest grades of chemicals, delicately balanced and blended to give the processor plating baths with long life, exceptional stability, consistent plating rates, self-maintaining pH and most importantly, reproducible quality. In addition, advancements in tank design, filtration systems, heating and agitation have virtually eliminated the problems that plagued the user years ago.

Furthermore, in the past decade, advancements have been made in autocatalytic nickel plating solutions. Reducing agents other than sodium hypophosphite are used for special applications; composites of nickel with diamonds, silicon carbide and PTFE are available; and ternary alloys may be applied. Also, baths have been formulated to yield specific results, i.e., high corrosion resistance, brightness, high plating rate, improved ductility and low levels of magnetic response. Today, chemistries that utilize extended life strategies are becoming more common.

TYPES OF EN

All electroless nickel coatings are not the same. Different types have been developed to provide special properties, depending on the end-use requirement. Table I lists deposit characteristics and suggests suitable EN types or systems.

Nickel-phosphorous Baths

Acid nickel phosphorus: Deposits from these baths can be identified by phosphorus content, which, in turn, determines deposit properties. 2-5% = Low phosphorus; 6-9% = Mid phosphorus; 10-12% = High phosphorus. Low phosphorus deposits offer improved hardness and wear characteristics, higher temperature resistance, and increased corrosion resistance in alkaline environments. Mid phosphorus coatings are bright and aesthetically pleasing and have good hardness and wear resistance, along with moderate corrosion resistance. High phosphorus coatings provide very high corrosion resistance and a complete lack of magnetic response.

Alkaline nickel-phosphorus: These baths plate at a relatively low temperatures (75-140°F, 24-60°C), making them suitable for plating on plastics and other nonconductive materials or for use on zincated aluminum. In addition, because of the low phosphorus content deposited (3-4%), they offer enhanced solderability and bondability, especially in electronic applications.

Nickel-boron Baths

Low boron, nickel-boron coatings (less than 1%B), reduced with amine boranes, are most often used in electronic applications to provide high electrical conductivity, good solderability and good ultrasonic bonding characteristics. Deposits with higher levels of boron (2-3%) have high hardness values and better wear resistance than other coatings. In addition, the melting point of nickel-boron alloys is higher than that of nickel-phosphorus coatings. The chemical cost of amine borane reduced coatings is five to 10 times that of nickel-phosphorus deposits.

Sodium borohydride reduced nickel-boron plating solutions, deposit higher levels of boron (3-5%) than amine borane baths and are usually co-alloyed with thallium. These coatings provide exceptionally high hardness and wear resistance, usually equal to hard chromium.

Polyalloys

Several electroless nickel plating solutions produce deposits having three or four elements. These include nickel-cobalt-phosphorus; nickel-iron-phosphorus; nickel-tungsten-phosphorus; nickel-rhenium-phosphorus; nickel-molybdenum-boron; nickel-tungsten-boron; and others.

Each of the above is designed to maximize qualities such as corrosion resistance, hardness, high-temperature resistance, electrical properties and magnetic or non-magnetic characteristics.

Composite Coatings

The excellent wear resistance of electroless nickel can be further enhanced by co-depositing hard particulate matter with the nickel-phosphorus alloy. Usually, particles of silicon carbide (4,500 VHN) or synthetic diamonds (10,000 VHN) are used in this process. A uniform dispersion of particles (20 to 30 pct by volume) is held in place in the deposit by the nickel-phosphorus matrix. These deposits are very brittle and require a sound substrate to prevent cracking in use. Composites containing silicon carbide are most often used in mold and die applications. Those containing diamonds have found use in textile and cutting tool applications.

The code position of PTFE particles in an electroless nickel coating can significantly improve its lubricity and release properties. These coatings typically contain 15 to 25% (by volume) PTFE particles and can provide coefficients of friction nearly as low as solid Teflon ® or dry film lubricants.

Table I

Electroless Nickel Coating Most Suitable For Specific Deposit Characteristics

Characteristic Desired	Most Suitable Electroless Nickel Coating
Wear resistance	1. Composite coating with SiC or diamonds
	2. Nickel-boron, with 3 ½% or more B and 3 ½% or more Ti
	3. Nickel-phosphorus with 11% or more P, heat treated
	4. Nickel-phosphorus, with 3-5%P
Corrosion resistance	1. Nickel-phosphorus with 11% or more P
Hardness	1. Composite coatings with SiC or diamonds
	2. Nickel-boron, with 3 ½% or more B and 3 ½% or more Ti
	3. Nickel-phosphorus, with 10 ½% or more P, heat treated
	4. Nickel-phosphorus, with 3-5% P
Ductility	1. Nickel-phosphorus with 11% or more P
	2. Nickel-phosphorus, with 2% or less phosphorus
Lubricity	1. Composite coatings with Telflon®
	2. Nickel-phosphorus
Chemical resistance	1. Nickel-phosphorus, with 10% or more P

Solderability and bonding	1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
Non-magnetic response	1. Nickel-phosphorus, with 10% or more P
Electrical conductivity	1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
Electrical resistivity	1. Nickel-boron, with 1% or less boron 2. Nickel-phosphorus, with 2% or less phosphorus
Precious metal replacement	1. Nickel-boron, with 1% or less phosphorus 2. Nickel-phosphorus, with 2% or less phosphorus
High temperature resistance	1. Nickel-boron 2. Nickel-phosphorus
Brightness/pleasing appearance	1. Nickel-phosphorus, with 6-9% P, brightened

APPLICATIONS OF EN

Electroless nickel coatings have many unusual properties, which make them very useful in a broad range of functional applications. Most applications take advantage of the hardness, lubricity, corrosion resistance, electrical and magnetic properties of electroless nickel, as well as its ability to cover complex geometries and internal as well as external surfaces. Table II lists many of the common applications and indicates which properties of EN are of value in each of these applications.

TABLE II
ELECTROLESS NICKEL APPLICATIONS

APPLICATION	Base Metal	Deposit-Mils Approx.	Wear Resistance	Corrosion Resistance	Repair & Salvage	Fretting Resistance	Release Properties	Magnetism	Solderability	Base for Electroplating	Infinite Throw	Thickness Control	Uniform Coating	Electroless Forming
			REASON FOR USE											
AUTOMOTIVE														
Heat Sinks	Al	.4		X					X		X			
Pistons	Fe	.6	X	X										
Engine Bearings	Al		X	X										
Hose Couplings	Fe	.2	X											
Gears and Gear Assemblies	Fe	0.4–1.0										X	X	
AIRCRAFT														
Engine Overhaul	Fe	1.0+	X	X	X						X	X		
Struts	S/S	1.0–2.0			X							X		
Landing Gear	Fe	1.0+	X	X	X									
Hydraulics	Fe	1.0+												
Propellers	Fe	1.0+	X	X	X									
Hinges	Fe	.4	X							X				
Tape Guides	Al	.2	X											
Engine Mounts	4130 4140	1.0–2.0	X	X									X	
Turbine Parts	Fe	1.0–2.0											X	
Gyro Parts	Fe	0.5–1.0	X											
CHEMICAL EQUIPMENT														
Tanks	Steel and SS	2.0–5.0		X										
Pumps	Steel and SS	2.0–5.0	X	X										
Filters	Steel and SS	2.0–5.0	X	X										
Heat Exchangers	Steel and SS	2.0–5.0		X										
Spray Nozzles	Fe/Cu	0.3–1.0	X	X							X	X	X	
Tubing	Cu/Al Fe/SS	0.5–2.0	X	X							X	X	X	
RAILROAD														
Diesel Shafts	Fe	1.0+	X		X	X					X	X		
ELECTRICAL MOTORS														
Variable Speed Shafts	Fe	0.5+	X		X							X		
Rotor Blades, Starter Rings	Fe/Al	0.5–5.0	X	X										
PRINTING ROLLS	Fe/Cu	0.8–1.5	X	X									X	

TABLE II (Continued)
ELECTROLESS NICKEL APPLICATIONS

APPLICATION	Base Metal	Deposit-Mils Approx.	REASON FOR USE: Wear Resistance	Corrosion Resistance	Repair & Salvage	Fretting Resistance	Release Properties	Magnetism	Solderability	Base for Electroplating	Infinite Throw	Thickness Control	Uniform Coating	Electroless Forming
OIL WELLS & MINING														
Drills & Pipes	Fe	1.0+	X	X	X	X					X			
Oil Drilling Equipment	Fe/SS	2.0-3.0		X										
MOLDS														
Mold for ZDC	Fe	1.0-3.0	X	X	X		X				X	X		
Extrusion Dies	Fe	0.3-3.0	X	X	X		X				X	X		
MILITARY														
Fuse Assemblies	Fe	.5		X										
Mortar Detonators	Fe	.4		X							X	X		
Wave Guides	Al	0.3-1.5		X									X	
Mirrors	Al/Be	5.0-7.0										X	X	
VALVES (Gate)	Fe/Al	0.5-2.0	X	X							X	X	X	
VALVES (Ball)	Fe/Al	0.5-2.0	X	X							X	X	X	
VALVES (Plug)	Fe/Al	0.5-2.0	X	X							X	X	X	
TEXTILE														
Drop Wires	Fe	.01	X	X								X		
Spinnerettes	S/S		X	X	X		X				X	X		
ELECTRONICS														
Heat Sinks	Al	.4		X				X	X					
Memory Drums	Al	.1								X				
Terminals	Fe	.1						X	X	X	X			
Lead Wires	Fe	.1							X	X	X			
Chassis	Al	.5		X					X	X	X			
Transistors	Fe	.2		X						X	X	X		
Al High Frequency Signal Selectors	Al	0.5-1.5		X							X			
Form Complex Parts/Small Electrical	Al	1.0-4.0												X
Al & High Temp. Plastic and Other Electronic Junction	Al/Plastic	0.3-0.5	X	X					X					
P.C.	P.C. Boards	0.2-0.5						X	X					
MATERIAL HANDLING														
Hydraulic Shafts	Fe	1.0	X	X		X	X				X	X		
Hydraulic Cylinders	Fe	1.0	X	X		X	X				X	X		

PROPERTIES OF EN

It is the superior properties of electroless nickel coatings that caused the rapid expansion of its use. No other coating has the combination of properties offered by electroless nickel.

Corrosion Resistance and Corrosion Protection

One of the most common reasons for the use of electroless nickel coatings in functional applications is its excellent corrosion resistance. In the very corrosive conditions encountered in drilling and producing oil wells, for example, electroless nickel has shown its ability to withstand the combination of corrosive chemicals and abrasion.

The alloy content of the EN deposit influences its performance in most environments. Phosphorus alloys typically provide better protection than boron reduced coatings. In hot, highly alkaline solutions, low phosphorus deposits are more corrosion resistant than high phosphorus alloys. However, in most other chemical environments, high phosphorus alloys provide superior corrosion resistance.

Density

The density of EN coatings declines with increasing phosphorus content. An electroless nickel deposit containing 3 percent phosphorus has a density of 8.5 g/cm^3, while that of a deposit with 11 percent phosphorus has a density of 7.75 g/cm^3. These values are lower than those of pure metallurgical nickel (8.91 g/cm^3).

Coefficient of Thermal Expansion

The coefficient of thermal expansion of a deposit containing 8 to 9 percent phosphorus is about $13 \times 10^{-6}/^{\circ}C$. This compares to values for electrodeposited nickel of 14 to $17 \times 10^{-6}/^{\circ}C$.

Thermal Conductivity

The thermal conductivity of an electroless nickel deposit containing 8 to 9 percent phosphorus is 0.0105 to 0.0135 cal/cm/sec/°C. Electrodeposited nickel has a value of 0.19 to 0.26 cal/cm/sec/°C.

Melting Temperature

The final melting temperatures of electroless nickel deposits vary widely, depending upon the amount of phosphorus alloyed in the deposit. The initial melting point is about 1630 °F (890 °C) for all deposits. This temperature corresponds to the eutectic point for nickel phosphorus.

Magnetism

Electroless nickel deposits containing greater than 8 percent phosphorus are considered to be essentially nonmagnetic as plated. The coercivity of 8.6 percent and 7.0 percent phosphorus content deposits has been reported at 1.4 oersteds and 2.0 oersteds respectively. A 3.5 percent phosphorus content deposit produces a magnetic coating of 30 oersteds. When the phosphorus content is increased to 11 percent, the deposit is completely nonmagnetic.

Coating thickness measurements with devices that rely on the nonmagnetic characteristic of the coating become inaccurate if phosphorus content is below 9 percent.

Heat treatment of electroless nickel at temperatures over about 520 °F (270 °C) will increase the magnetism of the deposit. Even deposits that are completely non-magnetic as plated, will become highly magnetic when heat-treated above 625 °F (330 °C). At these temperatures amorphous solid solutions of phosphorus in nickel decompose to form nickel phosphide (Ni_3P) and magnetic nickel.

Electrical Resistivity

The electrical resistivity of EN deposits also varies with their phosphorus content. Pure metallurgical nickel has a value of 6.05 microohm-cm. Electroless nickel deposits containing 6 to 7 percent phosphorus have resistivities between about 52 to 68 microohm-cm. The resistivity of a deposit containing 2.2 percent phosphorus is 30 microohm-cm, while that of a deposit with 13 percent phosphorus is 110 microohm-cm.

Heat treating electroless nickel reduces its electrical resistivity. Beginning at about 520° F (270 °C), heat treating decreases electrical resistivity due to the precipitation of nickel phosphide in the coating. The resistivity of an electroless nickel deposit with 7 percent phosphorus, heat treated to 1100 °F (600 °C), was reduced from 72 to 20 microohm-cm.

Solderability/Weldability

Electroless nickel-phosphorus alloys are easily soldered with a highly active acid flux. Soldering without a flux or with mildly active fluxes can be more difficult if the parts are allowed to form oxides by extended exposure to the atmosphere. The heat processing of electroless nickel plated parts can make soldering very difficult unless a highly active acid flux is used.

Welding of electroless nickel deposits is not commonly done. The dissolution of phosphorus in the weld can produce low melting point compounds and “hot cracks” and disintegration of the weld.

Adhesion

Excellent adhesion of electroless nickel deposits can be achieved on a wide range of substrates, including steel, aluminum, copper and copper alloys. Typical bond strengths reported for electroless nickel on iron and copper alloys range from 50 to 60,000 psi (340 to 410 MPa). The bond strength on light metals, such as aluminum, tends to be lower, in the range of 15 to 35,000 psi (100 to 240 Mpa).

Low temperature, heat treatment is commonly employed to improve adhesion of EN on all metals, particularly on light metals such as aluminum or titanium. During this heat treatment diffusion can occur between the atoms of the coating and the substrate.

The surface preparation and activation is one of the most important factors for producing excellent adhesion.

Thickness

Electroless nickel can be deposited to produce a wide range of coating thicknesses, with uniformity and minimum variation from point to point. This uniformity can be maintained in plating both large and small parts and on components that are fairly complex, with recessed areas. Electroplating of such parts, on the other hand, would produce thickness variation and possible voids in the plating when coating holes and inside diameters. The range of thicknesses for electroless nickel in commercial applications is 0.1 to 5 mils (2.5 to 125 μm), although deposits as thick as 40 mils (1000 μm) have been reported. The typical plating rate of most baths is 0.3 to 0.8 mil/hr (7.5 to 20 μm/hr).

Brightness

The brightness and reflectivity of electroless nickel can vary significantly, depending on the specific formulation. The reflectivity of the deposit is also affected by the surface finish of the substrate. Thus, a very bright electroless deposit may appear dull if the substrate is rough.

The appearance of most electroless nickel coatings is similar to that of electrodeposited nickel.