PALM

Electroless Nickel: Alternative to Chromium Coatings

By Ronald N. Duncan

Electroless nickel is an alloy of nickel and phosphorus normally used for functional, rather than decorative, applications. As deposited, the coating is a metallic glass, containing about 10.5% P dissolved in nickel and less than 0.05% other impurities. Unlike chromium and other electroplates, electroless nickel coatings are completely amorphous — they have no crystal structure and contain no internal segregation or separate phases.

An example of this coating is the 75 μm (3 mil) thick deposit shown in Fig. 1. It is the lack of structure which produces its unusual properties and makes it well suited for protection against corrosion, erosion, and wear. Some of the properties of electroless nickel are compared with those of commercial hard chromium coatings in Table I.

Because of their high phosphorus content, purity, and homogeneity, the internal stress of electroless nickel deposits is very low on most substrates. On steel, the coating is typically compressively stressed at 4 MPa (500 psi). This helps to insure the deposit's integrity and the coating's performance.

The internal stress of commercial hard chromium coatings is always very highly tensile, and usually exceeds 200 MPa (30 000 psi). This, combined with chromium's brittleness, causes the coating to be cracked and often produces fissures through its thickness to the substrate.

A similar problem occurs with electroless nickel coatings containing less than 10% P. The internal stress level of low phosphorus deposits is also high. This also causes these deposits to be cracked and porous. A secondary problem with many coatings is that they contain large amounts of co-deposited contaminants, such as cadmium, sulfur, or phosphides, which further increase their stress and porosity. An example of one of these coatings is shown in Fig. 2. The discontinuities present in both chromium and low phosphorus, electroless nickel coatings reduce their strength, ductility, and wear and corrosion resistance.

***Gate for 1.2 m (48 in.) flow line gate valve was coated with 75 μm (3 mils) of electroless nickel for corrosion protection.* (Courtesy Schumacher Co., Houston)**

Coating is Uniform All Over the Part

Electroless nickel is applied without an electric current — by autocatalytic chemical reduction. It is plated onto a substrate by

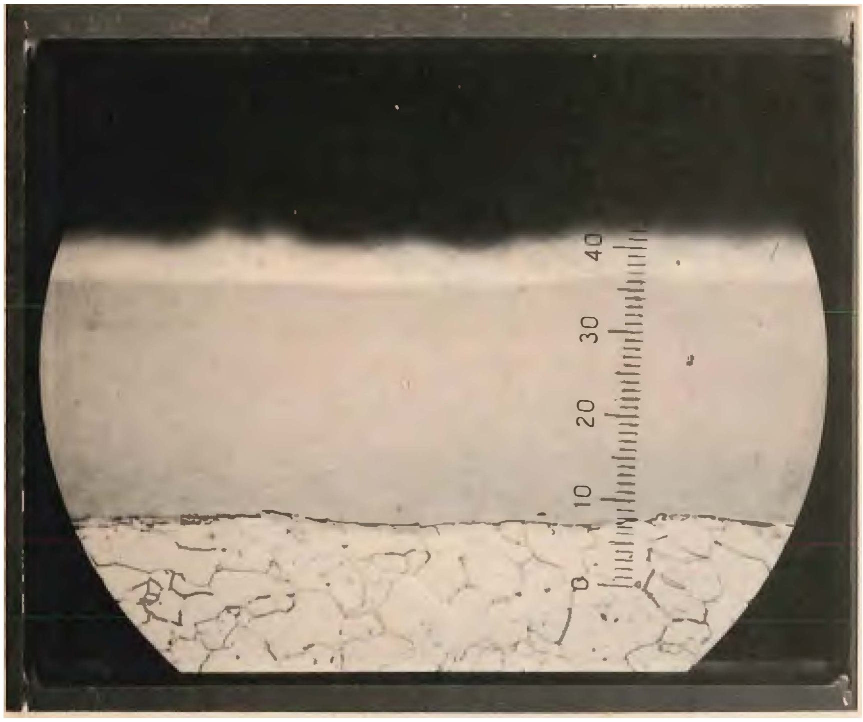

Fig. 1 — Amorphous gray area is a typical 10.5% P electroless nickel deposit on AISI 1010 steel substrate. Coating thickness is 75 μm (3 mils). Lighter layer on top is copper overplate applied to enhance edge resolution. Nital. 400X.

Fig. 2 — Typical low phosphorus (<10% P) electroless nickel deposit on AISI 4140 steel substrate. Coating thickness is 20 μm (0.8 mil). Cracks and pores are due to high stress level of deposit and co-deposited contaminants. Nital. 400X.

reducing nickel ions to metallic nickel with sodium hypophosphite. The chemical process avoids the nonuniformity associated with most other metallic coatings.

The thickness of electroplated coatings like chromium varies significantly, depending upon the part's configuration and proximity to the anodes. These coatings tend to build up on corners and edges, while the reverse is true on internal surfaces.

With electroless nickel, coating thickness is the same on any area of the part exposed to fresh plating solution. Grooves, slots, blind holes, and even the inside of tubing will have the same amount of coating as the outside surface.

The uniformity of an electroless nickel coating on the internal threads of a small spray nozzle is shown in Fig. 3.

Electroless nickel's uniformity is the reason for its substitution for chromium on many of the cylinders and rolls used in the printing and textile industries. This change has significantly reduced the finishing costs of these components. Previously they had to be ground, plated to a thickness of about 250 μm (10 mils), and ground a second time before they could be balanced and installed. Now they are ground only once, balanced, plated to the desired diameter — usually with 25 to 37 μm (1 to 1.5 mils) of coating — and installed. The cost of plating has been reduced by 40%, grinding time by 55%.

Coating thickness can be controlled to suit the application. Coatings as thin as 2.5 μm (0.1 mil) are commonly applied to electronic components, while those as thick as 75 μm (3 mils) are typical for chemical or petroleum equipment. Coatings thicker than 250 μm (10 mils) are also easily applied, but because of cost are normally used only for salvage or repair of worn or mismachined parts.

High in Strength, Low in Ductility

The mechanical and physical properties of electroless nickel resemble those of other glasses. It has high strength, limited ductility, and relatively low conductivity. Its ultimate tensile strength exceeds 700 MPa (100 000 psi), equal to that of many alloy steels, and five to ten times higher than that of chromium.

The coating can therefore withstand considerable abuse without damage. Accordingly, it is commonly used to protect compressor blades, turbines, valves, pumps, extruders, and blowers, and has often replaced stainless steel and exotic alloys. An example is the turbogenerator shaft shown in Fig. 4. Its bearing surfaces were coated with a 100 μm (4 mil) thick electroless nickel coating to protect them against the vibration produced during startup and shutdown.

The ductility of electroless nickel is only about 1 to 1.5%, which is adequate for most coating applications and much superior to that of chromium and lower phosphorus coatings. Thin films of the deposit can be bent completely upon themselves without fracture, and the coating

Fig. 3 — A 25 μm (1 mil) electroless nickel coating reproduces profile of internal threads on leaded steel part. Note nonuniformity of copper overplate. Picral. 100X.

Fig. 4 — Bearing surfaces of 8200 kg (18 000 lb) shaft for turbogenerator are coated with 100 μm (4 mils) of electroless nickel to protect against vibration produced during startup and shutdown of equipment. **(Courtesy Schumacher Co., Houston)**

has been used successfully for springs and bellows. Electroless nickel, however, should not be applied to articles which subsequently will be bent or drawn. Severe deformation will crack the deposit, reducing corrosion and abrasion resistance.

The electrical and thermal conductivity of electroless nickel is low. Its conductivity can be increased by heat treatment, but is still much less than that of conventional conductors like copper or silver. Because of the relatively thin layers used, however, for most applications this is not significant. For example, these coatings are being selected for such applications as heat exchanger tubing and electrical switches and contacts.

As deposited, electroless nickel is completely nonmagnetic. Its magnetic susceptibility is on the order of 10^{-4} at ambient temperature. Heat treatments at temperatures above 260 C (500 F), however, increase the deposit's susceptibility and can provide coercivities in excess of 150 oersteds (12 kA/m).

Electroless nickel can be easily soldered, brazed, and bonded. It is often used to ease joining of nonmetals and aluminum and stainless steel. This, combined with its uniformity and corrosion resistance, have made electroless nickel an ideal coating for electrical components. Accordingly, it is being increasingly used to reduce or eliminate gold and other precious metal requirements in the electronic and computer industries.[1]

Resistance to Wear Rated Excellent

One of the most important properties of electroless nickel for many industrial applications is its hardness and wear resistance. As-deposited coatings have a microhardness of 480 to 500 HV$_{100}$ (approximately 48 HRC). Heat treatments similar to age hardening procedures for aluminum alloys can provide significant increases in coating hard-

Table I – Properties of Electroless Nickel (10 to 11% P) and Hard Chromium Coatings

Property	Electroless Nickel	Hard Chromium
Internal stress on steel, MPa (10^3 psi)	<7 (<1)	200-300 (29-44)
Density, g/cm^3 (lb/in.^{3})	7.75 (0.28)	6.90-7.18 (0.25-0.26)
Melting point, C (F)	890 (1635)	1610 (2930)
Electrical resistivity, µΩ•m	0.90	0.14-0.66
Thermal conductivity, W/m•K	8	67
Tensile strength, MPa (10^3 psi)	>700 (>100)	<200 (<29)
Elongation, %	1-1.5	<<0.1
Modulus of elasticity, GPa (10^6 psi)	200 (29)	100-200 (15-29)
Coefficient of thermal expansion, 10^{-6}/C (10^{-6}/F)	12 (6.7)	6 (3.3)
Adhesion strength, MPa (10^3 psi)	300-400 (44-58)	Good
Hardness, HV$_{100}$	480-500[1]	800-1000
Coefficient of friction vs steel (lubricated)	0.13	0.16
Taber wear resistance, mg/1000 cycles	15-20[2]	2-3

1. As-deposited; coating is heat treatable to 1100 HV$_{100}$.
2. As-deposited; 2 to 9 after heat treatment.

Table II – Wear Resistance of Different Coatings

Coating	Heat Treatment	Taber Wear Index, mg/1000 cycles[1]
Watts nickel	None	25
Electroless nickel	None	17
Electroless nickel	300 C (570 F) for 1 h	10
Electroless nickel	500 C (930 F) for 1 h	6
Electroless nickel	650 C (1200 F) for 1 h	4
Hard chromium	None	2

1. Taber Wear Index (TWI) determined using Taber Abraser, CS-10 wheels, and 1000 g load. TWI is the average weight loss per 1000 cycles for total test of 6000 cycles.

ness. As shown in Fig. 5, values as high as 1100 HV_{100} (69 HRC) can be produced. This is equal to the hardness of commercial hard chromium and comparable to that of some hard facing alloys and ceramics.

Hardening of electroless nickel is due primarily to the formation of nickel phosphide particles within the alloy. At temperatures above 260 C (500 F) coherent and then distinct particles of Ni_3P begin to form, and at temperatures above 320 C (600 F) the glass begins to crystallize. This causes its hardness and wear resistance to increase rapidly. Maximum hardening is obtained through treatments at 400 C (750 F).

Both heat treated and non-heat treated coatings are commonly used to combat erosion, abrasion, and wear. Laboratory tests have shown fully hardened coatings to have wear resistance equal to that of hard chromium under both dry and lubricated conditions. The comparative performance of electroless nickel coatings, electroplated nickel, and chromium [2] in wear tests is indicated in Table II. The excellent wear resistance of electroless nickel often allows it to replace high alloy materials and hard chromium.

Example — An aluminum bowl with a 125μm (5 mil) thick electroless nickel coating was in service for two months (pelletizing polyethylene) with no measurable loss or attack. Previous uncoated bowls failed in less than three weeks after 40% of their weight was eroded away. Other typical wear applications include feed screws and extruders, computer drive mechanisms, textile and fiber equipment, hydraulic components, molds and dies, and packaging equipment.

Because of the phosphorus they contain, electroless nickel deposits have a low coefficient of friction, typically 0.13 (lubricated) to 0.4 (unlubricated). This is approximately 20% lower than that of chromium, one-half that of steel, and significantly better than that of aluminum or stainless steel.

Table III — Corrosion Rates of Chromium and Electroless Nickel Coatings

	Corrosion Rate, μm/year		
Environment[1]	Commercial Hard Chromium at 12 C (54 F)[2]	Cast Chromium Metal at 16 C (61 F)	Electroless Nickel at 20 C (68 F)[3]
Acetic Acid	nil	660	25
Citric acid	nil		19
Hydrochloric acid (conc)		100 000	46
Hydrofluoric acid	25 000		30
Lactic acid	nil		19
Malic acid	51		17
Nitric acid	nil		44
Nitric acid (conc)	nil		>25 000
Phosphoric acid	25	5	16
Sulfuric acid	280		12
Sulfuric acid (conc)	760		25
Sodium hydroxide	nil		nil
Ammonium chloride	nil		nil
Cupric chloride	380		25
Cupric nitrate	51		12
Ferric chloride	nil		780
Sodium chloride	nil		0.5

1. Concentrations are 10% unless otherwise noted.
2. Corrosion rates less than 25 μm/year reported as nil.
3. Ni-10.5P (<0.05% other elements).

Adhesion Strength and Corrosion Resistance

The adhesion of these coatings to steels and to aluminum, copper, and their alloys normally exceeds the shear strength of the substrate. High bond strength is due to the ability of the plating solution to completely remove microscopic contaminants from the substrate surface prior to the deposition of the first Ni-P layer. This allows the coating to develop both mechanical and metallic bonds.

The adhesion of electroless nickel coatings to steel and aluminum is typically 300 to 400 MPa (40 000 to 60 000 psi), superior to results usually obtained with chromium coatings.

One of the most important differences between electroless nickel and chromium coatings is their corrosion resistance.

Both are barrier coatings. Both protect the underlying metal by sealing it off from the environment rather than by sacrificial action.

But, because of the cracks present through even thick deposits, chromium coatings offer only limited protection. Cracks offer pathways through the coating for a corrosive environment to reach the substrate. Chromium coatings will often develop a network of rust spots across their surface. In addition, unlike electroless nickel, chromium coatings are subject to interface

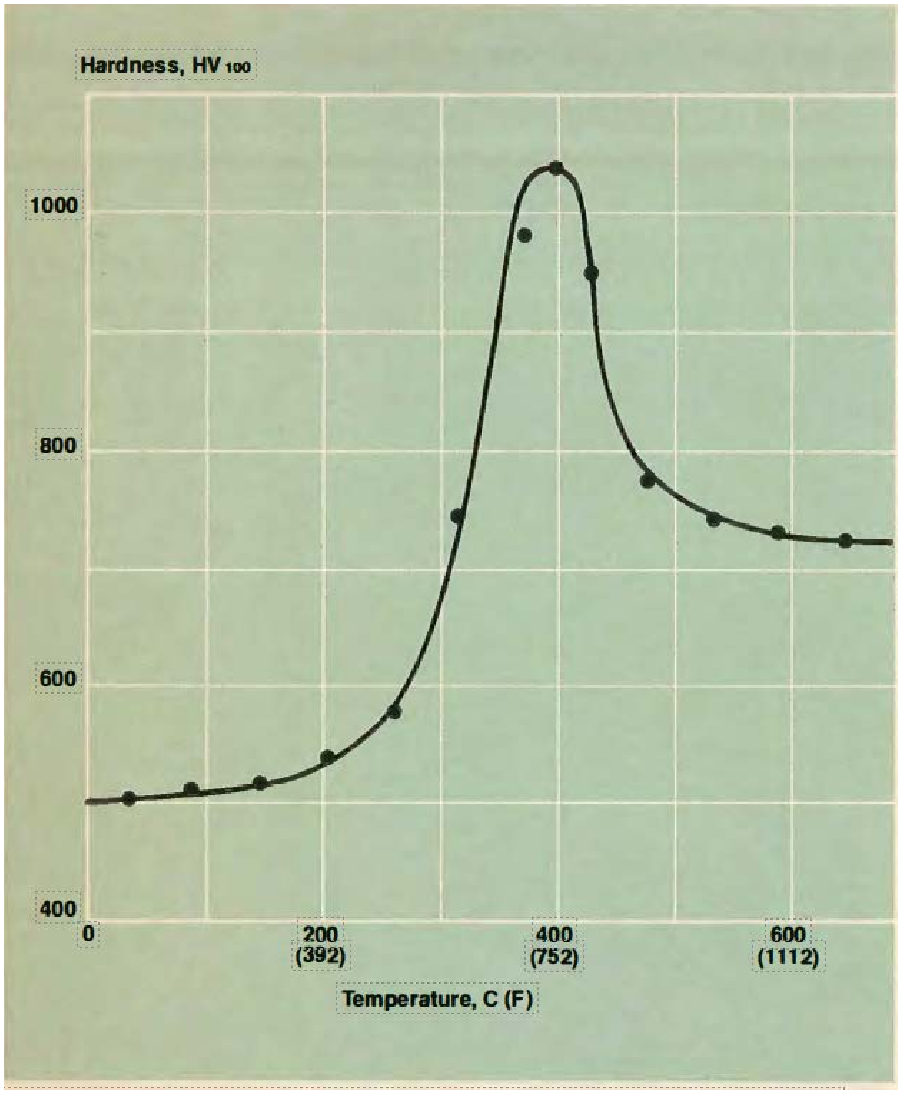

Fig. 5 — Effect of 1 h heat treatments on hardness of electroless nickel (10.5% P).

or underdeposit attack. With chromium, corrosion not only will extend into the substrate at the bottom of cracks or pores, but will also travel out from these areas along the coating-to-substrate interface, loosening and lifting the coating.[3]

Because of their homogeneity and freedom from defects, electroless nickel coatings provide a true barrier to corrosion. They do not offer any pathways to the substrate. The metallic bonds they form with the substrate also prevent underdeposit attack. Even if a pore were to be produced by improper processing or mechanical damage, in most environments it rapidly fills with corrosion product, stifling further attack. Corrosion will not spread out from the defect and thus it is contained.

The corrosion resistance of electroless nickel is similar to that of other high nickel alloys. Coatings are almost totally resistant to alkalis, like caustics and potash; to salt solutions and brines, like seawater or those present in food or chemical environments; to acid gas environments, like those found in the petroleum industry; and to all types of organic media and solvents.

The coating also has good resistance to ammonia solutions; to organic acids, like lactic or acetic; and to reducing acids, like hydrochloric or sulfuric. It is significantly attacked only by oxidizing solutions like oleum or nitric acid.[4]

In most environments, the corrosion resistance of hard chromium is much less than that of electroless nickel. Chromium is rapidly attacked by reducing environments and is subject to pitting and localized attack in halogens, especially oxidizing halogens like ferric chloride. The corrosion performances of electroless nickel and chromium in different environments are compared in Table III.[3-5]

The petroleum and chemical process industries are the largest users of electroless nickel coatings for corrosion protection. They are often used in place of more critical or expensive materials, especially stainless steel. For instance, oil field valves with 75 μm (3 mils) of coating cost approximately one-third that of equivalent stainless steel valves and in most environments provide equal protection.[6]

Many petroleum components now coated with electroless nickel were originally plated with hard chromium.[7] Specific applications include ball, gate, plug and check valves, blow out preventers, chokes, heat exchange equipment, pumps, compressors, tubing, vessels, packers, and all types of downhole equipment.[6] An example of one of these applications is the 1.2 m (48 in.) valve gate shown in the lead photo.

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Ronald N. Duncan

BIOGRAPHICAL SKETCH

In Memory of Ron Duncan

Ron Duncan served as Vice President of Palm International, Inc., where he led the company's technical and educational initiatives. Prior to joining Palm, he was Director of Research at Elnic, Inc., focusing on electroless nickel formulation and materials research.

Before entering the metal finishing industry, Ron spent 12 years in the oil sector with Exxon and Caltex Petroleum Corporations, tackling materials and corrosion challenges. His work took him across the globe—including the United States, Middle East, Europe, South America, and Africa—where he developed a reputation for his deep expertise and practical problem-solving.

Ron held a BE in Mechanical and Metallurgical Engineering from Vanderbilt University. He was a Registered Professional Engineer and a certified Corrosion Specialist through NACE. A leader in technical standards, he chaired NACE task groups T-1G-19 and T-6A-53, contributing to authoritative reports on electroless nickel and other metallic coatings. He also served on the AESF's Electroless Committee.

Throughout his distinguished career, Ron authored more than fifty technical papers on corrosion, coatings, and electroless nickel. His work appeared in Materials Performance, Plating and Surface Finishing, Metals Progress, Products Finishing, and Finishers Management, as well as in numerous industry conferences. He was the principal author of the electroless nickel chapter in Volume 5 of the Metals Handbook and was honored with the AESF Gold Medal in 1996 for the best paper published in Plating and Surface Finishing.

Ron also directed the Electroless Nickel School, a comprehensive four-day seminar presented by Palm, which educated professionals in all aspects of electroless nickel technology.

Ron Duncan passed away on December 15, 2006. He is deeply missed by his family, colleagues, and the broader surface finishing community. His legacy of innovation, mentorship, and integrity continues to inspire all who had the privilege of working with him.