WHAT IS ELECTROLESS NICKEL?

EN plating is a chemical process that involves several simultaneous reactions in an aqueous solution which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by the reducing agent (sodium hypophosphite), and oxidized thus producing a negative charge on the surface of the part. The charge causes a layer of nickel and phosphorus to form and this continues until the part is removed from the solution. Since the plating process requires no electrical current, the coating produced is very uniform and has a dense amorphorus structure that can be applied over various metals and substrates to provide corrosion and wear resistance.

One of problems with EN is its generic name. "Electroless Nickel" is the term used to describe the deposition of an alloy on a substrate, however, there are many different types of EN coatings and processes available to meet a wide range of unique applications. Physical and mechanical properties vary considerably from one EN process to another depending on the phosphorus content, the formulation of the bath and both the preplate and postplate treatments, yet all the EN coatings offer excellent deposit uniformity and superior corrosion protection.

FEATURES OF EN COATINGS

Corrosion resistance
Precise thickness control
Uniformity of deposit
Increased hardness
Abrasion resistance
Inherent lubricity
Anti-galling and fretting wear protection
Quick release properties
Non-magnetic properties
Conductivity
Solderability/Weldability/Brazeability

TCP

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UNIFORM COATING: Because it is an electroless process, the plating rate and coating thickness are the same on any section of the part exposed to fresh plating solution. Even on the most complex and irregular surfaces, close tolerances can be held without any additional machining or finishing. Unlike electroplating, no complicated fixturing or positioning of anodes is required. Shafts, rollers, gears, nuts and bolts, bearing journals, servo valves and oil nozzels all benefit from EN plating. See fig. 1 for the effects of plating on thread dimensions.

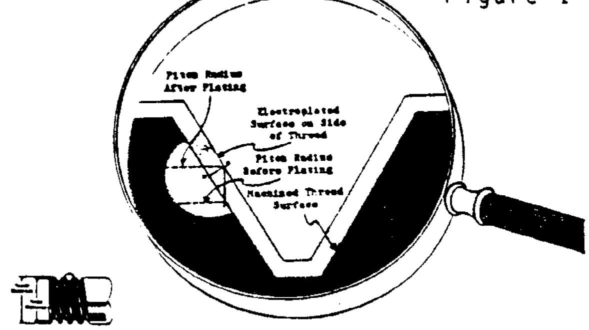
THICKNESS: EN can be accurately and uniformly deposited in a wide range of coating thicknesses. The majority of commercial applications utilize a thickness between 0.1 -1.0 mils while holding a tolerance of $\pm$.00005. Thicknesses of 1.0 - 3.0 mils are common for corrosive service, while deposit thicknesses above 3.0 mils are typical of repair and rework. Deposition of heavier coatings requires careful process control to avoid roughness and pitting.

CORROSION RESISTANCE: EN is a barrier coating, protecting the substrate by sealing it off from the environment, rather than using sacrificial action. EN is an amorphous alloy; it has no crystal or phase structure and is, therefore, more resistant to attack than equivalent polycrystalline materials. Incapsulation is the principal method of protection and corrosion control of the substrate. The EN plating solution generally penetrates into small voids and surface imperfections as well as on the surface providing excellent corrosion resistance that, in many environments, is superior to pure nickel or chromium alloys. The better the surface finish prior to coating the better the corrosion resistance. Coating thickness, substrate condition and surface preparation are important factors that determine both coating porosity and the ultimate resistance to corrosive attack. Fig. 2.

Figure 1

The Effect of Electroplating on Thread Dimension

Very often when specifying the plating thickness on screw threads, no allowance is made for the fact that the pitch diameter of an American Standard thread is increased by four times the thickness of the plating deposit, measured on the side of the thread at the pitch diameter. (The plating thickness is measured at right angle to the surface while the increase in pitch diameter is measured at an angle of 30° to the surface).



O = point on pitch radius before plating
P = same point as O after plating side of thread
NP = Thickness of plating deposit

$\angle NOP = 30^\circ$
$\sin 30^\circ = 0.5$
Assuming, NP = 0.001"
Then, $\sin \angle NOP = \frac{NP}{OP}$

$0.5 = \frac{0.001}{OP}$

$OP = \frac{0.001}{0.5} = 0.00$[illegible]"

Since OP, the increase in pitch radius, is shown to be double NP, the plating thickness, the increase in pitch diameter is four times the thickness of the plating deposit.

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HARD FINISH: EN coatings offer outstanding protection against wear and abrasion. Additional heat treatment of the EN coating causes the alloy to age harden and, under lubricated conditions, produce hardness values and wear resistance levels equal to most commercial hard chromium coatings. For some applications high temperature treatments cannot be tolerated because parts may warp, the strength of the substrate may be reduced or maximum corrosion protection may be effected. For these applications, longer times amd lower temperatures are used to obtain the desired hardness.

<u>HARDNESS OF EN - ROCKWELL C HARDNESS*</u>

Phos level	As Plated	Heat treated
1 - 3%	58 - 62	68 - 70
6 - 8%	46 - 50	65 - 68
10 -12%	44 - 48	65 - 67

* Approximate values based on Vickers hardness.

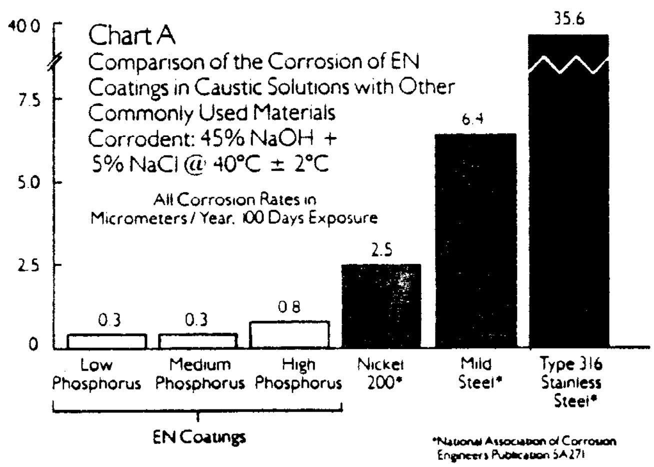


Fig. 2

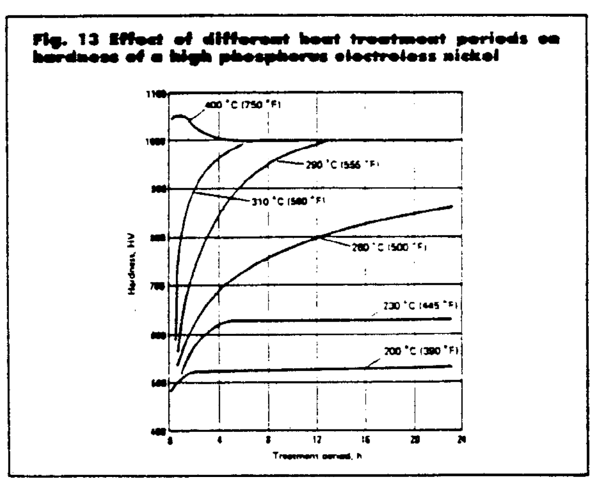


Fig. 13 Effect of different heat treatment periods on hardness of a high phosphorus electroless nickel

Fig. 3

WEAR RESISTANCE: Wear is the mechanical loss of material on a surface. There are many types of wear and nearly 200 specific wear tests, making for a complex evaluation of many applications. Wear can be combined into four categories which define most situations.

1. *Fretting Wear* is produced when the surface is mechanically deformed, causing material to be fractured and removed. Fretting wear generally occurs when there is small movement at high loads. An example of a fretting situation involved diesel valve spring retainers on locomotive engines. As the springs and valve stems moved, the retainer clips, made of hardened RC 35 steel, exhibited fretting, causing movement and wear debris on the valve stem. An EN coating of .0003" was applied and the retainers did not show any sign of fretting at overhaul.

2. *Adhesion Wear* is the most common in metal-to-metal wear situations. It is produced when microwelds cause the material interface to join, and the adhesive failure of the coating or wearing material occurs below the weld. Any metals of similar hardness will gall and eventually cold weld to each other. EN provides the lubricity and hardness at the interface to significantly reduce adhesion wear and improve the service of the plated article.

3. *Abrasion Wear* is the result of solids being cut from the surface. It is produced when paper, textiles, debris, etc. pass over the wearing surface and cut into the substrate, removing material. Again, the lubricity and hardness of EN reduces abrasion wear and improves the service of the substrate.

4. *Erosion Wear* is the most complex of the four. It involves the movement of liquids, solids, and gasses near or on the surface producing micro failure and abrasion. It eventually causes macro amounts of material to be removed. EN deposits have been used in several environments with good success. These include: alkalies, salts and brine solutions, petroleum, sweet and sour applications, solvents and hydrocarbons.

BRIGHTNESS: The brightness or reflectivity of EN varies significantly, depending upon the specific formulation, the presence of brightening agents, and the surface finish. An EN solution which is producing a bright deposit on smooth surfaces may provide a much duller deposit on a surface that is rough from machining, sand blasting, etching etc.

POROSITY: The porosity of EN varies with deposit type, thickness of plate, pretreatment, post-treatment and surface condition. EN baths with a high phos content are preferred for applications where minimal or no porosity is critical. Deposit thickness should be a min of .7 -1 mil on smooth surfaces - up to 50 RMS and 2-3 mils on rougher surfaces >100 RMS. Improper cleaning of the metal surface will increase coating porosity as well as produce poor adhesion. Heat treatment of EN deposits above 300 degrees C. will tend to create microcracking, significantly increasing coating porosity. Rough surfaces or coarsely machined or milled areas, produce sites where some porosity of the final plate may be unavoidable without the introduction of special processing techniques.

LUBRICITY: The phosphorus in EN coatings provides natural lubricity and release properties which can be very useful for applications such as plastic molding. The coefficient of friction for EN is 0.6 for unlubricated conditions and up to .13 for lubricated conditions. Heat treatment or the level of phosphorus does not significantly affect the frictional properties of the EN. EN/PTFE composite coatings *(PEN-TUF/EN)* greatly enhances the inherent lubricity of EN. Coefficient of friction values range from 0.17 in a dry condition to 0.07 in a lubricated conditon.

SOLDERABILITY/WELDABILITY: EN alloys are easily soldered with a highly active acid flux. Soldering to EN will not be consistent if the there is EN oxidation due to heat treatment, steam aging, improper handling, or long storage times prior to soldering. Successful welding to EN can be correlated to the substrate and type of EN. Lower carbon steels (1008-1018) provide a good basis for subsequent welding operations whereas substrates with high levels of phosphorus, carbon and sulfur tend to yield inconsistent and unsatisfactory results.

ELECTROLESS NICKEL COATINGS

PRE-TREATMENTS

Proper pretreatment can be as important to the successful application of EN as the actual deposit. Part design, manufacturing processes and surface contamination must be evaluated before determining the pretreatment required to produce a quality EN coating.

1. *Design:* The design of the part may require special handling and surface treatments. A very large part may require external, manual finishing. Parts with deep recesses or blind holes require special handling and draining techniques to avoid cross contamination during the plating process. They also determine whether a soak or electrolytic surface treatment should be used.

2. *Select Plating:* When plating must be applied to only certain areas of parts, the areas not to be plated must be stopped off or masked, which means they must be covered with a material that will not let the EN plating solution come in contact with the surface of the substrate. Masking materials must adhere well to the metal surface, withstand the temperatures of the plating solutions, be resistant to chemicals used for cleaning, etching and plating, and easy to remove after plating. A sharp, uniform demarcation between plated and nonplated areas is sometimes difficult to produce and a transition area is helpful to bridge the gap. Plugs, waxes and rubber coatings are some of the different masks available but they all require extensive hand operations that contribute significantly to the cost of plating. One of the alternatives to masking is to machine the coating off the desired surface or to drill and tap holes after plating.

3. *Substrate:* Different base metals require different treatments. An aluminum part cannot be processed through a typical steel cleaning cycle without damage to the part. Alloy types of the same base metal require different preparations prior to plating, for example a 1100 series aluminum part will be processed differently than a 380 cast aluminum part.

4. *Metallurgy:* EN is sensitive to the metallurgical state of the substrate. Localized strains and stresses caused by poor machining or other mechanical handling practices will alter the surface energy of the material. This in turn will cause localized differences in the electrochemical potentials of the substrate surface and result in an EN deposit with pits,

poor adhesion and low corrosion resistance.

5. *Surface Contamination:* It is often difficult to achieve 100% effectiveness in cleaning the surface of the substrate especially in recessed areas, deep blind holes, rough surfaces and coarsely machined areas because of contaminants on the surface. The contaminants can be divided into two basic categories:

   5.1. *Organic soils* - Mineral oils, animal fats and vegtable oils used as lubricants in manufacturing. Usually, little or no attention is paid to the type or formulation of lubricants used during forming, stamping, machining and similar processes. Yet, many of the lubricants are formulated with active chemicals to inhibit corrosion by adhering or chemically bonding to the substrate surface. In some cases, a pre-plate bake in a reducing atmosphere may be necessary to remove thes soils from the surface.

   5.2. *Inorganic films* - Rust, oxidation and scale from heat treatment operations. Heavily scaled parts or those that have been in service generally require mechanical or abrasive cleaning, especially on the ID of tubular parts. Chemical cleaning alone is not generally effective in removing scale or rust from the substrate.

STRESS RELIEF/ HYDROGEN EMBRITTLEMENT RELIEF: During processes such as EN plating, hydrogen can be absorbed into the metal substrate especially if the metal is a high strength steel. This penetration causes cracking and failure of the metal and is known as hydrogen embrittlement. To prevent hydrogen embrittlement, components are baked to diffuse the absorbed hydrogen out of the steel. This restores the mechanical properties of the steel almost completely, helping to ensure against failure. The time required to remove hydrogen from a steel depends on the strength of the steel. Longer periods or higher temperatures are needed as the strength of a steel increases.

Stress Relief Recommendations

Tensile strength of steel (mpa)	Recommended HT time in hrs 190-230 degrees C	Allowable Delay for embrittlement relief in hours
up to 1050	-	-
1051-1450	2	8
1451-1800	18	4
>1800	24	immediate.

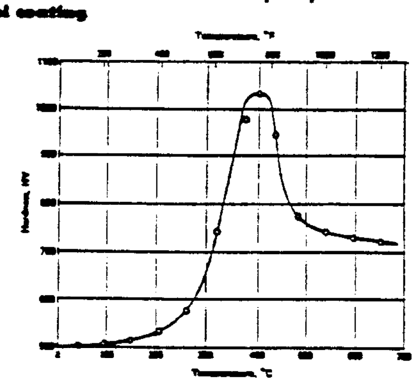
HEAT TREAT FOR HARDNESS: As plated, EN is one of the harder coatings available and its hardness may be increased by heat treatment. EN deposits have a maximum achievable hardness and once that level has been reached any further treatmennt will lower the hardness factor. Heat treating is generally done in an air circulating oven, but nickel oxides may form causing undesirable cosmetics or interference with subsequent soldering and bonding operations. An alternative would be to heat treat in an inert atmosphere to avoid this type of oxide formation. Polishing should be done prior to heat treatment when the deposit is softer. Improved corrosion resistance as a result of heat treatment is only partially true. Corrosion resistance improves up to a certain temperature because of oxide formation; once that temperature is exceeded crazing in the coating occurs and avenues for substrate corrosion are opened.

EFFECTS OF HEAT TREATMENT: As EN deposits are heated to temperatures above 430 degrees F, nickel phosphide particles begin to form, reducing the phosphorus content of the remaining material. This reduces the corrosion resistance of the coating. The particles also create small active/passive corrosion cells, further contributing to the destruction of the deposit. The deposit shrinks as it hardens, which can crack the coating and expose the substrate to attack. Baking treatments used for hydrogen embrittlement relief, cause no significant increase in corrosion. Hardening however, has caused the corrosion rate of the deposit to increase from 0.6 mil/yr to more than 35 mils/yr. Where maximum corrosion resistance is required, hardened coatings should not be used.

Table 5 The effect of heat treatment on the corrosion of a 10½% phosphorus electroless nickel in 10% hydrochloric acid

Heat treatment	Deposit hardness, HV_{100}	Corrosion rate	
		μm/yr	mil/yr
None	480	15	0.6
190 °C (375 °F) for 1½ h	500	20	0.8
290 °C (550 °F) for 6 h	900	1900	75
290 °C (550 °F) for 10 h	970	1400	55
340 °C (650 °F) for 4 h	970	900	35
400 °C (750 °F) for 1 h	1050	1200	47

Fig. 12 Effect of heat treatment at different temperatures on the hardness of 10½% phosphorus electroless nickel coating



SUMMARY OF ELECTROLESS NICKEL DEPOSIT PROPERTIES

	LOW	MID	HIGH
Composition			
Nickel	98%	92%	88%
Phosphorus	2%	8%	11%
trace	.02%	.05%	.5%
Elongation %	.1%	0.1 - 0.4%	0.5 - 1.5%
Density g/cm3	8.28	8.12 - 7.95	7.85
Thermal Expansion (10-6 m/m/C)	9	9 - 13	14
Resistivity microohm-cm	20 - 30	40 -70	120
Magnetic	30 oersteads	1.4 oersteads	0.2 oersteads
Tensil Strength	40 Kp/mm2	70 Kp/mm2	as plated
	80 Kp/mm2	25 Kp/mm2	2 hr 750C
Elasticity	1.2 to 2 x 10^-4 Kp/mm2		
Internal Stress	-3 to +30 MPa		
Melting Point			881 (C)
Hardness			
Vickers 100 gram load			
As plated	550 - 700	500 - 550	450 - 500
200 (C)	600 - 800	550 - 650	550 - 600
400 (C)	750 -1000	900 -1000	900 - 950
600 (C)	900 -1000	800 - 850	850 - 900
Taber Abrader Index			
Resistance			
mg/1000 cyc			
As Plated	12 - 16	18 - 28	20 - 25
400 (C)	8 - 12	12 - 16	12 - 18

Electroless Nickel vs Other Materials

Stainless Steel: The use on EN plating on carbon steel or cast-iron has key advantages when compared to stainless steel and other non-ferrous alloys.

* Lower cost.
* Ease of machining. Reduction of welding and fabrication problems because parts are plated after fabrication.
* Improved corrosion performance in many environments especially resistance to chloride attack.

Plastic Coatings: EN deposits offer advantages over phenolic or epoxy-type plastic coatings.

* EN will function over a broad temperature range.
* Better adhesion due to the metallurgical bond formed between the metals.
* Coating uniformity especially in recesses and on complex shapes.
* Electrical conductivity.
* Superior abrasion, wear resistance and durability. No cracking or tearing in threaded areas and better resistance to wire line damage.

Hard Chrome: EN coatings have several important advantages when compared to hard chromium.

* Coating uniformity holds critical tolerances even on complex geometries without subsequent machining.
* Superior corrosion resistance and lack of porosity. Hard chrome plating has a micro-cracked structure that is very porous and more susceptible to corrosion.
* Inherent lubricity offers galling resistance when mated against itself or stainless steel. Hard chromium tends to gall in these instances.
* Better total wear properties in many applications. The hardest part will not always provide the best wear.
* Increased pressure on chrome waste is causing corporate liability concerns about future compliance and cost of compliance.

WHY USE DIFFERENT EN FORMULATIONS?

The right nickel coating can eliminate the need for expensive high-alloy materials in corrosive environments, prolong the life of wear components by factors of four or more, improve release properties of molds, or improve the appearance of metal components.

Types of EN coatings include nickel-phosphorus, nickel-boron, poly alloys, and composite coatings. The variety of coatings available within these categories allows the design engineer to optimize an important property while retaining a good balance of all the properties common to EN.

Low Phos 1-4%

* Best for solderability.
* Magnetic.
* Corrosion resistance best in alkaline environments, poor in acidic environments.

Mid Phos 5-8%

* Faster deposition rate means lower costs.
* Generally suited for mild corrosive environments.
* Slightly magnetic.

High Phos 9-12%

* Corrosion resistence best in acid environments, fair to excellent in alkaline environments.
* Non-magnetic.
* Slow deposition rate results in higher cost.

Nickel boron

* Offers higher hardness and better solderability than conventional EN but has high tensile stresses that impair durability.
* Still very much in the developmental stages and under further evaluation.

Poly Alloys

* Copper-nickel-phosphorus poly alloys, offer the potential for better corrosion resistance, but currently are not durable enough for commercial use.
* This coating is also still under development and futher evaluation.

Composite Coatings

* Silicon carbide particles incorporated in the deposit for enhanced abrasion/erosion resistance. Used in such applications as barrel tubes at bottoms of oil wells, where sand in the incoming slurry causes rapid abrasive wear. Also suitable for farm implements, machinery parts, sawblade tips, etc.
* PTFE particles are uniformly dispersed throughout the coating to offer reduced friction, improved lubricity and wear, and non-stick and anti-fouling properties. EN/PTFE coatings, such as *PEN-TUF/EN* are gaining widespread use in numerous applications such as mold plates and ejector pins for plastic injection molding, threaded parts for robotics, computer and other hardware applications, cylinders and rollers, and various parts for the printing, automotive and food industry.

TRY "PEN-TUF/EN"

FRONT RANGE PLATING'S ANSWER TO PTFE COMPOSITES

REFERENCES

1. ASM Metals Handbook 9th Edition, Volume 5 Surface Cleaning, Finishing, and Coating, 1982

2. Clayton J. Graham, Hardness and Wear Implications with Respect to Electroless Nickel, 1980.

3. Neal Smith, Electroless Nickel Post Treatments, 1980.

4. Frank Beer, The Importance of the Metallurgical State and Surface Condition, 1980.

5. Tom Bleeks and Gary Shawhan, New Electroless Nickel Technology as an Alternative to Hard Chromium Plating, Metal Finishing October 1989.

6. Ronald N. Duncan, The Effect of Heat Treatment Upon the Hardness and Abrasion Resistance of EN Coatings, Metal Finishing March 1990.

7. Robert A. Jeanmenne, EN for Hard Chromium, Products Finishing January 1990.

8. Diane M. Tramontana, Electroless Nickel News, Spring 1989.

9. Enthone Inc., Enplate Electroless Nickel for Oil/Gas and Chemical Processing Industry Applications, 1987.

10. Dr. Oscar E. Roberto, Electroless Nickel/PTFE Composite Coatings, Products Finishing April 1989.

11. Enthone Inc., The Nuts and Bolts of Electroless Nickel Plating, 1988.

12. Robert P. Tracy Using Electroless Nickel Coatings, Materials Engineering November 1989.

13. Stapleton Company, Electroless Nickel State of the Science, July 1985.