Electroless Nickel Overview

Minnesota Chapter
MNAMF
National Association for Surface Finishing

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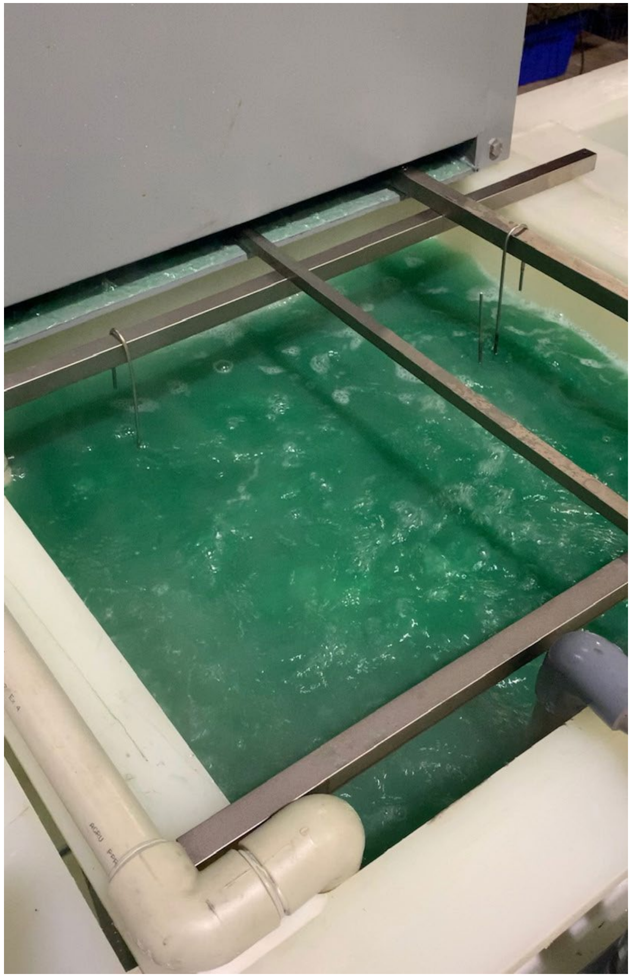
Minnesota Association of Metal Finishers
Training Seminar

MetalChem, inc.

What is Electroless Nickel?



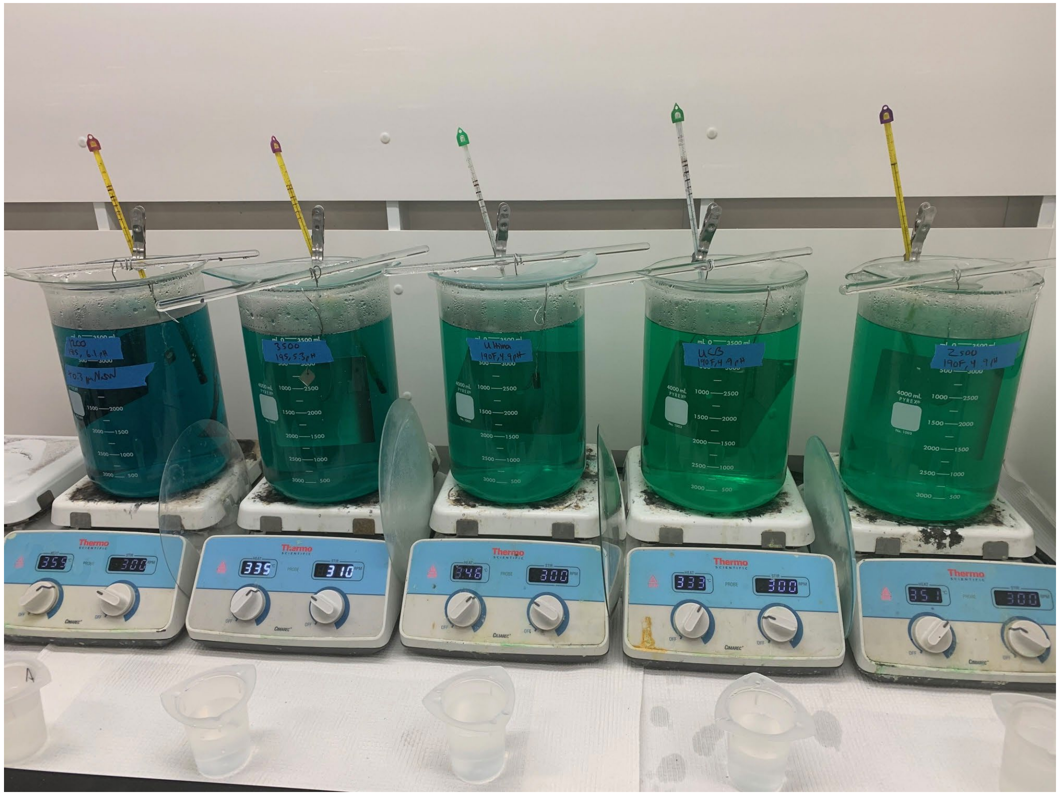
1. Plated Deposit of Nickel and Phosphorous
2. Primary Advantages
   A. Corrosion Protection (Barrier Mechanism opposed to Sacrificial)
   B. Mechanical Properties: Improved Wear and Hardness
3. Can Be Applied to a Multitude of Base Materials

Contents

The Science of Electroless Nickel

Bath Composition

- Nickel Ions
- Hypophosphite Ions
- Chelators
- Stabilizers
- Buffers
- pH Regulators
- Wetters



The Science of Electroless Nickel

Nickel Ions

The source of metal to be deposited onto the substrate by reduction. Typically provided by: Nickel Sulfate, Nickel Chloride, or Nickel Acetate.

Hypophosphite Ions

Hypophosphite is the reducing agent required to facilitate the electroless mechanism. Hypo supplies the phosphorous incorporated into the deposit and becomes the by-product orthophosphite.

Oxidation Reduction Reaction

I $$Ni^{+2} + H_2PO_2^- + H_2O \xrightarrow{cat.} Ni + H_2PO_3^- + 2H^+$$

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

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

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Figure 2.1
Electrolytic Plating

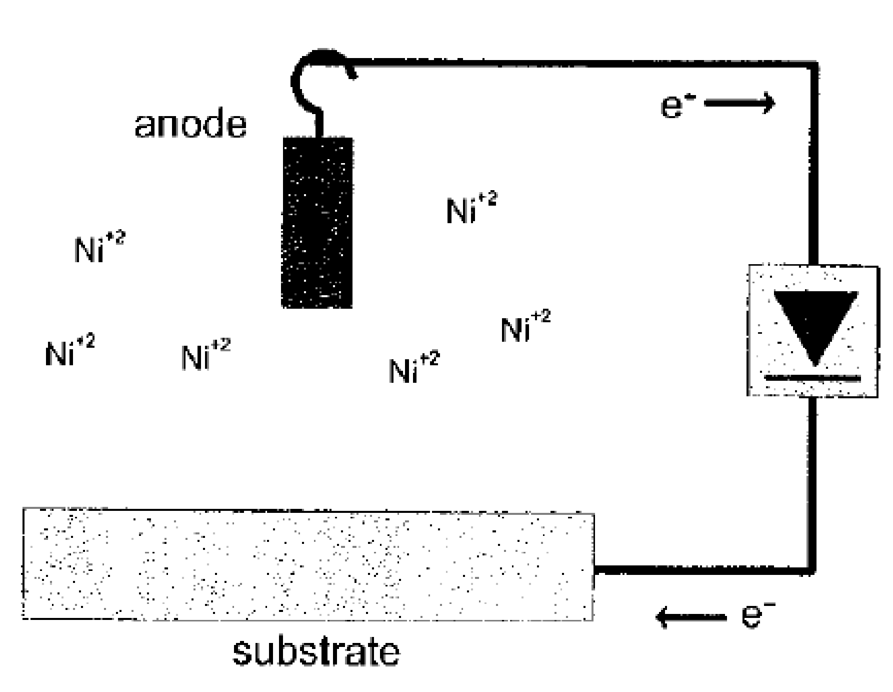

Figure 2.2
Electrolytic Plating

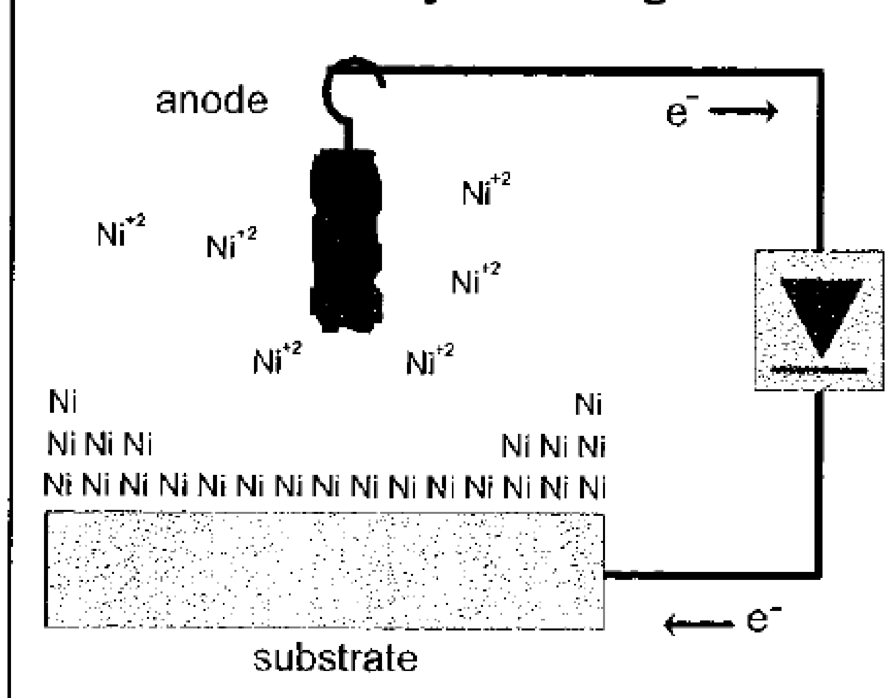

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Figure 2.5
Electroless Plating

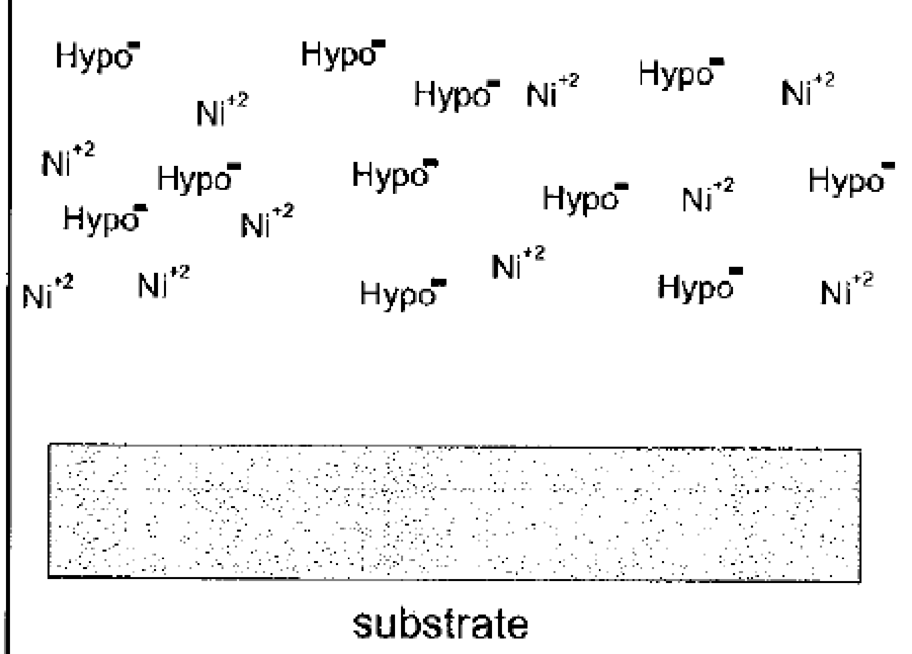
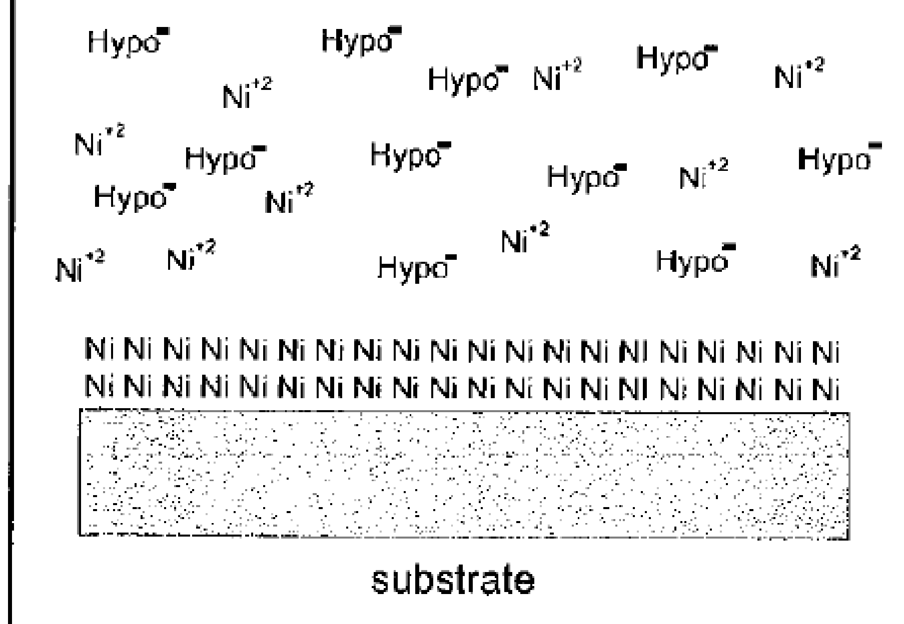


Figure 2.6
Electroless Plating



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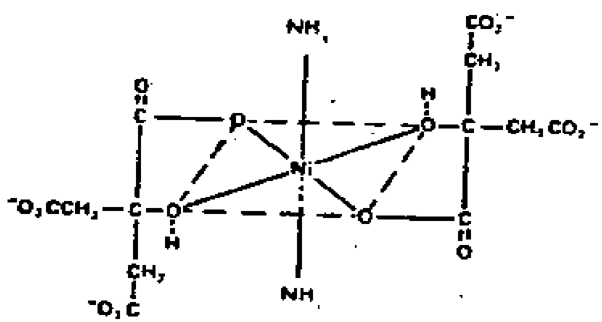
Chelators

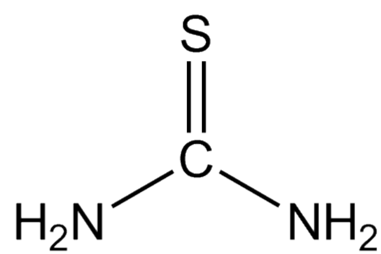
Chelators are organic compounds that form complexes with the nickel ions. The strength of various chelators controls the plating rate and % phosphorous. They also prevent nickel phosphite (white-out).

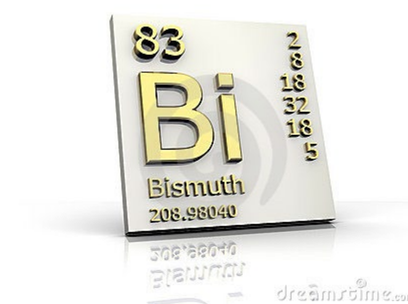


Citrate Complex

Stabilizers

Stabilizers make up the smallest part of the EN bath, usually a few ppm or less, but play a significant role. Examples: heavy metals ($Pb^{2+}$and Bi^{2+}) and organic sulfur compounds. Stabilizers prevent the bath from plating out or decomposing.





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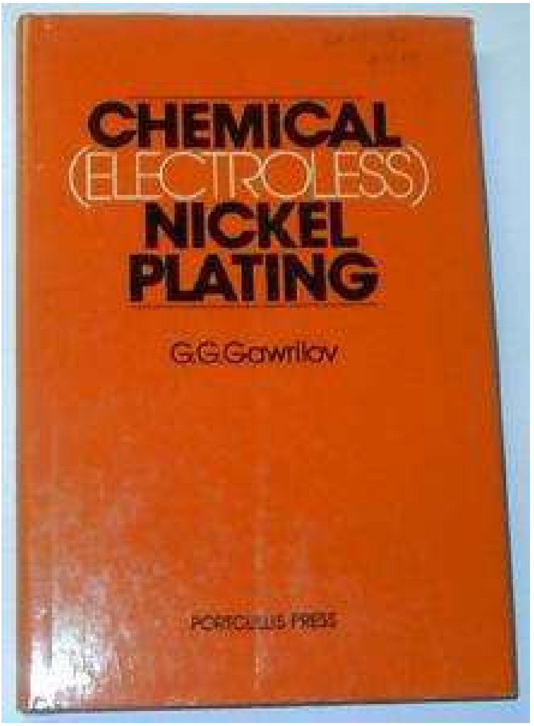
The Four Groups of Stabilizers

Group 1: Water soluble organic dipolar anions, including:
- a. 6+ C, aliphatic compounds. Na^+ Oleate
- b. Functional acid groups. Some organic acids
- c. Unsaturated organics, such as maleic acid

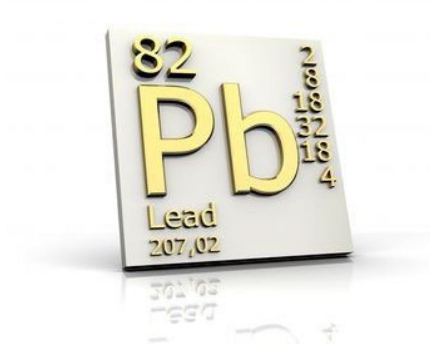
Group 2: Heavy Metals: Pb^{++}, Sn^{++}, Bi^{++}

Group 3: Organic and Inorganic compounds of S, Se, Te

Group 4: Compounds containing oxygen: MoO_3, H_2O_2



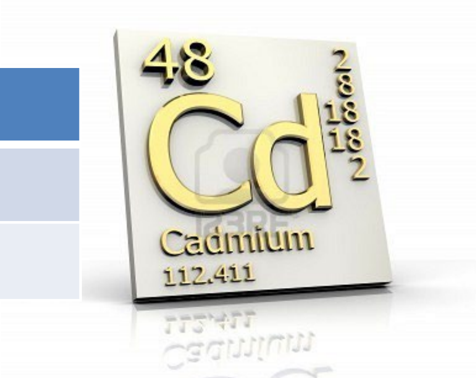
RoHS Compliancy



A Brief History

- Prior to RoHS in 2003 there were no limitations to the use of Pb and Cd in EN formulations.
- Amongst EN suppliers, there was very little variation between technologies.
- Mid Phos EN could plate all substrates with excellent coverage, including copper and its alloys. *Life was very good….Then*
- *2003 Hits*. Pb and Cd must be reduced/replaced from EN formulations to maintain RoHS limits.

Element	RoHS Deposit Limit
Lead	<1000 ppm
Cadmium	<100 ppm



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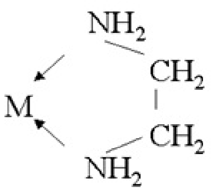
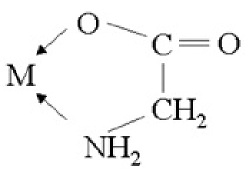
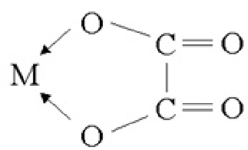
Chelator/Ligand Types



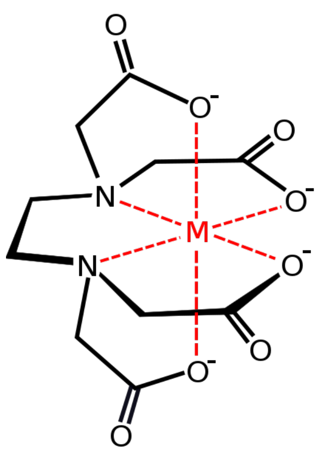
ethylenediamine



glycinato



oxalato complex
stable



1. Monodentate: acetic acid, proprionic acid
1. Bidentate: lactic acid, glycine, succinic acid
2. Tridentate: malic acid, aspartic acid
3. Tetradentate: citric acid, pyrophosphate

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Buffers

Buffers are compounds that resist small changes in pH. Their presence in the bath prevents drastic drops in pH while plating. Without buffers, the average plating rate would be much slower large drops in pH. Common examples include boric acid and acetic acid.

pH Regulators

Hydrogen ions are a reaction by-product which cause the pH to go down. Common pH regulators, like ammonia and potassium carbonate, neutralize the acid and keep pH maintained at the desired level.

High Phos: 4.6-4.9 pH

Mid Phos: 4.8-5.2 pH

Low Phos: 5.0-6.0 pH

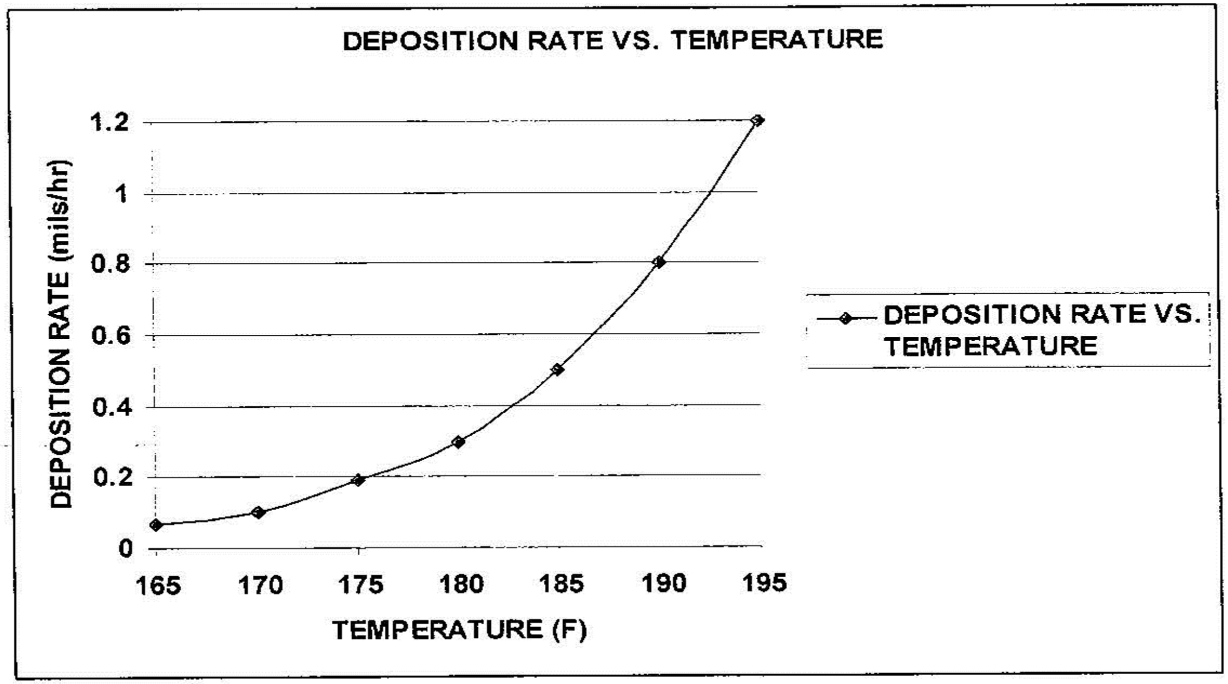
Wetters

Ionic and non-ionic surfactants. Wetters lower surface tension, make gas bubbles smaller, improve rinsing, and help reduce pitting.

The Science of Electroless Nickel

Effect of Temperatures

Temperature of solution can drastically affect the plating rate of EN chemistry. The graph below shows the Rate vs. Temperature.



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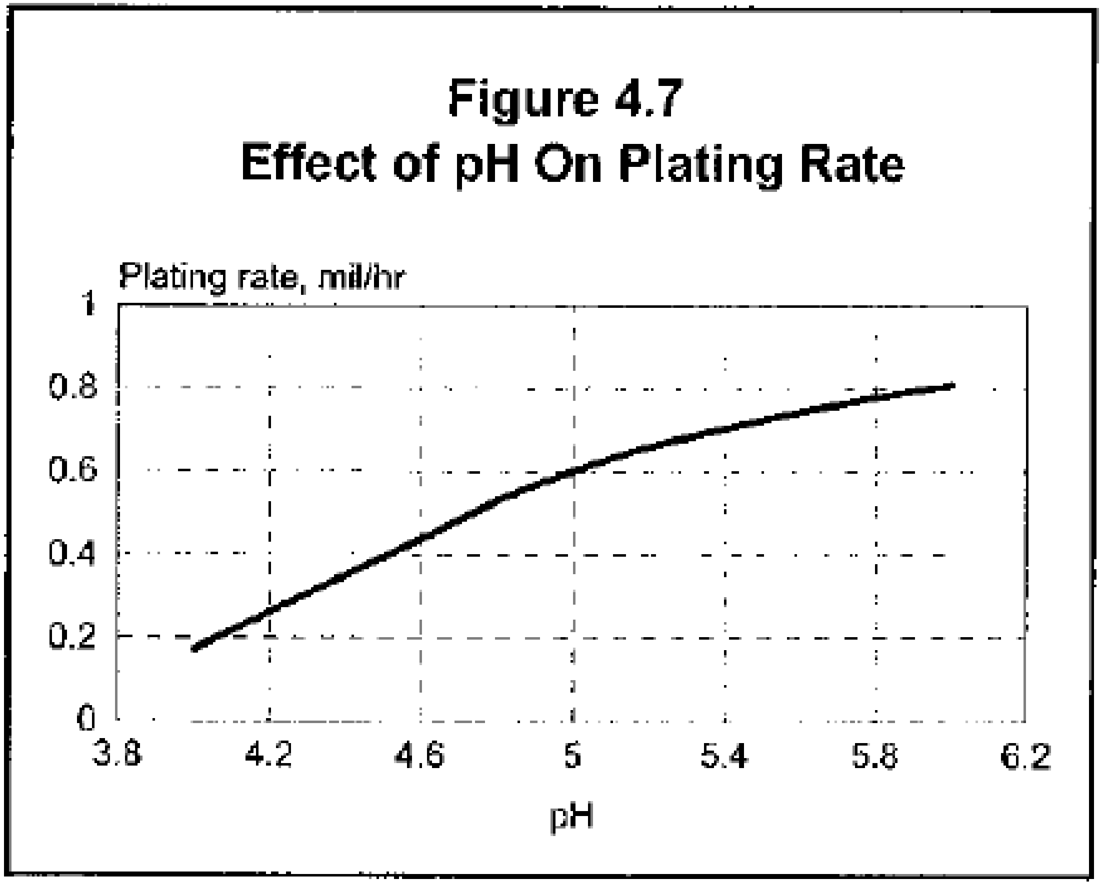


Different Baths/Different Objectives

- Low Phosphorous
- Medium Phosphorous
- High Phosphorous
- Nickel-Boron
- Nickel-Composite

Different Baths/Different Objectives

Low Phosphorous

- High as plated hardness (58-62 R_C)
- Excellent wear resistance
- Very resistant to corrosion in alkaline environments
- High melting point (1200^o C)
- Poor general corrosion resistance
- 1-4% phosphorous
- Applications include:

Chrome replacement and electronics

Different Baths/Different Objectives

Medium Phosphorous

- 49-54 R_C as-plated hardness, heat treatable to 65-68 R_C
- Good corrosion resistance in alkaline and acid environments
- Available in bright and semi-bright appearance
- Used for decorative as well as functional applications

- 5.0-9.0% Phosphorous
- Applications:

Aerospace, aluminum connectors, electronics, automotive, busbar,

Different Baths/Different Objectives

High Phosphorous

- Maximum corrosion resistance among all EN
- Highly ductile, good for high thickness
- Non-magnetic, as-plated hardness 46-48 R_C
- Heat treatable to 69 R_C

- 10.5-12.0% Phosphorous
- Highly engineered nickel used for the most severe environments, including:

Memory disk, oil and gas extraction, hydraulics, marine water environments

Different Baths/Different Objectives

Nickel-Boron

- High as plated hardness (up to 65 R_C)
- Reduced by DMAB or sodium borohydride, 0.5-5.0% Boron
- Low corrosion resistance, very good wear resistance
- Can be used for chrome replacement
- Applications:

Printed circuit board, POP,

firearm industry, saw blades, and

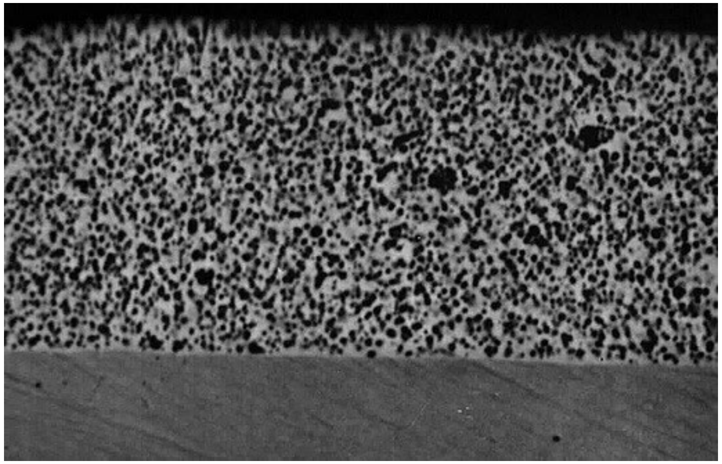
gear drives

Different Baths/Different Objectives

Nickel-Composite

- Ni-P alloy, containing a co-deposited particle
- PTFE, boron nitride, silicon carbide, and diamonds
- Composite material gives added properties to Ni-P deposit

- Wear resistance, lubricity, hardness, and low CoF
- Applications: Firearms, mold release, bearings, and oil and gas



APPENDIX A

TABLE A-1
Properties of Electroless Nickel-Phosphorus and Nickel-Boron Coatings(A)

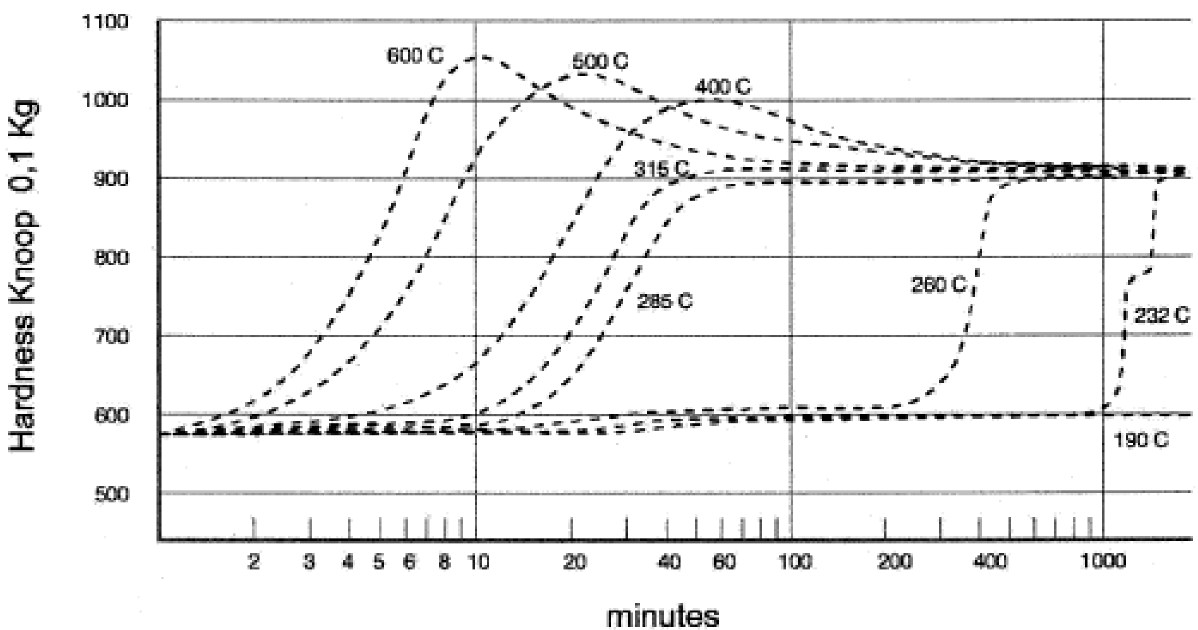
Property	Ni-3P	Ni-8P	Ni-11P	Ni-1/2B	Ni-5B-5Tl
Composition	3 to 4% P, balance Ni	6 to 9% P, balance Ni	11 to 12% P, balance Ni	0.5 to 1% B, balance Ni	3 to 5% B, 3 to 5% Tl, balance Ni
Structure	Micro-crystalline	Mixed crystalline and amorphous	Amorphous	Crystalline	Mixed crystalline and amorphous
Internal stress	-10 MPa	+40 MPa	-20 MPa	+500 MPa	+110 MPa
Final melting point	1275°C	1000°C	880°C	1440°C	1170°C
Density	8.6 g/cm^3	8.1 g/cm^3	7.8 g/cm^3	8.6 g/cm^3	8.25 g/cm^3
Coefficient of thermal expansion	12.4 µm/m-°C	13 µm/m-°C	12.0 µm/m-°C	ND	12.1 µm/m-°C
Electrical resistivity	30 µΩ-cm	75 µΩ-cm	100 µΩ-cm	10 µΩ-cm	89 µΩ-cm
Thermal conductivity	0.6 W/cm-K	0.05 W/cm-K	0.08 W/cm-K	ND	ND
Specific heat	1,000 J/kg-K	ND	460 J/kg-K	ND	ND
Magnetic coercivity	10,000 A/m	110 A/m	0	ND	ND
Tensile strength	300 MPa	900 MPa	800 MPa	ND	110 MPa
Ductility	0.7%	0.7%	1.5%	ND	0.2 %
Modulus of elasticity	130 GPa	100 to 120 GPa	170 GPa	ND	120 GPa
Hardness, as deposited	700 HV_{100}	600 HV_{100}	530 HV_{100}	580 HV_{100}	700 HV_{100}
Hardness, heat treated	960 HV_{100}	1000 HV_{100}	1050 HV_{100}	500 HV_{100}	1200 HV_{100}
Coefficient of friction	ND	0.38	0.45	ND	0.44
Taber Wear Index, as deposited	11 mg/ 1,000 cycles	16 mg/ 1,000 cycles	19 mg/ 1,000 cycles	8 mg/ 1,000 cycles	9 mg/ 1,000 cycles
Taber Wear Index, heat treated	9 mg/ 1,000 cycles	12 mg/ 1,000 cycles	12 mg/ 1,000 cycles	8 mg/ 1,000 cycles	3 mg/ 1,000 cycles
Corrosion protection, salt fog resistance	24 h	96 h	1,000 h	ND	24 h

(A) ND = not determined

EN Properties

Hardness

X4. HARDNESS VERSUS TIME AND TEMPERATURE



NOTE—These graphs are average and may vary with deviations from normal practice.

FIG. X4.1 Hardness and Annealing Time Versus Temperature
9 % Phosphorus Deposit

EN Properties Wear Resistance: Taber Wear

	Low Phos	Mid Phos	High Phos
As-Deposited	11 TWI	16 TWI	19 TWI
Heat Treatment	9 TWI	12 TWI	12 TWI

Temperature °C	Period hours	Hardness HV_{100}	Taber Wear Index mg/1000 cycles
As deposited		580	19.7
200	1	580	20.6
	8	560	—
	24	590	—
260	1	600	19.7
	2	580	—
	4	890	—
	8	910	—
	16	990	—
	24	940	13.4
	48	970	—
	96	960	—
	288	1000	—
290	1	750	17.6
	2	960	—
	4	1000	13.4
	8	1010	—
	10	1050	13.6
	24	970	—
340	1	970	13.3
	2	980	—
	4	1020	11.6
	6	1000	12.7
	8	1000	—
	24	960	12.0
400	0.2	970	—
	0.5	1020	—
	1	1040	11.5
	24	970	11.9

EN Properties

Wear Resistance: Hardness

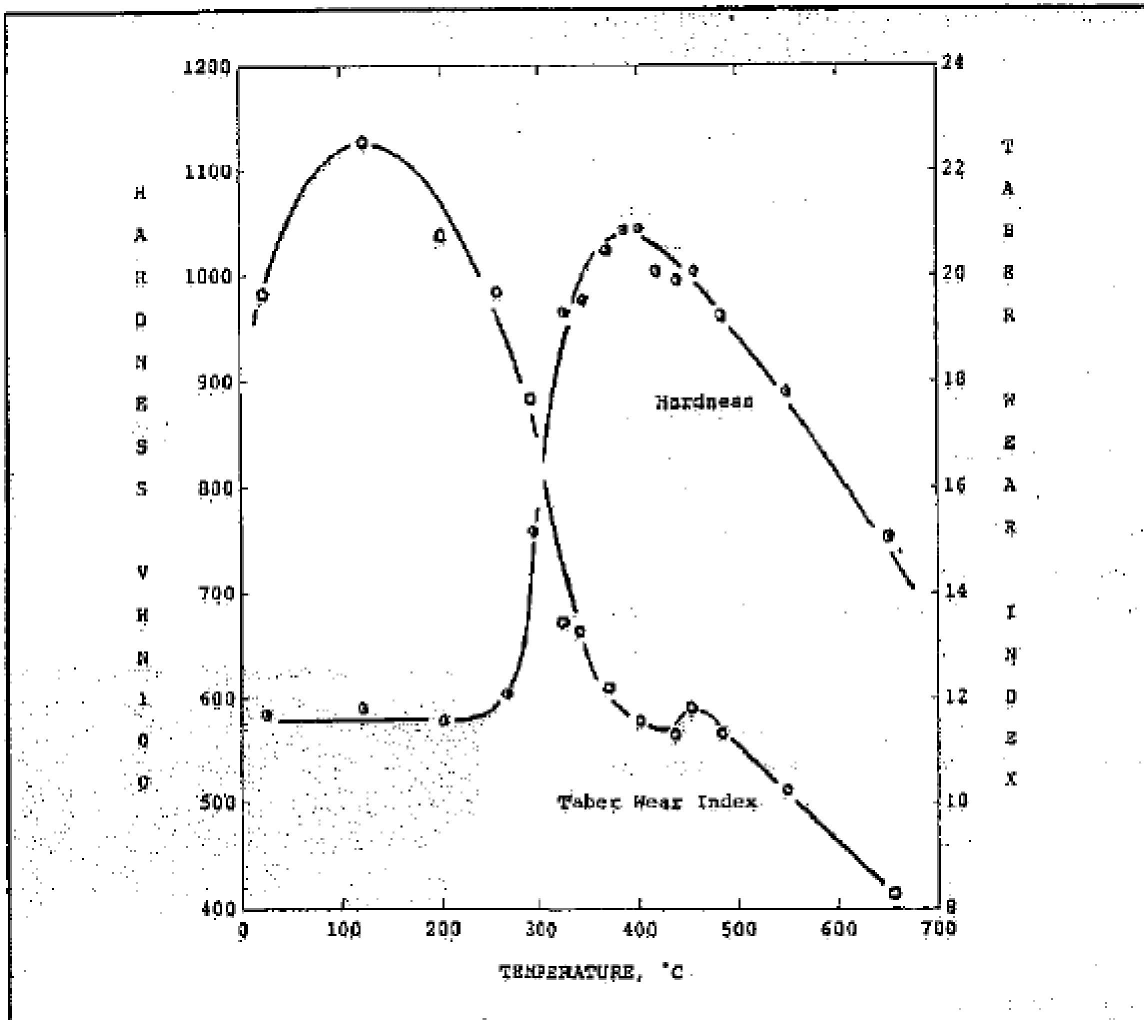


Fig. 1. Hardness and abrasive wear resistance of electroless nickel containing 11%P after one-hour heat treatment.