

An Overall Aspect of Electroless Ni-P Depositions—A Review Article

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Literature on electroless Ni-P deposition, in recent decades, has dwelled primarily on surface engineering and corrosion-resistant applications. By contrast, we have many research articles devoted to the engineering aspects of the electroless Ni-P depositions and their technology. The present article deals with the development of electroless Ni-P bath, advantages and mechanisms of deposition, and applications of the Ni-P deposits. We also present a comparison of the properties of electroless Ni-P and Ni-B as well as the recent developments in nickel-phosphorous research. We attempt to review these in a detailed manner. We also briefly discuss the future developments of electroless Ni-P.

I. INTRODUCTION

CONVENTIONAL plating, normally designated as “electroplating,” is accomplished when metal ions are reduced to the metallic state and deposited as such at the cathode by use of electrical energy. Electroless plating is a chemical reduction process, which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of the metal without the use of electrical energy.

The modern electroless nickel employs a completely different stabilizer system. It is designed for true economy and ease of control. This new system actually builds brightness on dull metals and builds thickness of 100 μm or more without pitting or producing roughness. Bath constituents do not break even at an operating temperature of 95 $^{\circ}\text{C}$.

Credit for the discovery of electroless plating goes to Brenner and Riddell.^[1,2] Their work in developing a process for plating the inner walls of tubes with nickel-tungsten alloy using an insoluble anode brought out the unusual reducing properties of the hypophosphites. This process was eventually covered by patent^[3] in 1950. While the initial acceptance of the chemically deposited coating was slow, subsequent development of the process on the improvements of both bath composition and techniques has increased its industrial use.

Ever since the discovery of these compounds in 1819, the reducing power of hypophosphorous acid and the hypophosphite has commanded considerable attention. Thus, Wurtz^[4] first observed the reduction of a nickel ion to nickel by hypophosphite in 1845. Subsequently, other investigators studied this reaction, including Bretean,^[5] Paal and Frederici,^[6] Scholder and Heckel,^[7] and Scholder and Haken.^[8]

Similarly, reduction of cobalt ion to cobalt was also studied by Paal and Frederici^[6] and by Scholder and Haken.^[8]

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In most instances, this spontaneous chemical reduction gave a black powder.^[9] However, occasionally, as in the case of Bretean, a nickel mirror was obtained. In 1916, Roux^[10] was granted a patent involving the deposition of nickel coatings on solid substrates from hot, ammoniacal nickel citrate and sodium hypophosphite solutions. This bath decomposed spontaneously to yield a coating on all objects immersed in it, including the walls of the vessel.

The difference between the electroless plating process and the deposition of nickel, as accomplished by Bretean and by Rouse,^[9] is that the reaction used by the latter was spontaneous and complete, whereas the process of Brenner and Riddell was catalytic. This process was controlled. Here, the deposition occurred only on activated surfaces immersed in the bath. It was recognized that the deposited metal was an alloy of nickel and phosphorous, and since the electroless process did not offer a satisfactory means of controlling the phosphorous content, an electrolytic process was developed for producing the alloys.^[12,13] Such deposit, a mixture of metallic nickel and nickel phosphide (Ni_3P), was shown to be amorphous, and the physical, mechanical, and chemical properties of electrodeposited nickel-phosphorous alloys are compared with electroless deposits having a similar phosphorous content.

A. Advantages of Electroless Plating over Electroplating

Since electroless plating is a chemical reduction process, the coatings obtained are of uniform thickness all over the object plated. The quality of the deposit, namely, the physical and mechanical properties, is also uniform because the composition of the coating is uniform at all thicknesses. By the proper choice of the solution composition, pH, and the operating temperatures, the rate of deposition can be seen to be as high as 20 to 25 $\mu\text{m}/\text{h}$, which is sufficiently fast for industrial applications. Recent advances in the electroless nickel system offer extremely bright deposits, which are comparable with electroplated bright nickel, while retaining the advantages of uniformity of thickness, especially for parts or products with complex geometry. The ductility of electroless nickel deposits is improved largely so that postplating operations such as crimping or forming can be easily carried out. However, the disadvantage is that the leveling ability is extremely poor.^[14]

In contrast to most electrodeposition baths, all electroless Ni baths possess certain characteristics, which may be summarized as follows. (1) The bath contains nickel ions and a reducing agent in metastable equilibrium. The bath will normally be stabilized such that two components will not spontaneously react with one another under normal operating temperatures. The above said "stability" of the bath is an important criterion, (2) The Ni content of the bath is very low (2 to 8 g/L), (3) The deposition rate is usually around 10 to 25 $\mu\text{m/h}$, *i.e.*, relatively low, (4) The deposition rate is very closely dependent on bath composition, temperature, and pH, and, to some extent, the age of the bath. The buffers, complexants, accelerators, and stabilizers added to commercial formulations of the bath ensure optimum deposition rate and bath stability, (5) Metal deposition is initiated and maintained by a catalyst, removal of which leads to the end of the reaction, (6) The reduction of Ni is accompanied by hydrogen evolution, and (7) Coatings formed by electroless deposition are not normally of the pure metal. They might also contain phosphorous or boron, which might be derived from the reducing agent.

II. COMPONENTS OF ELECTROLESS NICKEL BATHS

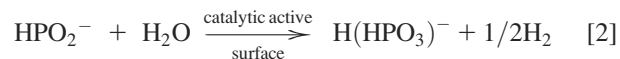
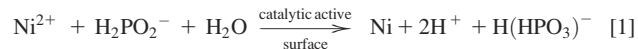
Electroless nickel plating is carried out by the immersion of objects with a catalytic coating in a solution containing nickel ions and a suitable reductant, which may include hypophosphite, borohydride, aminoboranes, hydrazine, *etc.* at temperatures above 90 °C. Further, some organic complexing agents for nickel ions, buffers, stabilizers, exulants, *etc.* are also present in this solution. Table I summarizes these components.

A. Electroless Ni-P Acid Baths^[14,15]

The acid solutions are the most popular and well investigated. The compositions of chemical nickel-plating solutions used by Brenner and Riddell have certain advantages over the alkaline solutions and, hence, are most popular. The rate of deposition is as high as 20 to 25 $\mu\text{m/h}$. The compositions are more stable since there is no loss of the complexant by evaporation. The coatings obtained from acid

solutions are of better quality. The properties of the electroless nickel-phosphorous alloy can be controlled easily by controlling the amount of phosphorous in the deposit. Hence, the acid solutions are generally preferred in many applications.

Reactions occurring in electroless nickel deposition with hypophosphite ion as the reducing agent may be represented as



Thus, the reaction proceeds forward due to the following factors: (1) reduction in nickel ion concentration, (2) conversion of the hypophosphite to phosphate, (3) increase in hydrogen ion concentration, and (4) adsorption of hydrogen gas by the deposit.

Amine boranes are also used as reductants instead of hypophosphite in electroless nickel deposition from acid solutions. The deposits obtained from these solutions contain boron, which enhances the hardness of the coating.

B. Alkaline Solution^[16-31]

The main disadvantages of the alkaline solutions are their high instability at temperatures greater than 90 °C and loss of ammonia, which is added to raise the bath pH at that temperature. The reduction of nickel in alkaline solutions follows the same pattern as in acid solutions. Another difference from the acid solutions is that the rate of deposition of nickel increases with hypophosphite concentrations. However, very high concentrations of hypophosphite make the bath unstable due to homogeneous deposition in the bulk.

Temperature influences the rate of deposition of nickel in the same way as in acid solutions. However, temperatures above 90 °C make the control of pH very difficult.

Borohydrides are also used as reducing agents in alkaline electroless nickel-plating baths. They are also operated at

Table I. Components of Electroless Nickel Baths and Their Functions

Component	Function	Example
Metal ions	Source of metal	Nickelchloride, Nickel Sulfate, Nickel acetates
Hypophosphite ions	Reducing agent	Sodium hypophosphite
Complexants	From Ni complexes, prevent excess free Ni ion concentration so stabilizing and preventing Ni phosphate precipitation; also act as pH buffers	Monocarboxylic acids, Dicarboxylic acids, Hydroxycarboxylic acids, Ammonia, alkanolamines, <i>etc.</i>
Accelerators (exulants)	Active reducing agent and accelerate deposition; mode of action opposes stabilizers and complexants	Anions of some mono- and di-carboxylic acids, fluorides, borates
Stabilizers (inhibitors)	Prevent solution breakdown by shielding catalytically active nuclei	Pb, Sn, As, Mo, Cd, or Th ions, thioures, <i>etc.</i>
Buffers	For long-term pH control	Sodium salt of certain complexants, choice depends on pH range used
pH regulators	For subsequent pH adjustment	Sulfuric and hydrochloric acids, Soda, caustic soda, ammonia
Wetting agents	Increase wettability of surfaces to be coated	Ionic and nonionic surfactants

low temperatures, *i.e.*, from 20 °C to 97 °C, the rate of deposition being lower at low temperature. The following bath is taken from related literature.

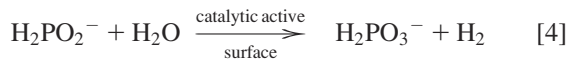
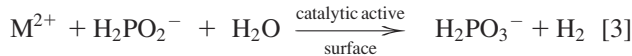
Nickel chloride NiCl ₂ · 6H ₂ O	20 g/L	24 g/L
Ethylene diamine (98 pct)	45 g/L	—
Sodium hydroxide NaOH	40 g/L	120 mL/L
Sodium borohydride NaBH ₄	0.67 g/L	0.4 g/L
pH	11 to 12	11 to 12
Temperature	97 °C	60 °C
Rate of deposition	7 to 8 to 9.2	0 to 12
	mgm/cm ² /h	mgm/cm ² /h

The deposit contains 4 to 7 pct boron and depends on the BH₄⁻/Ni⁺⁺ ratio. It is also claimed that thallium nitrate, stannous chloride, or sodium arsenate in mgm/L concentration acts as an exultant in the borohydride alkaline electroless nickel baths.

C. Mechanism for Electroless Nickel Deposition from Various Reducing Agents

1. Electroless nickel deposition with hypophosphite bath

Metal deposition by hypophosphite ion can be represented in a simplified manner by the following equations. All these reactions take place on catalytically active surfaces with input of external energy, *i.e.*, at higher temperatures (60 °C ≤ T ≤ 95 °C). In addition to metallic nickel, M, some molecular hydrogen is also formed. Then, it appears half of the hypophosphite is decomposed to evolve hydrogen.



However, in technical practice, the use efficiency of hypophosphite is around 35 pct at the best conditions.^[32] In other words, to deposit 1 g of nickel, 5 g of sodium hypophosphite are required.

The mechanism of reduction of metal ion by hypophosphite has been under constant revision in recent years. An electrochemical mechanism^[33] has been proposed in which it is supposed that hypophosphite ion is catalytically oxidized and nickel and hydrogen ions are reduced at the catalytic surface.

Anodic reaction:

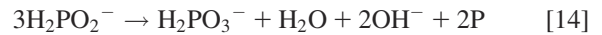
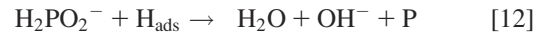
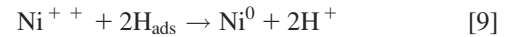
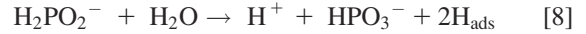


Cathodic reactions:



Atomic hydrogen theory^[34] received general support until the hydride ion mechanism was put forward and revised.^[35]

In the preceding studies, the following partial reactions were sent out:

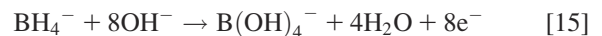


Electrochemical aspects of electroless metal deposition have been recently advocated.^[36] In this mixed potential theory, the overall electroless deposition mechanism is interpreted in terms of anodic and cathodic partial electrochemical reaction.

2. Electroless Ni-B deposits with boron compounds

a. Borohydride compound

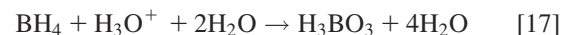
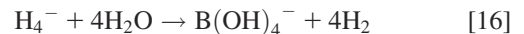
Borohydrides^[37] are good reducing agents in the alkaline medium. In acid and neutral pH ranges, borohydrides are readily hydrolyzed, and in the presence of nickel ions, nickel boride is formed. In alkaline solutions (pH above 13), borohydride is catalytically decomposed, as represented by the equation



One gram of nickel will be deposited by 0.6 g of sodium borohydride and the nickel deposits are more than 92.97 pct pure.

b. Boron-nitrogen compounds

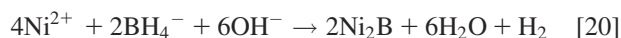
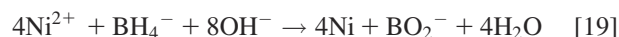
Borohydrides^[37] are good reducing agents in alkaline medium. In acid and neutral pH ranges, borohydrides are readily hydrolyzed, and in the presence of nickel ions, nickel boride is formed.



In the presence of nickel ions, the following reaction takes place:



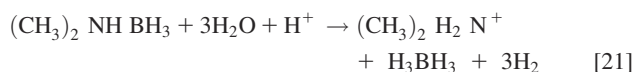
In alkaline solutions (pH above 13), borohydride is catalytically decomposed as represented by the following reactions.^[18] Here, the formation of borohydride is hindered and metallic nickel is the main product formed.



At higher temperatures, the undesirable Reactions [15] and [16] are accelerated, though the addition of alkali represses them. Moreover, by addition of stabilizers, the loss by decomposition of boron-hydrogen compounds can be significantly reduced with a commensurate increase in the rate of nickel and nickel-boron deposition. One gram of nickel will be deposited by 0.6 g of sodium borohydride and the nickel deposits are more than 92.97 pct pure.

c. Boron-nitrogen compounds

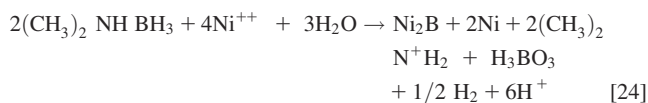
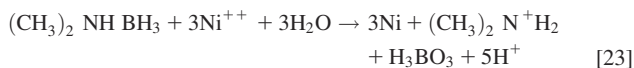
Amineboranes^[38-42] are effective reducing agents over a wider range of pH compared to the borohydrides and the nickel baths with N-dimethylamineborane. Amineboranes, which can work in both acid and alkaline baths, have been successfully used at pH ranging between 3.5 and 7 in acid baths. In addition to this, its properties with baths operating at alkaline pH ranges are also reported. At pH lower than 3.5, acid catalyzed hydrolysis sets in with BH_3 and BH_3OH^- as intermediates.



The major electronegative species responsible for reduction of nickel ions is BH_3OH^- produced by the following mechanism,^[36] even though direct oxidation of amine boranes is not ruled out.



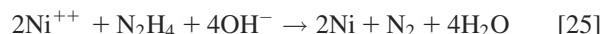
The boron content of the nickel deposit, obtained from the amine borane bath, varies from 0.2 to 4.0 wt pct,^[43] the higher boron content being obtained at higher pH range. The overall reduction reactions producing metallic nickel and nickel boride can be written as follows:



In practice, to produce 1 g of nickel, 1 g of dimethylamineborane is required. Amine boranes can be used as a good reducing agent for electroless deposition of other metals such as copper,^[44] gold,^[45] silver,^[46] and cobalt.^[47]

d. Hydrazine compound

More than 99 pct pure nickel^[48,49] is obtained (500- to 5000-Å thick) with hydrazine as a reducing agent in an alkaline solution of pH above 10.0. The reaction of hydrazine reduction can be written as follows:



Hydrazine in conjunction with hypophosphite has been used to deposit electroless nickel phosphorous at ambient temperatures (90 °C to 95 °C). The rate of deposition is approximately 25 to 30 $\mu\text{m}/\text{h}$. Without affecting the rate of deposition, palladium^[50] and gold^[51] baths containing hydrazine as a reducing agent are also reported.

D. Reasons for Spontaneous Decomposition of Electroless Nickel Bath

(1) local overheating;^[52] (2) rapid addition of sodium hypophosphite;^[52] (3) high phosphite concentration;^[53] (4) rapid addition of an alkali;^[52] (5) excessive deposits of nickel on tank walls or on heating coils;^[52] (6) high pH during bath preparation, causing the precipitation of nickel compounds;^[52] (7) incomplete removal of palladium after the use of palladium activation;^[52] (8) instability of fresh baths;^[52] (9) low bath loadings,^[53] and (10) over use of baths, leading to the precipitation of phosphates.^[52]

III. PROPERTIES OF ELECTROLESS NICKEL DEPOSITS^[14,53-62]

The electroless deposition technique of Ni-P alloy coatings has been a well-known commercial process that has found numerous applications in many fields due to excellent properties of coatings, such as high corrosion resistance, high wear resistance, good lubricity, high hardness, and acceptable ductility. Hypophosphite reduced electroless nickel is an unusual engineering material, because of both its method of application and its unique properties. Due to the presence of phosphorous/boron, the properties of electroless nickel deposits are significantly altered. As applied, Ni-P coatings are uniform, hard, and relatively brittle. A deposited Ni-P coating can be a lubricant, which is easily solderable and highly corrosion resistant. Properties of deposits from borohydride or amino borane reduced baths are similar to those of electroless Ni-P alloys with a few exceptions. The hardness of the Ni-B deposits is very high, and these alloys can be heat treated to high levels, equal to or greater than that of hard chromium deposits. The Ni-B has outstanding resistance to wear and abrasion. These coatings, however, are not completely amorphous and have reduced resistance to corrosive environments. Furthermore, they are much more costly than Ni-P coatings. The properties of electroless Ni-P coatings and comparison between properties of electroless Ni-P and Ni-B coatings are reviewed briefly in the following sections.

1. Melting Point

Pure nickel has a melting point of 1455 °C, and electroless deposited from the hydrazine reducing agent bath also melts in the range of ($T_m = 1440 \text{ °C} \pm 1.0 \text{ °C}$). The greater the proportion of codeposited alloying elements (phosphorous,

boron, thallium, lead, *etc.*) or codeposited organic or inorganic impurities, the lower the melting point of the deposits. Electroless Ni-P deposits containing 7.9 wt pct P have a melting point of 890 °C.

2. Density

The density of the electroless nickel coatings is inversely proportional to their phosphorus content. The density is lowered in proportion: electrodeposits, 8 to 9 g/cc; and electroless deposits, 7 to 9 g/cc.

3. Thermal properties

Thermal expansion measurements are made with a dilatometer instrument. A mean value for the coefficient of thermal expansion between 0 °C and 100 °C for Ni-P 8 ± 1 wt pct is around 13×10^{-6} per deg, while Ni-B deposits in the range 20 °C to 100 °C a value of 12×10^{-6} per deg. After heat treatment, the coefficient becomes smaller with a value of 10.8×10^{-6} per deg being reported in the literature. Specific thermal conductivity values for Ni-P deposits with 8.9 wt pct P are 0.0105 to 0.0135 cal · cm⁻¹ · s⁻¹ deg⁻¹.

4. Modulus value

The modulus value for Ni-P (7 wt pct deposits) is 2×10^5 N/mm², while low phosphorus deposits (1 to 3 wt pct) have a modulus of elasticity of 50 GPa, and those with higher phosphorous content (7 to 12 wt pct) have moduli from 50 to 70 GPa. The values of elasticity moduli for Ni-B deposits in the as-deposited condition are around 1.2×10^5 N/mm². After heat treatment 1 hour at 400 °C, their values increase to 1.8×10^5 N/mm².

5. Tensile strength

The tensile strength of electroless nickel is mainly dependent on the phosphorous content in the deposits. For deposits (in the as-deposited condition) with relatively low phosphorous content, values of tensile strength between 450 and 550 N/mm² were found. After heat treatment between 300 °C and 600 °C, these fall to 200 to 320 N/mm². Duncan^[54] sets a value of Ni-P of around 110 N/mm². Therefore, the tensile strength values of Ni-P deposits are higher than the Ni-B deposits.

The hardness of the Ni-P deposit is 480 VPN, which increased to 900 to 1000 VPN when heat treated at 350 °C to 400 °C for 1 hour. Above this temperature, the hardness starts decreasing, but is restored on subsequent cooling. Nickel-boron deposits retain the high hardness values even at high temperature. The deposits are generally amorphous (ultra microcrystalline). The hardness of the electroless Ni deposits can be increased by around a factor of 2, using heat treatment at temperatures above 250 °C. The phosphorus content in the deposits leads to the formation of intermetallic compounds. So, time and temperature of heat treatment variables are important factors.

6. Ductility

The ductility of electroless and electrodeposited nickel is arguably lesser (less than 2 pct) than those analogously formed from the molten state (3 to 30 pct). This is unfortunate, since good elastic and plastic properties are an important feature in the selection of metallic materials.

The preferred technique for quantitative measurements of ductility of the deposits is the micromechanical bulge test, a development of the long-established Ericsson technique.

7. Adhesion

Adhesion of electroless nickel deposits to iron, copper, nickel, and alloys of these metals are better than electrodeposited nickel and are further increased by heat treatment at 200 °C to 400 °C for 1 hour. Heat treatment is required for improving the adhesion of electroless nickel on aluminum alloys, stainless steel, chrome steels, and high carbon steels.

8. Wear resistance

Due to their high hardness and good ductility, electroless nickel deposits are usually held to have good wear resistance. Thus, the taber wear index (TWI) for watts nickel is around 25, for which Ni-P (9 wt pct) is 17, while Ni-B has a value of 9 and chrome plate has a value 2. The taber wear index is defined as weight loss per 1000 revolutions under a loading of 10 N with CS 10 wheels. A significantly better value of 9.6 was quoted for as-deposited Ni-P, while as-deposited Ni-B emerged with TWI 1.4 to 2, in contrast to hard chromium at 0.5 to 0.7. So, the wear resistance of electroless nickel coating is comparable to hard chromium in many respects and hence finds application as a substitute for hard chromium.

9. Structure of electroless Ni-P coatings

Hypophosphite reduced electroless nickel is one of the very few metallic glasses used as an engineering material. Depending on the formulation, commercial coatings may contain 6 to 12 wt pct P dissolved in nickel and as much as 0.25 pct of other elements. As applied, most of these coatings are amorphous; they have no crystal structure. Coatings containing more than 10 pct P and less than 0.05 pct impurities are typical continuous.

As electroplated Ni-P is heated to temperatures above 220 °C to 260 °C, structural changes begin to occur. First, coherent and then distinct particles of nickel phosphite (Ni₃P) form within the alloy. Then, at a temperature above 320 °C, the deposits begin to crystallize and lose their amorphous character. With continued heating, nickel phosphite particles conglomerate and a two-phase alloy forms with coatings more than 8 wt pct P matrix of Ni₃P form, whereas almost pure nickel is the predominant phase in deposits with lower phosphorous content. These changes are rapid increase in hardness, wear resistance, and decrease in ductility.^[55-58]

10. Internal stresses

Internal stresses in electroless nickel plating primarily depend on the coating composition, especially the amount of phosphorus in the deposits. Neutral, compressive stresses are developed when steel is coated more than 10 wt pct P. At the same time, phosphorous content below this value produces tensile stresses due to the difference in thermal expansion between the deposits and substrate. The high levels of stresses in these coatings promote cracking and porosity.^[59] Structural changes during heat treatment at temperatures above 220 °C cause volumetric shrinkage of electroless nickel deposits 4 to 6 wt pct. This volumetric

shrinkage increases tensile stresses and reduces compressive stresses.

11. Corrosion resistance

The corrosion resistance of electroless Ni-P coatings is a function of composition. Most deposits are naturally passive and very resistant to corrosion attack in most environments. Their degree of passivity and corrosion resistance, however, is greatly affected by their phosphorous content. Alloys containing more than 10 wt pct P are more resistant to attack than those with lower phosphorus content in neutral or acidic environment. Alloys containing low phosphorus content (3 to 4 wt pct P) are more resistant to strong alkaline environment than high phosphorus deposits. As Ni-P deposits are heated to high temperatures above 220 °C, nickel phosphide particles begin to form, reducing the phosphorus content of the remaining material. This reduces the corrosion resistance of the material of the coatings. The particles also create active/passive corrosion cells, further contributing to the destruction of the deposits. Baking at 190 °C, similar to the treatment used for hydrogen embrittlement relief, caused no significant increase in corrosion resistance. Hardening, however, caused the corrosion rate of the deposit to increase from 15 $\mu\text{m}/\text{year}$ to more than 900 $\mu\text{m}/\text{year}$.^[58] Amorphous alloy has better resistance to corrosion attack than equivalent polycrystalline materials because of their freedom from grain boundaries and glassy films that form on and passivate their surfaces.

12. Solderability

Electroless nickel coatings can be easily soldered and are used in electronic applications to facilitate soldering such light metals as aluminum. For most components, rosin mildly activated (RMA) flux is specified along with conventional Sn-Pd solder. Preheating the component to 100 °C to 110 °C improves the ease and speed of joints with moderately oxidized surfaces, such as those resulting from steam agings, activated rosin (RA) flux, or organic acid (which are usually required to obtain wetting of coatings).

13. Porosity

Generally, the porosity of electroless nickel deposits is equal to or lower than electrodeposited nickel under identical conditions of surface preparation and thickness. Heat treatment reduces porosity further and hence the electroless nickel deposits are more corrosion resistant than electrodeposited nickel at equal thickness values. The porosity of electroless nickel deposits are further reduced when a two or multistage deposition is carried out. The adhesion values are not impaired.

14. Fatigue strength

Generally, the fatigue strength of steels is slightly lowered by electroless nickel deposits in the as-deposited condition. However, heat treatment significantly lowers the fatigue strength if the steel is coated with electroless nickel. The magnitude of reduction of fatigue strength depends on the composition, heat treatment, and thickness of the coating, as well as original fatigue strength of the steel. Several investigations have shown that the use of

electroless nickel coatings causes a 10 to 50 pct reduction in fatigue strength and endurance limit of steel substrate. High-strength steel with tensile strength greater than 1400 N/mm² may be electroless nickel coated from hypophosphite bath without loss of strength. However, there are a number of reports suggesting that electroless nickel coating results in loss of strength and few reporting an increase in strength.^[59]

A. Comparison between Electroless Ni-P and Ni-B Deposits

Properties of deposits from borohydride or amino borane reduced baths are similar to those of electroless Ni-P alloys with a few exceptions. The hardness of the Ni-B deposits is very high, and these alloys can be heat treated to high levels equal to or greater than that of hard chromium deposits. Ni-B has outstanding resistance to wear and abrasion. These coatings, however, are not completely amorphous and have reduced resistance to corrosive environments. Furthermore, they are much more costly than Ni-P coatings, (1) Unlike nickel-phosphorous coatings in the as-deposited condition, electroless nickel-boron contains crystalline nickel, microstructurally nickel-boron (typically Ni₂B) glass. These coatings are not homogeneous and consist of phases of different composition, (2) Melting point of Ni-B coatings is relatively high and can approach that of the metallic nickel, (3) Electrical resistivity of 5 pct B coatings is similar to that of Ni-P alloys range from 49 $\mu\Omega \cdot \text{cm}$ in the as deposited condition to 43 $\mu\Omega \cdot \text{cm}$ after heat treatment at 1100 °C, (4) The strength and ductility of Ni-B coatings containing 5 pct B is only one-fifth that of high phosphorus deposits. The guided bend test of panels coated with 5 pct Ni-B showed strain at fracture to be 2.5 mm/m. In the same test, the breaking strain of hypophosphite reduced electroless nickel containing approximately 9 pct P was 5.3 mm/m. Unlike Ni-P coatings, however, heat treatment has little effect on the ductility of Ni-B deposits,^[58] (5) The principal advantage of electroless Ni-B is its high hardness and superior wear resistance than Ni-P deposits. In the as-deposited condition, microhardness values of 650 to 750 HV₁₀₀ are typical for borohydride and aminoborane reduced coatings. After 1 hour of heat treatment, at 350 °C to 450 °C, hardness values of 1200 HV₁₀₀ can be produced. Electroless nickel is naturally lubricious. Their resistance to friction vs steel is typically 0.12 to 0.13 in the lubricity condition and 0.43 to 0.44 for the dry wear condition.^[60] The wear resistance characteristic of various electroless nickel baths obtained from the taber wear index is given in Table II, (6) In general, the corrosion resistance of electroless Ni-B is less than that of electroless Ni-P alloys. In an environment that causes little corrosion of Ni-P, such as alkali and solvents, electroless Ni-B is also very restraint. However, in the environment, which causes moderate attack of Ni-P, such as acids and ammonia solutions, Ni-B coatings can be severely corroded. In a strongly oxidizing medium, of course, neither coating is satisfactory,^[61] and (7) The ductility value of Ni-B deposits is around five times worse than high phosphorous Ni-P deposits based on the bend test.

Table II. Comparison of Abrasion Resistance of the Different Coatings^[58]

Types of Coatings	Heat Treatment for 1 h	Taber Wear Index (mg/1000) Cycles
Watts nickel	None	25
Electroless Ni-P	None	17
Electroless Ni-P	300 °C	10
Electroless Ni-P	500 °C	6
Electroless Ni-P	None	9
Electroless Ni-P	400 °C	3
Hard chromium	None	2

IV. APPLICATIONS AND RECENT DEVELOPMENTS OF ELECTROLESS COATINGS

A. Applications of Electroless Nickel Deposits^[60,63-71]

Electroless nickel is primarily used for engineering applications where uniform thickness, high hardness, and wear resistance of the surface and improved corrosion resistance are required. Thus, (a) to deposit on complex shapes; (b) on large surfaces, especially large interior surfaces; (c) on surfaces subjected to wear; (d) to replace expensive stainless steel vessels in some processing industries; (e) to repair or salvage nickel-plated machine parts; (f) for nickel depositions where electrical power is not available or possible; (g) for improving the adhesion of enamels on steel; and (h) on printed circuit boards and electronics industries for corrosion resistance and solderability.

The inner surfaces of pumps, driers, tubes, gasoline containers and tanks, transport cars carrying various chemicals, storage tanks, valves, screws, nut fasteners, *etc.* are coated with electroless nickel for improved corrosion resistance and uniformity of deposition. Cylinders for hydraulic pumps, piston rings, piston cylinders, cranks, bearing surfaces, rotating shafts, printed press parts, motor blades, *etc.* are coated with electroless nickel for improved wear and abrasion resistance under lubricating conditions. Aluminum and aluminum parts used in aircrafts or spacecrafts are coated with electroless nickel for improved wear resistance and corrosion resistance. Nuclear reactor parts, light alloy dies, radar wave guides, and printed circuit boards are also coated with the electroless Ni. It is used on rollers and crimping tracks in textile industry to provide a uniform highly wear resistant and corrosion resistance surface. Electroless nickel, as an engineering coating, is used in many industrial applications in aerospace automotive computers, electronics, food processing, hydraulics machinery, nuclear engineering, oil petrochemicals, plastics, power transmission, printing, pump valves, textiles, *etc.* A list of items that are electroless nickel plated are available in a number of publications. Table III summarizes the industrial applications of electroless nickel plating and its thickness requirement.

With increased use of aluminum alloys in industrial equipment machinery, electroless nickel-plated aluminum has a bright future. Aluminum or beryllium parts coated with electroless nickel and precision turned to accuracy between 0.05- and 1.0- μm smoothness are used in paraboloid mirrors in space vehicles. Beryllium hemispheres

coated with diamond turnable electroless nickel are used in gyroscopes.

Electroless nickel is now being advocated as a preplate for additives and semiadditive circuitry because of its faster rates of build up, greater solution stability, and consistent results. Electroless nickel is found to be one of the metals that possesses a low catalytic effect on hydrazine and methyl hydrazine decomposition and has been used as a surface coating on maraging steel to delay the pressure build up during prolonged storage.

The excellent corrosion resistance of high phosphorous nickel coatings has found wide application in many industries because it is a cheaper substitute for nickel, monel, or stainless steel construction materials. The cost for nickel cladding or titanium as a construction material in the manufacture of reaction vessels in some chemical industries is prohibitive. Hence, electroless nickel, with high phosphorous, offers a cheaper alternative. Electroless nickel phosphorous has found application as a solar absorber in solar collectors. The bright Ni-P deposits can be blackened with dilute acids and thus produced black coating possesses good optical properties.

Plating on plastics is not a new thing. However, a hard metallic surface on plastics, capable of retaining its luster and shape for at least 5 to 7 years with the capability to withstand rough handling and aggressive environments, is not older than 15 years. This happened with the arrival of acrylonitrile buta diene styrene (ABS) polymer. At about the same time, bright copper and nickel-plating solutions also made their appearance. Nevertheless, the plating of ABS must be considered a major breakthrough in metal finishing technology. Within two years of its availability, the entertainment electronic industry made use of ABS plating to a great extent. The search by the automotive industries for plated light components with high heat resistance, high torsional strength, and better chemical resistance than ABS has resulted in mineral filled nylons such as capron, which is successfully plated in the United States, and is being extensively used in the automotive and marine hardware fields.

B. Recent Developments in Electroless Ni-P Depositions

It has been observed that permalloy films are suitable for soft magnetic materials for their high permeability, non-magnetostriction, and low coercive force. They have been widely used as the magnetic recording head core materials in computer applications. The effects of a small amount of P or B on the magnetic properties of permalloy films have been investigated, which improved the synthetic magnetic properties of films by increasing the resistivity value. In particular, electroless Ni-Fe-P alloys are deposited from a bath using boric acid as a buffer agent and sodium citrate as a complexing agent. The effects of deposition parameters, such as pH and mole ratios of $\text{FeSO}_4/(\text{FeSO}_4 + \text{NiSO}_4)$, on the plating rate and the composition of the deposits were examined. It was found that the presence of ferrous sulfate in the bath has an inhibitory effect on the alloy's deposition. Consequently, the percentage of iron in the deposits never reaches high values. In fact, it was observed to be less than 15.62 at. pct.^[72]

Carbon nanofibers (CNFs) were grown on a Ni-P alloy catalyst deposited on a silicon substrate in a microwave

Table III. The Industrial Applications of Electroless Nickel Plating and Their Thickness Requirement

Solution	Type of Work	Thickness (in in.)	Type of Work with Detailed Reason for Use
1	Chemical process equipment	0.002 to 0.005	Protects filters, heat exchanger pumps, tanks, and pipe fittings
2	Hydraulic parts, oil field drilling equipment	0.0005 to 0.002	Protects recessed areas such as O-ring grooves and other internal parts
3	Molds for zinc die casting	0.002 to 0.003	Resists chemical corrosion as well as provides hardness similar to chromium
4	Printing press bed and rolls	0.001 to 0.003	Offers good release characteristics
5	Plastics extrude dies	0.0008 to 0.00015	Improves release characteristics and reduction in mold cleaning requirements
6	Gyro parts	0.001 to 0.003	Protects against corrosion by ink
7	Gears and gear assemblies	0.0005 to 0.001	Provides hardness and wear resistances as well as high corrosion resistances similar to chromium
8	Spray nozzles	0.0004 to 0.001	Provides low friction and wear resistances
9	From complex parts, usually small electrical contacts	0.0003 to 0.0008	Makes possible accurate control of dimensions and uniform coverage on all areas
10	Complex stainless steel parts	0.001 to 0.004	Produces coating uniformity, which preserves the balance of the turbine
11	Aluminum and high-temperature plastic "Black Boxes" and other electronic junction fittings	0.0003 to 0.0005	Makes it possible to electroform over aluminum mandrels and then dissolve out aluminum
12	Printed circuits	0.0003 to 0.0005	Provides ease of solderability and allows welding of nickel alloy components to printed circuit boards
13	Turbine parts	0.0002 to 0.0005	Produces coating uniformity, which preserves the balance of the turbine

heating chemical vapor deposition system with methane gas at 650 °C. The Ni-P alloy catalyst films with various thicknesses were produced using an electroless plating nickel technique. The nanosized clusters on the clustered surface of the Ni-P alloy catalyst film directly provided the nucleation sites for CNFs without any pretreatment before the growth of the CNFs. The CNFs grown on the Ni-P alloy catalyst showed random orientation, and CNFs is composed of parallel graphite planes with defects tilted from their axis. Field emission measurement indicated that the Ni-P catalyzed CNFs exhibited excellent field emission properties.^[73] A novel process of electroless Ni-P plating by a nonisothermal method with an operating temperature as high as 180 °C or even higher has also been used in experiments.^[74]

Copper content in electroless Ni-Cu-P alloy coatings mainly depends on pH, temperature, and Cu₂P concentration in plating solution and has a significant effect on the corrosion resistance of the coatings. The anticorrosion properties of the Ni-Cu-P coatings in HCl and NaCl solutions were investigated. The results showed that the corrosion resistance of the Ni-Cu-P alloy coatings was superior to that of the electroless Ni-P coatings or copper. The optimum conditions for preparing these corrosion-resistant Ni-Cu-P coatings have been obtained.^[75]

Electroless deposition in nanotechnologies for the first time allows one to produce photo masks and microdevices with nanosized adjacent elements of different thicknesses made of various materials by single conventional optical photolithography.^[76] These advantages significantly extend functional capabilities of the device, simplify removal of undesirable gases, and heat dissipation. The proposed nanotechnologies are much more advantageous and simpler than other expensive and complicated methods such as e-beam, X-ray lithography, or production of the devices

using light phase shift photo masks. Methods of fabricating the ultrathin void-free and pore-free electroless coatings on micro-, meso- and nanosized particles (carbides, borides, nitrides, oxides, diamond, graphite, *etc.*) are also proposed. These methods allow one to obtain nanostructured composite materials and coatings with the specified properties. The developed technologies will be applied in these industries soon.

Wear tests on self-mated pairs of Ni, Cu, and Ni-P deposits have been carried out during the Ni-P electroless plating process onto the friction surfaces. The *in-situ* electroless plating of Ni-P enhanced the growth process of transfer particles during Cu/Cu and Ni/Ni rubbing. It also increased the coefficient of friction in both cases. In the rubbing of Ni-P, Ni-P plating had no effect on the growth of transfer particles and coefficient of friction. The hardness test showed that the transfer particles at the interface of pin and disk were harder than the bulk of pin and disk. The effect of Ni-P plating during wear is due to the enhancement of the shear strength of transfer particles compared to the original surface.^[77]

The electroless nickel deposition bath is known to have a major problem of sudden bath decomposition, which results in an increase in the operating cost of the process and the generation of environmentally hazardous waste. Bath stabilizers have normally been added to extend its life. It has been demonstrated that the addition of thiourea and maleic acid significantly improved the stability of the electroless nickel N bath. It has been observed that the stabilizers have a minor and a major effect on phosphorus content and the morphology of the electroless nickel deposits, respectively. It has also shown, for the first time, that the addition of the stabilizers has an effect on the nanograin size of the electroless nickel deposit.^[78]

Electroless nickel plating on hollow glass microspheres with hypophosphite as a reducing agent in an alkaline bath was studied.^[79] The hollow glass spheres *via* coupling agent solution adsorbed more palladium catalytic active centers on their surfaces during pretreatment. Hence, continuously and uniformly covered microspheres were achieved. The magnetic property of microspheres was improved by adjusting the pH and the concentration of the reducing agent in a certain range. The morphology, composition, and structure of deposits have been investigated, and it has been found that the deposits on hollow glass microspheres grew thicker with prolonged plating time. Post treatment of the coated Ni glass spheres improved the crystalline structure of the plated Ni layer.

Electromagnetic interference (EMI) shielding effectiveness (SE) of single-layer or double-layers electroless metals, such as nickel phosphorus–pure nickel (NiP-Ni), Ni-NiP, NiP-Cu, Ni-Cu, and coated carbon fiber reinforced acrylonitrile-butadiene-styrene (ABS) composites were investigated. The resistivity and antioxidization of conductive fillers were important factors for EMI shielding composites. Although the resistivity of electroless copper-coated carbon fiber (ECCF) is much lower than that of electroless nickel-coated carbon fiber (ENCF), electroless copper films on the carbon fibers readily oxidized during compounding processes. The resistivity of ECCFyABS composites increased significantly after composite fabrication. As a result, the EMI SE of the ECCFyABS composite showed a poor EMI SE (37 dBm) among those electroless metals-coated carbon fiber–reinforced ABS composites. The coated double-layer electroless metals on the conductive fillers were obtained by the electroless method. The outside metal layer, which possessed better antioxidization, provided suitable protection for the conductive fillers. Thus, the EMI SE of the ECCFyABS composite can improve effectively.^[80] The best EMI SE of double-layer electroless-coated metals yABS composites could be reached at 65 dBm.

V. FUTURE DEVELOPMENTS

The following future developments are expected: (1) New applications such as coating on ceramics or glass and shielding against electromagnetic radiation obtained by using electroless copper and nickel; (2) new thinking in terms of corrosion and wear protection of materials as opposed to the throwaway culture increasingly observed all over the world; (3) determining the theoretical reason that electroless nickel deposits should not be hard soldered; and (4) progressively reducing prices of electroless plating on plastics used for automotive industries.

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