Chapter 1

The Fundamental Aspects Of Electroless Nickel Plating

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The chemical deposition of a metal from an aqueous solution of a salt of said metal has an electrochemical mechanism, both oxidation and reduction (redox), reactions involving the transfer of electrons between reacting chemical species. The oxidation of a substance is characterized by the *loss* of electrons, while reduction is distinguished by a *gain* of electrons. Further, oxidation describes an anodic process, whereas reduction indicates a cathodic action. The simplest form of chemical plating is the so-called *metal displacement reaction*. For example, when zinc metal is immersed in a copper sulfate solution, the zinc metal atoms (less noble) dissolve and are spontaneously replaced by copper atoms from the solution. The two reactions can be represented as follows:

Oxidation: $Zn^0 \rightarrow Zn^{+2} + 2e^-$, anodic, $E^0 = 0.76$ V

Reduction: $Cu^{+2} + 2e^- \rightarrow Cu^0$, cathodic, $E^0 = 0.34$ V

Overall reaction: $Zn^0 + Cu^{+2} \rightarrow Zn^{+2} + Cu^0$, $E^0 = 1.1$ V

As soon as the displacement reaction begins, the surface of the zinc substrate becomes a mosaic of anodic (zinc) and cathodic (copper) sites. The displacement process continues until almost the entire substrate is covered with copper. At this point, oxidation (dissolution) of the zinc anode virtually stops and copper deposition ceases. Chemical plating by displacement yields deposits limited to only a few microns in thickness, usually 1 to 3 μm. Hence, chemical plating via the displacement process has few applications.

In order to continuously build thick deposits by chemical means without consuming the substrate, it is essential that a sustainable oxidation reaction be employed as an alternative to the dissolution of the substrate. The deposition reaction must occur initially and exclusively on the substrate and subsequently continue to deposit on the initial deposit. The redox potential for this chemical process is usually more positive than that for a metal being deposited by immersion. The chemical deposition of nickel metal by hypophosphite meets both the oxidation and redox potential criteria without changing the mass of the substrate:

Reduction: $Ni^{+2} + 2e^- \rightarrow Ni^0$ $E^0 = -25$ mV
Oxidation: $H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^-$ $E^0 = +50$ mV

$Ni^{+2} + H_2PO_2^- + H_2O \rightarrow Ni^0 + H_2PO_3^- + 2H^+$ $E^0 = +25$ mV

which is the sum of the oxidation and reduction equations. This reaction does not represent the true electroless plating reaction, since EN deposition is accompanied by hydrogen evolution. Figure 1.1 shows the difference between immersion and electroless deposition by comparing deposit thickness vs. time.

The term *electroless plating* was originally adopted by Brenner and Riddell (1) to describe a method of plating metallic substrates with *nickel or cobalt alloys* without the benefit of an external source of electric current. Over the years, the term has been subsequently broadened to encompass any process that continuously deposits metal from an aqueous medium.

In general, electroless plating is characterized by the selective reduction of metal ions only at the surface of a catalytic substrate immersed into an aqueous solution of said metal ions, with continued deposition on the substrate through the catalytic action of the deposit itself. Since the deposit catalyzes the reduction reaction, the term *autocatalytic* is also used to describe the plating process.

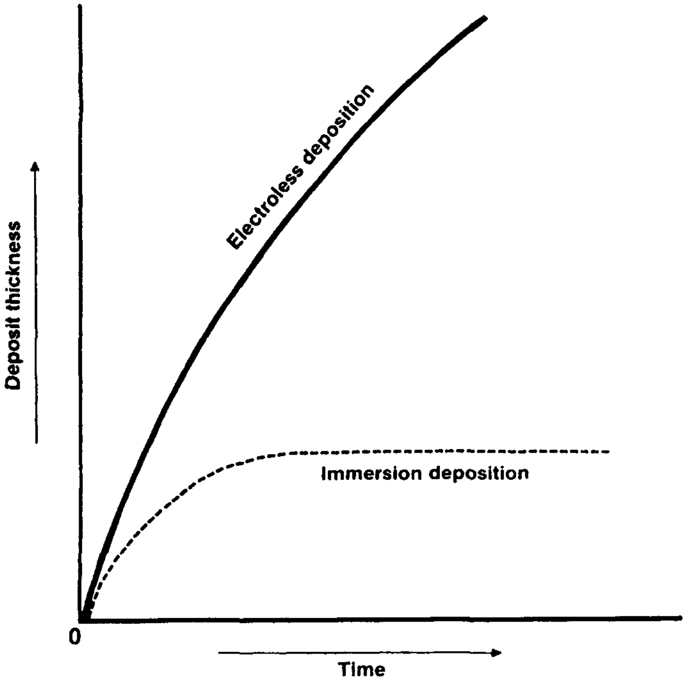


Fig. 1.1—Thickness vs. time—comparison between electroless and immersion deposition.

In 1844, Wurtz (2) observed that nickel cations were reduced by hypophosphite anions. However, Wurtz only obtained a black powder. The first bright metallic deposits of nickel-phosphorus alloys were obtained in 1911 by Breteau (3). In 1916, Roux (4) was issued the first patent on an electroless nickel plating bath. However, these baths decomposed spontaneously and formed deposits on any surface that was in contact with the solution, even the walls of the container. Other investigators studied the process, but their interest was in the chemical reaction and not the plating process. In 1946, Brenner and Riddell (1) published a paper that described the proper conditions for obtaining electroless deposition as defined above. Over the years, the process has been investigated further and expanded by many workers to its present state of development.

THE ELECTROLESS NICKEL PLATING BATH: COMPONENTS

Electroless nickel (EN) plating is undoubtedly the most important catalytic plating process in use today. The principal reasons for its widespread commercial and industrial use are to be found in the unique properties of the EN deposits. The chemical and physical properties of an EN coating depend on its composition, which, in turn, depends on the formulation and operating conditions of the EN plating bath. Typically, the constituents of an EN solution are:

- A source of nickel ions
- A reducing agent
- Suitable complexing agents
- Stabilizers/inhibitors
- Energy

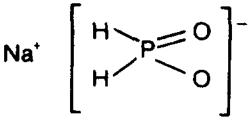
The Nickel Source

The preferred source of nickel cations is nickel sulfate. Other nickel salts, such as nickel chloride and nickel acetate, are used for very limited applications. The chloride anion can act deleteriously when the EN plating bath is used to plate aluminum, or when the EN deposit is used as a protective coating over ferrous alloys in corrosion applications. The use of nickel acetate does not yield any significant improvement in bath performance or deposit quality when compared to nickel sulfate. Any minor advantages gained by nickel acetate are offset by its higher cost vs. the cost of nickel sulfate. The ideal source of nickel ions is the nickel salt of hypophosphorus acid, $Ni(H_2PO_2)_2$. The use of nickel hypophosphite would eliminate the addition of sulfate anions and keep to a minimum the buildup of alkali metal ions while replenishing the reactants consumed during metal deposition. The concentration of nickel ions and its relationship to the reducing agent and complexing agent concentrations will be discussed in a succeeding chapter.

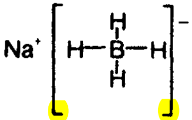
Reducing Agents

Four reducing agents are used in the chemical reduction of nickel from aqueous solutions:

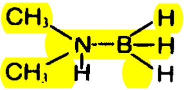
Sodium hypophosphite $NaH_2PO_2 \cdot H_2O$



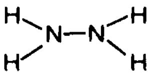
Sodium borohydride $NaBH_4$



Dimethylamine borane (DMAB) $(CH_3)_2NHBH_3$



Hydrazine $N_2H_4 \cdot H_2O$



The four reducing agents are structurally similar in that each contains two or more reactive hydrogens, and nickel reduction is said to result from the catalytic dehydrogenation of the reducing agent. Table 1.1 gives a summary of nickel reducing agents.

Electroless nickel deposition can be viewed, in a very elementary manner, as the sum of two chemical reactions occurring in an electrochemical cell—a chemical oxidation reaction that liberates electrons and a nickel reduction reaction that consumes electrons:

Oxidation of reducing agent

$\text{Red} \rightarrow \text{Ox} + ne$

Reduction of nickel ion

$mNi^{+2} + 2me^{-} \rightarrow mNi^{0}, 2m = n$

Overall or sum reaction

$$mNi^{+2} + Red \rightarrow mNi^{0} + Ox$$

The sum equation is a schematic illustration of the type of stoichiometric reactions usually written to describe the chemical reduction of nickel by a reducing agent. However, these overall reactions do not account for all of the phenomena that are observed during plating. Experimentally observed reaction characteristics indicate that the course of the reaction is considerably more complex than described by simple stoichiometric equations. Hence, it is necessary to attempt to ascertain the mechanism of the nickel reduction by the various reducing species.

Table 1.1
Nickel Reducing Agents

Reducing agent	Mol. wt.	Equiv. wt.	pH range	E^0, volts
Sodium hypophosphite			4-6	0.499
$NaH_2PO_2 \cdot H_2O$	106	53	7-10	1.57
Sodium borohydride				
$NaBH_4$	38	4.75	12-14	1.24
Dimethylamine borane				
$(CH_3)_2NHBH_3$	59	9.8	6-10	—
Hydrazine				
H_2NNH_2	32	8.0	8-11	1.16

An explicit understanding of the reaction mechanisms that govern electroless nickel deposition is necessary from both theoretical and practical viewpoints. Knowledge of the mechanisms of the reaction of a reducing agent with nickel ions can lead to the solution of a series of problems—development of methods to increase the plating rate, for enhancing hypophosphite efficiency, and for regulating the phosphorus or boron content of the deposit. It must be emphasized that an understanding of the course of the reaction, especially as it relates to the reduction of phosphorus or boron, is extremely important. It is the inclusion of P or B in the respective nickel alloys (Ni-P and Ni-B) that determines the properties of each alloy.

Before discussing the individual reducing agents and the proposed mechanisms of their reactions with nickel, it might be informative to recall certain characteristics of the process that the mechanism must explain:

- The reduction of nickel is always accompanied by the evolution of hydrogen gas.
- The deposit is not pure nickel but contains either phosphorus, boron or nitrogen, depending on the reducing medium used.
- The reduction reaction takes place only on the surface of certain metals, but must also take place on the depositing metal.
- Hydrogen ions are generated as a by-product of the reduction reaction.
- The utilization of the reducing agent for depositing metal is considerably less than 100 percent.
- The molar ratio of nickel deposited to reducing agent consumed is usually equal to or less than 1.

Hypophosphite

Nickel deposition by hypophosphite was sometimes represented in the literature by the following equations:

$$Ni^{+2} + H_2PO_2^- + H_2O \rightarrow Ni^0 + H_2PO_3^- + 2H^+ \quad [1]$$

$$H_2PO_2^- + H_2O \xrightarrow{cat} H_2PO_3^- + H_2 \quad [2]$$

overall

$$Ni^{+2} + 2H_2PO_2^- + 2H_2O \rightarrow Ni^0 + 2H_2PO_3^- + 2H^+ + H_2 \quad [3]$$

The reduction of nickel ions with hypophosphite yields alloys of nickel and phosphorus; however, Eqs. 1, 2, and 3 completely fail to account for the phosphorus component of the alloy. Further, if the plating reaction took place in accordance with the above equations, the rate of deposition would be proportional to the concentrations of the reactants. Gutzeit (5) has shown that in acid plating solutions ($pH > 3.0$), the plating rate has a first order dependence upon the hypophosphite concentration. That is, plating rate is dependent on the hypophosphite concentration, over a very wide concentration range. Gutzeit further showed the rate to be independent of the nickel ion concentration beyond about 0.02M Ni^{++}; the rate is said to have a zero order dependence on nickel concentration. In alkaline solution, the rate is dependent only on the hypophosphite concentration.

Since the publication in 1946 of the paper by Brenner and Riddell (1), four principal reaction mechanisms have been proposed to explain electroless nickel deposition, which is incompletely represented by the stoichiometric reactions in Eqs. 1 to 3. These reaction schemes attempt to explain nickel reduction by hypophosphite in both acid and alkaline media. To account for the phosphorus in the deposit, the proposed mechanisms involve a secondary reaction of hypophosphite to elemental phosphorus.

Each of the heterogeneous reaction mechanisms outlined below requires a catalytic surface on which the reaction sequence will proceed. Hence, electroless nickel plating occurs only on specific surfaces. The reduction reaction begins spontaneously on certain metals—almost all metals of Group VIII of the periodic table (Fe, Co, Ni, Rh, Pd, Pt) in active form. The active metals of Group VIII are well known as hydrogenation-dehydrogenation catalysts (5). Nickel, cobalt, palladium, and rhodium are considered to be catalytically active. Metals that are more electropositive than nickel, such as iron and aluminum, will first displace nickel from a solution of its ions as follows:

$$Fe + Ni^{+2} \rightarrow Fe^{+2} + Ni^0_{cat} \qquad [4]$$

or

$$2Al^0 + 3Ni^{+2} \rightarrow 2Al^{+3} + 3Ni^0_{cat} \qquad [5]$$

forming the catalytic surface, e.g., Ni^0cat. It is interesting to note that when steel or aluminum, the most commonly plated substrates, are electroless nickel plated, the initial phase in the deposition process is the displacement reaction.

If the substrate metal is more electronegative than nickel, it can be made catalytic by electrolytically depositing a thin nickel deposit on its surface. This can also be accomplished by providing contact, in the solution, between the substrate and a more electropositive metal, thereby forming an internal galvanic cell. For example, copper and its alloys are usually rendered catalytic to EN plating by either of these techniques.

A surface reaction, such as electroless nickel deposition, can be divided into the following elementary steps:

1. Diffusion of reactants (Ni^{+2}, $H_2PO_2^-$) to the surface;
2. Adsorption of reactants at the surface;
3. Chemical reaction on the surface;
4. Desorption of products (HPO_3^-, H_2, H^+) from the surface;
5. Diffusion of products away from the surface.

These are consecutive steps, and if any one has a much slower rate constant than all the others, it will become rate determining.

Appropriately, the first electroless nickel reaction mechanism proposed was advanced by Brenner and Riddell. They postulated that the actual nickel reductant is atomic hydrogen, which acts by heterogeneous catalysis at the catalytic nickel surface. The atomic hydrogen, generated by the reaction of water with hypophosphite, is absorbed at the catalytic surface:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H_{ad} \qquad [6]$$

The absorbed atomic hydrogen reduces nickel ions at the catalytic surface:

$$Ni^{+2} + 2H_{ad} \rightarrow (Ni^{+2} + 2H^+ + 2e) \rightarrow Ni^0 + 2H^+ \qquad [7]$$

The evolution of hydrogen gas, which always accompanies catalytic nickel reduction, was ascribed to the recombination of two atomic hydrogen atoms:

$$2H_{ad} \rightarrow (H + H) \rightarrow H_2 \qquad [8]$$

Gutzeit (5) essentially agrees with the Brenner-Riddell atomic hydrogen concept of nickel reduction. However, Gutzeit attributes the formation of atomic hydrogen to the dehydrogenation of the hypophosphite ion during formation of the metaphosphite ion:

$$H_2PO_2^- \xrightarrow{cat} PO_2^- + 2H \qquad [9]$$

followed by the formation of an orthophosphite molecule and an hydrogen ion according to:

$$PO_2^- + H_2O \rightarrow HPO_3^{-2} + H^+ \qquad [10]$$

A secondary reaction between hypophosphite and atomic hydrogen results in the formation of elemental phosphorus:

$$H_2PO_2^- + H \rightarrow P + OH^- + H_2O \qquad [11]$$

Although the atomic hydrogen mechanism, which has received the support of several authors, sustains the observed results, it fails to explain certain other phenomena. The scheme does not account for the simultaneous reduction of nickel and hydrogen, nor does it explain why the stoichiometric utilization of hypophosphite is always less than 50 percent.

The second mechanism, known as the *hydride transfer* mechanism, was first suggested by Hersch (6), who claimed that the behavior of hypophosphite is analogous to the reduction of nickel ions by borohydride ions. That is, Hersch assumed that hypophosphite acts as the donor of hydride ions (H^-). Hersch's proposed mechanism was later modified by Lukes (7).

In acid solutions, the primary step in the mechanism involves the reaction of water with hypophosphite at the catalytic surface, and may be described by the following equation:

$$2H_2PO_2^- + 2H_2O \xrightarrow{cat} 2H_2PO_3^- + 2H^+ + 2H^- \qquad [12]$$

The corresponding reaction in alkaline solution is given by:

$$2H_2PO_2^- + 6OH^- \xrightarrow{cat} 2H_2PO_3^- + 2H_2O + 2H^- \qquad [13]$$

The reduction of nickel ion in this mechanism proceeds as follows:

$$Ni^{+2} + 2H^- \rightarrow (Ni^{+2} + 2e^- + 2H) \rightarrow Ni^0 + H_2 \qquad [14]$$

The hydride ion can also react with water or a hydrogen ion:

Acid

$H^+ + H^- \rightarrow H_2$ [15a]

Alkaline

$H_2O + H^- \rightarrow H_2 + OH^-$ [15b]

According to Lukes, the hydrogen that appears as hydride ion was originally bonded to phosphorus in the hypophosphite. If Eq. 11 is included in this scheme, the codeposition of phosphorus is also accounted for. The hydride mechanism presents a satisfactory explanation for the coupled reduction of nickel and hydrogen.

The third mechanism is the so-called *electrochemical* mechanism, originally proposed by Brenner and Riddell, and later modified by others. This theory can be represented as follows:

An anodic reaction where electrons are formed by the reaction between water and hypophosphite:

$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^-$, $E^0 = 0.50$ V [16]

Cathodic reactions that utilize the electrons generated in Eq. 16:

$Ni^{+2} + 2e \rightarrow Ni^0$, $E^0 = -0.25$ V [17]

$2H^+ + 2e \rightarrow H_2$, $E^0 = 0.000$ V [18]

$H_2PO_2^- + 2H^+ + e \rightarrow P + 2H_2O$, $E^0 = 0.50$ V [19]

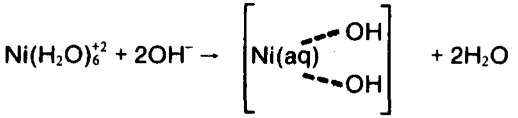
According to this mechanism, the evolution of hydrogen gas that takes place during nickel deposition is a result of the secondary reaction represented in Eq. 18. The electrochemical mechanism implies that the nickel ion concentration should have a significant effect on the rate of deposition; however, the converse is true.

The fourth mechanism involves the coordination of hydroxyl ions with hexaquonickel ion. This mechanism was proposed by Cavallotti and Salvago (8), and later supported by the results of calorimetric studies on electroless nickel plating by Randin and Hintermann (9). The chemical reduction of nickel at a catalytic surface can be represented by the following reactions:

Ionization of water at catalytic nickel surface:

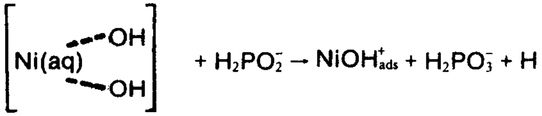
$2H_2O \rightarrow 2H^+ + 2OH^-$ [20]

Coordination of hydroxyl ions to solvated nickel ion:



$$Ni(H_2O)_6^{+2} + 2OH^- \rightarrow \left[Ni(aq) \begin{matrix} OH \\ OH \end{matrix} \right] + 2H_2O \qquad [21]$$

Reactions of hydrolized nickel species with hypophosphite:



$$\left[Ni(aq) \begin{matrix} OH \\ OH \end{matrix} \right] + H_2PO_2^- \rightarrow NiOH_{ads}^+ + H_2PO_3^- + H \qquad [22]$$

$$NiOH_{ads} + H_2PO_2^- \rightarrow Ni^0 + H_2PO_3^- + H \qquad [23]$$

where $NiOH_{ads}$ represents a hydrolyzed Ni^+ species adsorbed at the catalytic surface. The hydrogen atoms formed by reactions 22 and 23 result from P-H bonds. The two hydrogen atoms can react and evolve as hydrogen gas:

$$H + H \rightarrow H_2 \qquad [24]$$

Salvago and Cavallotti (10) proposed the direct interaction of the catalytic nickel surface with hypophosphite to give phosphorus codeposition:

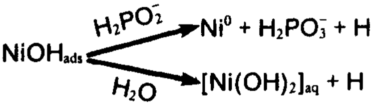
$$Ni_{cat} + H_2PO_2^- \rightarrow P + NiOH_{ad}^+ + OH^- \qquad [25]$$

The authors point out that copper, silver, and palladium can be reduced by $H_2PO_2^-$ without P codeposition, and hence, show the direct intervention of the chemical nature of the metal in the codeposition reaction.

According to the reaction scheme proposed by Salvago and Cavallotti (10), the hydrolyzed Ni species can react with water as follows:

$$NiOH_{ads}^+ + H_2O \rightarrow [Ni(OH)_2]_{aq} + H \qquad [26]$$

Reactions 23 and 26 are seen to be competing reactions, that is:



$$NiOH_{ads} \xrightarrow{H_2PO_2^-} Ni^0 + H_2PO_3^- + H \qquad [27a]$$

$$NiOH_{ads} \xrightarrow{H_2O} [Ni(OH)_2]_{aq} + H \qquad [27b]$$

Salvago and Cavallotti further argue that the adsorbed NiOH species plays a role in the lamellar morphology observed in electroless nickel deposits. Gutzeit (5) attributes the lamellae of the EN deposit to a periodic variation of the phosphorus content in the coating. As long as there is a constant supply of adsorbed NiOH species on the catalytic surface and reaction 23 takes place, the deposition of phosphorus via reaction 25 cannot occur. The metallic Ni_{cat} surface must be available for a direct interaction with $H_2PO_2^-$ to deposit phosphorus. However, if reaction 26 occurs, the metallic catalytic nickel surface that was previously covered by adsorbed NiOH species is now free to interact with $H_2PO_2^-$. It is evident that any periodicity between reactions 23 and 26 will lead to a lamellar morphology.

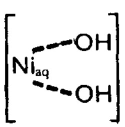
The reaction of hypophosphite ions with water must also be included in the reaction scheme:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2 \qquad [28]$$

According to Randin and Hintermann (9), the overall reaction can be written as:

$$Ni^{+2} + 4H_2PO_2^- + H_2O \rightarrow Ni^0 + 3H_2PO_3^- + H^+ + P + 3/2H_2 \qquad [29]$$

From Eq. 29, the mole ratio $[Ni^{+2}]/[H_2PO_2]$ is observed to be ¼ (0.25).



is a schematic representation of the reacting species formed by loosely bonded OH^- ion in the coordination sphere of partially solvated $Ni(H_2O)_4^{+2}$ ions, and not nickel hydroxide. Cavallotti and Salvago, in fact, point out that when nickel hydroxide precipitates, inhibition phenomena are evident. If the hydroxyl ions are bonded too tightly to the nickel, they will not react with the hypophosphite ion. The adsorption of the hydrolyzed species on the active surface probably increases the lability of the coordination bonds.

The results of the studies by Franke and Moench (11) and later by Sutyagina, Gorbunora and Glasunov (12) on the origin of the hydrogen gas evolved from the interaction between water and hypophosphite ion can be explained by the reaction mechanism proposed by Cavallotti and Salvago.

Reducing Agents Containing Boron

In the forty or so years since the discovery of "electroless" nickel plating by Brenner and Riddell, hundreds of papers describing the process and the resulting deposits have been published. Although other electroless systems depositing metals such as palladium, gold, and copper are covered, the vast majority of these publications (papers and patents) are concerned with nickel and cobalt-phosphorus alloys and the plating solutions that produce them.

Attempts to develop alternative reducing agents led several workers to investigate the boron-containing reducing agents, in particular, the borohydrides and amine boranes. Subsequently, several patents were issued covering electroless plating processes and the resulting deposits.

The deposits obtained from electroless systems using boron-containing reducing agents are nickel-boron alloys. Depending on the solution operating conditions, the composition of the deposit can vary in the range of 90 to 99.9

percent nickel, with varying amounts of reaction products. In some cases, a metallic stabilizer will be incorporated in the deposit during the plating reaction.

As is the case with nickel-phosphorus alloys, nickel-boron deposits are characterized by their unique chemical and physical properties.

The Borohydride (BH_4^-) Ion

The borohydride reducing agent may consist of any water soluble borohydride compound. Sodium borohydride is generally preferred because of its availability. Substituted borohydrides in which not more than three of the hydrogen atoms of the borohydride ion have been replaced can also be used; sodium trimethoxyborohydride ($NaB(OCH_3)_3H$) is an example of this type of compound.

The borohydride ion is a powerful reducing agent. The redox potential of BH_4^- is calculated to E_{ca} = 1.24 V. In basic solutions, the decomposition of the BH_4 unit yields 8 electrons for the reduction reaction:

$$BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e^- \qquad [30]$$

Then, each borohydride ion can theoretically reduce four nickel ions. That is, adding Eq. 30 to:

$$4Ni^{+2} + 8e^- \rightarrow 4Ni^0 \qquad [31]$$

gives the overall reaction:

$$4Ni^{+2} + BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4Ni^0 + 4H_2O \qquad [32]$$

However, it has been found experimentally that one mole of borohydride reduces approximately one mole of nickel.

There are only a few published articles that are concerned with the mechanism of nickel deposition with borohydride, and most of the proposed schemes are not supported by experimental data. Experimental evidence to the contrary, several authors still assume that each borohydride ion reduces four nickel ions.

Although the authors of three separate mechanisms agree that nickel reduction proceeds as expressed in Eq. 31, the reduction to boron is approached differently in each case.

Case 1 (13)

Here the author assumes that only three hydride ions are oxidized to protons and that the fourth hydride is oxidized to a hydrogen atom, which leads to the formation of a molecule of evolved hydrogen gas:

$$4Ni^{+2} + 2BH_4^- + 6OH^- \rightarrow 2Ni_2B + 6H_2O + H_2 \qquad [33]$$

Case 2 (14)

In this instance, it is assumed that all hydride ions are oxidized to protons, so that:

$$5Ni^{+2} + 2BH_4^- + 8OH^- \rightarrow 5Ni^0 + 2B + 8H_2O \qquad [34]$$

Case 3 (15)

Boron reduction is, as assumed by these authors, the catalytic decomposition of borohydride to elemental boron that takes place independently of nickel reduction:

$$2BH_4^- + 2H_2O \rightarrow 2B + 2OH^- + 5H_2O \qquad [35]$$

Gorbunova, Ivanov and Moissev (16) raised an objection to the three above hypotheses. They argue that, based on data relating to the reduction reactions by hypophosphite, it is doubtful that the hydrogen atoms, formed during the oxidation of the hydride ions of BH_4^-, are intermediate products that can take part in either nickel or boron reduction:

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H + 4H^+ + 4e \qquad [36]$$

Data obtained from mass-spectrometric measurements of the isotope composition of hydrogen gas evolved during electroless Ni-B deposition experiments using heavy water (D_2O), led Gorbunova et al. to propose a mechanism that more nearly fit the results of their studies. Their experiments were carried out using plating solutions prepared with D_2O, and also containing NaOD. It should be noted that calculations based on previously proposed schemes yielded results that deviated by almost 200 percent from the experimental data obtained in isotope experiments.

The proposed scheme of Gorbunova et al. for the reaction mechanism of nickel-boron plating consists of three main steps:

Reduction of nickel

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H + 4H^+ + 4e^- \qquad [37]$$

$$2Ni^{+2} + 4e^- \rightarrow 2Ni^0 \qquad [38]$$

$$BH_4^- + 2Ni^{+2} + 4H_2O \rightarrow 2Ni^0 + B(OH)_4^- + 2H_2 + 4H^+ \qquad [39]$$

Reduction of boron

$$BH_4^- + H^+ \rightarrow BH_3 + H_2 \rightarrow B + 5/2H_2 \qquad [40]$$

Hydrolysis of borohydride

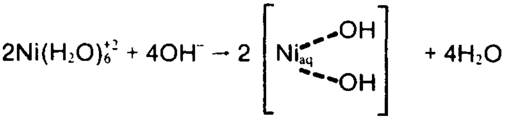
$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H + 4H^+ + 4e^- \rightarrow B(OH)_4^- + 4H_2 \qquad [41]$$

Mallory (17) has also investigated the reduction of nickel ions by amine boranes. On the basis of experimental data (16,17), he suggests that the hydrolyzed nickel mechanism of Cavallotti and Salvago, proposed to explain nickel reduction with hypophosphite, can be adapted to explain nickel reduction with both borohydride and amine boranes. The modified hydrolyzed nickel mechanism with borohydride can be represented by the following sequence of reactions:

Ionization of water

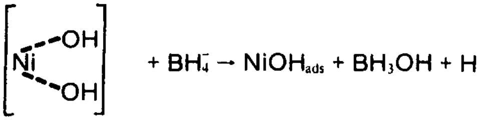
$$4H_2O \rightarrow 4H^+ + 4OH^- \qquad [42]$$

Coordination of hydroxyl ions to solvated nickel ion



$$2Ni(H_2O)_6^{+2} + 4OH^- \rightarrow 2\left[Ni_{aq}\begin{array}{l}\cdots OH\\ \cdots OH\end{array}\right] + 4H_2O \qquad [43]$$

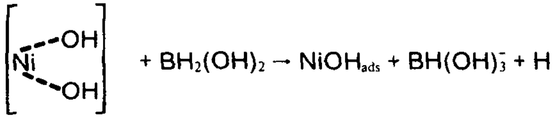
Reaction of hydrolized nickel species with borohydride ion



$$\left[Ni\begin{array}{l}\cdots OH\\ \cdots OH\end{array}\right] + BH_4^- \rightarrow NiOH_{ads} + BH_3OH + H \qquad [44]$$

$$NiOH_{ads} + BH_3OH^- \rightarrow Ni^0 + BH_2(OH)_2^- + H \qquad [45]$$

The $BH_2(OH)_2^-$ species reacts with the second hydrolyzed nickel ion in a similar manner:



$$\left[Ni\begin{array}{l}\cdots OH\\ \cdots OH\end{array}\right] + BH_2(OH)_2 \rightarrow NiOH_{ads} + BH(OH)_3^- + H \qquad [46]$$

$$NiOH_{ads} + BH(OH)_3 \rightarrow Ni^0 + BO_2 + 2H_2O + H \qquad [47]$$

The four atoms of atomic hydrogen react to form hydrogen gas

$$4H \rightarrow 2H_2 \qquad [48]$$

Thus, Eqs. 42 through 48 can be represented by the overall reaction:

$$2Ni^{+2} + 4H_2O + BH_4^- \rightarrow 2Ni^0 + B(OH)_4^- + 2H_2 + 4H^+ \qquad [49]$$

The reduction of boron is accounted for in the reaction of BH_4^- with a hydrogen ion:

$$BH_4^- + H^+ \rightarrow BH_3 + H_2 \rightarrow B + 5/2H_2 \qquad [50]$$

Equations 49 and 50 can be combined to obtain:

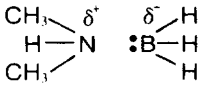
$$2Ni^{+2} + 2BH_4^- + 4H_2O \rightarrow 2Ni^0 + B + B(OH)_4^- + 3H^+ + 9/2H_2 \qquad [51]$$

The mechanism proposed by Gorbunova et al. and the modified Cavallotti and Salvago proposal lead to the same overall reaction. Also, in both schemes, the increase in acidity observed in the process is a result of hydrogen ions that originate from water molecules only. Finally, the two mechanisms indicate that the mole ratio of nickel reduced to borohydride consumed is 1:1, which is supported by experimental evidence.

The Amine Boranes

In the BH_3 molecule, the boron octet is incomplete, that is, boron has a low-lying orbital that it does not use in bonding, owing to a shortage of electrons. As a consequence of the incomplete octet, BH_3 can behave as an electron acceptor (Lewis acid). Thus, electron pair donors (Lewis bases), such as amines form 1:1 complexes with BH_3 and thereby satisfy the incomplete octet of boron. The linkage between BH_3 and dimethylamine is illustrated by the following:

The amine boranes are covalent compounds whereas borohydrides such as $Na^+BH_4^-$ are completely ionic, that is, $Na^+ BH_4^- = Na^+ + BH_4^-$. Although the amine boranes do not ionize, one of the atoms has a greater affinity for the electrons than the other and the bond will therefore be polar:



In this case, the electrons are displaced toward the boron atom, giving the boron atom excess negative character, whereas the nitrogen atom displays excess positive charge. The electrical polarity of a molecule, expressed as its dipole moment, plays an important role in the reactions of covalent compounds.

The commercial use of amine boranes in electroless nickel plating has, in general, been limited to dimethylamine borane (DMAB), $(CH_3)NHBH_3$. DMAB has only three active hydrogens bonded to the boron atom and, therefore, should theoretically reduce three nickel ions for each DMAB molecule consumed (each borohydride will theoretically reduce four nickel ions). The reduction of nickel ions with DMAB is described by the following equations:

$$3Ni^{+2} + (CH_3)_2NHBH_3 + 3H_2O \rightarrow 3Ni^0 + (CH_3)_2NH_2^+ + H_3BO_3 + 5H^+ \qquad [52]$$

$$2[(CH_3)_2NHBH_3] + 4Ni^{+2}\ 3H_2O \rightarrow Ni_2B + 2Ni^0 + 2[(CH_3)_2NH_2^+] + H_3BO_3 + 6H^+ + \tfrac{1}{2}H_2 \qquad [53]$$

In addition to the above useful reaction, DMAB *can be consumed by wasteful* hydrolysis:

Acid

$$(CH_3)_2NHBH_3. + 3H_2O + H^+ \rightarrow (CH_3)_2NH_2^+ + H_3BO_3 + 3H_2 \qquad [54]$$

Alkaline

$(CH_3)_2NHBH_3 + OH^- \xrightarrow{H_2O} (CH_3)_2NH + BO_2^- + 3H_2$ [55]

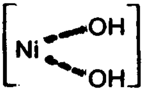
The theoretical expressions for nickel reduction are not supported by experimental findings, however. The results of studies on chemical nickel plating with DMAB indicates that the molar ratio of nickel ions reduced to DMAB molecules consumed is approximately 1:1 (17). A modified hydrolyzed nickel mechanism satisfactorily accommodates the experimental data.

Based on his studies, Lelental (18) suggests that nickel deposition with DMAB is dependent on the adsorption of the reducing media on the catalyst surface, followed by cleavage of the N-B bond of the adsorbed amine borane. The adsorption step is consistent with the polar nature of the DMAB molecule. The mechanism can be illustrated as follows:

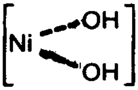
N-B bond cleavage

$2R_2NHBH_3 \xrightarrow{cat} 2R_2NH + 2BH_{3ads}$ [56]

Reduction of hydrolized nickel with BH_{3ads}

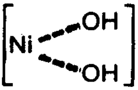


$+ BH_{3ads} \rightarrow Ni^0 + BH(OH)_{2ads} + 2H$ [57]



$+ BH(OH)_{2ads} \rightarrow NiOH_{ads} + B(OH)_3 + H$ [58]

$NiOH_{ads} + BH_{3ads} \rightarrow Ni^0 + BH_2OH + H$ [59]



$+ BH_2(OH) \rightarrow Ni^0 + B(OH)_3 + 2H$ [60]

The sums of the above equations, including the ionization of water, is:

$3Ni^{+2} + 2R_2NHBH_3 + 6H_2O \rightarrow 3Ni^0 + 2R_2NH_2^+ + 2B(OH)_3 + 3H_2 + 4H^+$ [61]

Boron reduction

$R_2NHBH_3 \xrightarrow{cat} R_2NH + BH_3 + H_2 + H^+ \rightarrow R_2NH_2^+ + B + 5/2\ H_2$ [62]

Equations 61 and 62 can be combined to give:

$$3Ni^{+2} + 3R_2NHBH_3 + 6H_2O \rightarrow 3Ni^0 + B + 3R_2NH_2^+ + 2B(OH)_3 + 9/2H_2 + 3H^+ \quad [63]$$

Hydrazine

Soon after Brenner and Riddell published their findings on nickel reduction with hypophosphite, Pessel (19) was issued a patent (1947) claiming the use of hydrazine as a metal reductant. During the succeeding 16 years, many papers and patents were published detailing electroless nickel-phosphorus deposition. It was not until 1963, however, that Levy (20) reported the results of his investigation of electroless plating with hydrazine. Later, Dini and Coronado (21) described several electroless nickel-hydrazine plating baths and the properties of the deposits obtained from their solutions, which contained >99 percent nickel.

Hydrazine is a powerful reducing agent in aqueous alkaline solutions:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-,\ E_b = 1.16\ V \quad [64a]$$

$$2Ni^2 + 2e \rightarrow 2Ni^0,\ E^0 = -0.25\ V \quad [64b]$$

Levy (20) proposed the following reduction reaction for nickel ions with hydrazine in an alkaline solution:

$$2Ni^{+2} + N_2H_4 + 4OH^- \rightarrow 2Ni^0 + N_2 + 4H_2O,\ E^0 = 0.91\ V \quad [64c]$$

which is the sum of Eqs. 64a and 64b.

This reaction implies a reducing efficiency of 100 percent for hydrazine, since the hydrazine is involved in the reduction of nickel ions only. Equation 64c does not account for the hydrogen evolved during the nickel plating reaction with hydrazine.

The hydrolyzed nickel ion mechanism can be modified to represent the experimental observations made during nickel reduction with hydrazine:

$$Ni^{+2} + 2OH^- \rightarrow Ni(OH)_2^{+2}$$

$$Ni(OH)_2^{+2} + N_2H_4 \rightarrow Ni(OH)_{ad}^{+1} + N_2H_3OH + H$$

$$Ni(OH)^{+1}_{ad} + N_2H_3OH \rightarrow Ni + N_2H_2(OH)_2 + H$$

$$2H \rightarrow H_2$$

The overall reaction can be written as:

$$Ni^{+2} + N_2H_4 + 2OH^- \rightarrow Ni^0 + N_2 + 2H_2O + H_2 \quad [65a]$$

The above mechanism does not account for the formation of hydrogen ions (H^+) during the course of the deposition reaction. In the reaction sequence given above, the hydroxyl ions (OH^-) in the first step are present in the solution through the addition of alkali metal or ammonium hydroxides. However, if the hydroxyl ions coordinated to nickel are generated by the dissolution of water molecules, a slightly different reaction mechanism results:

$$2H_2O = 2H^+ + 2OH^-$$

$$Ni^{+2} + 2OH^- = Ni(OH)_2$$

$$Ni(OH)_2 + N_2H_4 = Ni^0 + N_2H_2(OH)_2 + 2H$$

$$N_2H_2(OH)_2 + 2H = N_2 + 2H_2O + H_2$$

Now the overall reaction is given by:

$$Ni^{+2} + N_2H_4 \xrightarrow{H_2O} Ni^0 + N_2 + H_2 + 2H^+ \qquad [65b]$$

The two plausible reaction mechanisms proposed for the reduction of nickel with hydrazine lead us to speculate that there are separate mechanisms for the reduction of nickel with hypophosphite (and possibly DMAB) in acidic and alkaline solutions. This assumption is based on the acceptance of the nickel hydroxide mechanism, or some modification of it.

In acidic solutions, the first stage of the process is the dissociation of water ($H_2O = H^+ + OH^-$) at the catalytic surface. The hydroxyl ions (OH^-) replace the hydrogen in the P-H bond of hypophosphite and as a result, an electron and a hydrogen atom are produced. The consumption of OH^- ions results in the accumulation of hydrogen ions (H^+) in the solution with a concurrent decrease in pH of the solution.

In alkaline solutions, the sources of hydroxyl ions are the basic compounds ($NaOH$, NH_4OH, etc.) that are added to the plating solution to adjust the pH into the alkaline range of >7.0 to 14.0. As a result of the reaction of OH^- with the P-H bond, the pH also decreases in the alkaline solution. In this case, however, the pH decrease is due to the consumption of OH^- ions rather than the formation and accumulation of H^+ ions.

Van Den Meerakker (22) claims that electroless deposition processes can be explained by a so-called universal electrochemical mechanism, regardless of the nature of the reducing agent. Each process can be divided into a series of elementary anodic and cathodic reactions, where the first anodic step is the chemical dehydrogenation of the reductant. Thus in alkaline media:

Anodic

(1) Dehydrogenation $RH \xrightarrow{cat} R + H$

(2) Oxidation $R + OH^- \rightarrow ROH + e$

(3) Recombination $H + H \rightarrow H_2$

(4) Oxidation $H + OH^- \rightarrow H_2O + e$

Cathodic

(5) Metal deposition $M^{+n} + ne \rightarrow M^0$

(6) Hydrogen evolution $2H_2O + 2e \rightarrow H_2 + 2OH^-$

In acid media, reactions 4 and 6 in this set of equations become:

(4a) Oxidation $H \rightarrow H^+ + e$

(6a) Hydrogen evolution $2H^+ + 2e \rightarrow H_2$

Subsequent discussion in this section will show that a universal mechanism for electroless metal deposition is not feasible.

Each of the mechanisms discussed for the various reducing agents, and in particular for hypophosphite, explain most of the characteristics of electroless nickel deposition. However, each mechanism fails to account for some experimentally observed characteristic of the plating reaction. According to the hydride ion theory, the utilization of hypophosphite is always less than 50 percent, which is contrary to an observation of Pearlstein and Weightman (23). Experimental data indicates that the hydrogen gas evolved during the plating reaction originates, in the main, from the reducing agent; this fact is not supported by the electrochemical mechanism.

Electrochemically speaking, an electroless deposition reaction can be considered the combined result of two independent electrode reactions:

- The cathodic partial reactions (e.g., the reduction of metal ions)
- The anodic partial reactions (e.g., the oxidation of the reductant)

The electrons required for the reduction of the metal ions are supplied by the reducing agent. Mixed potential theory interprets many electrochemical processes in terms of the electromechanical parameters of the partial electrode reactions. Paunovic (24) was the first to identify electroless metal deposition in terms of mixed potential theory. He suggested that electroless deposition mechanisms could be predicted from the polarization curves of the partial anodic and cathodic processes. In simple terms, mixed potential theory leads to the assumption that electroless nickel plating can be considered as the superposition of anodic and cathodic reaction at the mixed (deposition) potential, E_M. Accordingly, the rates of the anodic reactions are independent of the cathodic reactions occurring simultaneously at the catalytic surface, and the rates of the separate partial reactions depend only on the electrode potential, the mixed potential. If these assumptions are correct, it should be possible, experimentally, to separate the anodic and cathodic reactions at different electrodes.

The partial anodic and cathodic reaction for electroless nickel deposition with hypophosphite are usually written as follows:

Anodic

Oxidation of H_2PO_2

$H_2PO_2 + H_2O \rightarrow H_2PO_3 + 2H^+ + 2e$; i_{Red} = hypophosphite oxidation current

Cathodic

$Ni^{+2} + 2e \rightarrow Ni^0$; i_{Ni} = nickel deposition current

$2H^+ + 2e \rightarrow H_2$; i_H = hydrogen evolution current

$H_2PO_2 + 2H^+ + e \rightarrow P + 2H_2O$; i_p = phosphorus deposition current

At steady state equilibrium potential (mixed potential), the rate of deposition is equal to the rate of oxidation of hypophosphite (anodic current, i_{Red}), and to the rate of the cathodic reactions (cathodic current, $i_{Ni} + i_H + i_p$). That is:

$$i_{deposition} = i_{Red} = i_{Ni} + i_M + i_p$$

Using Faraday's law, the rate of nickel deposition can be expressed as:

$$Rate_{(mg/cm/hr)} = 1.09 \times i_{dep(mA/cm2)}$$

The mixed potential, E_M, and the deposition current, i_{dep}, are obtained by the intersection of the partial anodic and cathodic polarization curves. Figure 1.2 is a schematic representation of the superposition of anodic and cathodic polarization curves, showing E_M and i_{dep}.

deMinjer (25) experimentally tested the validity of the mixed potential theory as applied to electroless nickel plating with hypophosphite. She found that it was possible for the anodic and cathodic reactions to occur at separate electrodes. The anodic oxidation of hypophosphite was observed to take place at a nickel or Ni-P electrode placed in a nickel-free hypophosphite solution, while the reduction of nickel metal takes place at a separate nickel or nickel-phosphorus electrode in a hypophosphite-free nickel-containing catholyte. It should be noted that deMinjer's experiments were run under acidic conditions (pH 4.2 to 4.3). We refer the reader to Ref. 25 for the details of her experiments.

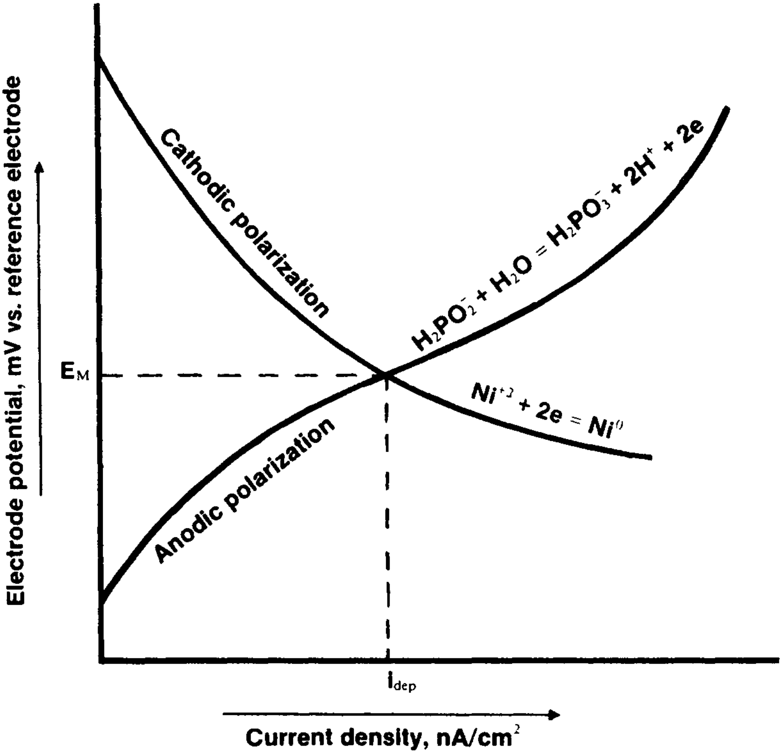


Fig. 1.2—Schematic representation of anodic and cathodic polarization curves combined in an Evan's diagram for deposition potential (E_M) and deposition current (i_{dep}).

Hydrogen evolution is usually considered to be a cathodic process (see above). However, studies by El-Raghy and Salama (26) on electroless copper plating lead to a different conclusion. They investigated electroless copper deposition electrochemically using a two-chamber galvanic cell and observed that hydrogen gas formation is an anodic process. That is, hydrogen evolution in electroless copper plating is the result of the anodic oxidation of the reducing agent formaldehyde.

Pearlstein (27) used the two-chamber technique to study electroless silver deposition with DMAB. A schematic representation of the two-chamber system used by Pearlstein is reproduced in Fig. 1.3. At open circuit, an extremely small amount of gas evolution was noted at the silver electrode in the silver-ion-free DMAB solution; there was no visible gassing on the silver electrode in the DMAB-free solution containing silver ions. When the silver electrodes in the two chambers were connected, he observed "a very evident increase in gas evolution

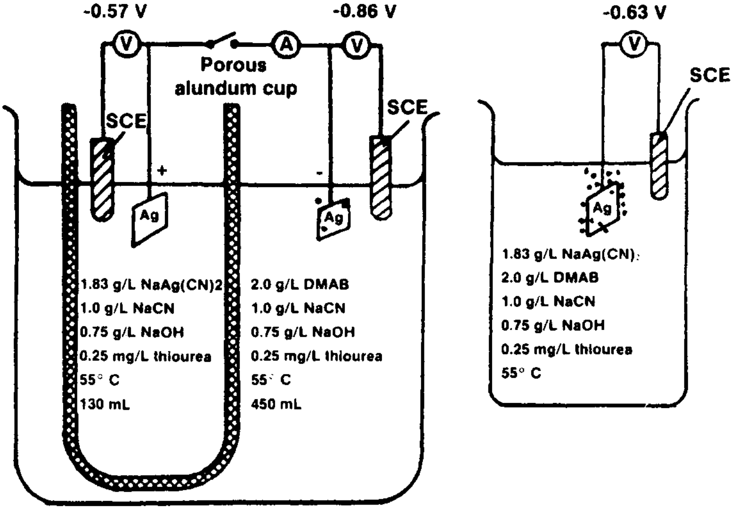


Fig. 1.3—Schematic representation of two-chamber system used to study electroless silver.

on the electrode in the DMAB-containing solution". No gassing was produced on the electrode in the silver-ion solution. Therefore, hydrogen evolution in electroless silver plating with DMAB is the product of the anodic oxidation of the DMAB.

Unfortunately, deMinjer did not report at which electrode (anode or cathode or both) hydrogen evolution occurred in her two-chamber electroless nickel experiments with hypophosphite.

Using polarization techniques, Ohno, Wakabayashi and Haruyama (28) studied the anodic oxidation of the reducing agents used in electroless plating—$H_2PO_2^-$, BH_4^-, DMAB, N_2H_4, and HCHO. The experiments were carried out in alkaline solutions on different metal electrodes (Ni, Co, Pd, Pt, Cu, Ag, Au), with special attention being paid to the catalytic aspect of electroless deposition. The authors found that the rate of anodic oxidation of a particular reductant depended on the pH of the solution, the concentration of the reductant, and the nature of the metal electrodes. Anodic polarization curves for hypophosphite on nickel electrodes exhibit a peak current that increases with increasing hypophosphite concentration. Similarly, the anodic current was also observed to increase with increasing pH (at constant $H_2PO_2^-$), with the current maximum shifting to less noble potentials. The polarization curves for the anodic oxidation of the other nickel-reducing agents (BH_4^-, DMAB, and N_2H_4) also exhibited current maximum behavior on nickel electrodes. The effects that concentration and pH have on the anodic oxidation current for $H_2PO_2^-$ on nickel electrodes are illustrated in Figs. 1.4 and 1.5, respectively.

Ohno et al. did not detect an anodic current attributable to the oxidation of hypophosphite or DMAB on copper electrodes. They found that the shape of the

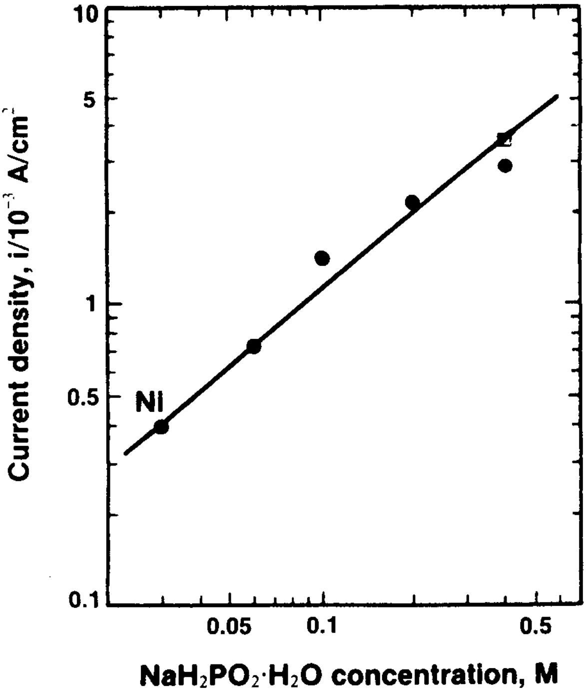


Fig. 1.4—Effect of $NaH_2PO_2 \cdot H_2O$ concentration on the anodic oxidation current on nickel electrodes at constant potential.

polarization curves of the nickel-reducing agents on Pd, Pt, Ag, and Au was similar to the shapes of Tafel curves. These two facts support the contention that the nature of the metal electrode strongly affects the polarization behavior of the reductants.

Prior to the start of the polarization experiments, Ohno et al. observed that hydrogen gas evolution occurred on some electrodes at open-circuit condition, especially in solutions containing $H_2PO_2^-$, BH_4^-, or DMAB. During the experiment, shifting the potential to more noble values resulted in an increase in hydrogen gas evolution on Cu, Ag, or Au electrodes. Thus, the anodic oxidation of a reducing agent on a Group IB metal is accompanied by the formation of hydrogen gas that comes from hydrogen bonded directly to the reductant molecule. These observations coincide with and support the experimental findings of Pearlstein (27).

On the other hand, shifting the potential of the Group VIII (Co, Ni, Pd, Pt) metal electrodes to more noble potentials resulted in a decrease in hydrogen gas

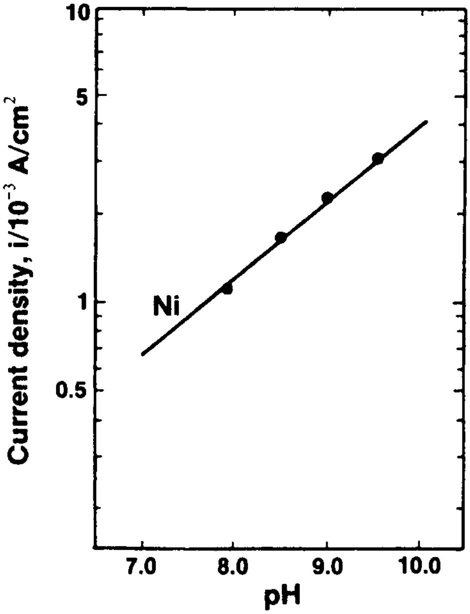


Fig. 1.5—Effect of pH on the anodic oxidation current of hypophosphite (0.2M) on nickel electrode.

evolution, and finally, its cessation during the anodic oxidation of hypophosphite, borohydride, and dimethylamine borane.

At this point, it would be premature to draw any conclusions or make assumptions as to the mechanism of electroless deposition based solely on the results reported in Refs. 26 through 28. This is especially true since the experiments undertaken in these studies were limited to alkaline solutions. What has been learned, however, is that hydrogen gas formation and evolution cannot be considered as strictly a cathodic process. A more cogent insight as to a possible mechanism or mechanisms can be gained by also reviewing the literature that is concerned with the anodic oxidation of the acid-compatible reducing agents in acid media. Therefore, of particular interest are the hypophosphite anion and DMAB.

Paunovic (29,30) reported on the electrochemical aspects of electroless nickel plating with DMAB in neutral (pH 7.0) solutions. Using polarization and other techniques, the author investigated the partial electrochemical processes. Most germane to this discussion on mechanisms, however, is the development of the kinetic diagnostic criteria $i_p/\sqrt{v}$ vs. v, where i_p is the peak current and v is the potential scan rate, mV/sec. Paunovic determined that if the ratio $i_p/\sqrt{v}$ decreases with an increase in scan rate v, then the charge-transfer reaction is preceded by a chemical reaction(s). He gave as the general kinetic scheme for this case:

(i) $Y \rightleftharpoons Red$

(ii) $Red \rightarrow Ox + ne$

where the substance Y is not directly oxidized at the applied potential, but is converted to the electroactive form, Red, by the preceding chemical reaction (i).

The direct oxidation of DMAB is usually written as:

$$(CH_3)_2NHBH_3 \xrightarrow{3H_2O} (CH_3)_2NH_2 + H_3BO_3 + 5H^+ + 6e \qquad [52a]$$

However, reactions involving DMAB are probably preceded by cleavage of the N-B bond:

$$(CH_3)_2NHBH_3 \rightarrow (CH_3)_2NH + BH_3 \qquad [56]$$

Hence, Eq. 56 is a homologue of reaction i and BH_3 is the electroactive species formed by a chemical reaction, which is subsequently oxidized and which supplies electrons for the reduction of nickel. The BH_3 unit also supplies the atomic hydrogen that is involved in H_2 evolution. The following scheme illustrates the cleavage of the N-B bond, the oxidation of BH_3, generation of electrons and evolution of hydrogen gas in acid or neutral solutions:

(1) $(CH_3)_2NHBH_3 \rightarrow (CH_3)_2NH + BH_3$

(2) $BH_3 \xrightarrow{3H_2O} BH_2(OH) + 3H^+ + 2OH^- + H + e$
(water dissociation $3H_2O = 3H^+ + 3OH^-$)

(3) $BH_2(OH) + 2OH^- \rightarrow BH(OH)_2 + OH^- + H + e$

(4) $BH(OH)_2 + OH^- \rightarrow B(OH)_3 + H + e$

Adding steps 1 through 4:

$$(CH_3)_2NHBH_3 + H^+ \xrightarrow{3H_2O} (CH_3)NH_2 + B(OH)_3 + 3H^+ + 3/2\ H_2 + 3e$$

A similar scheme can be written for these elementary steps in neutral or alkaline solutions.

More recently, Mital, Shrivastava and Dhaneshwar (31) sought to ascertain the validity of mixed potential theory as applied to electroless nickel deposition. Their studies involved the use of potentiostatic and voltammetric techniques on electroless nickel baths containing hypophosphite or DMAB in acid solutions (pH 6.0).

The current potential curves obtained by Mital et al. for the anodic oxidation of hypophosphite are similar in shape to those reported by Ohno et al. (28). The anodic curve attains a current maximum at which point there is a sudden rise in the anodic potential, indicating the possibility of formation of a passivating film on the electrode surface. In the case of DMAB, however, the anodic curves show a smooth monotonic increase in current with increasing anodic potential.

The deposition rate calculated from i_{dep} was compared to the rate obtained by the gravimetric method. Mital et al. (31) found the calculated rate to be significantly lower than the rate determined gravimetrically, the values being 1.63 and 10 mg/cm^2/hr, respectively. This fact indicated that an electrochemical mechanism under mixed potential control is not applicable in the case of Ni-P deposition.

The results reported (31) for plating with DMAB show the predominance of an electrochemical mechanism; i.e., the rates obtained from i_{dep} and the gravimetric method were 7.0 and 8.0 mg/cm^2/hr at 70° C, respectively.

Mital et al. state that mixed potential theory is applicable only to those electroless systems where the reduction of metal ions and the oxidation of reductant is electrochemically feasible at E_{Mix}, which they claim is the case with DMAB. On the other hand, when the reducing agent is not oxidizable electrochemically at E_{Mix}, as it is in the case of $H_2PO_2^-$, they assert that a chemical mechanism predominates. It is not clear if Mital et al. are proposing that each elementary step is a chemical reaction in an overall chemical reaction, or if at least one step is a charge-transfer reaction and the remaining steps in the overall reaction are chemical reactions. (A chemical reaction, as distinguished from an electrochemical reaction, is a reaction whose rate depends only on the concentrations of the reactants and is independent of the potential; i.e., a chemical reaction has a rate constant that is independent of the potential. If one of a number of elementary reactions is a charge-transfer reaction, then the overall reaction is an electrochemical reaction.)

It is obvious from the lengthy discussion above that considerably more experimental data will be required in order to formulate a reaction mechanism for EN deposition that satisfies all observed results for each reducing agent.

Complexing Agents

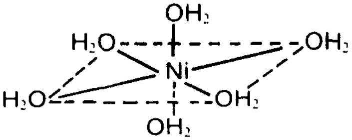
The additives referred to as complexing agents in electroless nickel plating solutions are, with two exceptions, organic acids or their salts. The two exceptions are the inorganic pyrophosphate anion, which is used exclusively in alkaline EN solutions, and the ammonium ion, which is usually added to the plating bath for pH control or maintenance. Examples of the complexing agents commonly used in electroless nickel solutions are given in Table 1.2.

There are three principal functions that complexing agents perform in the EN plating bath:

- They exert a buffering action that prevents the pH of the solution from decreasing too fast.
- They prevent the precipitation of nickel salts, e.g., basic salts or phosphites.
- They reduce the concentration of free nickel ions.

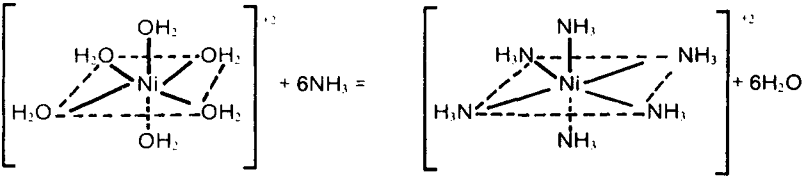
In addition to these functions, complexing agents also affect the deposition reaction and hence the resultant nickel deposit. These factors will be discussed throughout this chapter.

Nickel ions in aqueous solution interact with and are bound to a specific number of water molecules. The water molecule is oriented so that the negative end of the dipole, oxygen, is directed toward the positive nickel ion. The number of water molecules that can attach to the nickel ion is called the *coordination number*. Divalent nickel has two coordination numbers, 4 and 6. Aqueous solutions of simple inorganic nickel salts, e.g., $NiSO_4 \cdot 6H_2O$, contain the green, octahedral hexaquonickel ion $[Ni(H_2O)_6]^{+2}$. A schematic representation of a 6-coordinate nickel ion in aqueous solution is shown below:



When water molecules coordinated to the nickel ion are replaced by other ions or molecules, the resulting compound is called a *nickel complex* and the combining, or donor, group is called a *complexing agent* or *ligand*. The formation of the blue ammonium complex by displacement of the 6 water molecules by ammonia is illustrated below:

$$[Ni(H_2O)_6]^{+2} + 6NH_3 = [Ni(NH_3)_6]^{+2} + 6H_2O$$



Green Blue

The chemical properties of nickel ions in aqueous solution are altered when they are combined with complexing agents. Some of the common properties of solvated nickel ions that can be affected are color, reduction potential, and solubility. The effects complexing agents have on some of the common properties of nickel ions, such as color, reduction potential, and solubility are illustrated below:

$$[Ni(H_2O)_6]^{+2} + 6NH_3 = [Ni(NH_3)_6]^{+2} + 6H_2O \quad [66]$$

Green Blue

$$[Ni(H_2O)_6]^{+2} + 2e^- = Ni^0 + 6H_2O,\ E^0 = -0.25\ V \quad [67a]$$

$$[Ni(CN)_4]^{+2} + 2e^- = Ni^0 + 4CN^-,\ E_{ca} = -0.90\ V \quad [67b]$$

$$[Ni(H_2O)_6]^{+2}C_4H_8N_2O_2 = [Ni(C_4H_7N_2O_7)_2]^0 + 6H_2O + 2H^+ \quad [68]$$

Dimethyl-glyoxime

Equation 68 represents the classical method for separating nickel from aqueous solutions, and shows that the nature of the complexing agent determines whether the nickel complex remains in solution or precipitates.

Table 1.2
Ligands Commonly Used In Electroless Nickel Plating Baths

Anion	**Structure (acid)**	**No. of chelate rings**	**Ring size**	**pK**[a]
Monodentate				
Acetate	CH_3COOH	0	—	1.5
Propionate	CH_3CH_2COOH	0	—	—
Succinate	$HOOCCH_2CH_2COOH$	0	—	2.2
Bidentate				
Hydroxyacetate	$HOCH_2COOH$	1	5	—
α-Hydroxypropionate	$CH_3CH(OH)COOH$	1	5	2.5
Aminoacetate	NH_2CH_2COOH	1	5	6.1
Ethylenediamine	$H_2NCH_2CH_2NH_2$	1	5	13.5
β-Aminopropionate	$NH_2CH_2CH_2COOH$	1	6	5.6
Malonate	$HOOCCH_2COOH$	1	6	4.2
Pyrophosphate	$H_2O_3POPO_3H_2$	1	6	5.3
Tridentate				
Malate	$HOOCCH_2CH(OH)COOH$	2	5,6	3.4
Quadridentate				
Citrate	$HOOCCH_2(OH)C(COOH)COOH$	2[b]	5,6	6.9

---

[a] pK = -log K, where K is the stability constant for the nickel-ligand complex.
[b] See text for explanation.

Thermodynamics is of great help in predicting equilibria in electrochemical reactions. It is the Gibbs free energy that is the criterion as to whether or not an electrochemical cell reaction will occur spontaneously at a constant temperature and pressure. There is an important relation between the change in free energy, ΔG, and the amount of electrical work done, nFE, in a reversible cell:

$$\Delta G = -nFE \qquad [69]$$

where n is the number of electrons transferred in the reaction, F is the Faraday number (96,500 coulombs), and E is the voltage or EMF of the cell. If ΔG has a negative value, the reaction is spontaneous; if $\Delta G > 0$, the reaction will not go spontaneously.

Consider Eq. 67b combined with the half-cell reaction of hypophosphite with water (Eq. 16):

$$[Ni(CN)_4]^{-2} + 2e^- = Ni^0 + 4CN^-, \ E^0 = -0.90\ V \qquad [67b]$$

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3 + 2H^+ + 2e^-, \ E^0 = 0.50\ V \qquad [16]$$

$$[Ni(CN)_4]^{-2} + H_2PO_2^- + H_2O = Ni^0 + 4CN^- + H_2PO_3^- + 2H^+, \ E^0 = -0.40\ V \qquad [70]$$

From Eq. 70:

$$\Delta G^0 = -nFE^0 = (-)\ \frac{(2)\ (96{,}500)\ (-0.40)}{(4.184)} = +18\ \text{Kcal}$$

Since $\Delta G^0 > 0$, the reaction is not spontaneous and hypophosphite will not reduce nickel from the nickel tetracyanide complex. On the other hand, consider the half-cell reaction of the nickel hexamine ion, $[Ni(NH_3)_6]^{+2}$, combined with the half-cell reaction of hypophosphite in alkaline solution:

$$[Ni(NH_3)_6]^{+2} + 2e^- = Ni^0 + 6NH_3(aq), \ E^0 = -0.49\ V \qquad [71]$$

$$H_2PO_2^- + 3OH^- \rightarrow HPO_3^{-2} + 2H_2O + 2e^-, \qquad E^0 = 1.57\ V \qquad [72]$$

$$[Ni(NH_3)_6]^{+2} + H_2PO_2^- + 3OH^- = Ni^0 + HPO_3^{-2} + 2H_2O + 6NH_3(aq), \ E^0 = 1.08\ V \qquad [73]$$

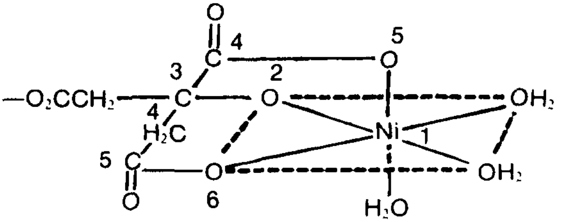
Then:

$$\Delta G^0 = -nFE^0 = \frac{-(2)\ (96{,}500)\ (1.08)}{(4.184)} = -49.8\ \text{kcal}$$

Since $\Delta G^0 < 0$, the cell reaction is spontaneous and hypophosphite will reduce nickel from ammoniacal solutions, as is well known. The above examples illustrate that complexing agents can have a profound effect on the reduction reaction.

An EN complexing agent can coordinate to a nickel ion through an oxygen or nitrogen atom, or both. The blue ammonium (amine) complex is an example of the general class of complexing agents (ligands) known as *monodentate* (one-tooth) ligands (see Table 1.2). Monodentate ligands use only one donor atom per ligand molecule or ion to occupy a single coordination position of the nickel ion. The monocarboxylate anions, acetate and propionate, are examples of monodentate ligands.

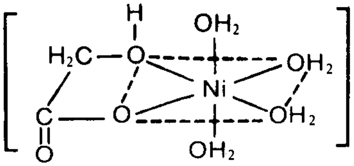
Nickel chelate compounds are defined as complexes in which the donor atoms. of the complexing agent are attached to each other as well as to the nickel ion. Thus, the nickel ion becomes part of a heterocyclic ring. Complexing agents having two or more donor atoms that can simultaneously fill two or more nickel coordinate positions are called *polydentate* complexing agents (ligands). Polydentate ligands whose structures are favorable for the attachment of two atoms are called *bidentate.* Those with three, four, five, and six donor sites are called *tri-*, *tetra-*, *penta-*, and *hexadentate* ligands, respectively. A polydentate ligand might not necessarily utilize all of its donor atoms when coordinating to a nickel ion, due to steric hinderance. The citrate ion, although tetradentate, probably coordinates to the nickel ion with the formation of two chelate rings, a 5-membered ring and a 6-membered ring. For pictorial simplicity, only one citrate molecule is shown coordinated to the nickel ion in the following representation:



Note that the succinate anion is listed in Table 1.2 as monodentate even though it has two donor atoms per ligand molecule. The succinate ion, functioning as a bidentate ligand, would form a 7-membered ring. When the chelate ring is 7-membered or more, it becomes more probable that the one end of the ligand molecule will coordinate to another metal ion rather than form the 7-membered ring (32,33).

If the complexing agent does not have a sufficient number of donor atoms to satisfy the coordination number (sites) of the nickel ion, the remaining sites may be occupied by other ligands and/or water molecules. For example, partial chelation of the hexaquonickel ion by hydroxyacetate anion can be represented schematically by:

$[Ni(H_2O)_6]^{+2} + HOCH_2COO^- =$



$+ 2H_2O$

It is important to note that some of the chemical properties of the initial aquometal ion are retained when the nickel chelate contains one or more free aquo positions.

Aquometal ions tend to be acidic, that is, they hydrolyze in aqueous solution in a manner represented by:

$$[M(H_2O)_a]^{n+} = [M(H_2O)_{a-1}(OH)]^{(n-1)+} + H^+ \qquad [74]$$

The complete hydrolysis of hexaquonickel ion can be represented by:

$$[Ni(H_2O)_6]^{+2} = [Ni(H_2O)_5OH]^{+1} + H^+ = [Ni(H_2O)_4(OH)_2]^0 + 2H^+ \qquad [75]$$

at pH $\geqslant$5.0.

The superscript 0 in this case means that the hydrated basic nickel salt has precipitated. Thus, the equilibrium between the aquonickel ion (Lewis acid) and the hydroxylated nickel ion can be considered to involve the displacement of the weak Lewis base, the water molecule, by the strongly coordinating hydroxyl ion. The chelation of an aquonickel ion occurs only when the ligand is a much stronger base than water, and analogously, may be considered an acid-base reaction. It should be noted that hydrolysis here occurs in the bulk of the solution and should not be confused with the hydrolyzed nickel species that originates at the catalyst surface.

Partial chelation of the nickel ion increases its resistance to hydrolysis, and it is possible to keep the nickel ion in solution at a higher pH than would otherwise be possible. However, as the pH increases, the disassociation of protons from the remaining coordinated water molecules frequently occurs and further hydrolysis of the nickel ion will result. For maximum stability against hydrolysis, the nickel ion must be completely coordinated.

In aqueous solutions, chemical reactions with nickel ions are said to take place at "free" coordination sites, that is, those sites that are weakly bound to coordinated water molecules, so that the kinetics of the electroless nickel plating reaction is a function of free nickel ion concentration. Of the several functions of complexing agents in electroless nickel plating solutions, one of the most important is the regulation and maintenance of the free nickel ion concentration, or activity; i.e., the nickel complex dissociates to form some small equilibrium amount of free nickel ions:

$$NiL_3^{2-3n} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL_2^{2-2n} + L^{-n},\ k_1 = \frac{[NiL_2^{2-2n}]\,[L^{-n}]}{[NiL_3^{2-3n}]} \tag{77}$$

$$NiL_2^{2-2n} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NiL^{2-n} + L^{-n},\ k_2 = \frac{[NiL^{2-n}]\,[L^{-n}]}{[NiL_2^{2-2n}]} \tag{78}$$

$$NiL^{2-n} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni^{+2} + L^{-n},\ k_3 = \frac{[Ni^{+2}]\,[L^{-n}]}{[NiL^{2-n}]} \tag{79}$$

The overall equilibrium constant for three independent equilibria is defined by:

$$K_3 = k_1k_2k_3 = \frac{[Ni^{+2}]\,[L^{-n}]^3}{[NiL_3^{2-3n}]} \tag{80}$$

In general:

$$K_m = k_1k_2 \ldots k_m = \frac{[Ni^{+2}]\,[L^{-n}]^m}{[NiL_m^{2-mn}]} \tag{81}$$

The constant K_m is also called the *instability constant*. The term *stability constant* is more commonly used in the literature, and its value is the reciprocal of the instability constant:

$$K_{NiL} = \beta = \frac{1}{K_m} \tag{82}$$

Although not shown in the scheme, as each coordination site on the nickel ion is exposed by a leaving ligand atom, a water molecule becomes attached at that site. As one bidentate ligand molecule dissociates, for example, two water molecules associate at the sites opened by the leaving bidentate ligand. It is obvious that the activity of a free nickel ion decreases as the number of ligand molecules bound to the nickel ion approaches m; m = 6 for monodentate ligands, m = 3 for bidentate ligands, and so forth.

The rate of nickel deposition is proportional to the rate at which the nickel complex dissociates to form free nickel ion. Thus, the plating rate is inversely related to the stability constant, i.e., the larger the stability constant, the lower the rate of complex dissociation and concomitantly, the lower the rate of deposition. As an example of this relationship, the stability constant (see Table 1.2) for the nickel-citrate complex is more than an order of magnitude greater than the stability constant for the nickel-lactate complex; and as predicted, the plating rate in the citrate bath is considerably slower than the plating rate in the lactate bath under similar conditions. Hence, the choice of complexing agent for use in the electroless nickel plating bath has a profound effect on the plating reaction.

Complexing agents, being electron donors, also have a considerable affinity for hydrogen ions. Complexing agents can be considered metal buffers in a manner analogous to the function of hydrogen ion buffers. When a complexing agent is added to a solution of free metal ions, M^{+z}, equilibrium is established as shown schematically:

$$M^{+z} + mL^{-n} = ML_m^{-(n-z)} \qquad [83]$$

Since:

$$K_{ML} = \frac{1}{K_m} \qquad [84]$$

therefore:

$$K_{ML} = \frac{[ML_m^{-(n-z)}]}{[M^{+z}]\,[L^{-n}]^m} \qquad [85]$$

or:

$$M^{+z} = \left(\frac{1}{K_m}\right)\frac{[ML_m^{-(n-z)}]}{[L^{-n}]^m} \qquad [86]$$

Analogous to the definition of pH, the negative logaritnm of the metal ion concentration, pM, is defined by:

$$pM = K_x + \log\frac{[L^{-n}]^m}{[ML_m{}^{(n-z)}]},\ K_x = +\log K_{ML} \qquad [87]$$

As pointed out earlier, the complexing agent shows an affinity for hydrogen ions, which can be expressed by the following equilibrium:

$$L^{-n} + H^{+} = HL^{-(n-1)} \qquad [88]$$

with equilibrium constant:

$$K_{HL} = \frac{[HL^{-(n-1)}]}{[H^{+}]\,[L^{-n}]} \qquad [89]$$

and:

$$[L^{-n}] = \left(\frac{1}{K_{HL}}\right)\frac{[HL^{-(n-1)}]}{H^{+}} \qquad [90]$$

Substituting the expression for $[L^{-n}]$ into Eq. 87 yields:

$$pM = K_x' + m\log\frac{[HL^{=(n-1)}]}{[ML_m{}^{(n-z)}]} + mpH = \frac{1}{\log[M]} \qquad [91]$$

where:

$$K_x' = K_x - m\log K_{HL} \qquad [92]$$

Since pM and pH are analogous concepts, an increase in the value of pM or pH results in a decrease in the concentration of the metal ion under consideration. Equation 91 indicates that as the pH increases (at constant m), pM increases and the free metal ion concentration decreases. The majority of commercial electroless nickel plating installations use acid plating baths that are operated in the pH range of 4.5 to 6.0. The complexing agents commonly used are most effective in this pH range.

Equation 91 also supports the statement made earlier that the nickel ion activity decreases as each coordinate position of the nickel ion becomes bound to a ligand atom. Using the example of the bidentate ligand (at constant pH), pM increases and the free nickel ion concentration decreases when m is increased from 1 to a maximum of 3.

Stabilizers

An electroless nickel plating solution can be operated under normal operating conditions over extended periods without adding stabilizers; however, it may decompose spontaneously at any time. Bath decomposition is usually preceded by an increase in the volume of hydrogen gas evolved and the appearance of a finely-divided black precipitate throughout the bulk of the solution. This precipitate consists of nickel particles, and either nickel phosphide or nickel boride, depending on the reducing agent being used.

Fortunately, chemical agents called *stabilizers* are available to prevent the homogeneous reaction that triggers the subsequent random decomposition of the entire plating bath. To use stabilizers effectively, the chemist must, first of all, be able to identify those problems that can be solved by the use of stabilizers. Second, the compatibility of the stabilizer with the process being used must be ascertained to avoid any adverse loss in catalytic activity due to a synergistic action with any other additive present in the bath. Third, when two or more stabilizers are employed, it is important to be sure that the action of one does not inhibit or lessen the effectiveness of the other stabilizers. Finally, the stabilizers must be selected on the basis that they only affect the plating process in a manner that the resultant deposit will be able to meet any required performance criteria.

Researchers (5) discovered the existence of hydroxyl ions at the surface of solid particles of colloidal or near-colloidal dimensions present in the solution. The hydroxyl ions are said to cause the localized reduction of nickel ions to the metal by the homogeneous reaction:

$$Ni^{+2} + 2H_2PO_2^- + 2OH^- \rightarrow Ni^0 + 2HPO_3^{-2} + 2H^+ + H_2 \qquad [93]$$

The finely divided nickel precipitate, in turn, acts as a highly efficient catalyst, because of its large surface area, thus triggering a "self-accelerating chain reaction."

The solid particles mentioned above are either formed in the solution or introduced into the solution by drag-in, dust, fumes, or other contaminants. The particles of extraneous origin can be the result of poor rinsing, poor cleaning, and/or poor housekeeping; good plating practices will eliminate their introduction.

Particles that form in the solution are insoluble nickel-phosphides and/or basic salts or metal hydroxides that precipitate at operating pH; e.g., the ions of iron and aluminum (Fe^{+2} and Al^{+3}) precipitate as gelatinous hydroxides when the bath pH is >5.0. These ions are introduced into the plating bath during the initial displacement reaction (discussed above) when steel or aluminum substrates are immersed in the plating bath. Steel and aluminum are by far the metals most likely to be plated in electroless nickel baths. Thus, the metal ions will accumulate in any production facility until their concentration exceeds their respective metal hydroxide solubility product limits and begin to precipitate.

Plating bath decomposition can be virtually eliminated by the addition of only trace amounts of stabilizer (sometimes referred to as *catalytic inhibitors*) to the plating bath. Gutzeit (5) pointed out that most of these so-called "anti-catalysts" (stabilizers/inhibitors) are identical with the materials that prevent hydrogenation/dehydrogenation catalysis.

The most effective stabilizers can be divided into the following classes:

(I) Compounds of Group VI elements: S, Se, Te
(II) Compounds containing oxygen: AsO_2^-, IO_3^-, MoO_4^{-2}
(III) Heavy metal cations: Sn^{+2}, Pb^{+2}, Hg^+, Sb^{+3}
(IV) Unsaturated organic acids: Maleic, itaconic

The stabilizer concentration in the plating bath can be very critical. The concentration of the stabilizer depends most importantly on its structural class.

Substances that fall into Class I or Class II can function effectively as stabilizers at concentrations as low as 0.10 ppm. In many cases, when the concentration of stabilizers from either of these two classes is increased much beyond 2 ppm, the plating reaction can be completely inhibited. On the other hand, certain Class I stabilizers such as thiourea, at optimum concentration will increase the rate of deposition substantially over that of a bath without any stabilizer (see Fig. 1.5).

The usage of stabilizers found in Classes III and IV is conveniently defined in terms of molar concentrations; e.g., the concentration range of Class III stabilizers is usually 10^{-5} M to 10^{-3} M, whereas the concentration of unsaturated organic acids (Class IV) is usually in the range of 10^{-3} to 10^{-1} M.

The activity of the catalytic substrate is altered appreciably by extremely minute concentrations of stabilizers. Substances that tend to inhibit catalytic activity are known as *poisons*; some substances actually enhance activity and increase deposition rate.

Several methods are available to determine the effectiveness of these compounds as stabilizers and to also ascertain their optimum concentration in the plating bath. One method consists of plotting the mixed or deposition potential of an electroless nickel solution against the concentration of stabilizer that is incrementally added to the solution (34). A curve similar to the one shown in Fig. 1.6 is usually obtained. The initial small addition of stabilizer causes an abrupt change in potential; subsequent additions cause only minor changes in the mixed potential. When the concentration of stabilizer reaches a critical value, the plating reaction stops, as is usually evidenced by the cessation of hydrogen evolution. The mixed potential abruptly changes to more noble values by 100 to 300 mV. The potential remains constant with further additions of inhibitor beyond the critical concentration.

Another method consists of measuring the deposition rate vs. stabilizer concentration, from which curves represented by the curve of Fig. 1.7 are obtained. Some curves will cover a smaller concentration range than others and show a very sharp maximum, but the one feature common to all is the critical concentration point. (Some stabilizers will increase the rate of deposition as indicated by a maximum in the rate vs. concentration curve.)

Stability can also be determined by adding 1 to 2 mL of a 100 ppm palladium chloride solution to a sample of the warm plating solution and measuring the time before visible black precipitate is formed. The plating bath is considered stable if the time required for precipitate formation is in excess of 60 seconds. Using one of the preceding methods, it will be found that the effective stabilizer concentration varies from 0.1 to about 300 ppm for Classes I to III. The concentration for the organic stabilizers can range up to several grams per liter.

Air agitation of electroless nickel solutions has been reported to significantly enhance the stability of the plating bath. Agitation using the inert gas argon was also found to be ineffective in increasing the stability of the electroless nickel plating solution (35). When pure oxygen was bubbled through an otherwise unstabilized experimental electroless nickel plating solution, the mixed (deposition) potential shifted from -625 mV vs. SCE to -550 mV vs. SCE. In other words, the oxygen-agitated solution showed increased stability vs. the quiescent solution.

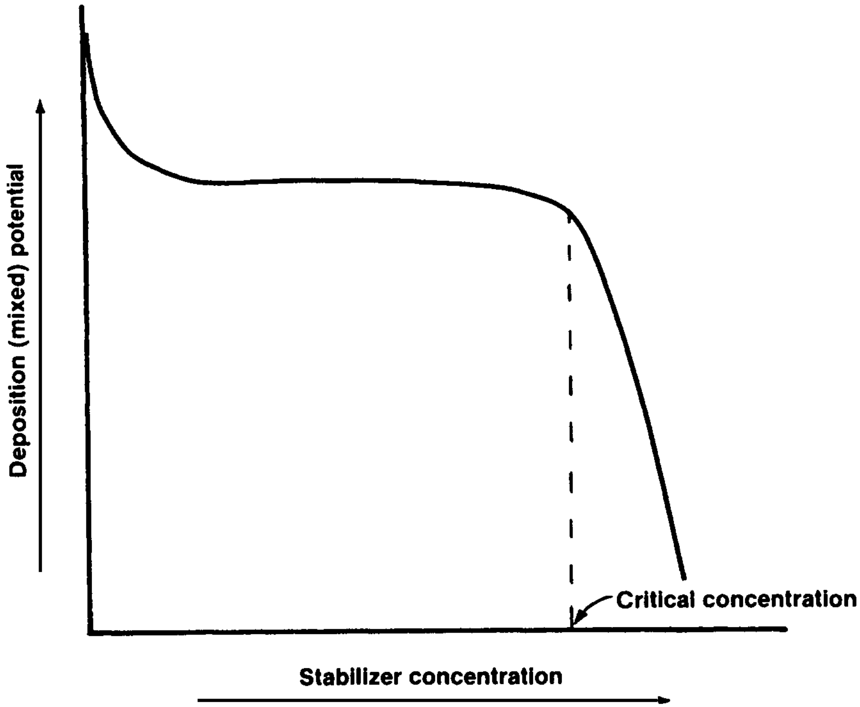


Fig. 1.6—Effect of stabilizer concentration on electroless nickel deposition potential.

Altura (36), using polarization techniques, studied the effect of stabilizers on the cathodic and anodic reactions. He first studied the partial processes in the absence of stabilizers. The initial cathodic polarization studies were made on solutions containing a complexing agent and nickel only. The initial anodic polarization studies were made in solutions containing a complexing agent (lactic acid) and sodium hypophosphite only.

Figure 1.8 presents the cathodic polarization results in solutions without hypophosphite or stabilizers. The solutions used in the cathodic studies, that is, those containing nickel, do not appear to reach a limiting current density down to -850 mV vs. SCE at the various nickel concentrations used.

The effect of hypophosphite concentration on anodic polarization curves is given in Fig. 1.9. Increasing the hypophosphite concentration at constant potential shows an increase in current density, which is to be expected. However, the shape of anodic polarization curves, especially curve D, shows limiting current behavior that indicates mass transfer as the most likely rate-controlling step for hypophosphite oxidation.

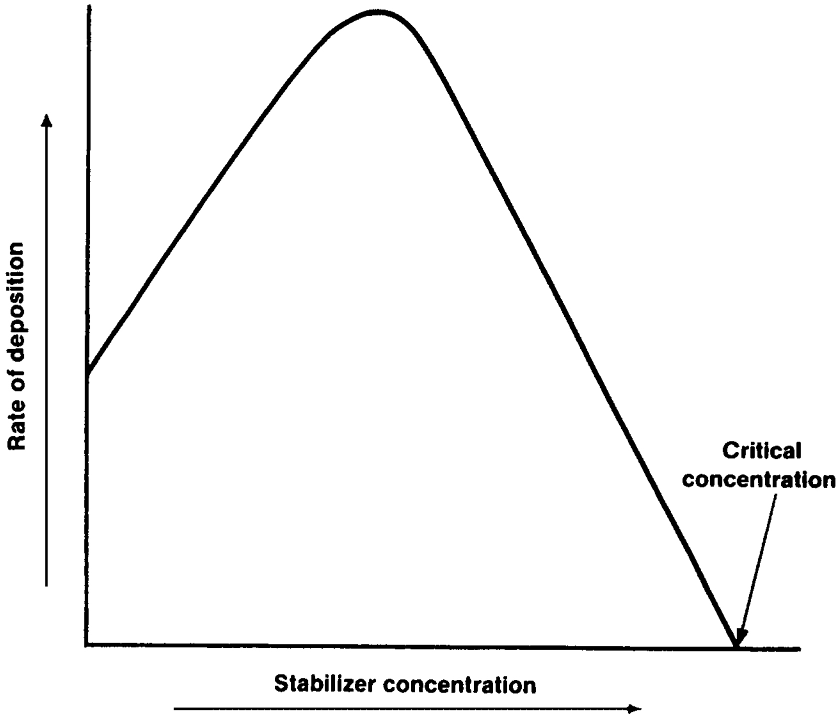


Fig. 1.7—Effect of stabilizer concentration on rate of electroless nickel deposition.

To determine the effect of stabilizers on the partial reactions, stabilizers were added to each solution used in the initial studies above. The cathodic polarization and the anodic polarization results in the presence of lead are presented in Figs. 1.10 and 1.11, respectively. Increasing the lead concentration causes a shift in cathodic curves in the cathodic direction, as shown in Fig. 1.10; curve G (Fig. 1.11) does not follow this behavior. The shift of the cathodic curves indicates an increasing inhibitive effect on the reduction reaction with increasing lead concentration. The anodic curves in Fig. 1.11 show a decrease in current density at constant potential for lead concentrations up to 2 ppm. When the lead concentration is 3 ppm or greater, the current density starts out lower than the zero lead case, but at about -600 mV. The current density increases, then decreases, causing an inflection in the curve. The inflection may be indicative of some other reaction, possibly involving lead, occurring at the surface of the electrode at lead concentrations of 3 ppm or greater.

Altura (36) also studied the effect of the widely used stabilizer, thiourea. The effect of the concentration of the sulfur-bearing substance on the cathodic

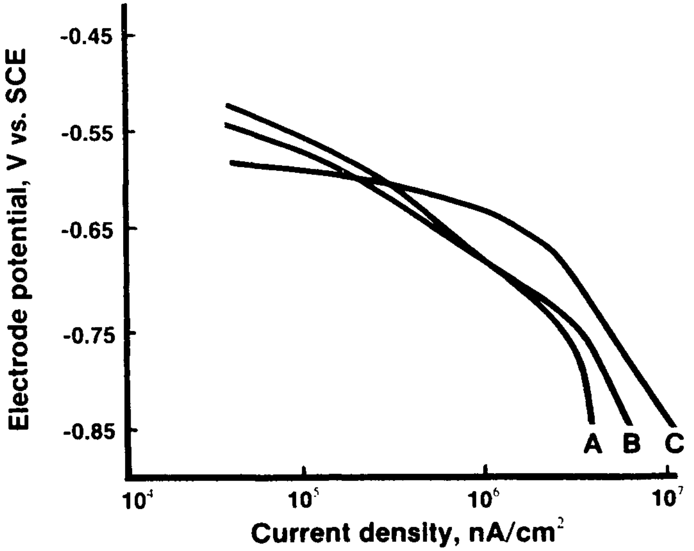


Fig. 1.8—Effect of nickel concentration on the cathodic polarization curves (no $NaH_2PO_2 \cdot H_2O$ or stabilizer). A = 0M Ni^{+2}; B = 0.02M; C = 0.15M.

polarization curves is shown in Fig. 1.12. The cathodic curves show an inconsistent shift in the location of the curve vs. thiourea concentration. This may be due to the combined or preferential inhibition of the hydrogen evolution reaction, nickel reduction, and/or the phosphorus reduction reaction. Assuming that thiourea inhibits phosphorus reduction, it could account for the decrease in the phosphorus content of deposits obtained from deposits containing thiourea. On the other hand, the family of anodic curves in Fig. 1.13 show a very consistent decrease in anodic current density with increasing thiourea concentration at constant potential. The shape of the anodic polarization curves suggests an enhanced effect on limiting current behavior vs. the stabilizer-free case, which indicates the likelihood of an anodic oxidation reaction involving thiourea to sulfur since it is well known that the potential of nickel deposits containing sulfur is different from sulfur-free Ni deposits.

Fontenals (37) suggested a theory that alternatively may explain the results obtained by Altura in his polarization studies on thiourea. The theory was developed to explain the characteristic relationship between the electroless nickel plating rate (which passes through a maximum) and the thiourea concentration in the plating bath. According to the theory, the rate increase as a

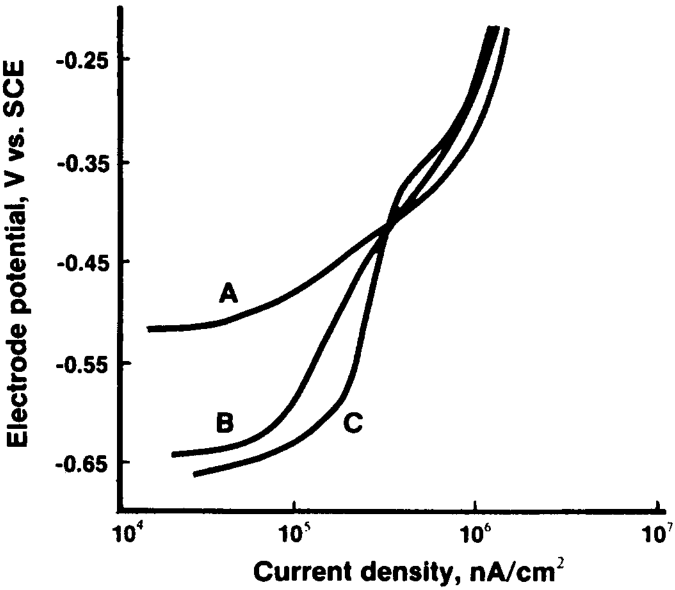
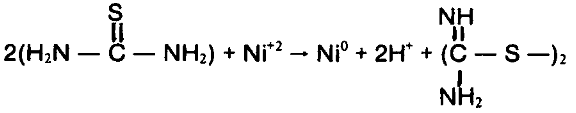


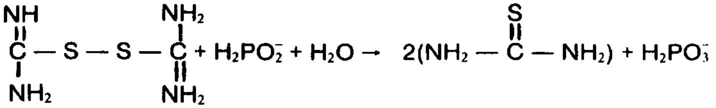
Fig. 1.9—Effect of hypophosphite concentration on the anodic polarization curves (no NH_3 or stabilizer). A = 0M $NaH_2PO_2 \cdot H_2O$; B = 0.1M; C = 0.6M.

result of the transfer of electrons from thiourea (anodic reaction) to the nickel ions, yielding elemental nickel and a dimer of thiourea:



$$2(H_2N-\overset{\overset{S}{\|}}{C}-NH_2)+Ni^{+2}\rightarrow Ni^0+2H^+ +(\underset{\underset{NH_2}{|}}{\overset{\overset{NH}{\|}}{C}}-S-)_2 \qquad [94]$$

The dimer is then reduced by the transfer of electrons from hypophosphite (anodic reaction) to the dimer to form thiourea:



$$\underset{\underset{NH_2}{|}}{\overset{\overset{NH}{\|}}{C}}-S-S-\underset{\underset{NH_2}{\|}}{\overset{\overset{NH_2}{|}}{C}}+H_2PO_2^-+H_2O\rightarrow 2(NH_2-\overset{\overset{S}{\|}}{C}-NH_2)+H_2PO_3^- \qquad [95]$$

The actions of KIO_3 (potassium iodate) on the partial cathodic and anodic reactions is quite different from those described for lead and thiourea. Figure 1.14 shows cathodic polarization curves for the nickel-only solution containing the oxy-anion IO_3^-. At constant potential of about -650 mV or greater, there is a

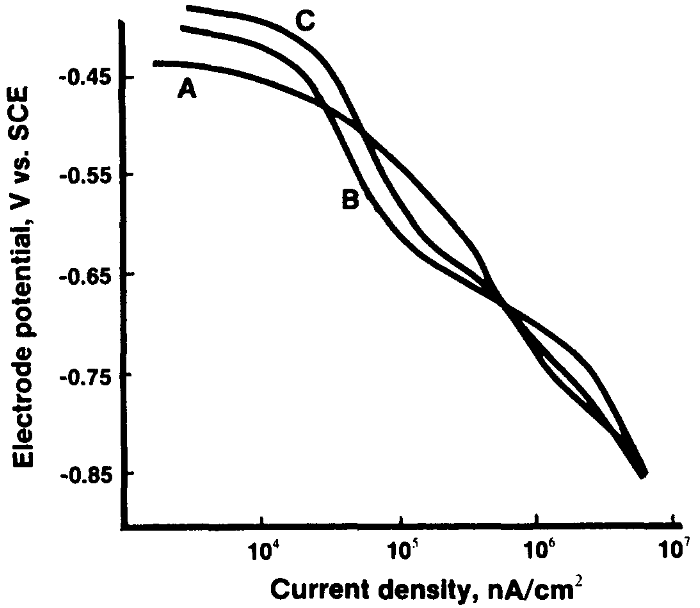


Fig. 1.10—Effect of Pb^{+2} concentration on the cathodic polarization curves. A = 0 ppm Pb^{+2}; B = 1 ppm; C = 10 ppm.

uniform shift in the curves to higher current densities as the concentration of KIO_3 is increased from 0 to 400 ppm. Also at potentials approximately ≥-650 mV, curves C and D reach a limiting current density where mass transfer is the controlling step. The cathodic polarization curves for the stabilizer-free case, and in the cases where thiourea or lead were present did exhibit limiting current behavior, over the range of potentials studied. If the reduction of IO_3^- is assumed to occur in the region of limiting current density, then a possible mechanism for bath stabilization by KIO_3 may be the competition of IO_3^- with Ni^{+2} for cathodic surface sites (catalysts), which would result in the reduction in the overall rate of the nickel reduction reaction. The cathodic curves at potentials below -650 mV (-650 to -850) are more or less linear and are similar to curves obtained for the stabilizer-free, lead and thiourea cases over the entire range of potentials. In this so-called linear region, the predominant reaction is most likely activation-controlled.

The results of anodic polarization in the presence of IO_3^- are shown in Fig. 1.15. There is a constant drop in current density (at constant potential) when the KIO_3 concentration is increased; curves E and F of Fig. 1.15 exhibit a dramatic shift in open circuit potential from about -650 mV to -387 mV and -354 mV, respectively. The theoretical E_{Mix} value for KIO_3 free case.

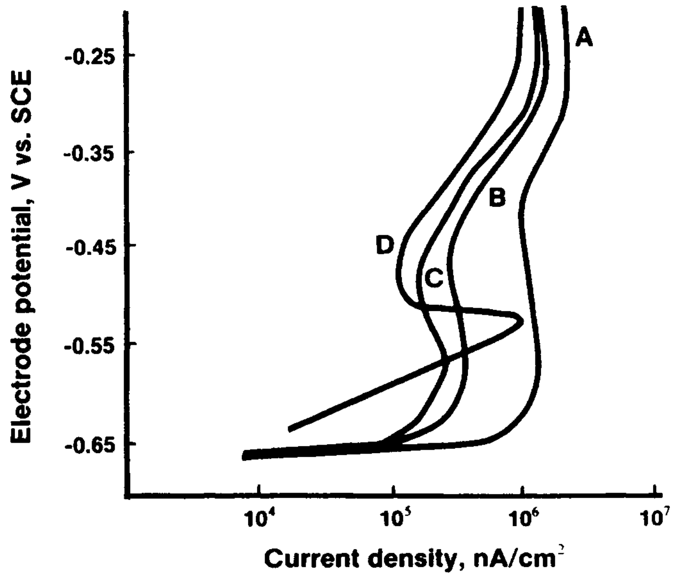


Fig. 1.11—Effect of Pb^{+2} concentration on the anodic polarization curves. A = 0 ppm Pb^{+2}; B = 1 ppm; C = 2 ppm; D = 10 ppm.

Feldstein and Amodio (38), in their study of the inhibition of EN deposition by oxy-anions, report that the steady-state potential decreases sharply when the concentration of IO_3^- is increased, resulting in a decrease in the plating rate. They propose that the inhibition effect associated with IO_3^- and other inhibiting oxy-anions (e.g., AsO_2^-, NO_2^-, BrO_3^-) is primarily by a surface adsorption mechanism. They further propose that the observed abrupt increase of inhibition (decrease in E_{Mix}) with increasing inhibitor concentration can be accounted for by one or any combination of the following mechanisms:

- A chemical reaction between the adsorbed IO_3^- (oxy-anions) and $H_2PO_2^-$ leading to a strengthening of the P-H bond in hypophosphite.
- The adsorbed IO_3^- (oxy-anions) alters the structure of the double layer, modifying (or increasing) the degree of surface adsorption and thereby affecting the kinetics of the redox reactions.
- The number of adjacent pair catalytic sites available for the catalytic dehydrogenation of the hypophosphite ion decreases rapidly once a critical concentration of adsorbed inhibitor is reached.

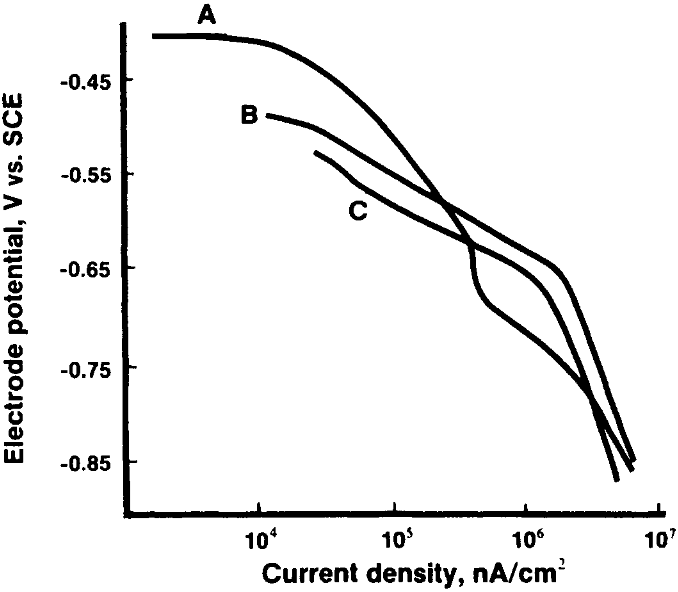
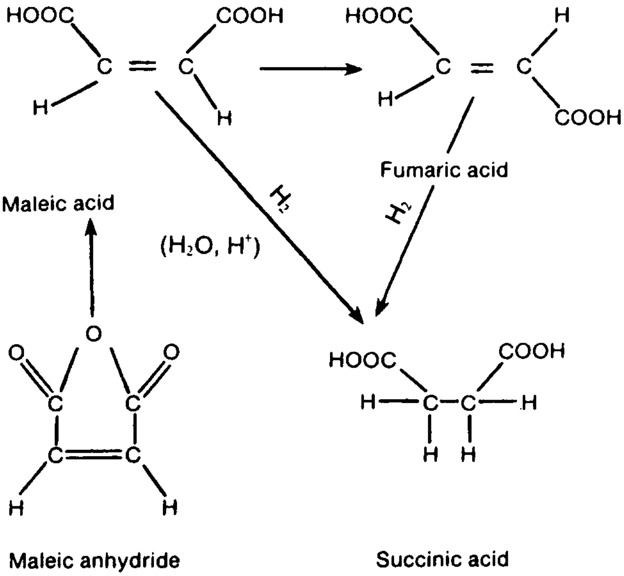
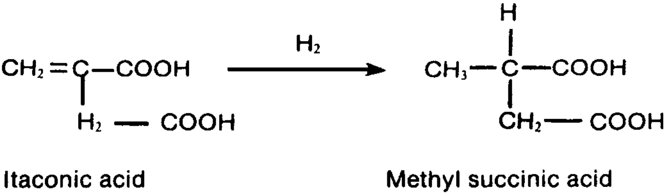


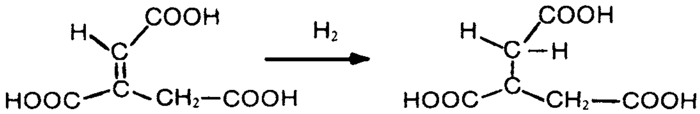
Fig. 1.12—Effect of thiourea concentration on the cathodic polarization curves. A = 0 ppm thiourea; B = 1 ppm; C = 10 ppm.

In 1966, Velemitzina and Riabchenkov (39) reported that the introduction of 1.5 to 2 g/L of maleic anhydride into an electroless nickel solution "sharply increased the resistance of the latter to self-decomposition . . . ". A large variety of unsaturated short chain aliphatic compounds are claimed to function as stabilizers or at least enhance the efficacy of other stabilizers, such as lead and thiourea. The unsaturated group of the stabilizer molecule may be either the carbon-carbon double bond (-HC = CH-) alkenes, or the carbon triple bond (—C≡C—) acetylenes. Obvious choices of this class of stabilizers are the short chain dicarboxylic acids, as represented by maleic and acetylene dicarboxylic acids. However, Linka and Riedel (40) observed that the unsaturated carboxylic acids are subject to chemical reaction. The catalytic conditions (during deposition) at the electrolyte-metal substrate interface are ideal for hydrogenation of the unsaturated acid. They demonstrated analytically that maleic acid was converted to succinic and fumaric acids by hydrogenation and isomerism, respectively. These reactions can be shown schematically as follows:

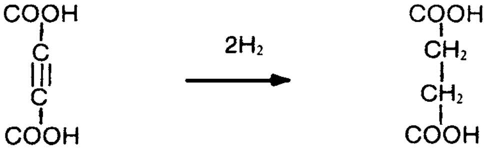


(For clarity, the hydrolysis of maleic anhydride to maleic acid has been included.) Based on the work of Linka and Riedel, it is assumed that the following conversions would take place:

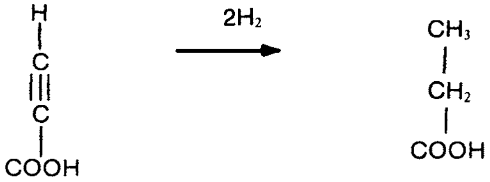




Aconitic acid → Tricarballylic acid



Acetylene dicarboxylic acid → Succinic acid



Propiolic acid → Propionic acid

The above examples illustrate that in some cases, the by-product of the hydrogenation reaction may be an innocuous addition to the plating solution. The formation of succinic acid can be considered a plus since its salts will help buffer the bath. On the other hand, the effect of tricarballylic acid on the plating reaction, as well as the deposit, must be determined. To reiterate, it is important to determine if the reaction by-product will have a deleterious effect on the deposition reaction and/or the final deposit.

The section on the unsaturated organic stabilizers illustrates the fact that all stabilizers in their active form are consumed during the deposition reaction, and therefore must be replenished periodically in order to maintain plating bath stability. The replenishment and maintenance of the optimum stabilizer concentration in the EN plating bath will be discussed further in the chapter on "Practical Electroless Nickel Plating."

The stabilization of an electroless nickel plating solution takes place at or near the catalytic substrate/double-layer interface. The mechanism of stabilization probably depends upon the degree of adsorption of the stabilizer onto the catalytic surface.

Class I and Class II stabilizers show a strong adsorption tendency (36,38); for example, Altura (36) reported that the steady-state potential (E_{Mix}) increases with increasing stabilizer concentration, indicating that the stabilizer is being adsorbed onto the working electrode (catalyst). Thiourea (Class I) is so strongly

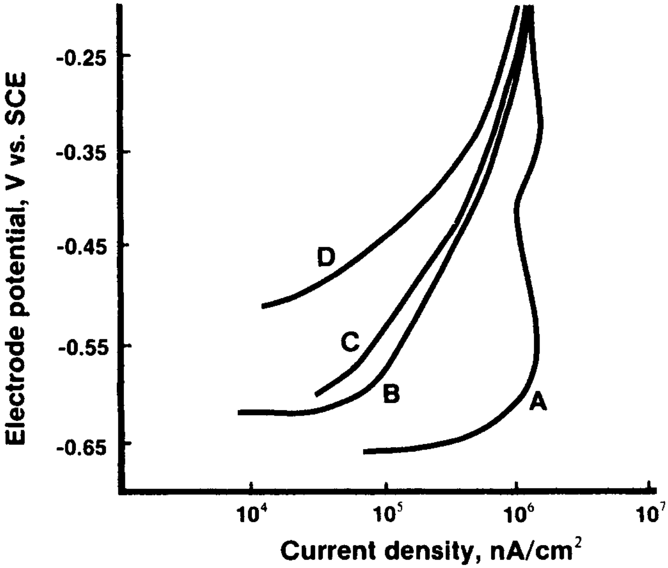


Fig. 1.13—Effect of thiourea concentration on the anodic polarization curves. A = 0 ppm thiourea; B = 1 ppm; C = 2 ppm; D = 10 ppm.

adsorbed that its use causes microporosity, as well as the codeposition of sulfur in the deposit. Feldstein and Amodio (38) show a proposed model for the interaction of adsorbed Class II anions with hypophosphite.

Solution agitation (mechanical or inert gas) in the presence of either a Class I or Class II stabilizer causes inhibition of the EN deposition reaction, as exhibited by a decrease in plating rate. Similar results were observed by Feldstein and Amodio (41). Each adsorbed stabilizer molecule or ion reduces the number of catalytic sites available for the dehydrogenation of hypophosphite. Solution agitation increases the rate of diffusion of stabilizer to the surface and, hence, increases its concentration at the surface. This condition leads to the shifting of the critical concentration of stabilizer to a lower value; for example, if the critical concentration of a particular stabilizer is 10 ppm in a quiescent solution, it may be lowered to 2 ppm when the solution is agitated vigorously. The actual stabilizer concentration can be safely maintained at concentrations below 10 ppm, say 5 to 8 ppm, in the unstirred case, whereas in the strongly agitated case, the actual concentration must be kept below 2 ppm. Skip-plating (edge-pullback) at sharp edges or corners is a visual example of the effect agitation has on the effective stabilizer concentration. In many cases, the so-called "edge

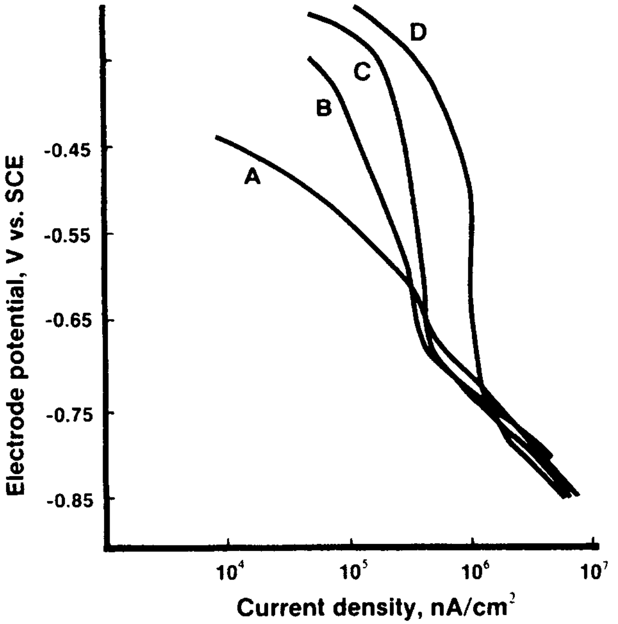


Fig. 1.14—Effect of KIO$_3$ concentration on the cathodic polarization curves. A = 0 ppm KIO$_3$; B = 50 ppm; C = 100 ppm; D = 400 ppm.

effect" can be eliminated by either decreasing or discontinuing agitation until the actual stabilizer concentration in the bath is reduced below the effective critical concentration for the agitated case.

Class III (e.g., Pb^{++}, Sn^{++}) stabilizers have a minimal effect on the steady-state potential of an EN plating bath, even at stabilizer concentrations that greatly reduce the plating rate; for example, when lead concentration in an EN bath was increased from 1 ppm to 10 ppm, the mixed potential of the working (plating) electrode changed from -625 mV to -609 mV, respectively, a E_{Mix} of only 16 mV. However, for the same change in Pb^{++} concentration, the rate of deposition decreased from 15 μm/hr to less than 2 μm/hr. Hence, it appears that lead is only loosely adsorbed onto the catalyst, but its diffusion in the double layer adjacent to the catalytic surface has a profound effect on bath stability.

In the Cavalotti and Salvago mechanism for electroless nickel deposition with $H_2PO_2^-$, Eqs. 23 and 26 were seen to represent competing reactions. When reaction 26 occurs:

$$Ni(OH)_{ads} + H_2O \rightarrow [Ni(OH)_2]_{aq} + H_{ads} \qquad [26]$$

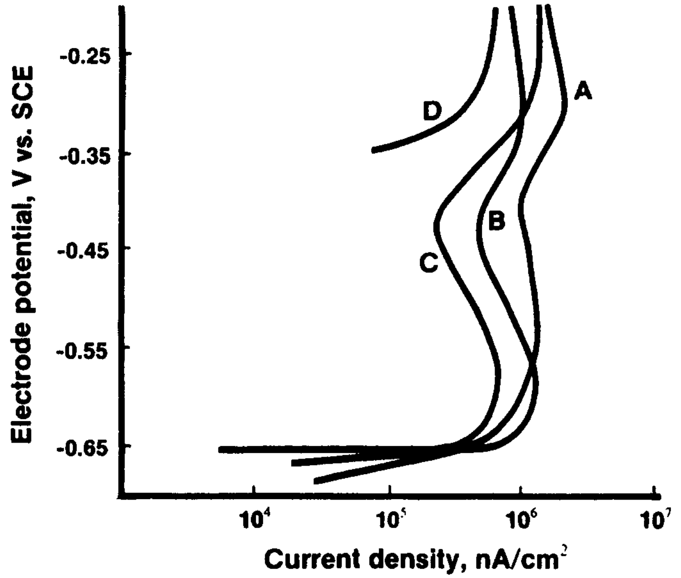


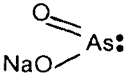
Fig. 1.15—Effect of KIO_3 concentration on the anodic polarization curves. A = 0 ppm KIO_3 B = 50 ppm; C = 100 ppm; D = 400 ppm.

the hydrolyzed Ni^{+2} species can desorb from the catalytic surface into the double layer, forming colloidal particles. The heavy metal stabilizers are adsorbed on these particles, importing a net positive charge to each particle, which causes them to repel each other. The action of the heavy metal thus prevents the aggregation of the particles to form micelles. In the absence of these stabilizers, the formation of micelles can result in the decomposition of the plating bath.

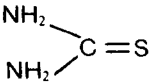
In a further attempt to characterize the observed phenomena, it is suggested that Class I and Class II stabilizers, which are adsorbed on the catalytic surface, inhibit the reaction expressed by Eq. 26. This allows Eq. 23 to proceed at the expense of Eq. 25. Since adsorption is reversible, the net effect of the addition of Class I or II stabilizers is to lower the frequency at which reactions 25 and 26 occur. This would result in a lower phosphorus content in the deposit. It is well known that EN plating baths utilizing Class I stabilizers yield deposits with lower phosphorus content than similar baths containing a Class III or no stabilizer.

In order for an unsaturated carboxylic acid to become hydrogenated during the operation of an EN plating bath, the acid must be adsorbed onto the catalytic surface. If the acid is hydrogenated, it can no longer function as a stabilizer; however, if the acid is isomerized at the surface, the isomer retains the stabilizing property; for example, both maleic acid and its isomer fumaric acid function as EN stabilizers.

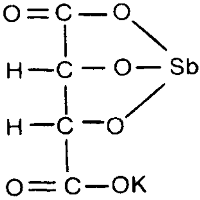
At this point, it is necessary to digress and briefly discuss adsorption of substances on metallic nickel surfaces, including EN deposits. The nickel atoms at the surface of an EN deposit have unsatisfied coordinate valences in a direction perpendicular to, and away from the interior of the deposit, as seen in Fig. 1.16. These surface nickel atoms will combine with a variety of substances known as *electron donors*. When these electron donors are adsorbed on the surface, they share their unpaired electrons with the nickel atoms, thereby satisfying the coordinate valency of the nickel atoms. Examples of Class I, II, and III stabilizers that are electron donors are given below:



Sodium
arsenite



Thiourea



Potassium
antimony
tartrate

The hydrogenation and isomerism of unsaturated carboxylic acids on the the depositing nickel surface are examples of heterogeneous or surface catalysis. The exact mechanisms of these reactions are not fully understood, however, information obtained for the catalytic hydrogenation of ethylene at nickel surfaces should be helpful in constructing a model for the reactions of interest.

It has been shown experimentally that ethylene combines exothermically (-60 kcal/mole) and reversibly with nickel surfaces (42). The bonding of the adsorbed ethylene to the surface nickel atoms most likely involves the electrons in the double bond, which satisfies the coordinate valency of nickel (33,42). Figure 1.17 is a schematic representation of ethylene adsorbed at the nickel surface. This model can be used as a basis for constructing a model of the heterogeneous catalysis of the unsaturated carboxylic acids on the EN film as it is being deposited.

The hydrogenation reaction takes place when a hydrogen molecule and an anion of the unsaturated acid, e.g., maleic acid, occupy sites on the nickel surface close enough to react, which is shown in Fig. 1.18. After hydrogenation, the saturated acid anion desorbs and diffuses into the bulk of the solution.

Because of the geometry of the carbon-carbon double bond, rotation about this bond is restricted. When the double bond of the anion is adsorbed on the

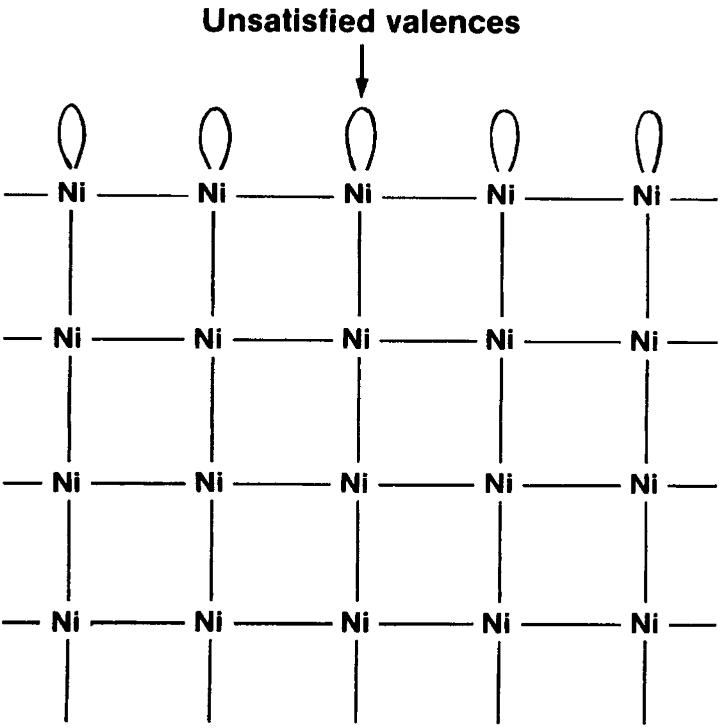


Fig. 1.16—Schematic representation of unsatisfied valences at surface of nickel deposit.

metal surface, one-half of the bond is broken in order to donate electrons to the surface nickel atoms. Now the two parts of the anion are free to rotate about the residual carbon-carbon single bond. Hence, if no hydrogen is available to react with adsorbed anions, isomerism can occur, as in Fig. 1.19, which is a representation of the conversion of maleic acid to the fumaric structure.

The stabilizing action exhibited by unsaturated compounds can be assumed to be the result of their adsorption on the nickel surface, where they inhibit one or more of the elementary EN deposition reactions in a manner analogous to that of the Class I or II stabilizers. Another method of stabilizing the EN bath might consist of the double bond combining with any colloids that are present, and preventing the formation of micelles. The two proposed methods, singularly or together, explain the stabilizing activity of the Class IV compounds.

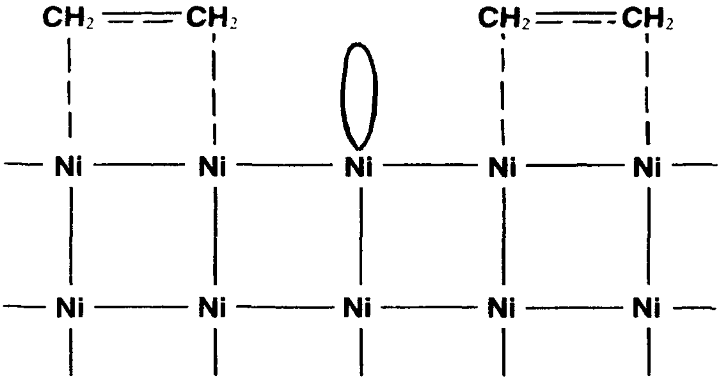


Fig. 1.17—Schematic representation of ethylene adsorbed at EN deposit surface. Dashed lines indicate sharing of electrons in double bond of ethylene with nickel.

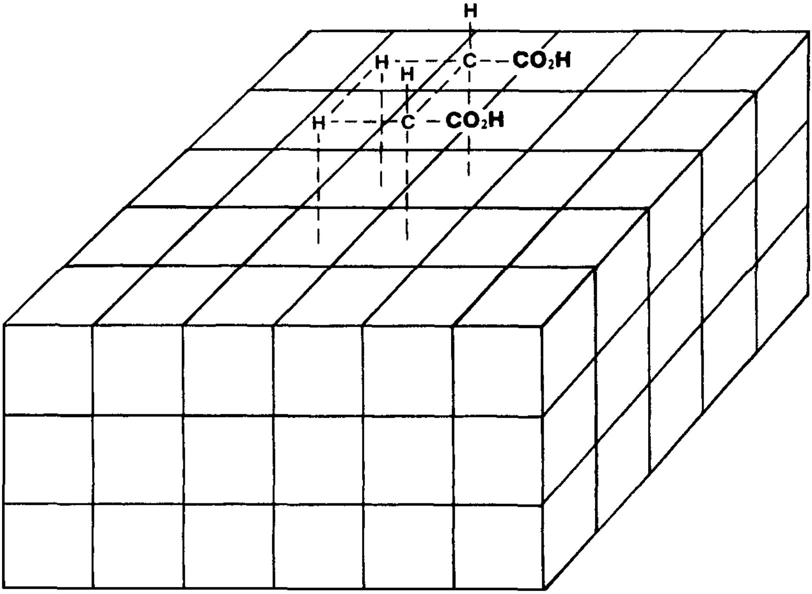


Fig. 1.18—Schematic representation of hydrogenation of maleic acid on EN deposit surface.

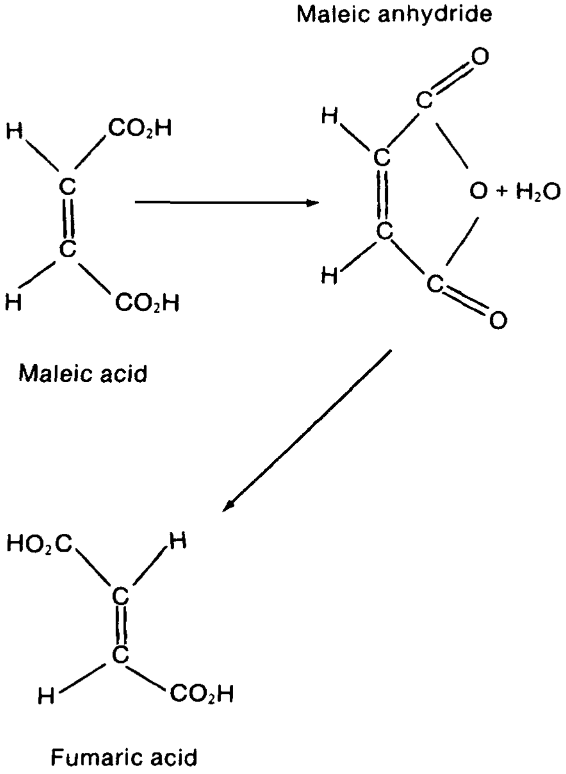


Fig. 1.19—Isomeric conversion of maleic acid to fumaric acid.

Although the above discussion on stabilizers was concerned with hypophosphite-reduced electroless nickel plating solutions, the principles also apply to amine borane-reduced baths. Stabilizers such as lead, and divalent sulfur compounds such as thiodiglycolic acid are commonly found in amine borane plating solutions. When a borohydride reducing agent is employed, the situation is different, however. As a result of the combination of high pH (>12.0) and high temperature (90° C), some of the stabilizers used in the former cases are not applicable because of their decomposition or precipitation. In borohydride baths, thallium salts at concentrations in the range of 40 to 50 ppm have proven to be extremely effective (16).

Energy

Catalytic reactions, such as electroless nickel plating, require energy in order to proceed. The energy is supplied in the form of heat. Temperature is a measure of the energy (heat) content of the plating solution. In the context of this chapter, energy, which is added to the plating bath, is considered a bath variable like the other reactants. The quantity of energy required by the system or added to it is one of the most important factors affecting the kinetics and rate of the deposition reaction. The dependence of reaction rate on temperature is illustrated in Fig. 1.20. The rate-energy relation is shown schematically because the exponential nature of the relation is common to all electroless nickel plating systems, even though their absolute plating rates will differ.

The rate of a chemical reaction may be studied by measuring the rate of decrease in the concentration of the reactants or the rate of increase in the concentration of the products. In electroless nickel deposition, we measure the rate of formation of the deposit. These relationships are expressed mathematically by:

$$\text{Rate} = \pm \frac{dC_i}{dt} = K\,(\pi_{i,j}\, C_i^j) \qquad [96]$$

where (+) is used if C_i is a product and (-) if C_i is a reactant; K is a numerical proportionality constant called the rate constant; C_i^j is the concentration of the *i*th reactant (product) present in the system at time t; and j is the reaction order of the *i*th species.

To reiterate, the dominant variable affecting reaction rate is the temperature at which the process occurs. Many reactions that take place close to room temperature double their rates of reaction for each 10° C rise in temperature. Note that 100° C is considered close to room temperature.

The variation of rate constant K (in Eq. 96) with temperature T is given by the Arrhenius equation:

$$\frac{d}{dT} \ln K = \frac{E_a}{RT^2} \qquad [97]$$

The quantity E_a is the activation energy of the reaction, and R is the gas constant. Since it is assumed that E_a is sometimes independent of temperature, T, integration of Eq. 97 yields:

$$\ln K = -\frac{E_2}{RT} + 1_{nA} \qquad [98]$$

where I_{nA} is the constant of integration.

Equation 98 is of the form y = mx + b, which is an equation for a straight line. Hence, a plot of I_{nk} vs. the reciprocal of the absolute temperature, 1/T, should be a straight line whose slope is $-E_a/R$.

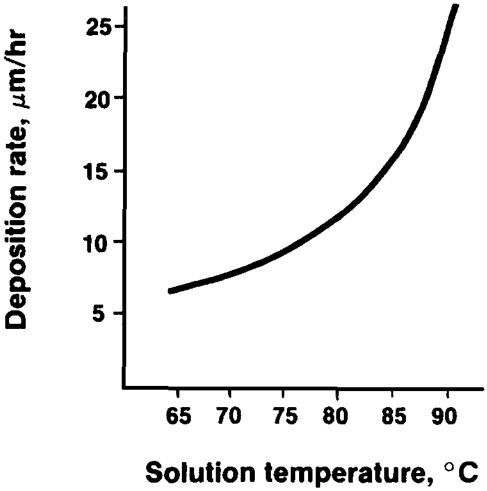


Fig. 1.20—Effect of temperature on plating rate.

Equation 98 yields an expression for the rate constant K:

$$K = A\exp\left(-\frac{E_c}{RT}\right) \qquad [99]$$

Here A is called the *pre-exponential* or *frequency* factor. According to this equation, the reacting molecules or ions must acquire a certain critical energy E_a before they can react. The term $\exp(-E_a/RT)$ is the Boltzmann factor, which denotes the fraction of the reacting species that have managed to attain activation energy E_a. The activation energy can be considered as a potential *energy barrier that the reactants must climb before they can react.*

Substituting the expression for K (Eq. 98), Eq. 96 can now be written as:

$$\text{Rate} = \pm\frac{dC_i}{dt} = A\left(\pi_{i,j}\, C_j^i\right) \exp\left(-\frac{E_a}{RT}\right) \qquad [100]$$

Equation 100 shows that the reaction rate is dependent on the addition of energy to the system as measured by temperature.

When operating an electroless nickel plating bath, it is necessary to know which conditions yield deposits with the desired properties. The deposits should be produced with minimum cost and difficulty and optimum efficiency. In some cases, it is more efficacious to operate the plating bath at a temperature that does not give the maximum plating rate. The composition of Ni-P deposits can be altered slightly by merely raising (decrease P) or lowering (increase P) the temperature of hypophosphite-reduced nickel plating solutions. The amine borane reducing agents are more temperature sensitive and will hydrolyze excessively at high temperatures, causing wasteful side reactions.

In this chapter we have discussed, in some detail, the chemistry of the principal components of electroless nickel plating solutions. Each component was shown to have a unique effect on the course of the deposition reaction. The discourse was mainly concerned with the theoretical, or better, ideal aspects of the nickel reduction reaction.

However, in real time, EN solutions are used to plate a myriad of commercial and industrial substrates. In subsequent chapters, the real time operation of EN plating solutions will be discussed.

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