Chapter 2
The Electroless Nickel Plating Bath:
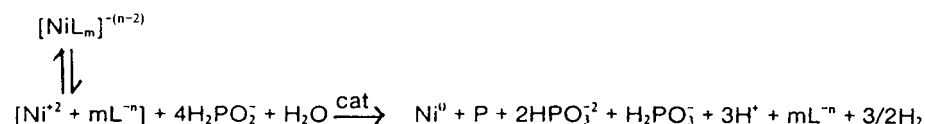# Effect of Variables on the Process

G.O. Mallory

In the previous chapter, the components of electroless nickel plating baths were discussed from the viewpoint of the function each performs in the bath, with little attention paid to their effect on the plating process. The metal and the electron source (the reducing agent) are consumed in the electroless plating reaction and so their concentrations in the bath are continuously decreasing. There are no anodes available to maintain a near-constant metal concentration, and no external electron source (rectifier) to keep a constant flow of electrons moving into the system, as in an electrolytic plating process. In order to have a continuous and consistent electroless plating process, the reactants must be replenished. The frequency at which additions of the reactants are made to the bath depends on how far the concentrations of the reacting species can be allowed to vary from their optimum concentrations without adversely affecting the plating process, or concurrently the deposit.

The electroless plating reaction not only yields a nickel alloy deposit; it also generates by-products, which accumulate in the solution. As the concentrations of the by-products increase, their influence on the plating reaction also increases. In the following sections, the effects on the plating reaction of the reactants and by-products, as variables, will be discussed.

ELECTROLESS NICKEL PLATING
WITH HYPOPHOSPHITE

Acid Plating Baths

A chemical equation that represents the aggregate electroless Ni-P plating reaction can be written as:

$$[NiL_m]^{-(n-2)}$$

$$\updownarrow$$

$$[Ni^{+2} + mL^{-n}] + 4H_2PO_2^- + H_2O \xrightarrow{cat} Ni^0 + P + 2HPO_3^{-2} + H_2PO_3^- + 3H^+ + mL^{-n} + 3/2H_2$$

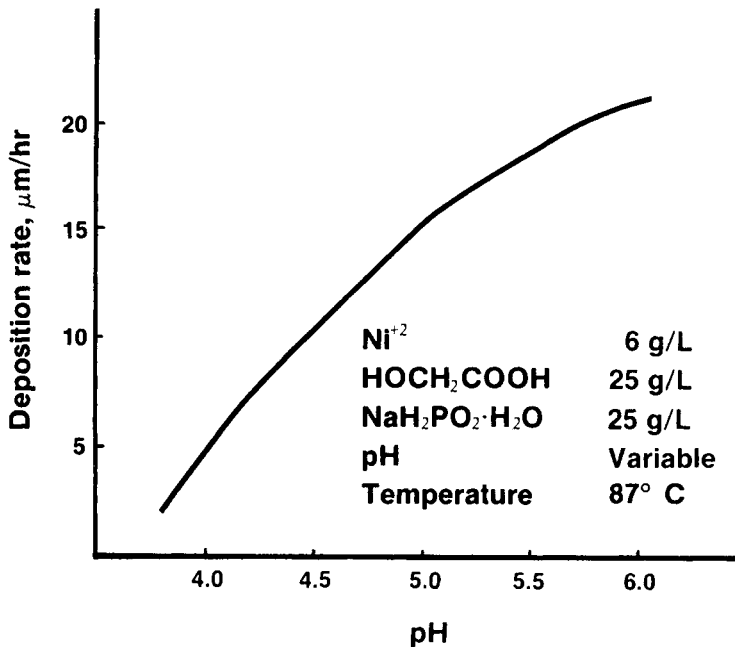where $[NiL_m^{-(n-2)}]$ denotes the nickel complex and mL^{-n} the "free" complexing agent.

Fig. 2.1—Effect of pH on rate of deposition.

Equation 1 shows that there are at least five variables (components) that influence the deposition reaction: the reactants Ni^{+2} and $H_2PO_2^-$; the products H^+, $H_2PO_3^-$, and L^{-n}. To these five variables, at least three more are added: temperature, the anion of the nickel salt used (e.g., sulfate from $NiSO_4 \cdot 6H_2O$), and one or more stabilizers. Hence, there are at least eight variables that must be monitored during electroless nickel plating.

The number of variables illustrates the complexity of operating and maintaining these solutions. As an aside, it should be pointed out that the suppliers of proprietary electroless nickel plating solutions have reduced the number of variables the plater must be concerned with through judicious formulations and clever packaging of replenishing solutions.

The Influence of H^+

In laboratory tests, it is observed that for every mole of Ni^{+2} deposited, three moles of H^+ are generated, which is in agreement with Eq. 1. The accumulation of hydrogen ions (H^+) in the plating bath lowers the pH of the solution. When the pH decreases, the most noticeable change in the plating process is a concurrent decrease in the rate of deposition. If the pH is allowed to drop too far in acid solutions (pH <4.0 for commercial plating baths), a very low plating rate is observed. Figure 2.1 illustrates the effect of solution pH on deposition rate. The
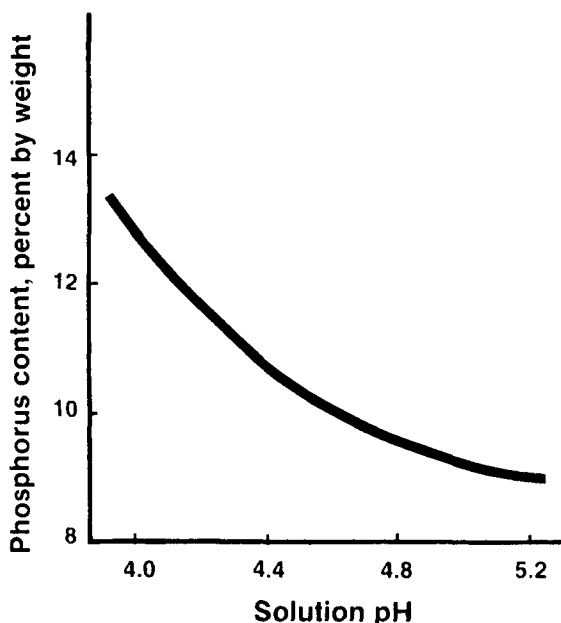
Fig. 2.2—Effect of pH on phosphorus content.

most dramatic effect of lowering the pH is on the composition, and concomitantly, the properties of the Ni-P deposit. The effect of solution pH on alloy composition is shown in Fig. 2.2.

The physical and chemical properties of electroless Ni-P deposits are dependent on the composition of the alloy in question. (A detailed discussion of the properties of electroless nickel-phosphorus deposits is covered elsewhere in this book.) As a rule of thumb, when the phosphorus content of the deposit is in excess of 10 percent by weight, the Ni-P alloy has the following characteristics:

- Low internal intrinsic stress, usually near zero or slightly compressive.
- Good corrosion resistance; low porosity.
- Non-magnetic in as-plated state.

If one or more of these properties is required, then a decrease in plating bath pH is not harmful, since the phosphorus content will be increased, allowing the deposit to achieve and maintain the desired property. On the other hand, if a particular application requires that the phosphorus content remain invariant or within a narrow range, say between 5.5 and 6.0 percent by weight, then a moderate decrease in pH can result in increasing the phosphorus content beyond the specified limit.
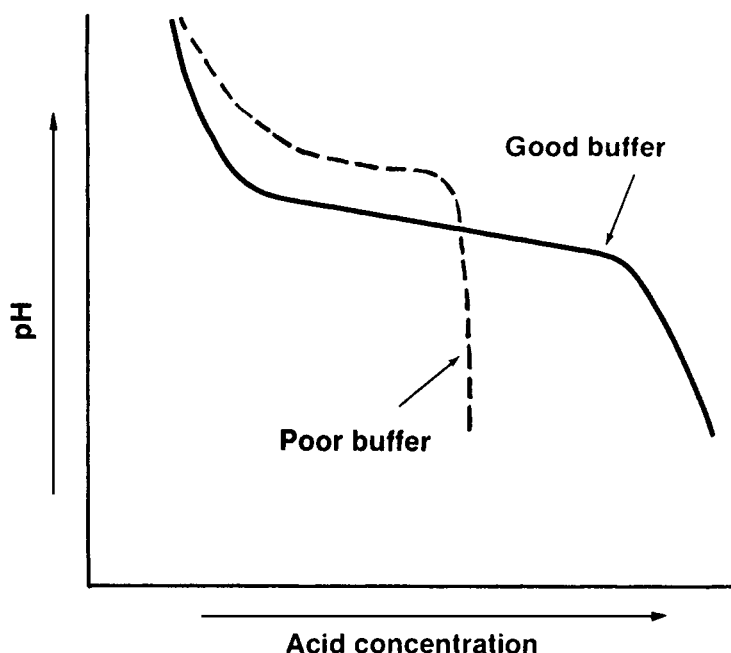
Fig. 2.3—Effect of buffering agents.

The amount that the pH changes as a result of the formation of H⁺ is related to the buffer capacity of the complexing agents and certain other materials called *buffers* that are present in the plating bath. In simple terms, a buffer is a substance or mixture of substances that, added to a solution, is capable of neutralizing both acids and bases without appreciably changing the original pH of the solution. A measure of buffer capacity is the amount of acid (H^+) required to change the pH by a given amount. The greater the amount of acid required, the better the buffer. The practical buffer capacity, P_B, of an electroless nickel plating bath can be determined by titrating the bath with a standard acid solution and plotting pH vs. acid concentration. Figure 2.3 is a schematic illustration of data obtained by this technique. The slope of the linear portion of the curve can be expressed mathematically by:

$$|\alpha| = \frac{\triangle pH}{\triangle[H^+]}$$

Table 2.1
Organic Acids Used as Buffers
In Electroless Nickel Plating Solutions

Acid	Structure	Dissociation constants at 25° C	
		K_1	K_2
Acetic	CH_3CO_2H	1.75×10^{-5}	—
Propionic	$CH_3CH_2CO_2H$	1.4×10^{-5}	—
Succinic	$HO_2C(CH_2)_2CO_2H$	6.6×10^{-5}	2.5×10^{-6}
Glutaric	$HO_2C(CH_2)_3CO_2H$	4.7×10^{-5}	2.9×10^{-6}
Adipic	$HO_2C(CH_2)_4CO_2H$	3.7×10^{-5}	2.4×10^{-6}

where $\triangle pH = pH_{initial} - pH_{final}$ and $\triangle[H^+] = [H^+]_{initial} - [H^+]_{final}$. P_B can then be defined as $1/\alpha$. The larger P_B is, the greater the buffer capacity of the plating bath. This method can be used to compare the buffer capacity of various combinations of complexing agents and buffers.

The most efficient buffers will not prevent the pH from eventually decreasing, therefore it is necessary to monitor the pH and neutralize the excess H^+ being generated in the solution by the addition of ammonium or alkali metal hydroxides or carbonates. The time interval between additions of base solutions to an electroless nickel bath with a large P_B is less critical than for a bath with a much smaller P_B. A list of the commonly used buffers is given in Table 2.1. The aliphatic carboxylic acids also function as monodentate ligands (complexing agents); however, their principal action is that of buffer. Additionally, the anions of propionic, succinic, and glutaric acids are said to *exalt* the plating reaction. Exaltants are defined as those compounds that activate the hypophosphite anion and enhance the EN plating rate.

With few exceptions, it would appear that the ideal operating pH range for an acid Ni-P plating bath would be about 5.0 to 7.0. However, Gutzeit (1) points out that there are two important factors to be considered in the choice of the optimum pH range:

- The solubility of the orthophosphite $(H_2PO_3^-)$ produced by the reduction reaction.
- The adhesion of the coating, particularly on ferrous substrates.

The first factor will be discussed in a subsequent section of this chapter. Data obtained from comparative adhesion tests on steel (1) reveal that the adhesion of a specimen plated at pH 4.4 was 60,000 psi, compared to values of less than 30,000 psi for a test specimen plated at pH 6.0. The optimum pH range for acid hypophosphite EN plating baths is usually 4.5 to 5.2. In the majority of EN applications, satisfactory deposits will be obtained if the solution pH is

Table 2.2
Effect of pH Change on Electroless Nickel Process

Change	Effect on solution	Effect on deposit
Raise pH	Increased deposition rate; lower phosphite solubility.	Decreased P content; shift in stress to tensile direction.
	Decreased stability with resultant plateout.	Poorer adhesion on steel.
Lower pH	Decreased deposition rate; improved phosphite solubility.	Increased P content; shift in stress to compressive direction.
		Improved adhesion on steel.

maintained within the stated range. The effects of raising or lowering the pH on the process itself as well as the resultant deposits are discussed in Table 2.2.

The importance of maintaining an essentially constant solution pH during the plating sequence should now be readily apparent; therefore, in the discussions on the remaining bath variables, a constant pH should be inferred unless otherwise stated.

The Influence of Nickel and Hypophosphite Ion Concentration

Brenner and Riddell (2) discovered that autocatalytic nickel plating would proceed on an immersed catalytic substrate at temperatures near 90° C in the pH range of 4 to 6. Plating was shown to occur over a wide range of nickel and hypophosphite concentrations—3 to 100 g/L (0.05 to 1.7M) for nickel and 10 to 100 g/L (0.09 to 0.94M) for hypophosphite. Under these conditions, the authors found that nickel deposition would occur on a suitable substrate without the simultaneous random reduction of nickel throughout the plating solution.

Gutzeit and Krieg (3) observed that to achieve optimum plating conditions, a narrow, more limited concentration range for hypophosphite is required. They also found that the molar ratio of $Ni^{+2}/H_2PO_2^-$ should be maintained within a limited range of 0.25 to 0.60, with the preferred range being 0.30 to 0.45.

The nickel concentration of commercial acid-type (pH 4 to 6) electroless nickel solutions lies within the range of 4.5 to 11 g/L (0.08 to 0.19M). Simple calculations based on the nickel concentration range and the preferred molar ratio of $Ni^{+2}/H_2PO_2^-$ yields a molar concentration range of 0.18 to 0.27M for sodium hypophosphite.

The nickel concentration of EN solutions used for most industrial applications is usually 6.5 ±1.0 g/L (0.09 to 0.13M). When the nickel concentration is equal to or greater than approximately 5 g/L (0.085M), it has little or no effect on the plating rate (4); the plating reaction is said to be zero order with respect to the
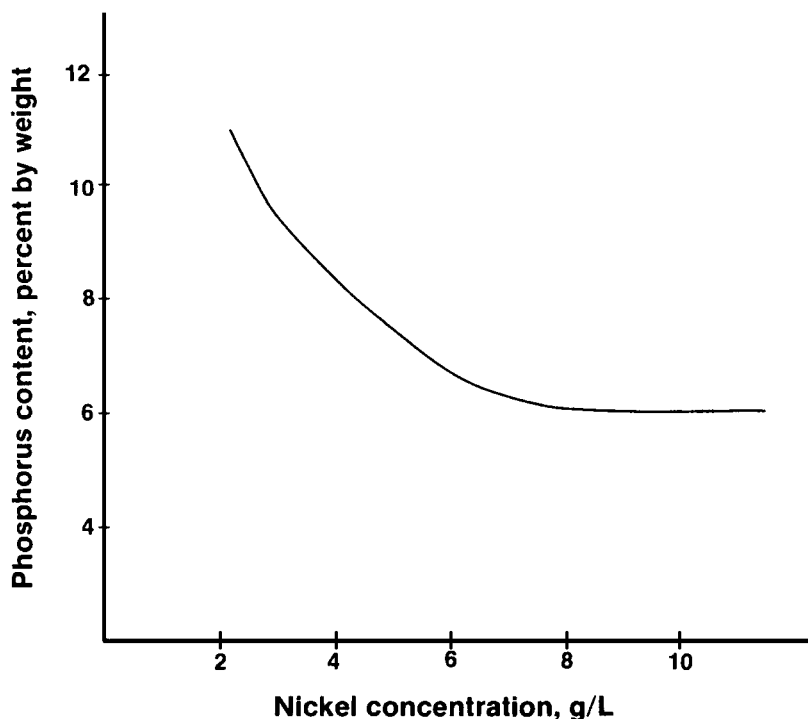
Fig. 2.4—Effect of nickel concentration on Ni-P alloy composition (4).

nickel ion concentration. The phosphorus content of Ni-P deposits is influenced by the nickel concentration in the plating baths only when the nickel concentration is less than about 0.1M. If the nickel concentration is increased beyond 0.1M (5.8 g/L), the phosphorus content will remain invariant, provided that the hypophosphite concentration is held constant. Figure 2.4 shows the effect of the nickel concentration on Ni-P alloy composition.

Lee (5) reported the influence of the reactants on the phosphorus content of the Ni-P coatings. Generally, increasing the $H_2PO_2^-$ concentration in the plating bath results in an increase in the phosphorus content of the deposit, as shown in Fig. 2.5.

Whereas nickel deposition is first order with respect to the hypophosphite concentration, Lee found a second order dependence on hypophosphite for phosphorus deposition. He derived the following empirical kinetic equation from experimental data:
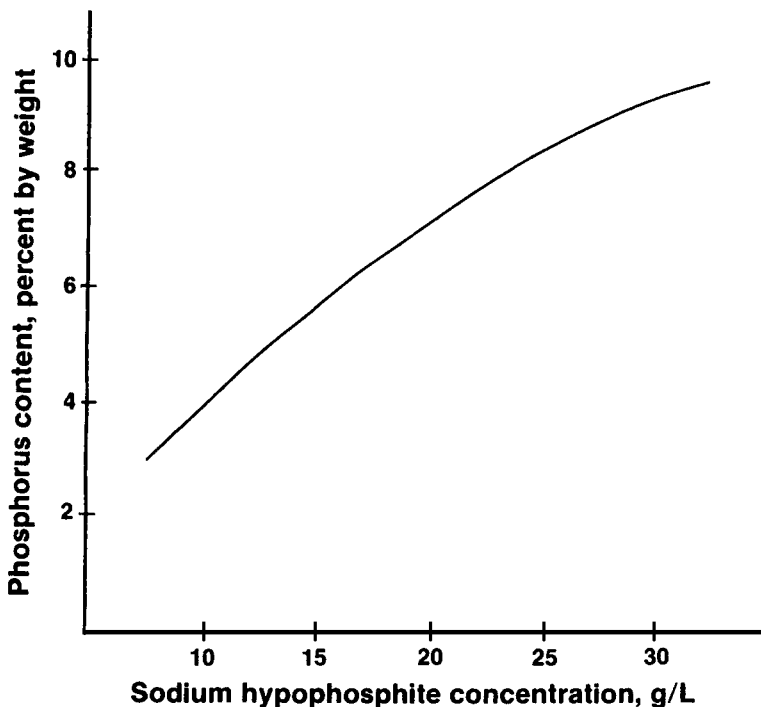
Fig. 2.5—Effect of hypophosphite concentration on Ni-P alloy composition (4).

$$\frac{dp}{dt} = K[H_2PO_2^-]^{1.91} [H^+]^{0.25} \qquad [2]$$

Equation 2 indicates that phosphorus deposition is acid-catalyzed (increase phosphorus content by increasing H^+). On the other hand, experimental data for nickel deposition leads to an empirical rate equation of the form:

$$\frac{dNi^0}{dt} = K \frac{[H_2PO_2^-]}{[H^+]^\beta} \qquad [3]$$

where β is the order of the reaction with respect to H^+ concentration. Hence Eq. 3 shows that nickel reduction is base-catalyzed (increase nickel deposition by decreasing H^+).

In addition to determining the effects of individual reactants on the electroless nickel plating process, it is equally instructive to ascertain the role their interdependence plays on the plating reaction. This is usually done by observing how the relationship expressed by the molar ratio $H^+/H_2PO_2^-$ affects the plating

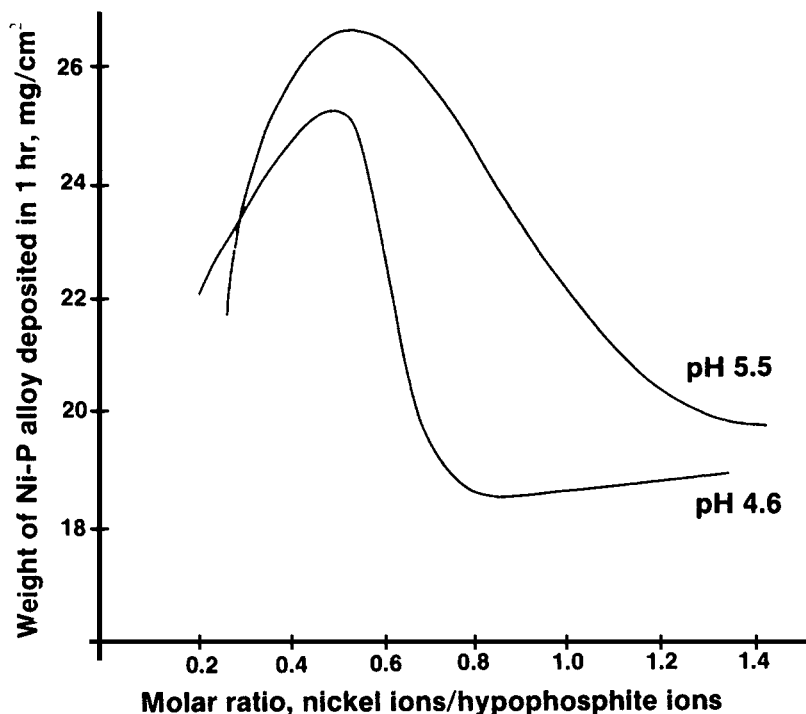Fig. 2.6—Rate of deposition from acetate baths as a function of $Ni^{+2}/H_2PO_2^-$ molar ratio at two different pH values (1).

rate. Figure 2.6, taken from Gutzeit (1), illustrates the effect of the molar ratio on the plating rate (constant $H_2PO_2^-$, varying Ni^{+2}). The results given in Fig. 2.6 were obtained from an uncomplexed acetate bath, and it in no way infers that all electroless nickel solutions, especially those containing chelating agents, will yield equivalent results.

The Phosphite Anion

The phosphite anion is generated by the oxidation of hypophosphite during the plating reaction (see Eq. 1). For each nickel ion reduced to metal, approximately three phosphite ions are produced; or, for each gram of Ni^{+2} reduced, approximately four grams of phosphite are formed. For continuous operation of the plating bath, the depleted hypophosphite (as well as nickel) must be replenished. Hence, phosphite steadily accumulates in the plating bath. With time, phosphite becomes an important solution component. As the phosphite concentration increases, it will begin to compete with the complexing agent for nickel ions. This usually occurs when the phosphite concentration reaches 30 g/L. Nickel phosphite is relatively insoluble and exhibits the inverse solubility
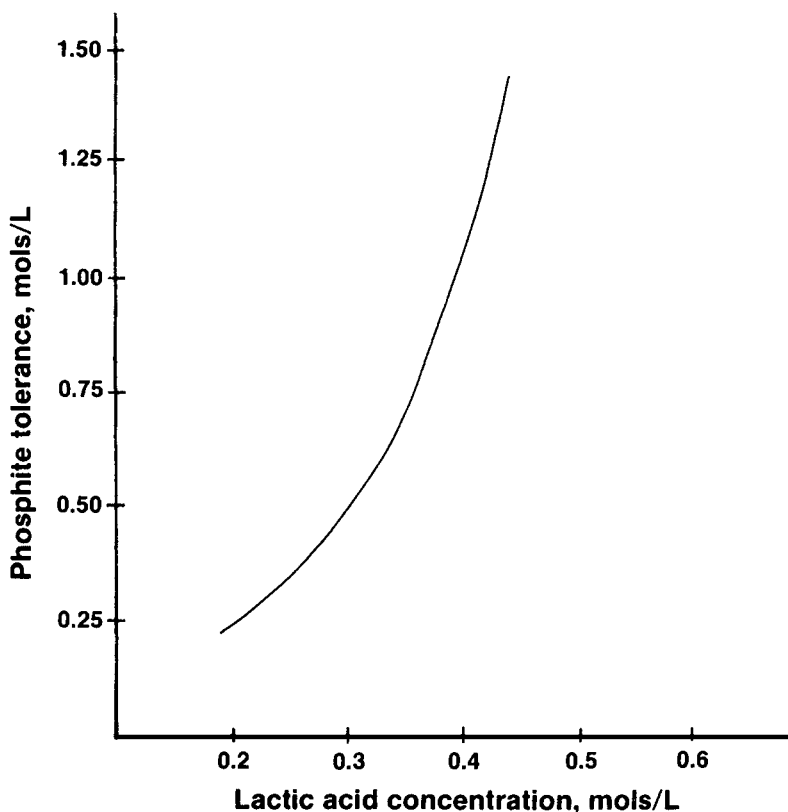
Fig. 2.7—Phosphite tolerance of plating bath as a function of lactic acid concentration (1).

phenomenon. That is, nickel phosphite is more soluble at low temperatures than at higher temperatures.

When the formation of nickel phosphite is first observed, the addition of excess complexing agent will solubilize the compound and prevent its precipitation. The hydroxy carboxylic acids (lactic and hydroxyacetic) are very effective in preventing the precipitation of nickel phosphite. Figure 2.7 illustrates the variation in phosphite tolerance with lactic acid.

Ultimately, the phosphite ion concentration becomes so large that further additions of complexing agent cannot prevent the precipitation of nickel phosphite. At this point the plating bath is discarded. Since nickel phosphite is more soluble at lower pH values, it may be more efficacious to sometimes operate the plating bath at lower pH values, say, 4.6 rather than 5.0. The solubility of phosphite vs. bath pH for two lactic acid concentrations is shown in Fig. 2.8.
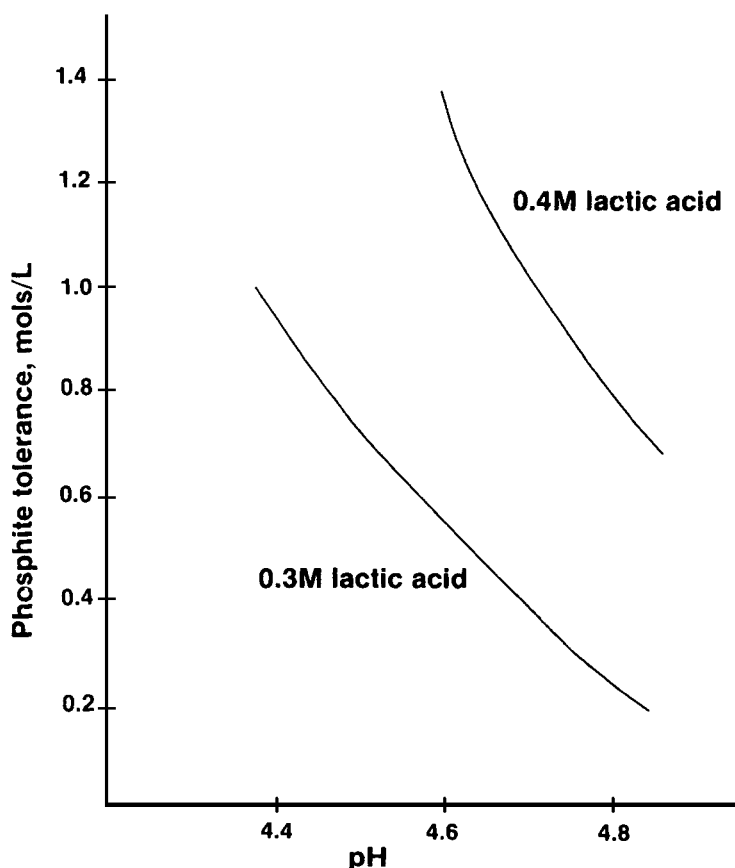
Fig. 2.8—Phosphite tolerance of plating bath as a function of pH at two lactic acid concentrations.

Nickel phosphite precipitation, which is visually observable, was considered the only harmful result of phosphite accumulation in the plating solution; however, there is a more serious consequence of phosphite presence in the solution. A definite correlation between the phosphite concentration and the internal stress of Ni-P deposits was observed by Baldwin and Such (4) and later verified by others (6). The effect of phosphite concentration on the internal intrinsic stress of Ni-P deposits is shown in Fig. 2.9. As the phosphite concentration increases, the stress becomes more tensile. In many applications (e.g., corrosion, memory disks), tensile stress is to be avoided. The data reported in Fig. 2.9 indicates that solutions used for engineering purposes have a limited useful life expectancy, up to three metal turnovers.

Some plating baths are able to tolerate moderate concentrations of phosphite better than others. This depends on the formulation of the bath and the nature of
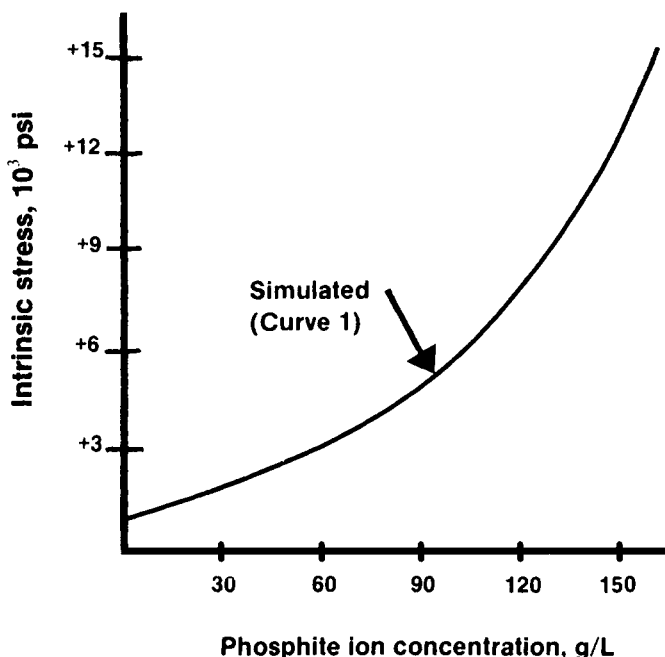
Fig. 2.9—Variation of intrinsic stress with phosphite ion concentration.

the complexing agent. A phosphite concentration of about 60 g/L will cause only a slight decrease in plating rate from some baths, while in other baths this concentration results in a marked decrease in rate. The phosphorus content in Ni-P deposits may be increased by 1 to 2 percent by weight at high phosphite concentrations in the bath.

To extend the life of an electroless nickel plating bath beyond a few metal turnovers, it is essential that the phosphite be removed from the solution, or at least reduced to a tolerable level. Methods of phosphite removal from EN plating baths have been investigated for many years.

The use of ferric chloride ($FeCl_3$) to precipitate the accumulated phosphite was proposed by Gorbunova and Nikiforova (7). Ferric chloride reacts with phosphite to form an insoluble complex compound according to the following equation:

$$2NaH_2PO_3 + FeCl_3 \xrightarrow{H_2O} Na_2[Fe(OH)(HPO_3)_2] \cdot xH_2O + 3HCl \qquad [4]$$
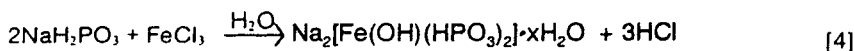
To avoid contamination of the plating bath with an excess of ferric chloride, the amount of $FeCl_3$ added must be less than the stoichiometric quantity required to precipitate all the $H_2PO_3^-$ in the bath. A considerable quantity of hypophosphite is

separated from the solution along with the phosphite that is precipitated; however, very little nickel is removed when the solution is treated with $FeCl_3$.

The formation of hydrochloric acid (HCl), as seen in Eq. 4, lowers the pH of the plating bath to inoperative levels. After removal of the insoluble iron complex by filtration, the pH of the bath must be raised to its optimum value. It is recommended that an acid neutralizing reagent be added simultaneously with the addition of ferric chloride.

Parker (8) discusses several procedures for precipitating the phosphite from spent EN plating baths. Of particular interest is his discussion of the ion-exchange treatment for the removal of phosphite. His data show that weak-base anionic resins are the most effective in adsorbing phosphite, as follows:

$$ROH + H_2PO_3^- \rightarrow RH_2PO_3 + OH^- \tag{5}$$

Parker claims that the ion exchange procedure is technically feasible and cost-effective, while on the other hand, the precipitation methods require further development to be practical.

The Role of the Complexing Agent
In the previous chapter, complexing agents were found to perform three principal functions in electroless nickel plating baths:

- Reduce the concentration of free nickel ions.
- Prevent the precipitation of basic nickel salts and nickel phosphite.
- Exert a buffering action.

de Minjer and Brenner (9) studied the relationship between ligand concentration and the plating rate. The data given in Fig. 2.10 are the results of their investigations.

Initially, a small addition of complexing agent is accompanied by an increase in plating rate. As the concentration of ligand is increased, the plating rate passes through a maximum. When the concentration of ligand is increased beyond the value where the rate maximum occurs, the plating rate decreases.

Several theories have been proposed to explain the maximum in the rate vs. ligand concentration curves. First, de Minjer and Brenner (9) argue that the maximum is the result of the low adsorption of ligand on the catalytic surface at low concentrations, which accelerates the reaction. At higher concentrations, there is a high adsorption of ligand on the surface, which poisons the reaction.

A more plausible explanation suggests that the rate increasing portion of the curve is due to the buffering action of the complexing agents. Maximum rates occur while there are uncoordinated (solvated) sites remaining on the nickel ions, that is, the nickel ions are only partially complexed or chelated. It must be remembered that partially complexed nickel ions retain some of the properties of free, solvated nickel ions. Hence, for ligand concentrations up to values where the maximum plating rates occur, buffering is the dominant function of the various ligands.
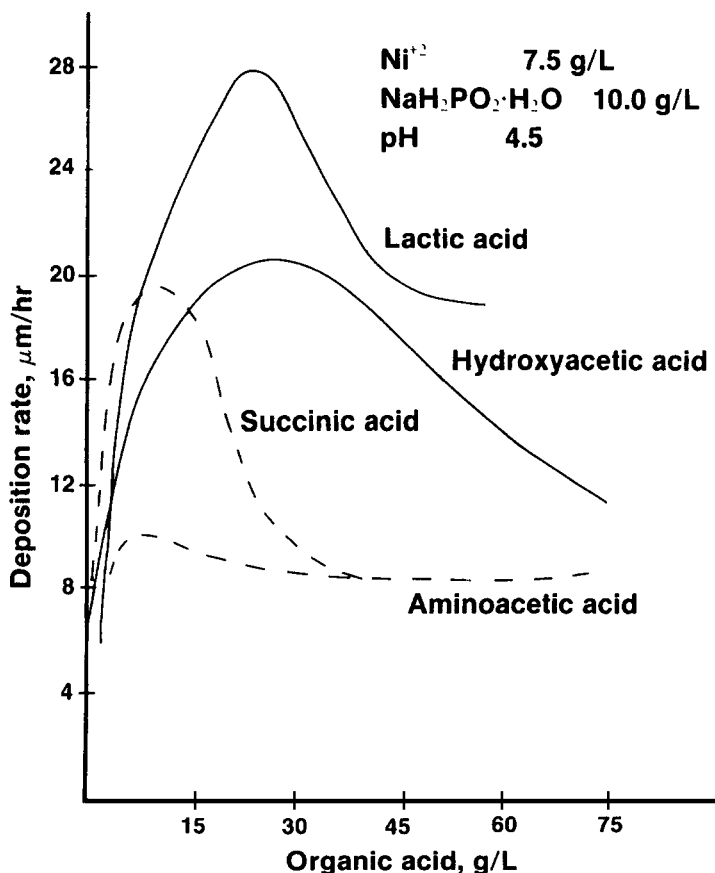
Fig. 2.10—Effect of concentration of organic acids on rate of deposition (9).

An explanation based on pH is inadequate to explain the decrease in rate for further increases in ligand concentration beyond the maximum point. The pH of the plating bath changes very little with continued plating. Moreover, the buffer capacity of the complexing agent does not parallel the plating rates obtained with them.

The decrease in plating rate, to the right of the maximum, is most likely due to the coordination of the remaining solvated sites with ligand atoms. The concentration of free nickel ions decreases and the metal ions take on the characteristics of complexed or chelated nickel ions.

The large differences in the rate maxima between the various complexing agents, as seen in Fig. 2.10, points to a specific property of ligands, vis-a-vis the nickel complex, that affects the rate of the plating reaction. The property in question is the stability constant of each nickel complex. Variations in the

maxima relative to the ordinate and absicca of each curve in Fig. 2.10 can be explained on the basis of the strength of the stability constant for each complex.

The difference in the rate of deposition between two plating baths containing different complexing agents is attributed to the differences in magnitude of the stability constants of the two nickel complexes. The nickel complex controls the number of free ions that are available to take part in the deposition reaction. Nickel complexes with low-value stability constants yield a larger quantity of free nickel ions when compared to complexes with numerically larger stability constants. It follows, then, that the larger the number of free nickel ions adsorbed on the catalytic surface, the greater the nickel plating rate.

The relationship between the nature of the nickel complex and the composition of the Ni-P deposit can be explained on the basis of the strength of the nickel complex. When the fraction of catalytic sites onto which nickel ions have been adsorbed is large (small stability constant), the number of sites available for phosphorus reduction is small and the phosphorus content of the deposit is lowered. On the other hand, when the stability constant is relatively large, the free nickel ion concentration is low, and the fraction of sites covered by adsorbed nickel is small; hence, in the latter case, the number of sites available for phosphorus reduction is large and the phosphorus content of the coating is increased.

In summary, electroless nickel complexes with low-value (weak) stability constants will show higher deposition rates and yield deposits with lower phosphorus content than baths with numerically larger (strong) stability constants. Electroless nickel plating baths based on lactic acid and citric acid are examples of complexing agents that form weak and strong nickel complexes, respectively.

The Selection and Replenishment
Of EN Stabilizers

Certain special compounds, called *stabilizers*, prevent or retard the spontaneous decomposition of electroless nickel plating solutions. This is especially true for acid EN solutions. Not only do these compounds stabilize plating solutions, but some of them also accelerate the plating rate. Other stabilizers can affect the phosphorus content and the internal stress of the electroless nickel deposits. If the stabilizer increases the reducing efficiency of the reducing agent, increases in plating rate and nickel content are observed. For example, thiourea increases the reducing efficiency of hypophosphite in acid EN plating solutions, with concomitant increases in plating rate and nickel content (lower phosphorus content) of the resultant deposits. Before incorporating a stabilizer in a production plating solution, it may be necessary to determine if it will affect the composition of the deposit.

Methods for determining the optimum stabilizer concentration were discussed in the previous chapter. The optimum stabilizer concentration is usually determined for some fixed set of plating conditions, e.g., temperature, pH, rate of agitation, and the surface area to solution volume ratio. However, in actual practice, these conditions vary and additionally, the stabilizer concentration

decreases as a result of its consumption during the deposition reaction. It is obvious that the control and replenishment of the stabilizer presents a difficult task.

The initial stabilizer concentration in the production bath is usually a compromise between the optimum concentration determined for the fixed set of conditions mentioned above, and the midpoint of a rate-vs.-concentration or potential-vs.-concentration curve in an unstirred solution.

The rate of consumption of the stabilizer is determined relative to the rate of nickel deposition, or even better, by the amount of nickel consumed. The stabilizer concentration can be monitored by several techniques, e.g., polarography, voltammetry, or atomic adsorption. Thus, when the nickel concentration is replenished to its initial value, a proportional quantity of stabilizer is also replenished. If more than one stabilizer is used, the above techniques are used to determine the working concentration of each stabilizer separately. However, when the stabilizers are combined in the working solution, synergistic effects must be compensated for by lowering the concentration of stabilizer component.

The working concentration of stabilizer(s) must be sufficient to prevent plate-out of nickel on the walls of the plating tank as well as solution decomposition. The concentration must be below the value where edge pull-back occurs on sharp edges of the parts being plated. Finally, replenishment additions must be able to maintain bath stability without poisoning the deposition reaction.

The Effect of Temperature

The temperature at which the plating reaction occurs is the principle variable that determines the rate of the reaction. Readers with intimate knowledge or experience with electroless nickel plating know that very little, if any, plating occurs at temperatures below about 60° C (140° F). As the temperature is increased, the plating rate increases exponentially.

Acid hypophosphite plating solutions are operated between 85 and 90° C. If the temperature is allowed to increase much beyond 90° C, the possibility of solution plate-out or even solution decomposition increases. Baldwin and Such (4) reported that the phosphorus content of deposits is decreased when the temperature of the plating bath is increased beyond its normal operating range, with all other variables held constant.

MISCELLANEOUS IONS

The term *miscellaneous* is used to describe certain cations and anions that accumulate in the plating bath by replenishment of consumed reactants, and the neutralization of H^+ ions that are generated during the plating reaction. The cations Na^+, K^+, and NH_4^+ are introduced into the solution by additions of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), sodium or potassium hydroxide (NaOH, KOH), and ammonium hydroxide or ammonium carbonate [NH_4OH or $(NH_4)_2CO_3$]. Nonreactive anions, such as SO_4^{-2} and Cl^- build up in the plating bath as the result

of nickel ion replenishment in the form of nickel salts such as nickel sulfate or nickel chloride ($NiSO_4 \cdot 7H_2O$ or $NiCl_2 \cdot 6H_2O$).

The actual effect that these so-called miscellaneous ions have on the plating process has not been clearly established in all cases. However, Haydu and Yarkowsky (10) show that sulfate anions ($SO_4^=$) in sufficient quantities will increase the phosphite tolerance of the plating bath. They found that the amount of phosphite required to precipitate metal ions from a new plating bath was increased from 28 g/L (0.25M) to 70 g/L (0.7M) by the addition of 152 g/L sodium sulfate at pH 5.0. This suggests that additional sodium sulfate be added along with maintenance additions of reactants to enhance phosphite solubility.

One can speculate as to the effect that the alkali metals ions (Na^+ and K^+) have on nickel deposition. From a previous section, it is known that Ni^{++} and H^+ ions compete for association with complexing and buffering agents. Sodium and potassium ions can be included in that competition. Once the concentration of Na^+ or K^+ exceeds some statistically significant quantity, the probability of an alkali metal reacting with the complexing agent or buffer is much greater than the probability of either the nickel or hydrogen ion reacting. Hence, as alkali metal ions accumulate in the bath, the equilibrium between "free" nickel ions and nickel complex is more likely to be affected, as shown in the following scheme:

$$M^{+2} = Ni^{+2} \qquad NiL_m^{2-n} \qquad [6a]$$

$$L_m^{-n} + M^+ \underset{M^{+2} = H^+}{\rightleftharpoons} HL_m^{1-n} \qquad [6b]$$

$$M^{+2} = Na^+ \qquad NaL^{1-n} \qquad [6c]$$

The decrease in plating rate observed in aged (replenished) plating baths may be attributed to the predominance of Eq. 6c over 6b.

Several authors have ascribed changes in solution and deposit properties to phosphite buildup in the plating solution as a result of prolonged replenishment of the solution. It is imputed, for example, that the decrease in plating rate in the bath and the increase in phosphorus content of the deposits from said bath, are due to phosphite buildup. Other researchers have added quantities of phosphite to new plating solutions (equivalent to the amount of phosphite formed corresponding to the number of turnovers and replenishments reported in prior studies) and found no correlation between phosphite and deposition rate or phosphorus content. However, the addition of both sodium sulfate (Na_2SO_4) along with phosphite ($NaHPO_3$) to new plating solutions does change the deposition rate and alter the phosphorus content. It must be noted that the addition of Na_2SO_4 does increase the alkali metal ion content of the bath. These
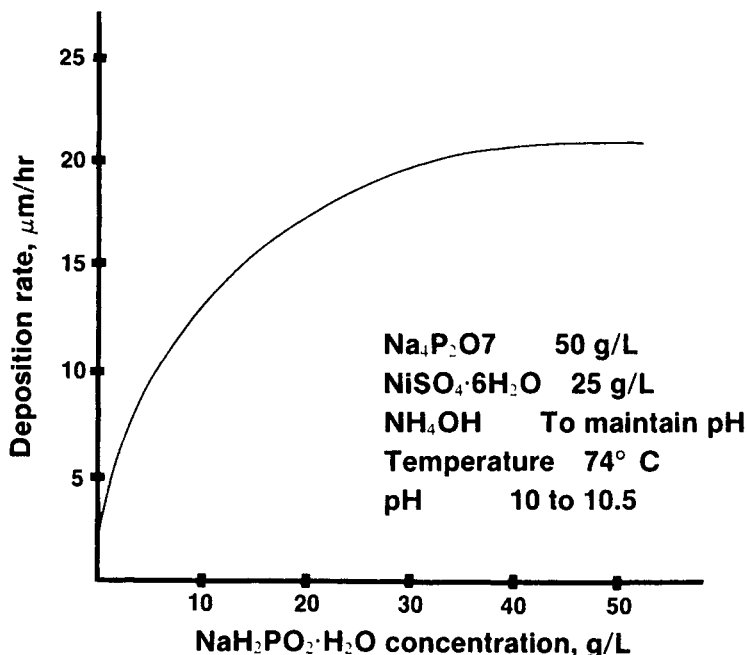
Fig. 2.11—Effect of sodium hypophosphite concentration on rate of deposition.

additions (Na_2SO_4 and Na_2HPO_3) do not account for all of the alkali metal ions that could be added over an equivalent number of replenishments.

Neutralization of H^+ by NaOH or K_2CO_3 increases the concentration of Na^+ or K^+. Hence, the changes in rate and percentage of phosphorus can just as well be justified by the alkali cation buildup; i.e., if the buffer associates with the excess sodium or potassium cations in preference to H^+ ions, then there are more H^+ ions available to lower the pH of the reaction layer adjacent to the substrate. This surplus of H^+ ions is also available to increase the phosphorus reduction reaction:

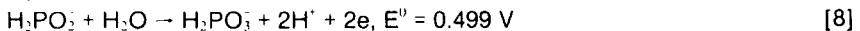$$2H_2PO_2^- + H^+ \rightarrow P + H_2PO_1^- + H_2O + \tfrac{1}{2}H_2 \qquad [7]$$
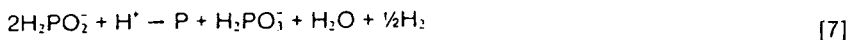
An increase in phosphorus reduction is concurrently accompanied by a decrease in nickel deposition.
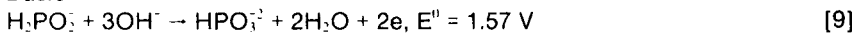
ALKALINE HYPOPHOSPHITE
PLATING SOLUTIONS

The industrial uses of alkaline plating solutions have been confined to a very few special applications, usually those that require plating at low temperatures, such as plating of various polymeric materials. In general, the phosphorus content of deposits obtained from alkaline solutions is lower than those produced in acid solutions. Alkaline solutions were used exclusively to produce low-phosphorus deposits. (Recently developed solutions that are slightly acidic [pH 6.0 to 6.6] yield deposits containing 1 to 2 percent phosphorus).

The plating reaction in alkaline solutions proceeds in a manner analogous to that in acid solutions; i.e., nickel deposition is accompanied by the production of hydrogen ions (H^+), hydrogen gas (H_2) evolution, and the oxidation of hypophosphite to phosphite. Further, the hypophosphite anion is a much more powerful reducing agent in basic solutions than in acid solutions, as shown by the following equations:

Acidic
$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e, \quad E^0 = 0.499 \text{ V} \tag{8}$$

Basic
$$H_2PO_2^- + 3OH^- \rightarrow HPO_3^{-2} + 2H_2O + 2e, \quad E^0 = 1.57 \text{ V} \tag{9}$$

The early investigations of Brenner and Riddell (2) were performed with alkaline solutions. As far as alkaline plating solutions were concerned, no significant advances were made until Schwartz (11) reported on the use of pyrophosphate solutions. The unique aspect of the alkaline pyrophosphate system is that it is composed of inorganic materials.

The Effects of Reactants on Alkaline
Electroless Nickel Plating Baths
The rate of deposition in alkaline electroless nickel solutions is proportional to the hypophosphite concentration; the plating rate increases with increasing reductant concentration. Although raising the hypophosphite concentration improves the plating rate, the stability of the plating bath is lowered, necessitating the use of stabilizers. Figure 2.11 is a graphical presentation of data for the pyrophosphate bath. It is evident that the hypophosphite ion concentration has a pronounced effect upon the plating rate.

The influence of the nickel concentration on plating rate in the citrate and pyrophosphate baths was found by Schwartz to be at variance with the results reported by Brenner and Riddell (2); i.e., in the citrate bath, the hypophosphite
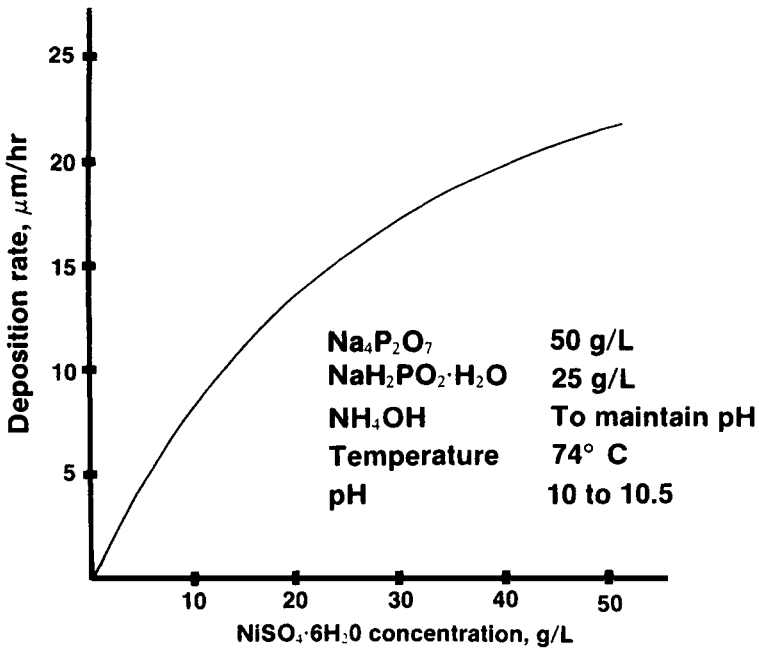
Fig. 2.12—Effect of nickel concentration on deposition rate (4).

ion has an appreciable effect on the rate, whereas the rate is only slightly increased by increasing the nickel ion concentration. The rate is increased significantly by increasing the nickel ion concentration in the pyrophosphate bath. The curve in Fig. 2.12 was plotted from data obtained by Schwartz for the pyrophosphate bath.

The Effect of Temperature on Rate

The rate of the deposition reaction is dependent on temperature in an exponential manner, and the relationship is independent of the acidity or alkalinity of the solution. A direct comparison between the two types of alkaline baths (citrate and pyrophosphate) is presented in Fig. 2.13. The deposition rate is seen to be considerably higher in the pyrophosphate bath than in citrate baths at equivalent temperatures; e.g., at 80° C, the rate in the pyrophosphate solution is nearly four times the rate in a citrate bath. It is also important to note that the initiation temperature is substantially lower in the alkaline pyrophosphate bath than in the alkaline citrate bath. In either case, the initiation temperatures are considerably lower for alkaline electroless nickel plating solutions than for
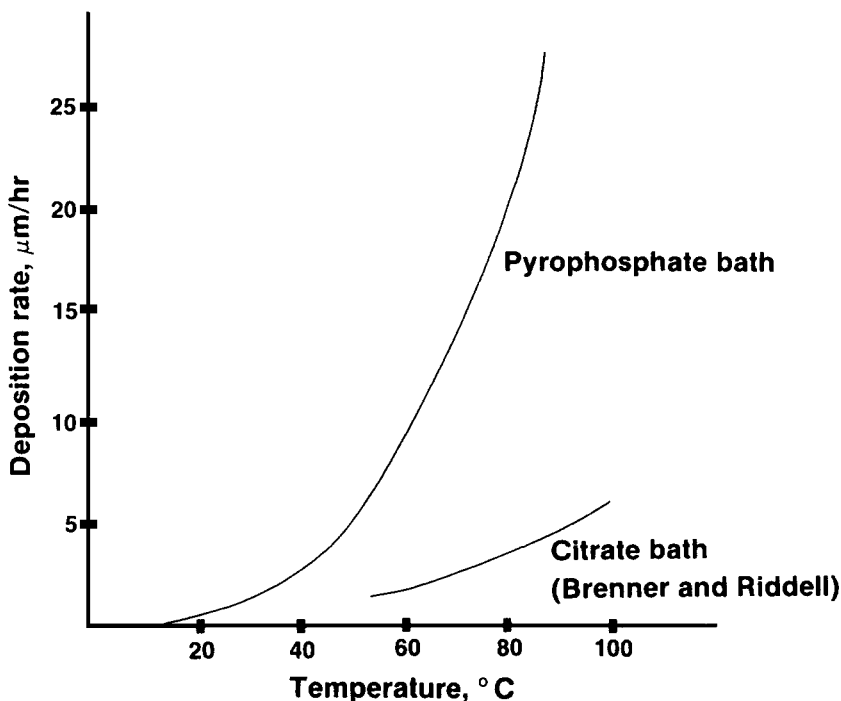
Fig. 2.13—Effect of temperature on deposition rate (11).

acidic plating systems. The fact that the pyrophosphate bath yields significant plating rates at "low" temperatures has led to its use in the so-called "low-temperature" applications.

The Effects of pH

As the plating reaction proceeds, the pH of an alkaline solution decreases. Figure 2.14 (taken from Schwartz) shows the effect of pH on plating rate in the pyrophosphate solution. Schwartz (11) points out that there is a lower limit for pH (about 8.5), below which the pH of the pyrophosphate solution must not be allowed to drop. Between pH 8.0 and 8.5, the operating solution turns turbid as a result of the precipitation of a basic nickel salt or complex.

The plating rates of non-proprietary alkaline electroless nickel solutions formulated with citrate are, with few exceptions, almost constant over the pH range of 8.0 to 11.0. The plating rate at 90° C lies in the range of 8 to 10 μm/hr. The maintenance of solution pH within its operating range is made easy by the intense blue color of the nickel ammine complex (a result of the addition of ammonium hydroxide) in the citrate baths. When the pH decreases, the color of
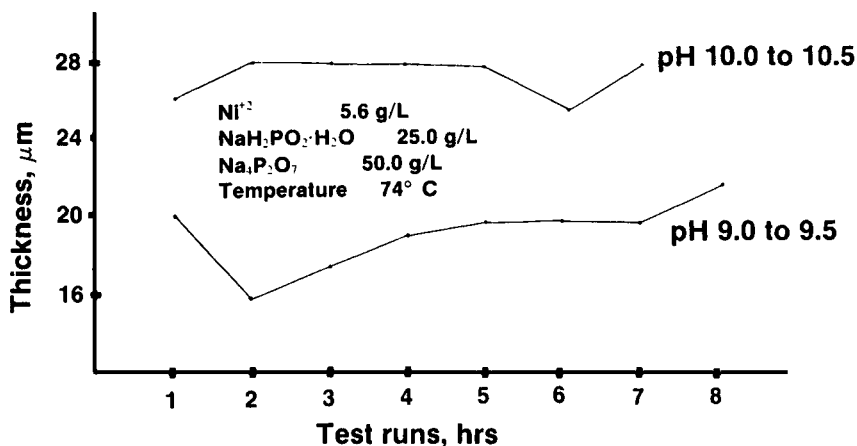
Fig. 2.14—Effect of pH on deposition rate (11).

the solution changes from dark blue to blue-green, to green, at which point ammonium hydroxide is added to restore the pH. Hence, the color, and intensity of the color, of the nickel-ammonia complex can serve as a qualitative indicator for both pH and nickel concentration. On the other hand, the color of the pyrophosphate nickel plating solution turns from intense dark blue to green when heated from ambient to operating temperature, even at optimum concentrations of the bath components.
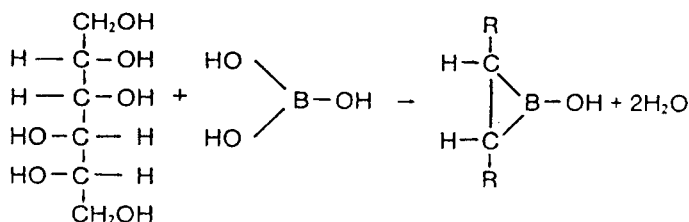
The Effect of Complexing Agents

Based on the high reduction potential given in Eq. 9, it might be assumed that the rate of deposition would be correspondingly higher in alkaline plating solutions than in acid plating solutions. However, the strong complexing agents used to prevent the precipitation of nickel hydroxide or basic nickel salts have a negative effect on the plating rate.

The complexing agents used to sequester nickel ions alkaline plating baths are generally combinations of citrate and ammonium ions or pyrophosphate and ammonium ions. EDTA and its substituted homologues are excellent chelators in basic solutions, but are seldom used as primary complexing agents because of the extremely low plating rate obtained in solutions containing these materials.
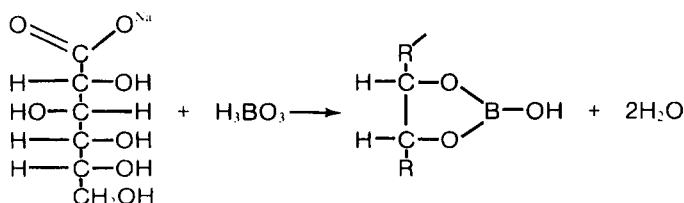
In 1975, Booze (12) reported a "nitrogen-free" alkaline plating solution, containing the so-called "borogluconate" addition compound. He observed that the complexing capacity of gluconate was greatly enhanced when sodium gluconate is reacted with boric acid to form the borogluconate complex. The mannitol/boric acid complex (from analytical chemistry) is the best known

homologue of this type of complex. The addition of boric acid to polyhydric materials is illustrated as:

$$CH_2OH$$
$$H-C-OH \quad HO$$
$$H-C-OH \ + \quad \ \ \ \ B-OH \quad \rightarrow \quad H-C \quad \ B-OH + 2H_2O$$
$$HO-C-H \quad HO$$
$$HO-C-H$$
$$CH_2OH$$

Mannitol/boric acid complex

and:

$$O=C-O^{Na}$$
$$H-C-OH$$
$$HO-C-H \ + \ H_3BO_3 \longrightarrow \quad B-OH \ + \ 2H_2O$$
$$H-C-OH$$
$$H-C-OH$$
$$CH_2OH$$

Sodium gluconate   Boric acid   Borogluconate complex

The pH of alkaline electroless plating baths based on borogluconate can be adjusted with alkali metal hydroxides or carbonates. The rate of deposition of these baths is a function of the borogluconate concentration, as shown in Fig. 2.15. Deposition rates in borogluconate solutions are comparable to those of pyrophosphate plating baths. Typical alkaline electroless nickel plating bath formulations are provided in Table 2.3.

Referring to Table 2.3, Baths 3, 4, and 5 are of particular interest. Iwasa et al. (13) observed that when electroless nickel plating silicon wafers with p-n junctions, and using conventional Brenner-type alkaline plating solutions, there was a pronounced difference in plating rate between the p- and n-type surfaces. They found that additions of EDTA to alkaline citrate solutions (Bath 3) resulted in an increase in deposition rate on p-type surfaces until it was essentially equal to the rate at n-type surfaces. The effect of EDTA concentration on plating rate of p-and n-type silicon as found by Iwasa et al. is shown in Fig. 2.16.

Electroless nickel plating of zinc die castings has generated considerable interest in alkaline pyrophosphate solutions (Bath 4) for use in this application. The pyrophosphate solution is claimed to have excellent tolerance to the zinc ions that build up in the solution. The pyrophosphate bath is also used as a
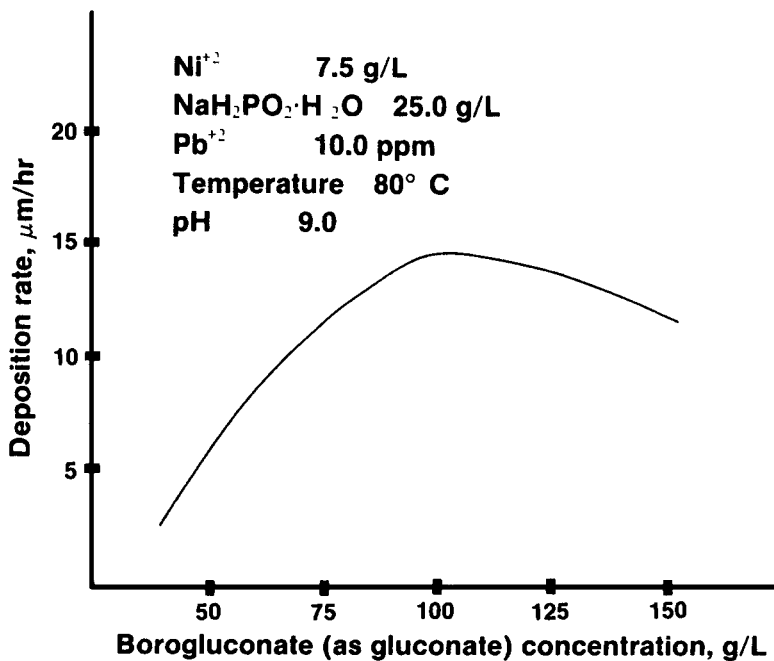
Fig. 2.15—Effect of borogluconate concentration on deposition rate (12).

Table 2.3
Typical Alkaline Electroless Nickel Plating Baths

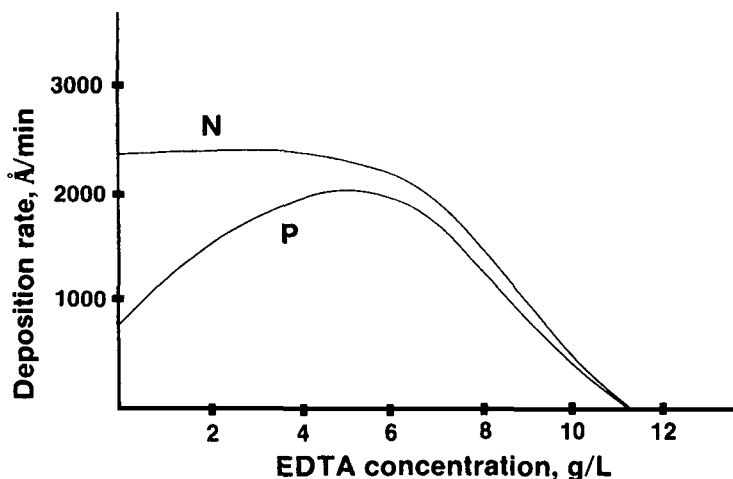|	Concentration, g/L				
	Bath				
Component	1	2	3	4	5
Ni^{+2}	7.0	7.5	7.5	6.0	7.5
NaH$_2$PO$_2$·H$_2$O	20.0	10.0	10.0	30.0	25.0
C$_6$H$_5$ONa^3·2H$_2$O	36.0	100.0	—	—	—
C$_6$H$_5$O$_7$(NH$_4$)$_2$	—	—	65.0	—	—
K$_4$P$_2$O$_7$	—	—	—	60.0	—
C$_6$H$_{11}$O$_7$Na	—	—	—	—	110.0
H$_3$BO$_3$	—	—	—	—	30.0
C$_{10}$H$_{10}$N$_2$O$_8$	—	—	5.0	—	—
NH$_4$Cl	—	50.0	50.0	—	—
pH (NH$_4$OH)	8 to 9	8 to 9	8 to 10	10.0	9.0
Temp., °C	90	90	90	75	80

Fig. 2.16—Effect of EDTA concentration on plating rate on p- and n-type silicon (13).

strike-plate over zincated aluminum prior to plating with acid-type electroless nickel solutions. It was pointed out earlier that the pyrophosphate plating solution will initiate deposition at much lower temperatures than other electroless nickel solutions, either acidic or basic.

The fact that Bath 5 can be operated without ammonium hydroxide should encourage further development on the efforts of Booze, and lead to an increase in the use of alkaline plating solutions.

PLATING WITH SODIUM BOROHYDRIDE

The borohydride anion hydrolyzes almost spontaneously in neutral or acidic aqueous solutions:

Neutral
$$BH_4 + 4H_2O \rightarrow B(OH)_4 + 4H_2 \qquad [10]$$

Acidic
$$BH_4 + H^+ \rightarrow BH_3 + H_2 \qquad [11]$$

When nickel ions are present in the solution, the homogeneous reaction represented by the following equation occurs, precipitating nickel boride:

$$8BH_4 + 4Ni^{+2} + 18H_2O \rightarrow 2Ni_2B + 6H_3BO_3 + 25H_2 \qquad [12]$$
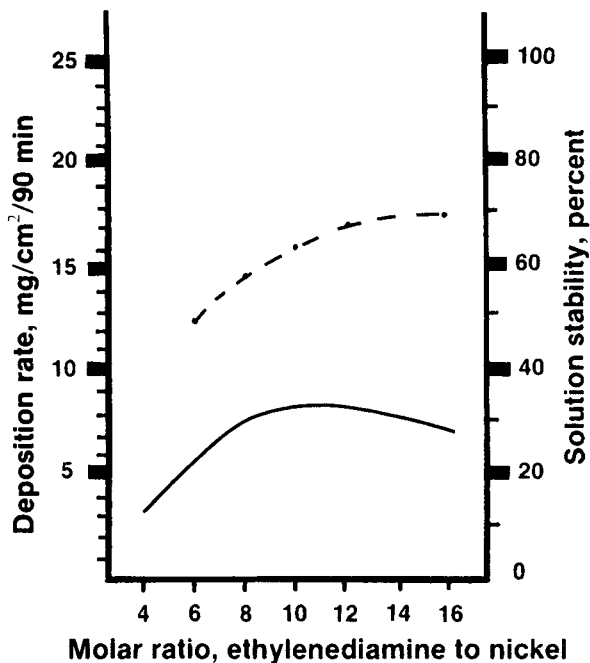
Fig. 2.17—Effect of the molar ratio of ethylenediamine to nickel on plating rate (solid line) and solution stability (dashed line). No stabilizer present (14).

The formation of the finely divided and extremely reactive Ni_2B is the basis for a method of waste-treating spent hypophosphite-reduced electroless nickel plating baths.

When the pH of an aqueous solution containing both nickel and borohydride ions is adjusted to values between 12 and 14, the formation of nickel boride is suppressed and the principal products of the reduction reaction are given by:

$$2Ni^{+2} + 2BH_4^- + 4H_2O \xrightarrow{n[OH^-]} 2Ni^0 + B + B(OH)_4 + 3H^+ + 9/2\ H_2 \qquad [13]$$
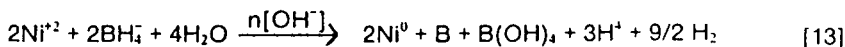
To prevent precipitation of basic nickel salts or nickel hydroxide, ligands that are effective in sequestering nickel ions within the operating pH range of 12 to 14 must be used. Ethylenediamine tetraacetic acid (EDTA), its analogues, and ethylenediamine, have been found to be the most effective complexing agents for use in these plating baths. On the basis of the results of experiments comparing several complexors, ethylenediamine is favored. The formation of completely coordinated nickel complexes with either zero or net positive charge imparts conditions that are favorable for the reduction process. Access to the nickel ions by water molecules or the borohydride ion is hindered by the
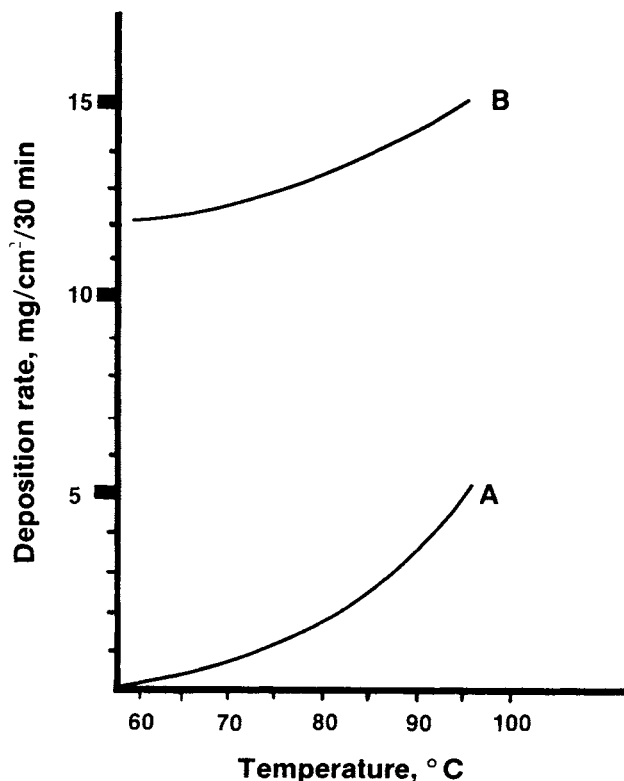
Fig. 2.18—Effect of temperature on plating rate. Curve A—no stabilizer in bath. Curve B—bath contains 100 ppm TlNO₃ (14).

structure of the complex. Under these conditions, the probability is quite small for the homogeneous reaction to occur in the bulk solution. Further, the zero or net positive charge on the complex favors the absorption of the complex at the negatively charged cathodic sites on the surface of the metal substrate catalyst. Figure 2.17 shows the influence of the molar ratio of ethylenediamine to nickel on the plating rate and solution stability (no stabilizer present).

As in all catalytic reactions, the temperature is the most important factor that influences the rate of the plating reaction. Borohydride-reduced plating solutions, which are operated at temperatures between 85 and 95° C, are no exceptions. The deposition rate will increase exponentially with an increase in the temperature of the plating bath, as illustrated in Fig. 2.18.

The plating rate is also affected by the concentration of borohydride. Figure 2.19 shows the relationships between BH_4^- concentration vs. plating rate, and BH_4^- concentration vs. bath stability. It is evident that as the concentration of BH_4^-
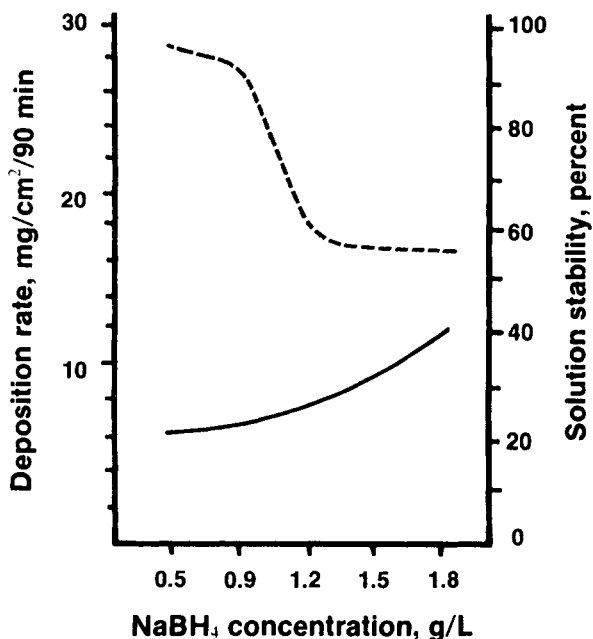
Fig. 2.19—Effect NaBH₄ concentration on plating rate (solid line) and solution stability (dashed line). No stabilizer present (14).

increases, the stability of the plating bath decreases. Lowering the operating temperature to accommodate high concentrations of borohydride ion enhances bath stability, but the lower temperature results in a sharp reduction in plating rate. It has been recommended that small quantities of the reducing media be added at very close intervals, along with additions of sodium or potassium hydroxide to maintain the concentration and activity of the borohydride ion, as well as the pH and the plating rate.

Studies on the effects of some stabilizers on the process indicates that bath stability can be sustained even at high BH₄ concentrations and high operating temperatures in the presence of certain stabilizing additives. The data obtained by Gorbunova, Ivanov and Moisseev (14) from their investigation of thallium nitrate, lead chloride, and 2-mercaptobenzothiazole (2-MBT) in these baths is very informative. The composition and operating conditions of several borohydride plating baths are given in Table 2.4. The effects of NaBH₄ concentration on plating rate and bath stability in the presence of stabilizers are given in Fig. 2.20. The results shown in Fig. 2.20 reveal a marked improvement in plating rate and bath stability when thallium is present, as compared to the data given in Fig. 2.19. The influence of the molar ratio of ethylenediamine to nickel

Table 2.4
Composition of Sodium Borohydride Electroless Nickel Plating Solutions

Concentration, g/L

	Bath					
Component	1	2	3	4	5	6
Ni^{+2}	7.4	7.4	2.5	7.6	5.0	6.0
Ethylenediamine (98%)	45	40	—	—	—	—
EDTA disodium salt	—	—	35	—	—	—
Triethylene-tetramine	—	—	—	87	—	—
Sodium potassium tartrate	—	—	—	—	65	—
Ammonium hydroxide (28%)	—	—	—	—	—	120 mL/L
Sodium hydroxide	40	40	40	40	40	—
Sodium borohydride	1.5	1.2	0.5	1.0	0.75	0.4
TlNO$_2$, mg/L	100	—	50	50	—	—
Pb(NO$_1$)$_2$, mg/L	—	40	—	—	10	—
2-MBT, mg/L	—	5	—	—	—	20
Temp., °C	95	95	95	97	92	60
pH	14	13	14	14	13	12

on plating rate and stability in the presence of stabilizers is presented in Fig. 2.21. The data of Fig. 2.17 is included in Fig. 2.21 to show by comparison the specific influence of thallium nitrate on the deposition rate. The use of TlNO$_3$ allows the process to be carried out at much lower temperatures, but with a considerably higher plating rate. The *overriding* aspect of the data in Figs. 2.19, 2.20 and 2.21 is that it draws attention to the fact that one stabilizer can so dramatically influence the process. It is not surprising that thallium codeposits into the alloy in significant quantities. Some nickel-boron alloys contain as much as 6 percent thallium.

The physical and chemical properties of the nickel-boron alloys, in particular those containing thallium, have generated considerable interest for their use in several applications. On the other hand, the baths used to produce these unique deposits present some operating limitations and disadvantages. The solution pH must be maintained in excess of 12 (preferably at 14) in order to suppress the homogeneous reaction expressed in Eq. 12. As a result of the high alkalinity of the plating bath, only substrate materials that are alkali-resistant can be plated in such solutions. Only substrates that are thermally stable at the operating temperature of borohydride-reduced baths can be coated in these plating
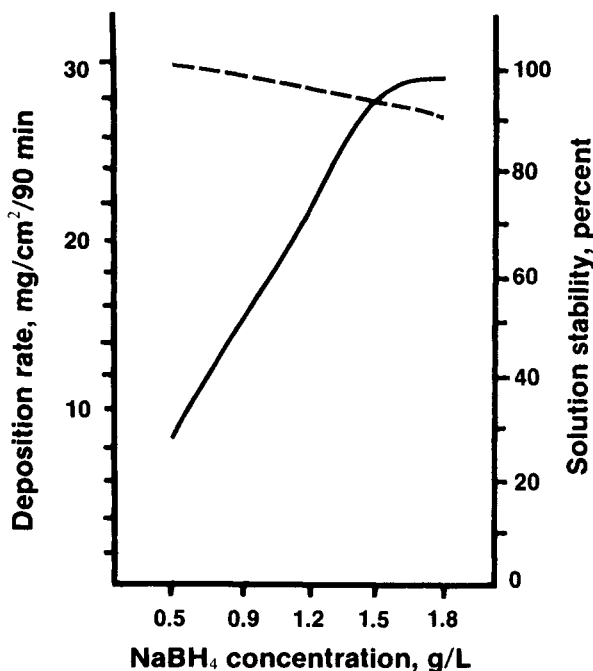
Fig. 2.20—Effect of NaBH₄ concentration on plating rate (solid line) and solution stability (dashed line). Bath contains 100 ppm TlNO₃ (14).

solutions. Finally, the use of thallium compounds is considerably more hazardous than, say, the use of lead salts and should be avoided whenever possible or whenever an alternative process is available. To circumvent the disadvantages and limitations proffered by BH₄⁻ plating baths and still retain most of the physical and chemical properties of the Ni-B coatings, the amine borane-reduced nickel baths are proposed as alternatives.

PLATING WITH AMINE BORANES

In general, the techniques of electroless nickel plating with hypophosphite as the reducing medium are applicable to plating with amine boranes (15); i.e., the substitution of water-soluble dimethylamine borane (DMAB) in a standard hypophosphite electroless nickel plating formulation will yield a workable plating bath. Typical acid and alkaline plating bath formulations are illustrated in Table 2.5.
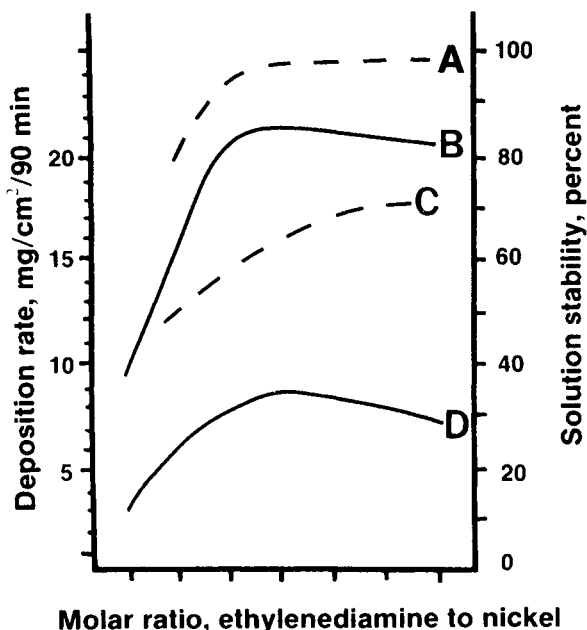
Fig. 2.21—Effect of molar ratio of ethylenediamine to nickel on plating rate (solid line) and solution stability (dashed line). Curves A and B contain 100 ppm TINO₃; curves C and D contain no stabilizer (14).

Table 2.5
Typical DMAB Electroless Nickel Plating Solutions

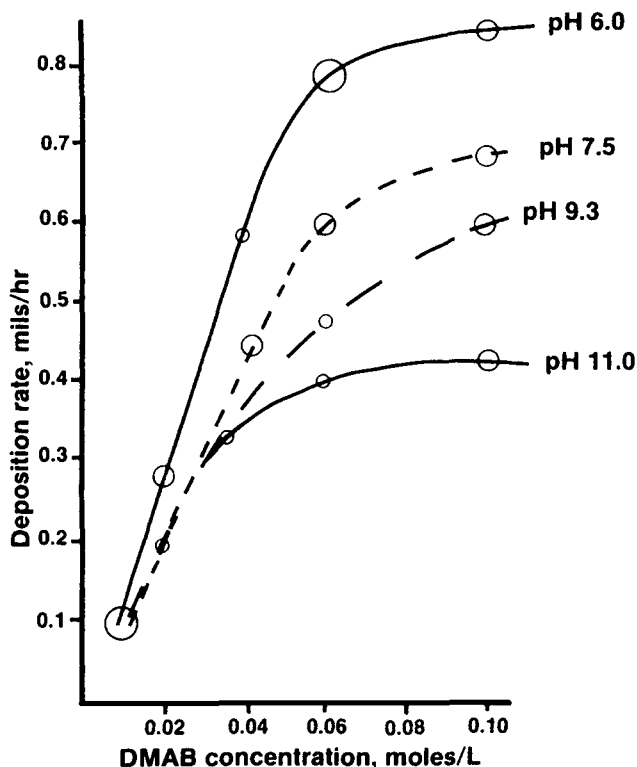| | Concentration, g/L | | | |
| | Bath | | | |
Component	1	2	3	4
Ni²⁺	6.0	11.0	7.5	7.5
Lactic acid (88%)	30.0	25.0	—	—
Citric acid	—	25.0	—	—
Sodium succinate	—	—	20	—
Sodium acetate	15.0	—	—	—
Sodium glycolate	—	—	40	—
Sodium pyrophosphate	—	—	—	60
DMAB	2.5	2.5	2.5	2.5
Thiourea, mg	1	—	2	—
Pb(NO₃)₂, mg	—	2	—	—
Thiodiglycolic acid, mg	—	70	—	50
pH (with NH₄OH)	6.1	6.3	7.0	9.0
Temp., °C	60	50	65	40

Fig. 2.22—Rate vs. DMAB concentration at various pH values. Bath operating temperature was 71° C (160° F) (15).

INFLUENCE OF VARIABLES ON PLATING RATE

Effect of DMAB Concentration

The concentration of the reducing medium is an important rate-determining factor, as shown in Fig. 2.22. The rate of deposition increases linearly with increasing DMAB concentration until the concentration is about 0.06M; above this point, increasing the DMAB concentration produces only small increases in the plating rate. The magnitude of the rate at the inflection point on the four curves in Fig. 2.22 is related to pH, since the lower the pH, the greater the magnitude of the rate at the inflection point.

Effect of Nickel Concentration

The rate of deposition is independent of nickel concentration when the nickel concentration is >0.06M (about 3.5 g/L). When the nickel concentration is less
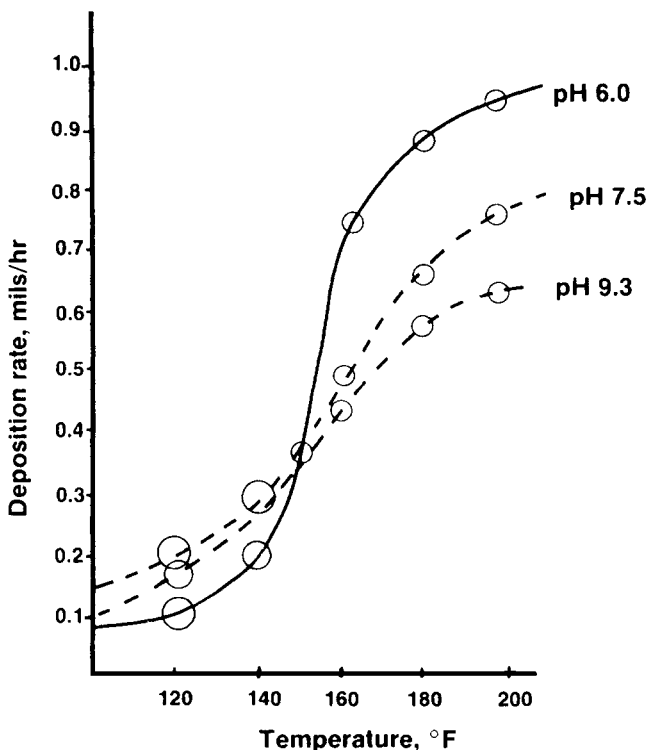
Fig. 2.23—Effect of temperature on deposition rate. DMAB concentration 0.06M (15).

than 0.06M, there is a strong dependence of rate on nickel concentration. However, plating baths are not operated at these low concentrations of Ni^{++} ions. Detailed studies on the effect of the molar ratio of nickel ions to DMAB are not available in the literature.

Effect of Temperature

DMAB-reduced nickel plating solutions show the same exponential dependence of plating rate on temperature that is typical of all catalytic nickel reduction reactions. Rate vs. temperature data are displayed as curves in Fig. 2.23. The exponential character of the rate vs. temperature relationship is maintained until the temperature exceeds some critical value that corresponds to the first inflection points on the curves. At this critical temperature, the rate of deposition becomes less dependent on temperature. The phenomena can be explained by the temperature dependence of DMAB hydrolysis reactions:
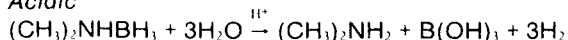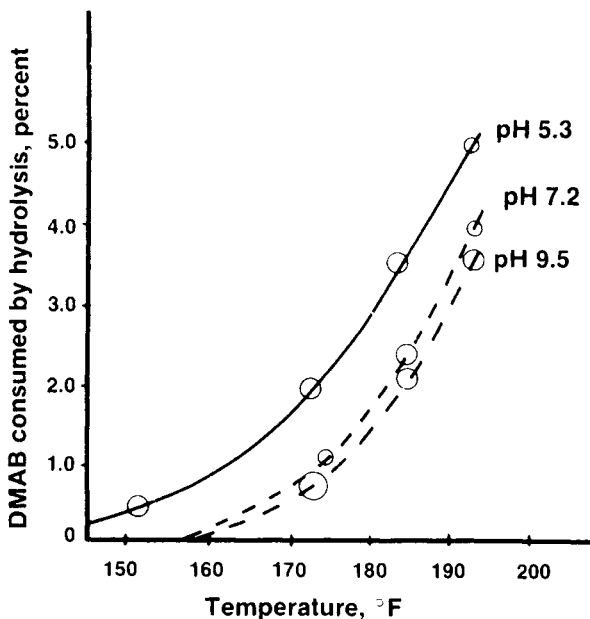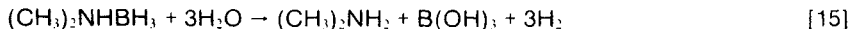
Acidic
$$(CH_3)_2NHBH_3 + 3H_2O \xrightarrow{H^+} (CH_3)_2NH_2 + B(OH)_3 + 3H_2 \qquad [14]$$

Fig. 2.24—Effect of temperature on hydrolysis of DMAB. Initial DMAB concentration 0.06M, operating time 90 minutes (15).

Neutral

$$(CH_3)_2NHBH_3 + 3H_2O \rightarrow (CH_3)_2NH_2 + B(OH)_3 + 3H_2 \qquad [15]$$

The effect of temperature on the hydrolysis of DMAB is shown in Fig. 2.24. When the temperature of the plating solution reaches a temperature that is equivalent to the first inflection point on the rate vs. temperature curve, the hydrolysis of DMAB becomes important; i.e., the hydrolysis of DMAB begins to compete with nickel reduction. At the second inflection point on each curve, hydrolysis of DMAB becomes the dominant reaction.

Effect of pH

The hydrolysis reaction expressed in Eq. 14 suggests that there is a practical lower limit for the operating pH of a DMAB plating solution. Figure 2.25 shows that above pH 5.0, the quantity of DMAB consumed by hydrolysis approaches a minimum almost asymptotically. The pH of a DMAB electroless plating bath, formulated to be operated in the acid pH range, should be maintained above pH 5.0 to minimize DMAB hydrolysis. The preferred operating pH range is the so-called "near-neutral" pH range (6.0 to 7.0).

At pH values below 5.0, the hydrolysis reaction is very temperature-dependent. Above pH 5.0, the hydrolysis of DMAB does not become a major consideration until the temperature exceeds 70° C. It has been shown experimentally that in the presence of reducible ions, such as Ni^{+2}, the hydrolysis of DMAB becomes

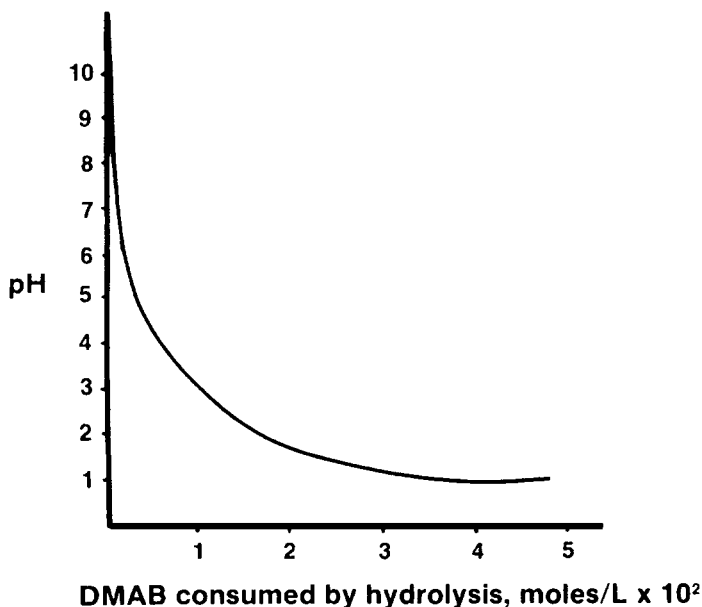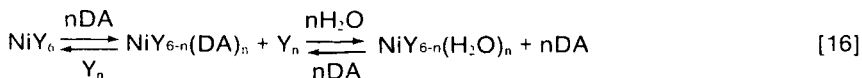**DMAB consumed by hydrolysis, moles/L x 10^2**

Fig. 2.25—Effect of pH on hydrolysis of DMAB. Temperature 65° C (150° F), operating time 1 hour (15).

more temperature-dependent, regardless of the pH.

The effect of pH on the plating rate in DMAB-reduced electroless nickel plating baths was found to be opposite to that observed in hypophosphite-reduced plating solutions. This result was alluded to in an earlier section. It was previously noted that the inflection point corresponding to the highest plating rate occurred on the curve (Fig. 2.22) representing data obtained from the plating bath with the lowest pH. Each successively lower plating rate (inflection point) occurred on a curve representing a successively higher pH value. In other words, the rate of deposition increases when the pH of the plating bath is decreased. The relationship of rate vs. pH is illustrated in Fig. 2.26.

There are probably several mechanisms that can be used to explain the effect pH has on plating rate in DMAB-nickel plating solutions. Two such reactions schemes are offered here:

• During the dissociation of the nickel complex to "free" solvated nickel ions and ligand molecules, a nickel-dimethylamine complex is formed as an intermediate; i.e., water molecules and dimethylamine molecules compete for nickel coordination sites that are available as the result of ligand groups leaving:
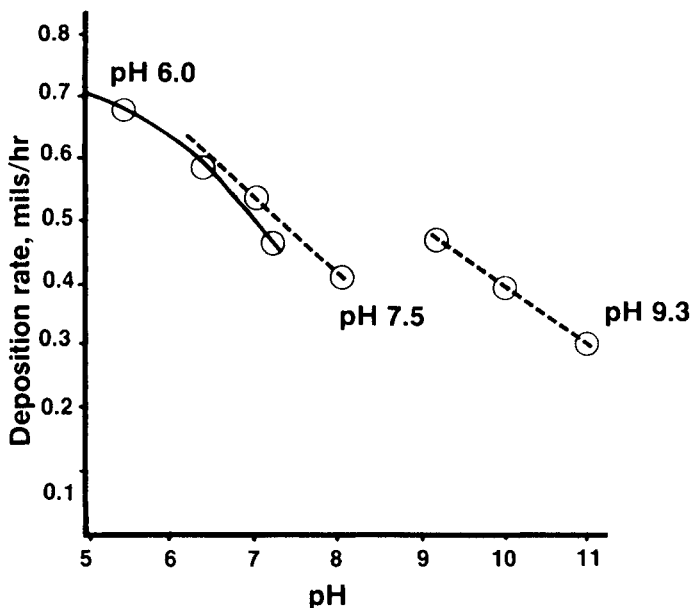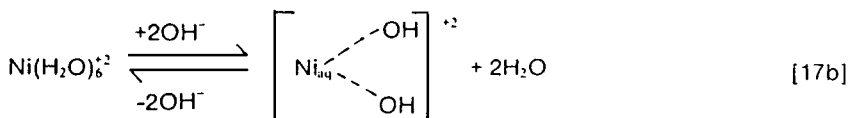
$$NiY_6 \underset{Y_n}{\overset{nDA}{\rightleftharpoons}} NiY_{6-n}(DA)_n + Y_n \underset{nDA}{\overset{nH_2O}{\rightleftharpoons}} NiY_{6-n}(H_2O)_n + nDA \qquad [16]$$

Fig. 2.26—Influence of pH on deposition rate. Temperature 71° C (160° F), DMAB concentration 0.06M (15).

where Y_6 represents the number of ligand atoms required to completely coordinate nickel, and DA denotes the dimethylamine molecule.

• After the dissociation of the nickel complex, dimethylamine (DA) molecules compete with hydroxyl ions (from dissociated water molecules) for the "free" solvated nickel ions:

$$Ni(H_2O)_6^{+2} \xrightleftharpoons[-2DA]{+2DA} \left[Ni_{aq} \begin{smallmatrix} -DA \\ \\ -DA \end{smallmatrix} \right]^{+2} + 2H_2O \qquad [17a]$$

$$Ni(H_2O)_6^{+2} \xrightleftharpoons[-2OH^-]{+2OH^-} \left[Ni_{aq} \begin{smallmatrix} -OH \\ \\ -OH \end{smallmatrix} \right]^{+2} + 2H_2O \qquad [17b]$$
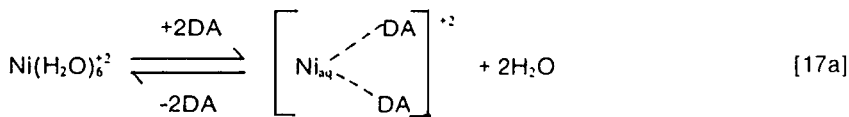
Either mechanism will affect the kinetics of the reduction reaction, and because intermediates are formed, the overall reaction rate will decrease. In a manner

analogous to the formation of the blue nickel-ammonium complex, as the pH of the solution is raised, the formation of the nickel-dimethylamine complex increases.

The practical operating limitations recommended for pH and temperature are unequivocal in their intent; at the present cost of DMAB, the consumption of the reducing media through nonproductive side-reactions can be hazardous to the bottom line.

Effects of Stabilizers

The compositions of Ni-B alloys produced with DMAB are 95 to 99.8 percent by weight nickel, the remainder is essentially boron. If these deposits are formed from solutions that do not contain stress reducers, their internal stress is extremely high and tensile in nature. Divalent sulfur compounds, such as thiourea and thiodiglycolic acid, are among the most effective stress reducing materials available. Not only do the organic divalent sulfur compounds reduce stress, they also act as stabilizers, preventing the homogeneous decomposition reaction from occurring. However, a sometimes-unwanted side effect occurs as a result of the use of the sulfur-containing materials: the boron content of the deposit is dramatically reduced. When the plating solution contains a divalent sulfur compound, its deposits usually contain less than 1 percent by weight boron. The high boron deposits (> 3 percent) produced with DMAB are, in general, so high in tensile stress that they cannot be used in the same applications as the borohydride-generated deposits. However, Mallory and Hohrn (18) were recently issued a patent detailing the deposition with DMAB of Ni-B alloys with low stress and whose boron content ranges from 3 to 8 percent by weight.

Effect of Reaction Products

Nickel plating with DMAB is accompanied by the formation of hydrogen ions, the evolution of hydrogen gas, and the formation of boric acid and dimethylamine. Boric acid and its salts, along with the amine, act as buffering agents in the plating bath and tend to decrease the effect of the H^+ ions. In certain plating baths, the pH actually increased slightly after using the baths for about one hour.

Electroless nickel plating baths utilizing DMAB are usually operated for a number of metal turnovers that exceeds, by a wide margin, the number of turnovers experienced with hypophosphite baths. One group of investigators (15) claim to have operated a DMAB-reduced plating bath for over 65 metal turnovers. One of the factors contributing to the exceptionally long operating life of these plating baths is that the reaction by-products are soluble, at least up to 65 metal turnovers.

Based on experimental data, it has been suggested that dimethylamine and boric acid form a polar, complexed amine borate. This proposition is a plausible explanation for two phenomena peculiar to these baths:

• The greatly enhanced solubility of boric acid in these aqueous plating solutions.

• The accumulation of reaction by-products does not cause a decrease in plating rate.

KINETICS OF ELECTROLESS NICKEL DEPOSITION

Empirical Rate Laws

The aim of chemical kinetics is to predict the rates of chemical reactions and to delineate the path or paths by which reactants proceed to products, i.e., the reaction mechanisms. Usually, reaction rates are determined under conditions of constant temperature, preferably at several temperatures. In a typical kinetic experiment, the data are records of concentrations of reactant and product species taken at various times and at constant temperatures.

Theoretical expressions for reaction rates as functions of concentrations of reactants and products are differential equations of the form:

$$\text{Rate} = \pm \frac{dC_i}{dt} = f(C_A, C_B, \ldots C_N) \qquad [18]$$

where t denotes the time, and C_i is the time-dependent concentration of the ith species (+ for product, - for reactant) that is followed to determine the reaction rate.

Generally, the concentrations of the reactants are known at the moment of mixing. The progress of the reaction is then studied as a function of time by any of a number of available techniques. Similar experiments may then be performed by using different initial concentrations of the reactants at different temperatures.

The rate of a reaction may be determined by measuring the rate of decrease in the concentration of a particular reactant, or, conversely, the rate of increase of by-products. In the case of electroless nickel plating, the rate of deposition is most commonly determined by measuring the rate of weight gain of the deposit in $mg/cm^2/hr$, or the rate of deposit thickness increase in $\mu m/hr$.

The next step is to express the resultant data from the rate measurements in some simple mathematical form; i.e., an expression (represented by the function f in Eq. 18) is needed for reactants and products. Usually, the relationship is expressed as:

$$\text{Rate} = \frac{dC_A}{dt} = k'C_A{}^\alpha C_B{}^\beta C_C{}^\gamma \ldots \qquad [19]$$

where K′ is a numerical proportionality constant called the *rate constant*; C_A, C_B, C_C, etc. refer to the concentrations of the chemical species A, B, C and so forth (reactants and products) present in the reacting system at time t; and α, β, γ, etc. are called the *reaction orders* of the respective chemical species.

In terms of this empirical rate equation, the particular reaction is said to α order with respect to A, β order with respect to B, etc.; and $\alpha + \beta + \gamma$ . . . is the overall reaction order. The individual time derivatives dC_A/dt, dC_B/dt, dC_C/dt are referred to as the rate of the reaction with respect to species A, B, and C, respectively.

The dominant variable in most reactions is the temperature. Many reactions occurring close to room temperature double their rates for each 10° C rise in temperature. Note that 100° C is considered close to room temperature. The expression for the rate constant K′ in Eq. 19 was given in Chapter 1 in the form:

$$K' = K_1 \exp \left(-\frac{E_a}{RT}\right) \qquad [20]$$

where K_1 is the frequency factor, E_a is the activation energy, T absolute temperature ° K, and R the universal gas constant. The empirical rate law, Eq. 19, can now be written as:

$$\text{Rate} = \frac{dC_A}{dt} = K_1[C_A]^\alpha[C_B]^\beta \ldots [C_N]^\gamma \exp \left(-\frac{E_a}{RT}\right) \qquad [21]$$

Empirical Rate Equation for Ni-P Deposition

An empirical rate equation for Ni-P plating, based on those variables that affect the plating rate, can be derived from Eqs. 1 and 21, and written as follows:

$$\text{Rate} = \frac{dNi^0}{dt} = K_1[H_2PO_2^-]^\alpha[Ni^{+2}]^\beta[L]^\delta [H^+]^\gamma[H_2PO_3^-]^\epsilon \exp \left(-\frac{E_a}{RT}\right) \qquad [22]$$

Putting Eq. 22 into logarithmic form yields:

$$\log \text{rate} = K_2 + \alpha\log[H_2PO_2^-] + \beta\log[Ni^{+2}] + \delta\log[L^{-n}] - \gamma pH + \epsilon\log[H_2PO_3^-] - \frac{E_a}{2.3\,RT} \qquad [23]$$

where $K_2 = \log K_1$, and log $(H^+) = -pH$.

From Eq. 23, the reaction orders $\alpha, \beta, \delta, \gamma, \epsilon$, and the activation energy E_a can be evaluated:

$$\left(\frac{\partial\log \text{rate}}{\partial\log[H_2PO_2^-]}\right)_q = \alpha \qquad [24a]$$

$$\left(\frac{\partial \log \text{ rate}}{\partial \log[Ni^{+2}]}\right)_u = \beta \qquad [24b]$$

$$\left(\frac{\partial \log \text{ rate}}{\partial \log[L^{-n}]}\right)_w = \delta \qquad [24c]$$

$$\left(\frac{\partial \log \text{ rate}}{\partial pH}\right)_x = -\gamma \qquad [24d]$$

$$\left(\frac{\partial \log \text{ rate}}{\partial \log[H_2PO_3]}\right)_y = \epsilon \qquad [24e]$$

$$\left(\frac{\partial \log \text{ rate}}{\partial(1/t)}\right)_z = -\frac{E_a}{2.3R} \qquad [24f]$$

The subscripts q, u, w, x, y, and z denote each set of variables held constant for the particular partial derivative.

The values of certain of the reaction orders can be ascertained, though not rigorously, from the discussions of the effect of the respective variables on the plating rate. For example, it was observed that the plating rate is independent of the nickel concentration in the concentration range where most hypophosphite-reduced baths are operated. Hence, in Eq. 24b $\beta = 0$, so that the term $[Ni^{+2}]$ in Eq. 22 reduces to $[Ni^{+2}] = 1$. Gutzeit (1) arrived at the same conclusion in a more elegant and rigorous treatment.

It was noted earlier that the buildup of phosphite in electroless nickel baths causes changes in the intrinsic stress of the Ni-P deposits, even at moderate concentrations. As the phosphite continues to accumulate in the bath, the relatively insoluble nickel phosphite will commence to precipitate. However, while these phosphite-induced phenomena are occurring, the soluble phosphite has little or no effect on the plating rate. In other words, the partial derivative, Eq. 24e, vanishes, i.e., $\epsilon = 0$ and $[H_2PO_3] = 1$. The remaining reaction orders, α, β, and γ can be determined by plotting log rate vs. log (concentration of species). The slopes of the straight lines obtained in these plots are the reaction orders.

Equation 22 can be simplified to:

$$\text{Rate} = K_1[L^{-n}]^\delta \frac{[H_2PO_2]^\alpha}{[H^+]^\gamma} \exp\left(-\frac{E_a}{RT}\right) \qquad [25]$$

Gutzeit (1) and later Lee (8) (see Eq. 3) have shown that the rate of nickel reduction is first order with respect to the hypophosphite ion concentration; i.e.,

$\alpha = 1$. Mallory and Lloyd (16) have evaluated γ for several electroless nickel solutions containing different complexing agents and found its value, in all but one case, to be $\gamma = -0.4$.

The activation energy, E_a, is computed from the slope of the straight lines obtained in log rate vs. $1/T$ plots, i.e.:

$$\left(\frac{\partial \log \text{rate}}{\partial 1/T}\right) = -\frac{E_a}{2.3R} = -\text{slope}$$

$$E_a = 2.3(1.98 \text{ cal deg}^{-1} \text{ mole}^{-1}) \text{ (slope)}$$

Table 2.6 gives the activation energies for several electroless nickel baths with different complexing agents.

In order to simplify computations, Eq. 25 can be put in the following form:

$$\text{Rate} = K_1 [L^{-n}]^\delta \frac{[H_2PO_2^-]}{[H^+]^{0.4}} \exp\left(-\frac{E_a}{RT}\right) \times \left[\exp\left(\frac{E_a}{360R}\right) \exp\left(-\frac{E_a}{360R}\right)\right]$$

since,

$$\left[\exp\left(\frac{E_a}{360R}\right) \exp\left(-\frac{E_a}{360R}\right)\right] = 1$$

so that after rearranging:

$$\text{Rate} = K_2 \frac{[H_2PO_2^-]}{[H^+]^{0.4}} \exp E \left(\frac{T-360}{T}\right) \qquad [26]$$

where:

$$K_2 = K_1 [L^{-n}]^\delta \exp\left(-\frac{E_a}{360R}\right)$$

and:

$$E = \frac{E_a}{360R}$$

The rate constant K_2 can be computed directly from Eq. 26. The straight line plots for the reaction orders are extrapolated to the point where the concentrations of the appropriate components are unity. At this point, the respective deposition rates can be read from the ordinate. The following identities are derived from Eq. 26, when T = 87° C (360° K):

$$\text{Rate} = K_2 \frac{1}{[H^+]^{0.4}} \quad [H_2PO_2^-] = 1 \qquad [27]$$

$$\text{Rate} = K_2 [H_2PO_2^-] [H^1] = 1 \qquad [28]$$

The rate constant K_2 is computed by solving Eqs. 27 and 28.

The specific rate constant, K_1, can be determined, if necessary, by solving the expression:

$$K_1 = \frac{K_2}{[L^{-n}]^\delta} \quad \exp\left(\frac{E_a}{360R}\right)$$

It has been shown (17) that the agreement between observed plating rates and those computed using Eq. 26 are in excellent agreement. The deviation from perfect correlation was found to be less than 5 percent.

Using arguments similar to those above, an empirical rate law for DMAB-reduced nickel baths can be derived. Since the development will not be given here, the interested reader is referred to Ref. 18.

Table 2.6
Activation Energies for Ni-P Baths
Containing Different Ligands

Ligand	Chelate ring size	Coordinating atoms	Activation energy, Kcal/g-mde
Hydroxyacetate	5	(O,O)	23
Lactate	5	(O,O)	16
Aminoacetate	5	(O,N)	17
β-alanine	6	(O,N)	13
Malate	5,6	(O,O,O)	17
Citrate	5,6	(O,O,O)	16

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