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Electroless Nickel Plating from Acid-acetate Baths Containing Hypophosphite as a Reducing Agent

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The properties of acid-acetate baths containing hypophosphite as a reducing agent were studied in an attempt to obtain an electroless nickel deposit; further, the protective property of such deposits with phosphorus contents of 4 to 13% was investigated. The hypophosphite utilization efficiency for the deposition of electroless nickel was found to be 0.33; the deposition rate indicates a first-order dependence on hypophosphite, but it is independent of nickel concentration, within the limits specified in the range of suitable conditions. The phosphorus content of the deposits increases with a decrease in the pH value of the bath and with an increase in the initial concentration of hypophosphite, but it is independent of that of nickel. An electoless nickel with a high phosphorus content affords more protection against metallic bases.

Since the deposition of nickel containing a low percentage of phosphorus on a catalytic surface from an aqueous solution by means of the reduction of nickel salts with hypophospite was first described by Brenner and Riddell[1] in 1946, the deposit has been called electroless nickel to distinguish it from electroplated nickel. Although much research has been done on the subject, most of the work has been concerned with practical applications of the process[2-5] or with the structure[6-8] and the mechanical properties[7,9] of the deposit. It has also been

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[1] A. Brenner and G. E. Riddell, *J. Res. Natl. Bur. Std.*, **37**, 31 (1946); **39**, 385 (1947).

[2] A. Brenner, *Metal Finishing*, **52** (11), 68; (12), 61 (1954).

[3] Am. Soc. Testing Materials, Spec. Tech. Publ., No. 265, "Symposium on Electroless Nickel Plating," Philadelphia (1959).

[4] G. Gutzeit, *Plating*, **46**, 1158, 1275, 1379 (1959); **47**, 63 (1960).

[5] K. M. Gorbunova and A. A. Nikoforova, "Physicochemical Principles of Nickel Plating (Translated from Russian by A. J. Aladjem)," Israel Program for Scientific Translations, Ltd., Jerusalem (1963).

[6] A. M. Goldenstein, W. Rostoker, W. Schossberger and G. Gutzeit, *J. Electrochem. Soc.*, **104**, 104 (1957).

[7] A. H. Graham, R. W. Lindsay and H. J. Read, *ibid.*, **109**, 1200 (1962).

[8] S. Urai and Y. Tanabe, *Kinzoku Hyōmen Gijutsu* (*J. Metal Finishing Soc. Japan*), **18**, 435 (1967).

[9] J. P. Randin and E. H. Hintermann, *Plating*, **54**, 523 (1967).

established that the electroless nickel affords far more protection to metallic bases than does the electroplated nickel.[3,5,10] However, little attention has been paid to the phosphorus content as an important variable with regard to the protective properties of electroless nickel, except for two reports of Ishibashi, Takano and Shimizu,[11,12] and they only intimated that it should not be ignored.

The present paper will be concerned with our fundamental studies of the electroless nickel plating from an acid-acetate bath; the reaction balance, the deposition rate, and the phosphorus content of the deposit will be described, and the life of the bath will be considered. In addition, the protective properties of the deposit will be discussed as a function of its phosphorus content.

Experimental

Reagents. All the chemicals used were of the reagent grade. Sodium hypophosphite monohydrate, nickel chloride hexahydrate and sodium acetate trihydrate were used to prepare the plating baths. The pH of the bath was adjusted to the desired value by adding hydrochloric acid using a Horiba M-3 pH Meter with a glass electrode.

Plating Procedure. The equipment used in the plating tests was simple. A plating solution buffered with 0.3M acetate was placed in a covered cylindrical glass vessel; the bath temperature was kept constant within ±0.3°C of the desired temperature by means of a water thermostat, the bath being left unagitated. A specimen, a brass or mild steel plate, which had previously been cleaned with trichloroethylene or electrocleaned, was immersed in the bath for the desired time. The deposition rate was obtained by weighing the dry specimens before and after the plating test. At each run, the nickel concentration was determined by the EDTA-titration method[13] and the phosphite and hypophosphite concentrations were determined by cerimetric procedures.[14,15]

The Determination of Phosphorus in the Deposits. The deposit on a bakelite coupon previousely sensitized with a palladium chloride solution[2] served to determine its phosphorus content. At the completion of a plating run, a calculated amount of the deposit was stripped from the base and dissolved in a small volume of hot nitric acid. The amount of phosphorus in the resulting solution was determined by spectrophotometric measurements[16] of the phosphomolybdic acid extracted with a mixed solvent composed of two parts of isobutyl alcohol and three parts of chloroform.

Estimation of the Protective Value of the Deposits. *Polarization Measurement.* Polarization curves in 1N sulfuric acid and 0.5N hydrochloric acid solutions were obtained by the galvanostatic method. Electroless nickel about 15 μ thick deposited on a brass plate, with a working area of 1 cm², was used as the working electrode. The potentials were measured by the direct method with a Luggin capillary using a saturated calomel electrode (SCE) as the reference electrode. A carbon plate was employed as the auxiliary electrode. All the measurements were made in 500-*ml* portions of the dilute acid solutions saturated with air, while the temperature was maintained at 30±0.1°C by means of a water thermostat.

Porosity and Salt-spray Resistance. Electroless nickel for both the porosity measurements and the salt-spray test was deposited on a mild steel plate. The porosity of the deposits up to 20 μ thick was evaluated by means of a ferroxyl test. A filter paper saturated with a solution containing 10 g of potassium ferricyanide, 10 g of potassium ferrocyanide, 60 g of sodium chloride, and 5 *ml* of 28% ammonia water in 1*l* was pressed to the surface of the deposit for 5 min, and the blue spots which appeared on the filter paper were counted. The salt-spray test was performed in an Itabashi Salt-spray Chamber with a 5% sodium chloride solution at room temperature (25—30°C). Cycles of spraying for 8 hr and stopping for 16 hr were periodically repeated for five days, and then the rust spots on the surface were counted. The results of these tests are given as the average for the five samples.

Results and Discussion

Reaction Balance. According to Brenner,[1] the significant overall reaction for the deposition of electroless nickel can be writen as:

$$H_2PO_2^- + Ni^{2+} + H_2O \longrightarrow H_2PO_3^- + Ni + 2H^+ \qquad (1)$$

Concurrently, more hypophosphite anions are oxidized to phosphite anions with the evolution of gaseous hydrogen according to the reaction:

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + H_2 \qquad (2)$$

Moreover, some of the hypophosphite anions supply the elemental phosphorus which alloys with the metallic nickel.

Table 1 lists the reaction balances for the deposition of electroless nickel from an acetate bath of pH 4.0. Attention is invited to Table 1, wherein the hypophosphite utilization efficiency, expressed as the molar ratio of the nickel deposited to the hypophosphite utilized, is always close to 0.33. Therefore, in order to examine whether this efficiency is independent of the plating conditions, a few tests were performed; the results are shown in Figs. 1 and 2. The discordance of the efficiencies in Figs. 1 and 2 must be considered as an inevitable consequence of the precision of the analytical method employed. It seems, therefore, as has been described by Gutzeit,[4] that the hypophosphite utili-

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[10] C. H. deMinjer and A. Brenner, *Plating* **44**, 1297 (1957).

[11] S. Ishibashi, O. Takano and T. Shimizu, "The 10th Symposium on Corrosion and Prevention," Takarazuka (1963), p. 214.

[12] *Idem*, *Kinzoku Hyomen Gijutsu* (*J. Metal Finishing Soc. Japan*), **16**, 236 (1965).

[13] K. Ueno, "Kireto-Tekiteiho (Chelatometric Titration)," Nankodo, Tokyo (1961), p. 287.

[14] D. N. Bernhart, *Anal. Chem.*, **26**, 1798 (1954).

[15] K. Ogawa, This Bulletin, to be published.

TABLE 1. REACTION BALANCE FOR ELECTROLESS NICKEL DEPOSITION*

Plating time min	%P of deposit	P deposited mmol	$H_2PO_2^-$ utilized mmol	$H_2PO_3^-$ formed moml	Ni deposited mmol	Molar ratio $\frac{\text{Ni deposited}}{H_2PO_2^- \text{ utilized}}$
30	9.8	0.49	7.1	6.4	2.37	0.33
60	9.4	0.88	16.5	14.4	4.82	0.29
90	10.5	1.37	20.4	20.0	6.15	0.33
120	9.0	1.88	30.6	28.6	10.00	0.32

* In each run, electroless nickel was deposited on a 25 cm² bakelite coupon from about a 350 m*l* bath containing 44.2 mmol of nickel, 49.3 mmol of hypophosphite and 12 mmol of acetate. All the initial pH values were 4.0 and the temperatures, 90°C.

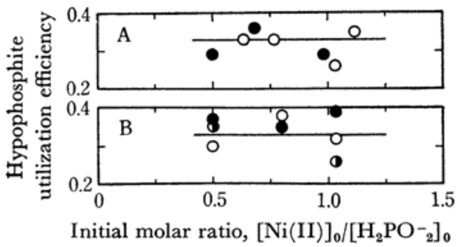

Fig. 1. Hypophosphite utilization efficiency for 30 min in electroless nickel deposition on a 25 cm² brass plate from a 400 m*l* bath at 90°C. The initial concentrations of baths are: (A) $[Ni(II)]_0=0.10$ M but $[H_2PO_2^-]_0$=variable, and (B) $[H_2PO_2^-]_0=0.10$ M but $[Ni(II)]_0$=variable.

○ pH 4.0; ● pH 4.5; ◑ pH 5.0

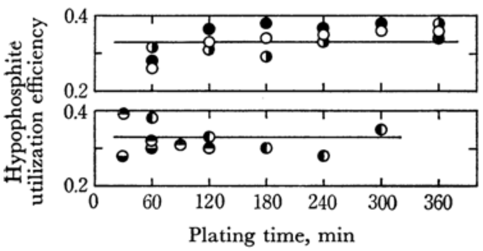

Fig. 2. Hypophosphite utilization efficiency in electroless nickel deposition on a 22.5 cm² mild steel plate from a 500 m*l* bath. The initial concentrations of baths are: $[Ni(II)]_0=0.10$ M, and $[H_2PO_2^-]_0=0.10$ M for pH 4.0, or 0.15 M for pH 4.5.

○ 80°C, ● 85°C, ◑ 90°C, ◐ 95°C at pH 4.0; ◒ 90°C at pH 4.5; ◓ 90°C at pH 5.0

zation efficiency is 0.33 independently of the plating conditions, within the range examined at least. This suggests that three moles of hypophosphite are consumed in order to deposit every mole of nickel, and that thus two moles of hydrogen are generated when one mole of nickel is deposited. However, we do not yet have an good explanation of why such a phenomenon occurs.

Deposition Rate. The deposition rates of electroless nickel from the baths of pH 4.0 and 4.5 are shown as the fucntions of nickel and of hypophosphite concentrations in Fig. 3. The deposition rate seems to be proportional to the hypophosphite concentration up to 0.1 M at pH 4.0 or up to 0.15 M at pH 4.5, but indepenent of the nickel concentration in the range of 0.05—0.2 M in the pH range of 4—4.5.

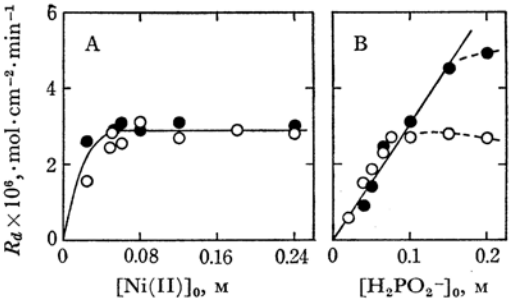

Fig. 3. The deposition rate of electroless nickel on a 25 cm² brass plate from a 400 m*l* bath at 90°C as the functions of nickel and of hypophosphite concentrations. The initial concentrations are:
(A) $[H_2PO_2^-]_0=0.10$ M but $[Ni(II)]_0$=variable, and
(B) $[Ni(II)]_0=0.12$ M but $[H_2PO_2^-]_0$=variable.
○ pH 4.0; ● pH 4.5

This can be verified by making the assumption, as has been described by Gutzeit[4] or by Ishibashi,[17] that the reaction undergoes an intermediate step as follows: the hypophosphite anion is converted into an active intermediate species, A*, which is then adsorbed or loosely bonded to the catalytic surface:[18]

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[16] M. Ura, *Bunseki Kagaku* (*Japan Analyst*), **7**, 420 (1958).

[17] S. Ishibashi *Kinzoku Hyomen Gijutsu* (*J. Metal Finishing Soc. Japan*), **12** 447 (1961).

[18] Gutzeit[4] postulated that an active intermediate species is atomic hydrogen produced by the catalytic dehydrogenation of hypophosphite anion to metaphosphite anion: $H_2PO_2^-\rightarrow PO_2^-+2H$; $PO_2^-+H_2O\rightarrow HPO_3^{2-}+H^+$. On the other hand, Ishibashi[17] departed from Gutzeit's concept and instead proposed that the hypophosphite anion converts from "normal type" into "active type" (probably adsorbed on the catalytic surface). A choice between the above explanations was not made.

$$H_2PO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^{\neq} \qquad (3)$$

thus taking part in the following simultaneous reactions:[19]

$$A^{\neq} + \mathrm{Ni(II)} \xrightarrow{k_2} \mathrm{Ni} \qquad (4)$$

$$A^{\neq} \xrightarrow{k_3} H_2 \qquad (5)$$

where Ni(II) represents bivalent nickel whether or not it forms complexes with acetate, and where the *k*'s denote the rate constants of the reactions. Reaction (5) can be considered, on the basis of the aforementioned reaction balance, to take place twice as fast as Reaction (4). Therefore, by making a steady-state treatment, the deposition rate can be derived as:

$$R_d = \frac{k_1{}^0 k_2 [H_2PO_2^-][\mathrm{Ni(II)}]}{k_{-1} + 3k_2[\mathrm{Ni(II)}]} \qquad (6)$$

where R_d represents the deposition rate in mol·min^{-1}·cm^{-2}, where $k_1{}^0$ is $k_1 V/A$, where V is the bath volume in *l*, and where A is the deposited area in cm^2. By transposing Eq. (6), the following equation is derived:

$$\frac{[H_2PO_2^-]}{R_d} = \frac{3}{k_1{}^0} + \frac{k_{-1}}{k_1{}^0 k_2} \frac{1}{[\mathrm{Ni(II)}]} \qquad (7)$$

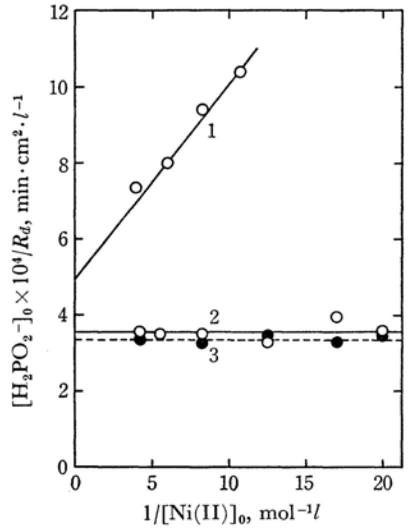

Fig. 4. Plots of $[H_2PO_2^-]_0/R_d$ *vs.* $1/[\mathrm{Ni(II)}]_0$. The pH values of baths are: (1) 3.5, (2) 4.0, and (3) 4.5. Other plating conditions are the same as in Fig. 3(A).

The experimental data plotted according to Eq. (7) are shown in Fig. 4. Although the expected linearity is apparent, there are some discrepancies between the results at different pH values. A plot of pH 3.5 produces a slopig line, for instance, but the values of $[H_2PO_2^-]/R_d$ at pH 4.0 and 4.5 are almost independent of $1/[\mathrm{Ni(II)}]$ in the concentration range examined. This suggests that the assumed active intermediate species, $A^{\neq}$, may react with Ni(II) at a much faster rate than it returns to hypophosphite anion in the pH range of 4—4.5. If this suggestion can be accepted as true, Eq. (6) takes a simpler form:

$$R_d = \frac{1}{3} k_1{}^0 [H_2PO_2^-] \qquad (8)$$

demonstrating that the deposition rate of electroless nickel is proportional only to the hypophosphite concentration.

The Change in the Hypophosphite Concentration of a Bath. From the aforementioned reaction balance, the hypophosphite concentration of a bath after *t* min can be expressed as:

$$[H_2PO_2^-]_t = [H_2PO_2^-]_0 - 3A\,x_{\mathrm{Ni}}/V \qquad (9)$$

where x_{Ni} is the molar amounts of nickel deposited on the unit area and where the subscripts 0 and *t* indicate the concentrations at the initiation of the reaction and after *t* min respectively. By substituting Eq. (9) into Eq. (8) and by integrating, the following equation can be derived:

$$\log [H_2PO_2^-]_t = \log [H_2PO_2^-]_0 - \frac{k_1{}^0}{2.3} \frac{A}{V} \qquad (10)$$

The examples of plots according to Eq. (10) shown in Fig. 5 demonstrate their consistency with the

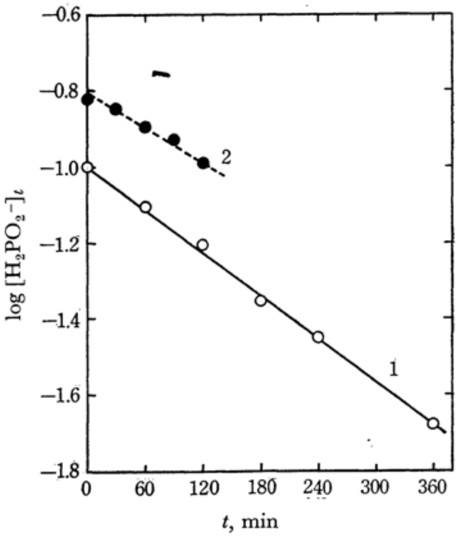

Fig. 5. Plots of $\log [H_2PO_2^-]_t$ *vs.* *t* at 90°C. The pH values of baths are: (1) 4.0 and (2) 4.5. Other plating conditions are the same as in Fig. 2.

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[19] According to West, both Reactions (4) and (5) may occur by electrochemical means: $\mathrm{Ni(II)} + 2e \rightarrow \mathrm{Ni}$ and $2H^+ + 2e \rightarrow H_2$ for cathode reaction, $H \rightarrow H^+ + e$ for anode reaction: J. M. West, "Denseki to Fushoku (Electrodeposition and Corrosion Processes) (Translated from English by T. Ishikawa and T. Shibata)," Sangyo Tosho Publ. Co., Ltd. (1968) p. 63. A similar local cell type model for electroless nickel deposition was also suggested by Ishibashi.[17] The present author will also support West's concept.

TABLE 2. RATE CONSTANTS AT 90°C

pH	k_1^0 $\text{min}^{-1}\cdot\text{cm}^{-2}\cdot l$ From Fig. 4	k_1^0 $\text{min}^{-1}\cdot\text{cm}^{-2}\cdot l$ From Fig. 5	k_{-1}/k_2 From Fig. 4
3.5	(6.1×10^{-5})	—	(3.2×10^{-1})
4.0	8.4×10^{-5}	9.6×10^{-5}	Negligible
4.5	8.9×10^{-5}	8.5×10^{-5}	Negligible

TABLE 3. RATE CONSTANTS, k_1^0, FOR pH 4.0 AT DIFFERENT TEMPERATURES

Temp. °C	k_1^0 $\text{min}^{-1}\cdot\text{cm}^{-2}\cdot l$
80	5.0×10^{-5}
85	6.8×10^{-5}
90	9.6×10^{-5}
95	12.2×10^{-5}

first-order mechanism. The values of k_1^0 calculated from Fig. 5 are tabulated in Table 2, together with those obtained from Fig. 4. The two values are in reasonable agreement. Table 3 gives the values of k_1^0 obtained at different temperatures from plots according to Eq. (10). A liner relation was found between the logarithmic values of k_1^0 and the reciprocal of the absolute temperature, in which the apparent activation energy was estimated to be 15 kcal/mol.

The Life of the Bath. The only stable anion produced during the reaction is phosphite, which forms a greenish nickel phosphite precipitate.[4,10,20] This precipitate is undesirable, because it initiates the nucleation of nickel and causes the spontaneous decomposition of the bath and the eventual roughness of the deposit.

As has been indicated in connection with the reaction balance, the phosphite concentration accumulated in the bath is nearly equal to the decrease in the hypophosphite concentration, while the latter is approximately three times the decrease in the nickel concentration. Therefore, no precipitation occurs under the following conditions:

$$3x_{\text{Ni}}\frac{A}{V}\left([\text{Ni(II)}]_0 - x_{\text{Ni}}\frac{A}{V}\right) < L\left(1+\frac{[\text{H}^+]}{K_2}+\frac{[\text{H}^+]^2}{K_1K_2}\right) = L_{\text{app}} \qquad (11)$$

where L and L_{app} are the absolute and the apparent solubility products of nickel phosphite, and K_1 and K_2, the first and the second acid dissociation constants of phosphorous acid; these values, determined at 90°C, are given in Table 4. The value of the left-hand of Eq. (11) cannot be above

TABLE 4. THE ACID DISSOCIATION CONSTANTS OF PHOSPHOROUS ACID AND THE SOLUBILITY PRODUCT OF NICKEL PHOSPHITE AT 90°C

H_3PO_3 *1 $\text{p}K_1$	H_3PO_3 *1 $\text{p}K_2$	NiHPO_3 *2 L $\text{mol}^2\cdot l^{-2}$
2.21	6.77	2.3×10^{-5}

*1 The values of $\text{p}K_1$ and $\text{p}K_2$ were determined by the pH titration method.

*2 The precipitation of NiHPO_3 was investigated in solutions containing 0.1 M of hypophosphite, 0.1 M of nickel and 0.3 M of acetate for various pH's and phosphite concentrations. The value of L was determined by observing whether a turbidity developed for 60 min at 90°C.

$3[\text{Ni(II)}]_0/4$. Therefore, if a set of conditions is selected where $[\text{Ni(II)}]_0 < 4L_{\text{app}}/3$, no precipitation is expected through the plating as long as no hypophosphite or nikcel salt is supplied. Calculations indicate that this limit is: $[\text{Ni(II)}]_0 < 0.13\text{M}$ for pH 4.0, $<0.06\text{M}$ for pH 4.5, and $<0.03\text{M}$ for pH 5.0.

On the other hand, when the bath compositions exceed the above limit, the life can be estimated by the following equations derived from Eqs. (10) and (11):

$$life = \frac{V}{A}\,\frac{2.3}{k_1^0}\log\frac{[\text{H}_2\text{PO}_2^-]_0}{[\text{H}_2\text{PO}_2^-]_0 - 3\dfrac{A}{V}x_{\text{Ni}}} \qquad 12)$$

$$\frac{A}{V}x_{\text{Ni}} = \frac{3[\text{Ni(II)}]_0 - \sqrt{9[\text{Ni(II)}]_0^2 - 12L_{\text{app}}}}{6}$$

Some examples of the estimated life are shown in Fig. 6.

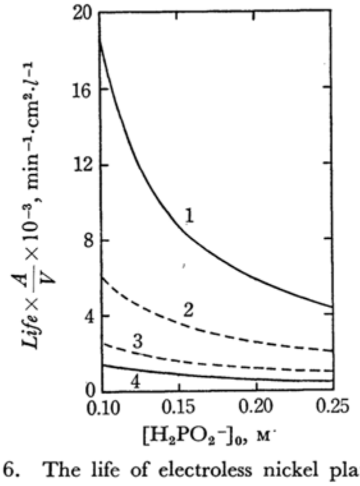

Fig. 6. The life of electroless nickel plating baths buffered with 0.3 M acetate at 90°C. (1) pH 4.0, $[\text{Ni(II)}]_0$=0.2M; (2) pH 4.5, $[\text{Ni(II)}]_0$=0.1 M; (3) pH 4.5, $[\text{Ni(II)}]_0$=0.2 M; (4) pH 5.0, $[\text{Ni(II)}]_0$= 0.1 M.

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[20] S. Ishibashi, S. Orii and N. Tezuka, *Kinzoku Hyomen Gijutsu* (*J. Metal Finishing Soc. Japan*), **12**, 94 (1961).

The Phosphorus Content of the Deposit.

As a result of the change in the bath compositions through the plating, it is expected that a phosphorus gradient exists across a deposit. However, as may be seen in Table 1, the phosphorus content of the deposit is almost constant, independent of the plating time, up to 120 min, in spite of the fact that the bath compositions change. Therefore, a phosphorus gradient across a deposit may be not very steep.

The phosphorus content for the deposits obtained at a constant plating time of 60 min was also investigated as a function of the bath compositions. The results in Figs. 7 and 8 reveal that the phosphorus content of a deposit increases as the pH rises and with an increase in the initial concentration of hypophosphite, but that it is independent of the concentration of nickel.

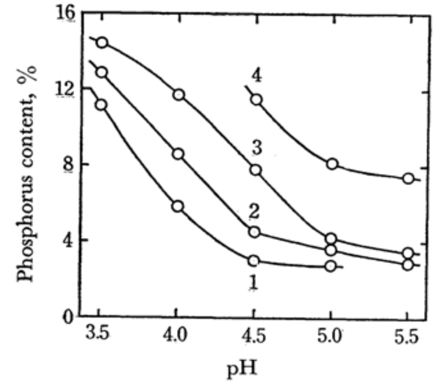

Fig. 7. The phosphorus content of electroless nickel deposit as a function of the initial pH value of bath. The initial concentrations of baths are: $[\mathrm{Ni(II)}]_0 = 0.09$ M, and $[\mathrm{H_2PO_2^-}]_0 =$ (1) 0.05 M, (2) 0.10 M, (3) 0.15 M, and (4) 0.20 M.

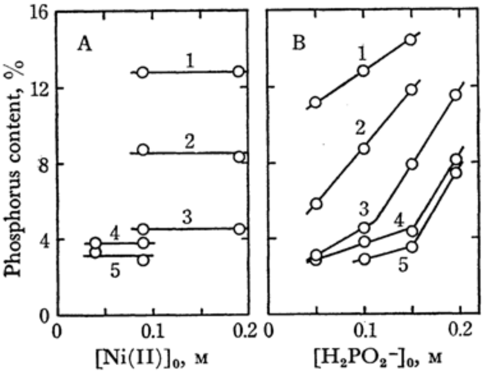

Fig. 8. The phosphorus content of electroless nickel deposit as the functions of bath compositions. The initial concentrations of baths are: (A) $[\mathrm{H_2PO_2^-}]_0 = 0.10$ M but $[\mathrm{Ni(II)}]_0 =$ variable, and (B) $[\mathrm{Ni(II)}]_0 = 0.09$ M but $[\mathrm{H_2PO_2^-}]_0 =$ variable. The initial pH values are: (1) 3.5, (2) 4.0, (3) 4.5, (4) 5.0, (5) 5.5.

The Protective Value of the Deposit. Examples of the polarization curves of the deposits in a 1 N sulfuric acid solution are shown in Fig. 9. Similar results were obtained in a 0.5 N hydrochloric acid solution. In all cases, both anodic and cathodic polarization curves exhibited Tafel-type behavior, and an increase in the phosphorus content moves the corrosion potential to a more positve value and reduces the corrosion currents. The corrosion rates calculated from the corrosion currents are given in Fig. 10, together with the minimum thickness free of pores and the salt-spray

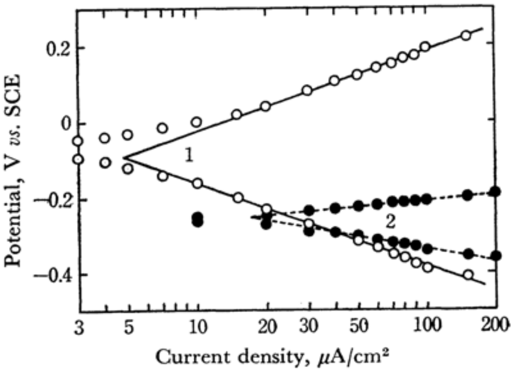

Fig. 9. The polarization curves of electroless nickel deposits in a 1 N sulfuric acid solution. The deposits contain (1) 8.7 and (2) 3.6% phosphorus.

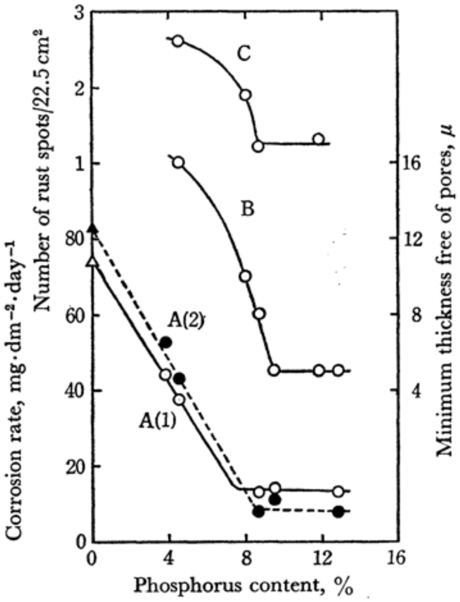

Fig. 10. The protective values of electroless nickel as the function of its phosphorus content.

(A) Corrosion rate in (1) 1 N H_2SO_4 and (2) 0.5 N HCl
(B) Minimum thickness free of pores
(C) Number of rust spots by salt spray
△, ▲ Pure nickel foil

resistance as functions of the phosphorus content. Generally, an electroless nickel with a high phosphorus content affords low porosity; it also exhibits a high resistance to dilute acid media and to salt-spray. These results are in qualitative agreement with some observations of deMinjer and Brenner,[10) who reported a rise in the resistance of similar electroplated alloys to salt-spray and outdoor exprosure with an increase in the phosphorus content. In Fig. 10 it is also shown that all of the curves change in the vicinity of 9% phosphorus; the corrosion rate by dilute acid solutions, the minimum thickness free of pores, and the number of rust spots caused by salt-spray, all decrease with a rise in the phosphorus content up to about 9%, while they remain practically as constant as the phosphorus content when it increases above 9%. This behavior seems to be connected with the fact that the as-deposited electroless nickel deviates gradually from a face-centered cubic lattice condition with an increase in the phosphorus content and is converted into an amorphous state above 7.4% of phosphorus.8)

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