The Role of Electroless Plating Bath Constituents in the Catalytic Oxidation of the Hypophosphite Ion

By N.K. Dirjal, K.A. Holbrook & P.B. Wells

Oxidation of the hypophosphite ion by water at the surface of a standard reference nickel catalyst (EuroNi-1) has been studied at 80 °C and pH 4. The effects of a number of bath additives, commonly used in electroless plating bath formulations, have been studied by measurements of the hydrogen evolved and the phosphorus deposited on the catalyst. This reaction occurs concurrently with the plating reaction in electroless plating baths, using hypophosphite as reducing agent. The results of this work are discussed in terms of their relevance to the mechanism of electroless plating.

Electroless plating is the term used to describe deposition of a metal coating from a solution containing a reducing agent (in the absence of an external current). When a catalytically active metal or suitably activated surface is present, the deposition occurs in a controlled way at the activated surface rather than by spontaneous deposition in the bulk of the solution. This process, which has well-known industrial applications, has received much attention, both in connection with the mechanism and with the chemical and physical properties of the deposit, and has been extensively treated in reviews and books.[1-5]

In aqueous plating solutions containing hypophosphite ions, a simultaneous catalytic oxidation of the hypophosphite ion by water occurs according to reaction (1).

$$H_2PO_2^- + H_2O \xrightarrow{\text{catalyst}} HPO_3^{-2} + H_2 + H^+ \qquad (1)$$

This represents inefficient utilization of the reducing agent as far as the plating process is concerned, and steps are normally taken to make the contribution of this competing reaction as low as possible. Although reaction (1) has been known for a long time,[6-10] little work has been reported on study of the mechanism of this reaction in solutions not containing nickel ions.[11,12]

The objective of this study was to carry out a detailed investigation of the catalytic oxidation of the hypophosphite ion by water on a standard EuroNi-1 catalyst. Variation in the concentration of additives, normally present in plating solutions as buffers, complexing agents or stabilizers, in this process in the absence of nickel was planned. The effects on the evolution of hydrogen and deposition of phosphorus on the catalyst were to be studied to understand more about the mechanism of the reaction and about the processes occurring in a nickel plating bath.

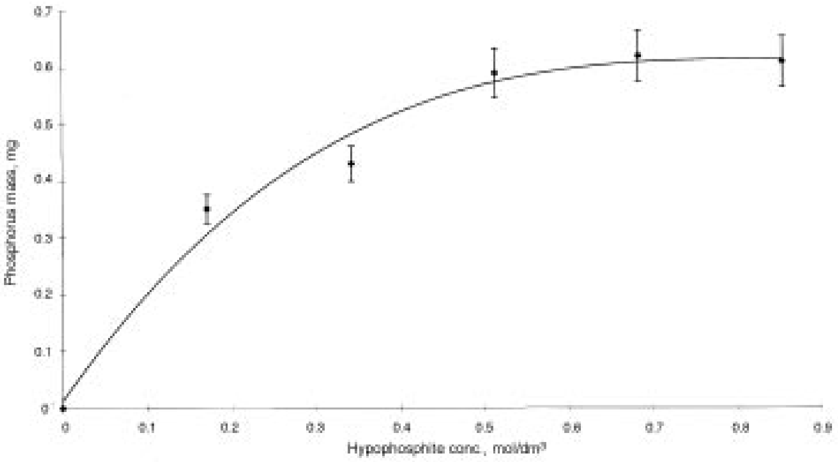

Fig. 1—Effect of hypophosphite concentration on incorporation of phosphorus on nickel catalyst.

Experimental Procedure

Apparatus

The apparatus used for hydrogen evolution measurements, as well as for the measurement of phosphorus deposited on the nickel catalyst is similar to the one described by Holbrook and Twist.[12] It consisted of a water bath (to maintain a constant temperature), containing a Pyrex glass reaction vessel (250 cm^3) with two screw openings. One opening was closed with a screw cap, used to inject the weighed catalyst-sample, while the other was connected to a water-condenser. The solution inside the reaction vessel was agitated by means of a magnetic stirrer bar driven by a magnetic stirrer revolving outside the water bath at a speed of 100 rpm. The condenser was connected to a gas-burette to enable measurement of the volume of hydrogen evolved.

Catalyst Preparation

EuroNi-1[13] was available as the precursor, consisting of high-area silica impregnated with nickel nitrate. The active catalyst was prepared in batches of 1.0 to 1.5 g by reduction of the precursor in hydrogen at atmospheric pressure in a static glass reactor for two hr at 400 °C. Hydrogen was changed at half-hourly intervals. After reduction, the vessel was cooled quickly under vacuum and the catalyst passivated by exposure to an atmospheric pressure of carbon dioxide at room temperature. The catalyst contained 25 percent by weight Ni, the metallic crystallites having a mean size of 3.5 nm.

Flow Injection Analysis

A variety of methods exists for the determination of phosphorus incorporated in Ni-P alloys, or deposited on nickel catalysts. A rapid and convenient technique used in the current study, which depends on the colorimetric determination of phosphorus as 12-molybdophosphate blue, is the technique of flow-injection analysis (FIA).[14] Injection of calibration solutions into the flow-injection apparatus produced a calibration graph of peak height vs. phosphate concentration that enabled phosphorus determination to be carried out with an average error not exceeding ± 4.4 percent.

Procedure for Handling FIA Samples

Phosphorus deposited on nickel catalyst

Each sample of catalyst, after removal from the hypophosphite solution by filtration, was dissolved in 10 cm^3 of 50-percent v/v HNO_3 at 80 °C. The residue, undissolved silica, was removed by filtration, and the solution was transferred into a 100-cm^3 graduated flask. The volume of the solution was made up to 100 cm^3 with deionized water. Samples were immediately analyzed for phosphorus.

The amount of nickel in each sample that came from the dissolution of the catalyst was added to each standard calibration solution. This was done by taking a weighed amount (0.1 g) of nickel catalyst dissolved in 10 cm^3 of 50-percent v/v HNO_3 at 80 °C and adding it, after filtration, to the standard solution, thus making the amount of nickel and the acid percentage the same as in the samples to be investigated. Both the nickel present in the solution and the acid have an effect on the blue complex that forms from the reaction between phosphate ions and the reagents. The acid was found to decrease the intensity of the blue color of the complex, whereas nickel ions in solution are green and absorb near the region of the blue color.

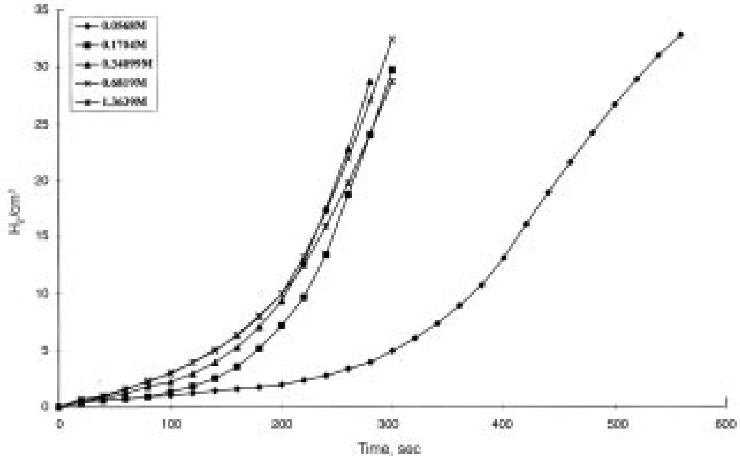

Fig. 2—Effect of hypophosphite concentration on rate of hydrogen evolution.

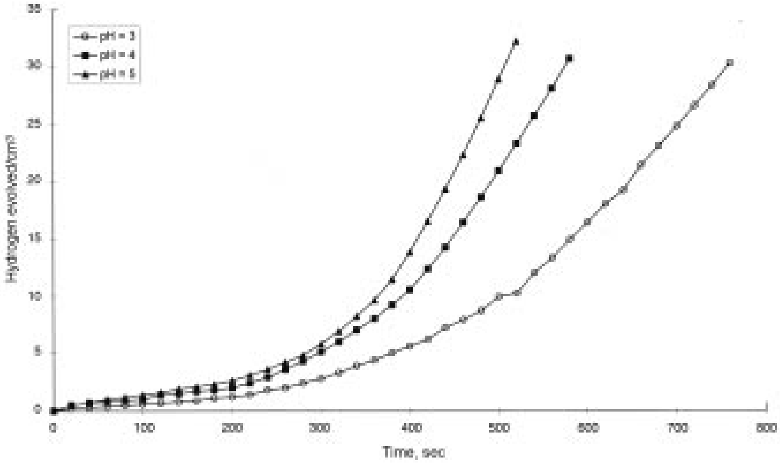

Fig. 3—Hydrogen evolution at different times as a function of pH.

Bath Composition for the Catalytic Oxidation of Hypophosphite

The composition of the bath and the operating conditions used are shown in Table 1. Experiments were carried out using this initial bath composition and set of operating conditions modified to allow independent variation of a number of components or factors such as pH. The independent variation of hypophosphite concentration, orthophosphite concentration (reaction product), solution pH, propionic acid concentration (buffering agent) and each of the following complexing agents: malonic, lactic, glycolic acids and glycine, was investigated.

Table 1
Bath Composition & Operating Conditions

Bath Composition	**Concentration, mol/dm³ †**
Hypophosphite (NaH_2PO_2)	0.341
Propionic acid (C_2H_5COOH)	0.6635
Catalyst mass	0.10 g
Operating conditions	
Temperature	80 ±1°C
pH (adjusted with NaOH)	4.0 ±0.1
Time	40 min

† 1 mol/dm³ = M g/L where M is the relevant relative molecular mass.
= 0.134 M oz/US gal.

The total volume of the solution was 200 cm^3 and deionized water was used in all experiments.

Run Procedure

A solution of sodium hypophosphite (200 cm^3) containing one of the specified additives was introduced into the reaction vessel. It was then placed into the water bath, connected to the condenser and heated to 80 ±0.1 °C. The whole system was at atmospheric pressure. A 0.1-g sample of nickel catalyst was then admitted to the reaction vessel through its second opening. This opening was immediately closed, and the reaction was followed as a function of time by measuring the volume of hydrogen evolved at atmospheric pressure, using the gas-burette. At the end of each run, when measurements of phosphorus deposited on the catalyst were required, the reaction vessel was disconnected from the condenser, cooled, and the catalyst retrieved by vacuum filtration. The apparatus allowed alternative experiments in which hydrogen was not measured but in which pH was measured continuously.

Results & Discussion

Preliminary experiments were carried out, using the solution described in Table 1, to check the stoichiometry of the reaction. Solution analyses at various times showed that orthophosphite ions and hydrogen gas are the main products of the reaction. Orthophosphite was detected by ^{31}P nmr spectrometry. Qualitative tests showed the presence of phosphorus deposited on the EuroNi-1 catalyst. Further identification of the presence of phosphorus was obtained by the use of Scanning Electron Microscopy (SEM), although this technique does not distinguish between elemental and combined phosphorus. Measurements of the pH during catalytic oxidation of the hypophosphite ion in unbuffered solutions showed a steady fall consistent with the production of H^+ ions in the reaction. In general, the results support previous studies,[1,6,15] and may be accounted for by the overall reaction steps

$$H_2PO_2^- + H_2O \xrightarrow{\text{catalyst}} HPO_3^{-2} + H_2 + H^+ \qquad (1)$$

and

$$H_2PO_2^- + H_{ads} \xrightarrow[\text{catalyst}]{} P + OH^- + H_2O \qquad (2)$$

where step (2) is slower than step (1).

Effect of Hypophosphite Ion

The effect of hypophosphite ion on the amount of phosphorus adsorbed on the nickel catalyst was established. Increase in the concentration of hypophosphite ion led to an increase in the amount of phosphorus deposited (Fig. 1). The phosphorus amount reached a plateau at about 0.7 mol/dm^3 hypophosphite concentration. Clearly, hypophosphite ion is a likely source of the phosphorus deposited on the nickel catalyst, and, consequently, it might also be a source of phosphorus incorporated in electroless nickel coatings. Baldwin, Such and others[16,17] have found that the phosphorus content of nickel coatings increased with increase in the concentration of hypophosphite in a plating solution.

Under conditions where the plateau is attained (Fig. 1) the number of phosphorus atoms deposited was 1.2 x 10^{19}. The mean size of the nickel particles in EuroNi-1[13] was 3.5 nm; supposing these particles to have been cubic (the precise morphology is not important) about 30 percent of the total number of nickel atoms (*i.e.*, 7.7 x 10^{19}) was present at the surface. From this, we conclude that phosphorus deposition occurred as an adsorbed monolayer and proceeded to saturation in competition with the adsorption of solvent and of the various phosphorus-containing ions in solution.

The manner in which hydrogen evolution varied with time is shown in Fig. 2. This process is clearly autocatalytic, in the sense that the changing surface conditions provided an increased hydrogen evolution rate.

Both of these observations are consistent with the overall reactions (1) and (2), and the limiting behavior observed may indicate that the surface becomes saturated with adsorbed $H_2PO_2^-$ ions at high concentrations.

The Effect of Orthophosphite Ion

Sodium orthophosphite was added to the bath in concentrations ranging from 0.02 to 0.21 mol/dm^3 to establish its effect on the amount of phosphorus in the deposit. An increase of 20 percent occurred. Similar experiments with measurement of hydrogen evolution showed that added orthophosphite ions had little or no effect on hydrogen production.

It is possible that reaction (3) proposed by Sutyagina *et al.* is responsible for a small amount of the phosphorus produced at later stages of the reaction under normal conditions:

$$H_3PO_3 + 3H_{ads} \xrightarrow[\text{catalyst}]{} H_2O + P \qquad (3)$$

The Effect of pH

Solution pH was an important factor affecting both the amount of phosphorus deposited on the catalyst surface, as well as the rate of hydrogen evolution. The amount of phosphorus decreased steadily with increase in pH from 3.0 to 7.0 (Table 2). In plating solutions, it is common to observe a decrease in percentage of phosphorus in the

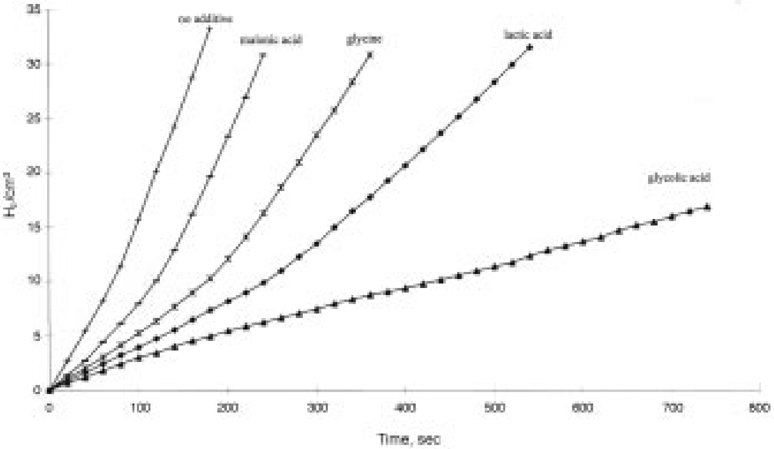

Fig. 4—Effect of different organic compounds on rate of hydrogen evolution at same molar concentration: 0.88 mol/dm^3.

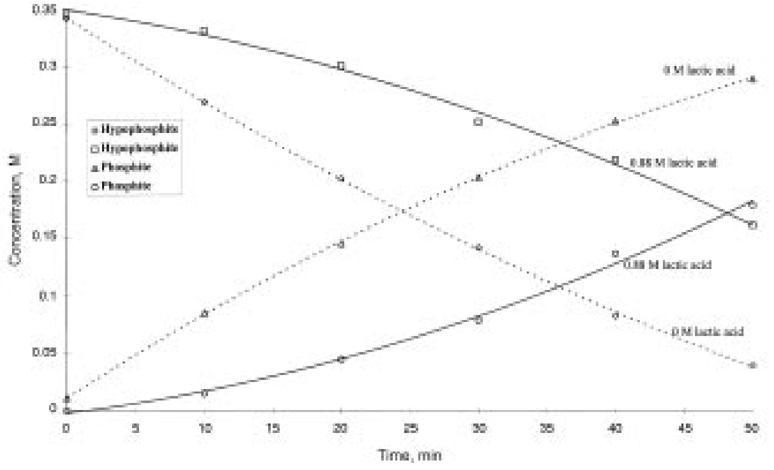

Fig. 5—Variation in $H_2PO_2^-$ and HPO_3^{-2} with time on nickel catalyst as function of lactic acid.

Table 2
Effect of pH on Phosphorus Deposited

pH	Mass P/mg
2.92	0.47
4.00	0.42
5.50	0.38
7.10	0.33

nickel deposit with increase in pH.[16-18] From the early work of Gutzeit,[9] it is possible to derive the weights of phosphorus deposited, which decrease by a factor of two with decrease in pH from 5.5 to 3.5, in contrast to the results presented here.

The production of phosphorus can be attributed to the occurrence of reaction (3) above to a small extent, but the more likely source, especially in the early stages of the reaction, is reaction (2), involving the hypophosphite ion. Increased pH would tend to inhibit reaction (2) and this can be interpreted as the cause of the decrease in deposited phosphorus. More adsorbed hydrogen atoms would then be available to recombine and form hydrogen gas. Experiments on varying the pH from 3.0 to 6.0 showed that the hydrogen evolution increased (Fig. 3).

An explanation of the observations in terms of adsorbed hydrogen atoms, however, is not unique. Recent mechanisms of electroless plating have favored electrochemical oxidation steps and alternative processes, such as (4), (5) and (6)

$$H_2PO_2^- + e^- \longrightarrow P + 2OH^- \qquad (4)$$

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^- \qquad (5)$$

$$2H^+ + 2e_- \longrightarrow H_2 \qquad (6)$$

could equally well describe these results.

The Effect of Organic Acids

Various organic acids have been used as additives to the catalytic oxidation of the hypophosphite ion. Propionic acid was added to the solution described in Table 1 in amounts varying from 0.06 to 0.66 mol/dm^3. The results showed a small increase in phosphorus deposition with increasing propionic acid concentration. Increase in propionic acid concentration produced a decrease in the rate of hydrogen evolution, in contrast to the effect observed on the plating rate in electroless nickel solutions, where an increased plating rate results.[19,20]

Similar effects have been observed for malonic acid, glycine, lactic acid and glycolic acid, all of which function as chelating agents for nickel ions in plating systems. Small changes in the phosphorus deposited on the catalyst are observed in the presence of these additives, but the more interesting results are the decreased rates of hydrogen evolution. These are illustrated in Fig. 4 for the same concentration of the various additives. The beneficial effect of the presence of these additives in plating solutions is clear, in that reaction (1), which is an unwanted side reaction in plating systems, is suppressed.

This effect is further illustrated in Fig. 5, which shows the rate of disappearance of $H_2PO_2^-$ and appearance of HPO_3^{-2} from ^{31}P nmr measurements to be strongly inhibited by the presence of lactic acid. The mechanism by which organic acid anions inhibit the heterogeneous oxidation of hypophosphite ions is not clear. One possibility is that these ions progressively adsorb at the catalytic surface and so inhibit catalytic processes such as (1) and (2), involving hypophosphite ions. In the case of glycolic acid additions, however, evidence has been obtained for the participation of another process, namely, the leaching of nickel from the catalyst. A quantitative test of the solution following the reaction with glycolic acid present, using dimethylglyoxime reagent, indicated the presence of nickel ions.

Conclusions

The results of this study confirm the previously accepted overall reactions (1) and (2) as important in describing the catalytic oxidation of hypophosphite ions by water.

Measurements of the hydrogen evolved and phosphorus deposited on the nickel catalyst EuroNi-1 were made. Hydrogen was evolved in an autocatalytic manner and the deposition of phosphorus was found to reach a maximum value, probably corresponding to saturation of the available surface Ni atoms. These results have important implications for the processes occurring in nickel-hypophosphite plating solutions. The presence of organic acids that function as chelating agents in plating solutions, causes a marked decrease in hydrogen evolution. It is clear that during plating, these acids act not only as chelating agents, but also in suppressing the concurrent catalytic oxidation of hypophosphite ions by water.

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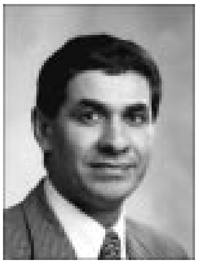
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