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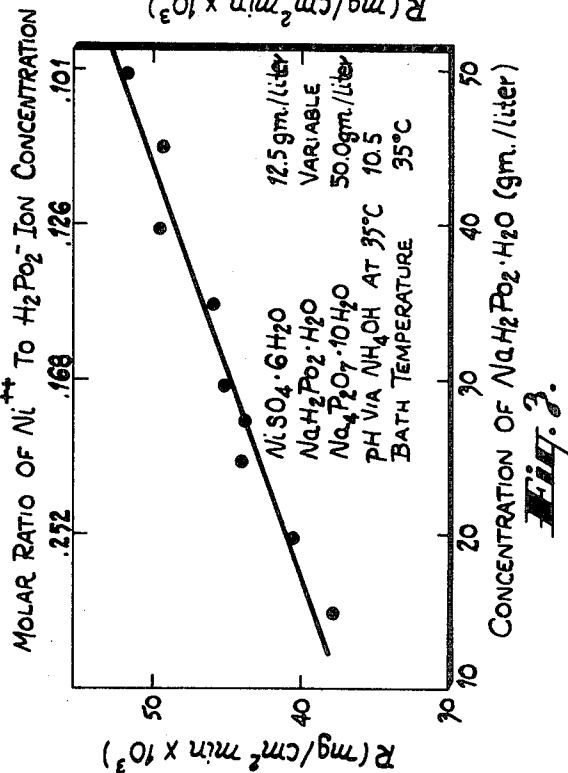
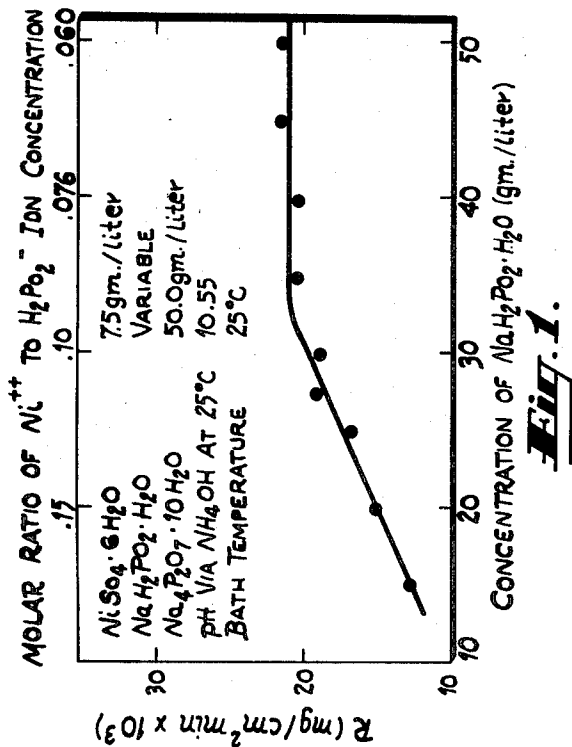
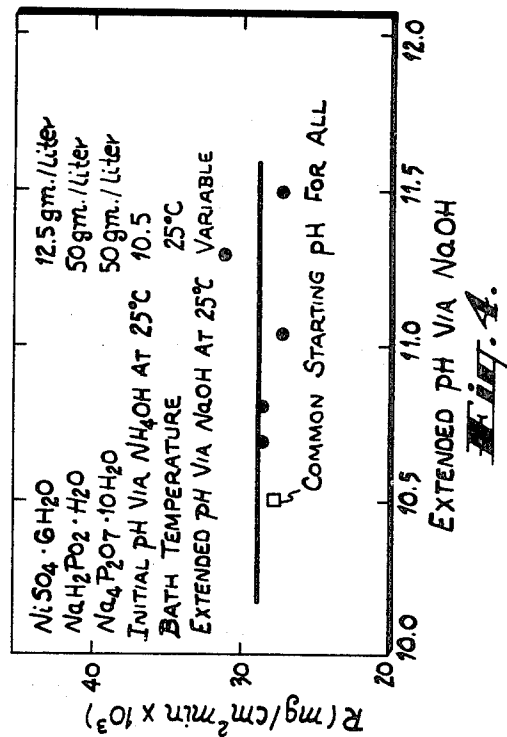
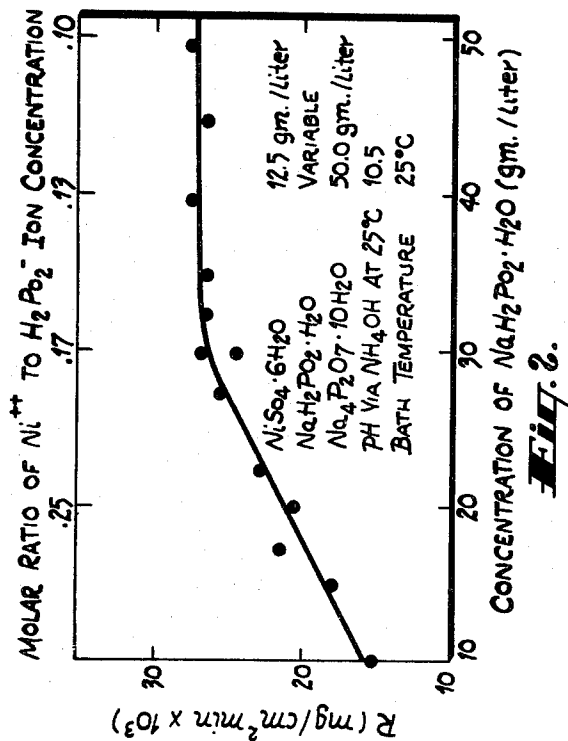
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3,690,944

ELECTROLESS NICKEL PLATING METHOD

Original Filed Feb. 20, 1968

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

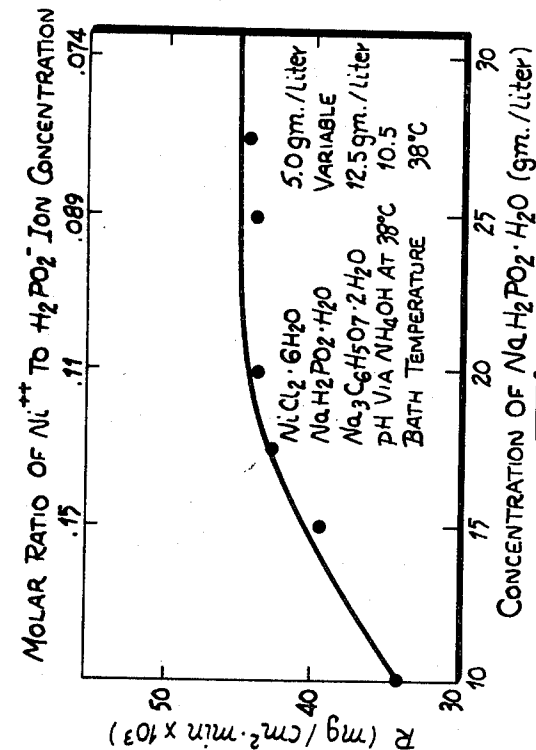


Fig. 6.

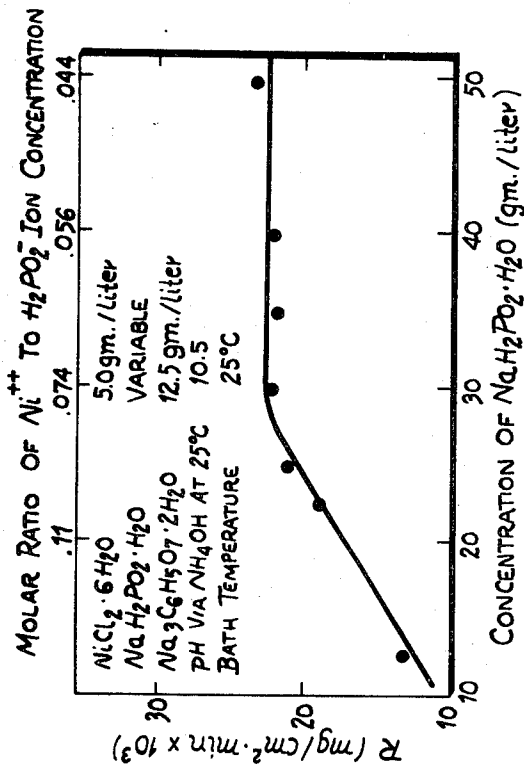


Fig. 5.

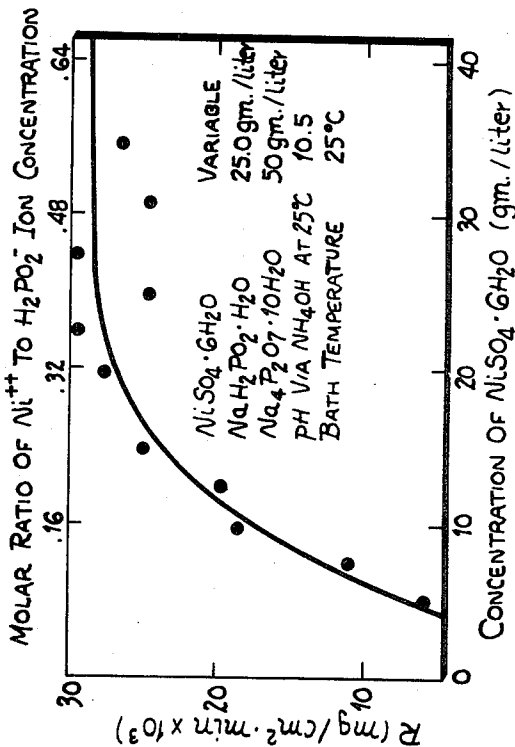


Fig. 7.

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3,690,944

ELECTROLESS NICKEL PLATING METHOD

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Continuation of application Ser. No. 706,822, Feb. 20, 1968. This application Mar. 10, 1970, Ser. No. 17,041

Int. Cl. C23c 3/02

U.S. Cl. 117—160 R

6 Claims

ABSTRACT OF THE DISCLOSURE

A method for electrolessly plating nickel from a bath comprising (i) a nickel salt; (ii) a nickel ion complexing agent; (iii) a source of hypophosphite ions; and (iv) ammonium hydroxide, in which the molar concentration ratio of nickel to hypophosphite ions is less than 0.2. The bath exhibits a plating rate substantially independent of hypophosphite ion concentration.

This application is a continuation of our application entitled, "Electroless Plating Baths Having Concentration Independent Plating Rates," Ser. No. 706,822, filed Feb. 20, 1968, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the electroless plating of metal from aqueous solution.

The electroless plating of metal by autocatalytic reduction of metal ions from aqueous solution is a technique well known in the art. Such plating solutions generally comprise (i) a salt of the metal to be deposited, (ii) a metal ion complexing agent, (iii) a reducing agent, and (iv) an acid or base for determining the pH of the plating bath.

When a substrate (suitably treated if the substrate is not itself catalytic for the electroless process) is immersed in the plating bath, the concentrations of metal and reducing agent ions are depleted as the deposition of metal onto the substrate progresses. Also, the pH of the bath decreases during the plating process.

In order to simplify production processes for deposition of a metal layer having a predetermined thickness, it is necessary to continuously sample and quantitatively analyze the plating bath for metal ion and reducing agent ion concentration. The proper amounts of metal salt and reducing agent may then be added to replenish the plating solution to restore its optimum composition. The pH of the solution must also be maintained, either by adding acid or base to the solution, or by otherwise stabilizing the bath to provide a deposition rate relatively insensitive to pH.

At present, the most extensively developed and widely used electroless baths are those employed for the deposition of nickel, and more specifically of nickel-phosphorus alloys. A technique for stabilizing alkaline electroless nickel plating baths employing hypophosphite ions as the reducing agent against variation in pH during the plating process is described in U.S. patent application Ser. No. 678,373, which I filed on Oct. 26, 1967 now U.S. Pat. No. 3,574,664.

U.S. patent application Ser. No. 6,783,373 is incorporated herein by reference and made a part of this specification.

In commercial electroless nickel plating baths employing a source of hypophosphite ions, such as sodium hypophosphite, as the reducing agent it is necessary to conduct periodic quantitative analyses for hypophosphite and nickel ion concentration in the nickel plating bath.

The nickel ion concentration can usually be determined

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with relative ease by (i) titration, (ii) electrochemical potential measurement utilizing a suitable reference electrode immersed in the plating bath, or (iii) spectroscopic or spectrophotometric methods. By utilizing titration, for example the nickel ion concentration can usually be determined within a few minutes.

The determination of hypophosphite ion concentration, however, is a difficult and time consuming process, and is complicated due to interference of phosphite anions which are generated as a by-product of the plating process. The hypophosphite ion analysis requires a skilled technician; utilizing the best analysis techniques presently available, the quantitative analysis for hypophosphite ions requires about 45 minutes.

Since a commercially used nickel plating bath must be analyzed and replenished at least two or three times per day, the required analysis for hypophosphite ion concentration represents a considerable economic expenditure.

An object of the present invention is to provide an electroless metal plating bath having a deposition rate substantially insensitive to reducing agent concentration over a predetermined concentration range.

SUMMARY

My invention provides a plating bath for the electroless deposition of a metal. The plating bath comprises (i) a salt of the metal, (ii) a metal ion complexing agent, (iii) a reducing agent and (iv) a pH determining substance. The molar concentration ratio of metal ions to reducing ions in the plating bath is less than 0.2.

According to a preferred embodiment of my invention, an aqueous alkaline electroless nickel plating bath is provided which comprises (i) a nickel salt, (ii) a source of hypophosphite ions, (iii) a nickel ion complexing agent and (iv) ammonium hydroxide, in which the molar concentration ratio of nickel ions to hypophosphite ions is less than 0.2.

IN THE DRAWINGS

FIGS. 1 to 4 show plating rate graphs relating to a preferred embodiment of the invention; and

FIGS. 5 to 7 show plating rate graphs relating to alternative embodiments of the invention.

DETAILED DESCRIPTION

The electroless plating of metals by autocatalytic reduction from aqueous solution is a chemical process whose rate, as in other chemical processes, may be determined by the availability of one of the reactants. In particular, the electroless reaction rate is dependent upon the relative concentrations of metal ions and reducing agent ions in the plating bath.

I have discovered that, for certain types of electroless plating baths, the plating rate can be made substantially independent of reducing agent ion concentration by employing a ratio of metal ion to reducing agent ion concentration which is below a specified value. While the precise explanation for this behavior is not completely understood at the present time, the plating rate under these conditions is believed to be governed primarily by the availability of metal ions in the vicinity of the substrate being plated. This metal ion availability, in turn, is dependent upon the rate of mass transfer of metal ions in the vicinity of the substrate and, consequently, upon the metal ion concentration gradient at the interface between substrate surface and the plating bath.

The relative insensitivity of the plating rate to reducing agent ion concentration, under the conditions disclosed herein, is upset by any environmental mechanisms which interfere with the metal ion mass transfer processes in the plating bath. Such environmental effects include turbulence caused by (i) agitation or by (ii) the increased

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bubbling of gases released from the plating bath at high deposition rates or at high temperatures.

My invention is particularly applicable to, and is explained in conjunction with, a bath for the electroless deposition of nickel from aqueous solution, in which hypophosphite ions are employed as the reducing agent. A typical bath of this type (employing pyrophosphate ions as a nickel ion complexing agent) may generally have a composition within the concentration ranges set forth in Table 1.

TABLE 1

Ingredient	Chemical formula	Concentration range
Nickel chloride.....	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10 to 45 grams/liter of bath.
or Nickel sulfate.....	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	10 to 50 grams/liter of bath.
Sodium hypophosphite...	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	Do.
Sodium pyrophosphate...	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	10 to 100 grams/liter of bath.
Ammonium hydroxide (58% by weight).	NH_4OH	5 to 40 cc./liter of bath.

The plating bath set forth in Table 1 is especially useful at room temperature, as described in U.S. patent application Ser. No. 678,373.

A graph showing the variation of plating rate, at room temperature (25° C.), as a function of reducing agent (sodium hypophosphite) concentration, is shown in FIG. 1. All plating rate measurements were carried out by depositing the nickel layer on a sensitized alumina substrate. The various compositions represented by FIG. 1 are obtained by preparing a plating solution, each liter of which contains (i) 7.5 grams nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), (ii) 50.0 grams sodium pyrophosphate complexing agent ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$), (iii) sufficient ammonium hydroxide to provide a pH of 10.55, and (iv) a quantity of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) varying from 15 to 50 grams.

A scale disposed parallel to and above the graph of FIG. 1 shows the molar concentration ratio of nickel to hypophosphite ions corresponding to each sodium hypophosphite concentration employed, at 25° C.

The electroless nickel plating rate (more specifically, the plating rate of the deposited nickel-phosphorus alloy) R initially increases with increasing sodium hypophosphite concentration (and decreasing $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio). As the sodium hypophosphite concentration is increased, however, to provide a $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio below a critical value on the order of 0.097, further increase of sodium hypophosphite concentration has no substantial effect on the nickel plating rate.

Therefore, a plating bath prepared with a composition corresponding to the flat portion of the graph shown in FIG. 1, i.e. with a $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio less than about 0.097, will exhibit a plating rate independent of the hypophosphite ion concentration, until plating from the bath has progressed to the point where the sodium hypophosphite concentration drops to a value (about 31 grams/liter) below that corresponding to the aforementioned critical ratio.

A similar graph, corresponding to a plating bath comprising the same ingredients utilized in the bath of FIG. 1 (at 25° C.), but containing a larger proportion of nickel ions, is shown in FIG. 2. The graph of FIG. 2 also exhibits a region in which the plating rate is substantially independent of sodium hypophosphite concentration. However, in this case the critical ratio has increased to a value on the order of 0.19 (corresponding to about 27 grams/liter sodium hypophosphite concentration).

The critical ratio, however, will in any event have a value less than 0.2 for all practical values of nickel salt concentration.

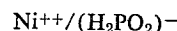
The plating baths whose performance is characterized by FIGS. 1 and 2 employ pyrophosphate ions as an agent for complexing the nickel ions in solution. I have found

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that the critical ratio for such pyrophosphate baths is quite temperature dependent. As the temperature of the bath is increased above 25° C., the critical ratio increases, until the flat portion of the plating rate/hypophosphite concentration curve completely disappears at a bath temperature on the order of 35° C., as is indicated in FIG. 3. FIG. 3 is plotted for the same bath compositions as those utilized in obtaining FIG. 2, but at a bath temperature of 35° C. It is seen that the plating rate is substantially proportional to the sodium hypophosphite concentration, and there is no region in which the rate appears to be substantially insensitive to sodium hypophosphite concentration. Sodium hypophosphite concentrations substantially in excess of 50.0 grams per liter, the upper limit of the graph, are not usually practical, since the plating bath tends to become unstable.

My invention may be employed in combination with that of U.S. patent application Ser. No. 678,373, to provide a plating bath which exhibits a plating rate substantially insensitive to variations in both pH and hypophosphite ion concentration, by utilizing the alkaline bath disclosed in U.S. patent application Ser. No. 678,373, but restricting the bath to those compositions which exhibit a $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ molar ratio of less than 0.2.

Such an alkaline bath, corresponding to a



ratio of 0.10, may comprise (i) 12.5 grams $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, (ii) 50 grams $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, and (iii) 50 grams $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ for each liter of bath (aqueous solution). The pH of the bath is initially set to a value of 10.5 at 25° C. by adding a sufficient quantity of concentrated ammonium hydroxide. The pH of the bath is then extended by adding another base such as, e.g., sodium hydroxide.

The graph of FIG. 4 shows, for this composition, the variation of plating rate with extended pH at 25° C. The plating rate is seen to be substantially insensitive to extended pH; it is evident that this bath (which corresponds to the composition at the 50 grams per liter sodium hypophosphite concentration point of the graph shown in FIG. 2) exhibits a plating rate which is also insensitive to hypophosphite ion concentration over a wide range.

My invention is not limited to the electroless deposition of nickel, but is also applicable to the electroless deposition of other metals, where an autocatalytic process is employed to reduce complex ions of the metal from solution. In order to obtain a plating rate substantially insensitive to reducing agent concentration, the molar concentration ratio of metal to reducing agent ions should be maintained at a predetermined value less than 0.2. The pH of the plating solution, however, should be set to a value corresponding to the optimum plating rate by means of a suitable pH determining substance, e.g., an acid or base or a substance which affects the pH of the bath upon hydrolysis. The invention is also applicable to electroless plating baths employing reducing agents other than hypophosphite salts.

In particular I prefer to employ the invention in conjunction with alkaline plating baths for the electroless deposition of nickel, cobalt, nickel-iron alloys and cobalt-iron alloys. In these preferred baths, a source of hypophosphite ions may be employed as the reducing agent, and ammonium hydroxide may be utilized both as a base and as a reactant which aids in the metal ion complexing process.

Another electroless nickel plating bath, according to an alternative embodiment of the invention, utilizes sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) rather than sodium pyrophosphate as the nickel ion complexing agent. A typical plating bath of this type may have a composition such that each liter of bath (aqueous solution) comprises (i) 5.0 grams $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, (ii) 12.5 grams $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, (iii) a sufficient quantity of ammonium hydroxide to pro-

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vide a pH of 10.5 at 25° C. and (iv) a variable quantity of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

A graph showing the plating rate of such a composition as a function of sodium hypophosphite concentration, appears in FIG. 5. It is seen that this citrate bath, as in the case of the pyrophosphate bath, exhibits a region in which the plating rate is substantially insensitive to hypophosphite ion concentration. In this case, the flat portion of the curve corresponds to those hypophosphite ion concentrations for which the $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio is less than a critical value on the order of 0.086.

The graph of FIG. 5 is plotted at a bath temperature of 25° C. As in the case of the pyrophosphate bath, the critical ratio increases as the bath temperature is raised. The graph shown in FIG. 6 is plotted for the same composition as that employed for FIG. 5, but at a bath temperature of 38° C. It is seen that the critical ratio has now increased to a value on the order of 0.12 (corresponding to a sodium hypophosphite concentration of about 17 grams/liter), but the phenomenon described has not disappeared as it did in the case of the pyrophosphate bath at 35° C.

It thus appears that the critical $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio is dependent upon both the bath temperature and, to a somewhat lesser degree, on the nature of the particular metal ion complexing agent employed. In all cases, however, practical compositions exhibit the phenomenon which I have discovered, i.e. the insensitivity of the plating rate to reducing agent concentration, at values of the critical $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio less than 0.2.

Where the pyrophosphate nickel plating bath is employed, sufficient ammonium hydroxide should be provided so that the bath exhibits an initial pH of at least 9.0. The pH may then be increased further in accordance with the teaching of U.S. patent application Ser. No. 678,373, so as to render the plating rate of the bath substantially insensitive to variation in pH over a wide range.

Wherever nickel sulfate is employed in the plating baths described herein, the equivalent weight of nickel chloride may alternatively be employed, and vice versa.

In the particular case of the alkaline electroless nickel bath which employs pyrophosphate ions as the nickel ion complexing agent, I have found that, rather than making the plating rate of the bath independent of hypophosphite ion concentration, the rate may alternatively be rendered independent of nickel ion concentration.

A bath of this type may, e.g., have a composition such that each liter of bath comprises (i) 25.0 grams $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, (ii) 50 grams $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, (iii) sufficient ammonium hydroxide to provide a pH on the order of 10.5, and (iv) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. A graph for compositions of this type, corresponding to various concentrations of nickel sulfate (other soluble nickel salts may be employed instead of nickel sulfate), is shown in FIG. 7 for a bath maintained at a temperature of 25° C. The plating rate is seen to be substantially insensitive to nickel ion concentration for those nickel sulfate concentrations which correspond to a $\text{Ni}^{++}/(\text{H}_2\text{PO}_2)^-$ ratio greater than about 0.26.

What is claimed is:

1. A method of electrolessly nickel plating a substrate, comprising the steps of:
 - providing at a temperature of about 25° to 35° C. an aqueous solution of which each liter contains:
 - 7.5 to 12.5 gms. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
 - 30 to 50 gms. of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$;
 - 30 to 50 gms. of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$;
 - sufficient ammonium hydroxide such that the bath exhibits an initial pH of at least 9;
 - immersing said substrate in said solution; and
 - plating said immersed substrate at a constant rate of

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deposition substantially independent of reducing agent and without replenishing said hypophosphite during deposition.

2. A method according to claim 1 in which said bath temperature is about 25° C.

3. A method of electrolessly nickel plating a substrate, comprising the steps of:

providing at a temperature of about 25° to 35° C. an aqueous solution of which each liter contains:

7.5 to 12.5 gms. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;

30 to 50 gms. of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$;

30 to 50 gms. of $\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$;

sufficient ammonium hydroxide such that the bath exhibits an initial pH of at least 10.5;

immersing said substrate in said solution; and

plating said immersed substrate at a constant rate of deposition substantially independent of reducing agent and without replenishing said hypophosphite during deposition.

4. A method according to claim 3 in which said bath temperature is about 25° C.

5. A method of electrolessly nickel plating a substrate, comprising the steps of:

providing at a temperature of about 25° to 35° C. an aqueous solution of which each liter contains:

5.0 to 12.5 gms. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$;

25 to 50 gms. of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$;

10 to 15 gms. of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$;

sufficient ammonium hydroxide such that the bath exhibits an initial pH of at least 10.5;

immersing said substrate in said solution; and

plating said immersed substrate at a constant rate of deposition substantially independent of reducing agent and without replenishing said hypophosphite during deposition.

6. A method of electrolessly nickel plating a substrate, comprising the steps of:

providing at a temperature of about 25° to 35° C. an aqueous solution of which each liter contains:

5.5 to 13.8 gms. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;

25 to 50 gms. of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$;

10 to 15 gms. of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$;

sufficient ammonium hydroxide such that the bath exhibits an initial pH of at least 10.5;

immersing said substrate in said solution; and

plating said immersed substrate at a constant rate of deposition substantially independent of reducing agent and without replenishing said hypophosphite during deposition.

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LORENZO B. HAYES, Primary Examiner

U.S. Cl. X.R.

70 106—1; 117—47 R