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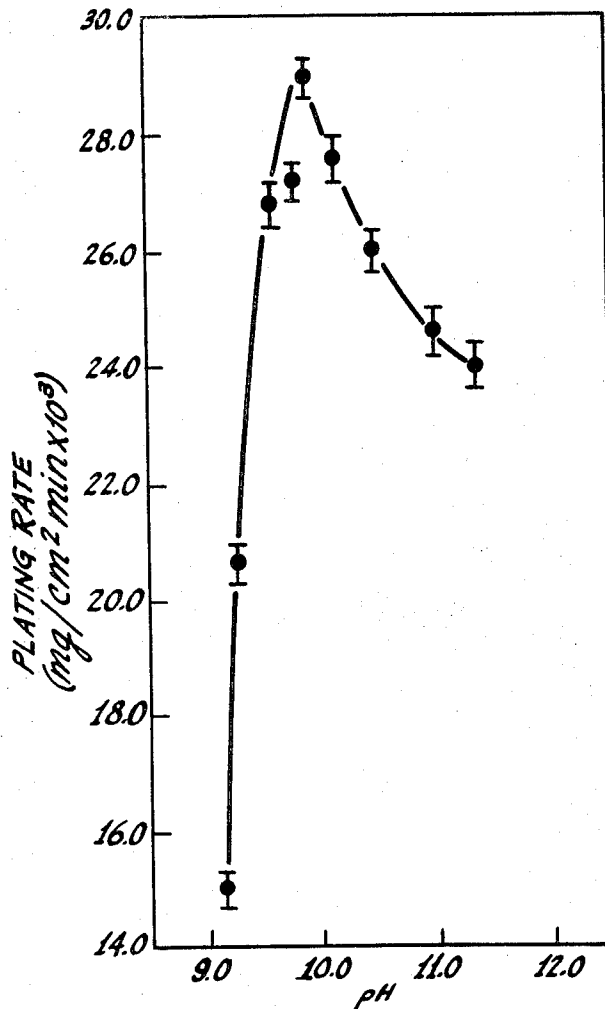
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3,574,664

ROOM TEMPERATURE ELECTROLESS NICKEL PLATING BATH

Filed Oct. 26, 1967

2 Sheets-Sheet 1



RATE OF DEPOSITION vs pH
VARIED BY NH_4OH FOR A
BATH CONTAINING NiSO_4

Fig. 1.

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2 Sheets-Sheet 2

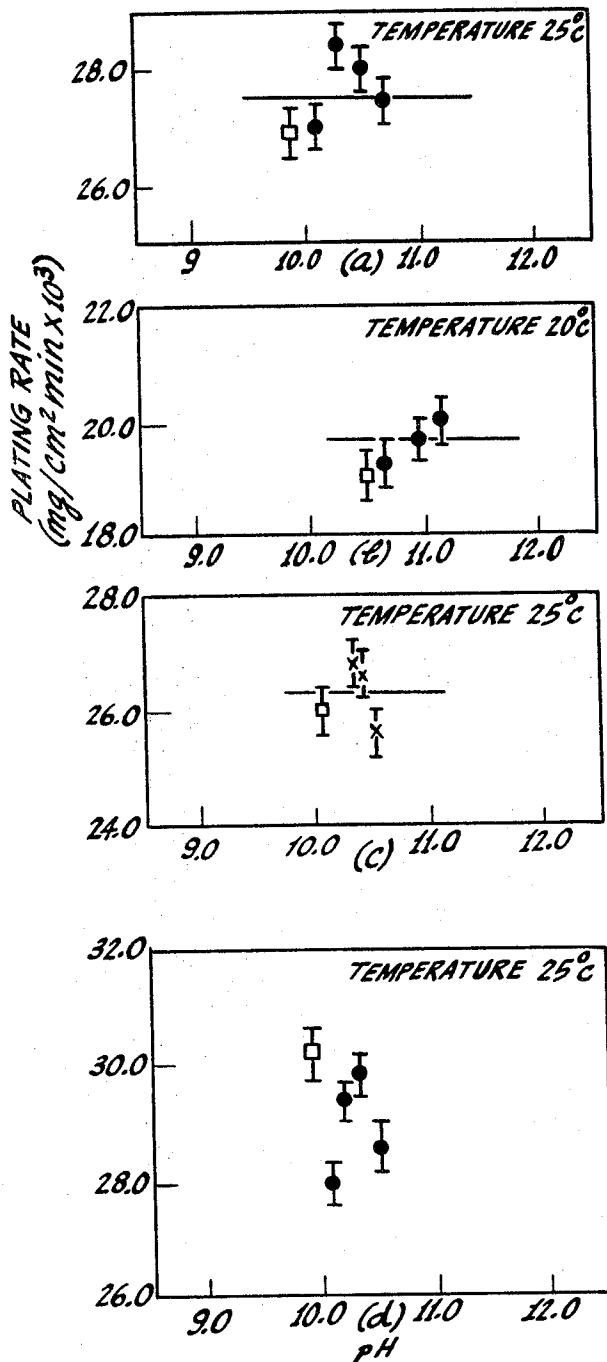
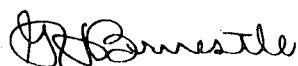


Fig. 2.

RATE OF DEPOSITION vs pH
(a) pH VARIED WITH LiOH
(b) pH VARIED WITH NaOH
(c) pH VARIED WITH KOH
(d) pH VARIED WITH $(\text{C}_2\text{H}_5)_4\text{NOH}$
□ DOES NOT CONTAIN THE ABOVE HYDROXIDES

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**ROOM TEMPERATURE ELECTROLESS NICKEL
PLATING BATH**Nathan Feldstein, Kendall Park, N.J., assignor to
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8 Claims

ABSTRACT OF THE DISCLOSURE

A process for depositing nickel onto a substrate from a room temperature electroless plating bath; the bath initially includes (i) a nickel salt, (ii) sodium hypophosphite, (iii) sodium pyrophosphate, and (iv) ammonium hydroxide.

The concentration of ammonium hydroxide is chosen so as to adjust the pH of the bath to an initial value (between 9.0 and 11.5) corresponding to the desired plating rate. A strong base such as sodium hydroxide is then added to increase the pH of the bath above the initial value without substantially affecting the plating rate.

In use, the pH of the bath decreases, but the plating rate remains relatively unaffected so long as the pH does not drop below the initial value set by the ammonium hydroxide. This permits wider tolerances in pH control of the bath and alleviates the need for adding an accurately controlled amount of hydroxyl ion when the bath is regenerated.

BACKGROUND OF THE INVENTION

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

The electroless plating of nickel on various types of substrates by autocatalytic reduction of nickel ions from aqueous solution is a technique well known in the art. In one particular electroless nickel process, the plating bath contains (i) nickel ions, (ii) hypophosphite ions (which serve as the reducing agent), (iii) pyrophosphate ions (which serve to complex the nickel ions to prevent the formation of undesired precipitates), and (iv) ammonium hydroxide (which serves to aid in complexing the nickel ions and to provide hydroxyl ions for increasing the pH of the bath).

One example of such a bath composition is disclosed in an article by M. Schwartz entitled "The Chemical Reduction of Nickel-Phosphorus Alloys From Pyrophosphate Solutions," and published in the Forty-seventh Annual Technical Proceedings of the American Electroplating Society, p. 176 (1960). Commonly employed electroless nickel solutions usually operate at relatively high temperatures, slightly below the boiling point of water (relatively low temperatures on the order to 68° to 74° C. are employed in the process described in the aforementioned Schwartz article). At these temperatures, instabilities in the plating rate and composition of the bath are introduced due to (i) the difficulty of accurately controlling the bath temperature under production line conditions, (ii) the rapid evaporation of ammonia from the solution, and (iii) spontaneous decomposition of the plating solution. In addition, the efficiency of utilization of the relatively expensive hypophosphite-containing material rapidly decreases at elevated temperatures.

Additional problems in utilizing the electroless nickel bath at elevated temperatures are due to (i) the undesired plating of nickel on non-metallized portions of ceramic or plastic substrates in the case of printed circuits and similar electronic applications, and (ii) the relatively high phosphorus content of the deposited nickel layer.

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The phosphorus renders the layer more brittle and, in the case of plating on semiconductor devices, introduces a source of donor impurities which may affect the characteristics of the underlying semiconductor material.

As the electroless deposition process proceeds, the pH of the bath tends to decrease. This reduction in pH decreases the reducing power of the hypophosphite ions, with the net result that the plating rate rapidly decreases.

An object of my invention is to provide an improved electroless nickel plating process especially suitable for use at room temperature.

Another object of my invention is to provide an improved electroless nickel plating process in which the plating rate is relatively insensitive to variation in pH.

SUMMARY

My invention provides a process for electrolessly depositing a nickel-phosphorus layer on a substrate surface. An aqueous plating bath is first prepared; the bath initially comprises (i) a nickel salt, (ii) a source of hypophosphite ions (iii) a nickel ion complexing agent, and (iv) sufficient ammonium hydroxide to adjust the pH of the bath to a value corresponding to a specified plating rate.

To this bath I add a quantity of a base to increase the pH of the bath without substantially affecting the specified plating rate. When the substrate to be plated is subsequently immersed in this bath, the electroless nickel-phosphorus layer is deposited at a plating rate which is relatively unaffected by the decrease in pH of the bath as the deposition progresses.

IN THE DRAWING

FIG. 1 shows the variation in plating rate versus pH for a plating bath similar to those heretofore known;

FIG. 2 shows plots of plating rate versus pH for various plating baths according to my invention.

DETAILED DESCRIPTION

The electroless plating of nickel, and more accurately nickel-phosphorus alloys, from aqueous solution is initiated by the reduction of nickel ions by hypophosphite ions in the presence of a suitable catalyst.

Elements which are catalytic for the electroless nickel plating process are iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum.

Elements which may be electrolessly nickel plated by virtue of an initial displacement reaction which deposits nickel thereon, either directly or through a galvanic effect, include copper, silver, gold, beryllium, germanium, aluminum, carbon, vanadium, molybdenum, tungsten, chromium, selenium, titanium, uranium, and zinc.

Examples of element which are non-catalytic and may not be ordinarily directly nickel plated by the electroless process include bismuth, cadmium, tin, and lead.

The activity of the catalytic materials varies considerably; iron, cobalt, nickel and palladium are particularly good catalysts for the electroless nickel plating process.

Where a non-catalytic surface is to be plated, it is common to activate the surface by forming thereon a thin film of a catalytic material. Palladium is most commonly employed for this purpose, usually in the form of palladium chloride.

I have found that an electroless nickel plating bath which comprises (i) a nickel salt such as, e.g., nickel sulfate or nickel chloride, (ii) a source of hypophosphite ions such as, e.g., sodium hypophosphite, (iii) a nickel complexing agent such as, e.g., sodium pyrophosphate and (iv) ammonium hydroxide is especially suitable for use at relatively low temperatures and particularly at room temperature (i.e., temperatures on the order of 20° to 30° C.).

In particular, I find plating baths having the following concentrations of the aforementioned ingredients to be especially useful at room temperature:

where n is an integer such that $1 \leq n \leq 4$

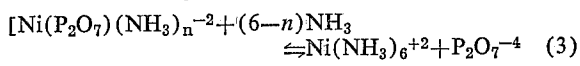


TABLE I

Ingredient	Chemical formula	Concentration range	Concentration for preferred composition
Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10 to 45 gms./liter of bath	22 gms./liter of bath.
Nickel sulfate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	10 to 50 gms./liter of bath	25 gms./liter of bath.
Sodium hypophosphite	$\text{NaH}_2\text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$	do.	Do.
Sodium pyrophosphate	$\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	10 to 100 gms./liter of bath	50 gms./liter of bath.
Ammonium hydroxide (58% by weight)	NH_4OH	5 to 40 cc./liter of bath	20 cc./liter of bath.

Since the solutions set forth in Table I operate at room temperature, their lifetime is generally limited to a few weeks unless the nickel nuclei which form spontaneously are filtered out or de-activated by adding a small amount of a stabilizing agent (usually including lead ions, thiol functional groups or other substances which act as poisons to render the nickel nuclei catalytic sites inactive).

Due to the limited lifetime of the plating solution, I have found it convenient to prepare the electroless plating bath as separate oxidizing and reducing agents. In one example, the oxidizing agent is produced as an aqueous solution each liter of which contains (i) 20 cc. of concentrated (58% by weight) ammonium hydroxide, (ii) 100 grams of sodium pyrophosphate, and (iii) 50 grams of nickel sulfate. For this example, the reducing agent is prepared as an aqueous solution each liter of which contains 50 grams of sodium hypophosphite.

The exact amount of ammonium hydroxide employed in the oxidizing solution depends upon the initial value of pH desired when the oxidizing and reducing solutions are mixed in the proper proportions (one part oxidizing solution to one part reducing solution). The mixing of the aforementioned (oxidizing and reducing) agents in the indicated proportions results in an initial pH of about 10.5.

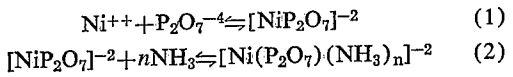
Since at room temperature the electroless solution is somewhat more sensitive to the presence of catalytic poisons than at elevated temperature, it is necessary to employ reagents of high purity which are free of such poisons (except, of course, where an extremely small controlled amount of catalytic poison is intentionally added as a stabilizing agent, usually in the relative proportion of no more than a few parts per million).

The preferred nickel plating bath composition set forth in Table I exhibits a large variation of plating rate with pH, when the pH is varied by changing the concentration of ammonium hydroxide in the bath. FIG. 1 shows a plot of this deposition rate as a function of pH for the aforementioned preferred composition.

It is seen from FIG. 1 that as the pH is increased from about 9.2 to 10, the plating rate nearly doubles. As the pH (and the concentration of ammonium hydroxide) is further increased, the plating rate reaches a peak (at a pH of 10.1) and then rapidly decreases.

This large variation of plating rate with pH makes it difficult to control the thickness of electroless nickel-phosphorus deposited, as the amount of material deposited is a complex function of time. Moreover, the pH of the bath must be accurately monitored during the deposition process, or accurately controlled (by adding additional hydroxyl ions to maintain the pH substantially constant), both of which requirements are somewhat difficult to embody in production line processes.

The curve shown in FIG. 1 is believed to be due to the formation of a nickel-ammonia-pyrophosphate complex and the dynamic equilibrium established between this complex and a nickel-ammonia complex, as shown by Equations 1 to 3 below



The mixed complex on the left-hand side of Equation 3 is relatively reactive, i.e., the nickel in the mixed complex is readily reduced to metallic nickel by the hypophosphite ions in the plating bath. On the other hand, the nickel-ammonia complex on the right-hand side of Equation 3 is relatively less reactive, i.e., the nickel in this (nickel-ammonia) complex exhibits a lower rate of reaction with the hypophosphite ions to form the metallic nickel plating.

The ammonia contributed to the solution as the concentration of ammonium hydroxide is increased from an initial pH of slightly over 9, enhances the formation of the mixed complex, as set forth in Equation 2. As more ammonium hydroxide is added to the plating solution, the dynamic equilibrium of Equation 3 is shifted to provide a lower concentration of the desirable, highly reactive mixed complex and a higher concentration of the less reactive nickel-ammonia complex, with a consequent decrease in plating rate.

I found that by adding a controlled amount of a (preferably strong) base (which does not contain ammonium ions) to the aforementioned preferred composition, the pH of the plating solution can be increased without substantially affecting the plating rate, which remains approximately at its initial value corresponding to the bath composition before addition of the base.

When this enhanced plating composition, containing the (strong) base, is employed to deposit electroless nickel-phosphorus, the plating rate remains substantially constant over a wide range of pH, so that the decrease in pH which necessarily takes place while the deposition progresses has no substantial effect on the plating rate.

It should be understood, however, that the plating rate will vary while the deposition progresses because the concentration of nickel and hypophosphite ions continuously decreases as the nickel-phosphorus layer is deposited. In order to maintain a constant plating rate, therefore, it is necessary to add controlled amounts of a nickel salt (such as the forementioned nickel chloride or nickel sulfate) and a source of hypophosphite ions (such as the aforementioned sodium hypophosphite) in order to maintain the nickel and hypophosphite ion concentrations substantially constant.

My invention alleviates the necessity of accurately controlling the pH of the bath in order to insure a substantially constant plating rate. Thus, nickel-phosphorus can be electrolessly deposited as a layer having an accurately controlled thickness, even where production line processes involving a loose pH control are employed.

FIG. 2 shows various plots of plating rate as a function of pH for the preferred composition set forth in Table I, in which:

- (i) the pH was initially set to a particular value (denoted by the square dot in each part of FIG. 2) by utilizing the appropriate concentration of ammonium hydroxide required to achieve this initial value of pH; and
- (ii) the pH was then increased above the initial value by adding a strong base such as lithium hydroxide (FIG. 2a), sodium hydroxide (FIG. 2b), potassium hydroxide (FIG. 2c), or tetraethylammonium hydroxide (FIG. 2d) to the bath.

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The resultant variation of plating rate as a function of pH, where the pH is modified by each of these bases, is shown in FIG. 2. It is seen that over a pH range of approximately one unit, the variation of plating rate with pH is approximately one-fourth as great as that exhibited by the preferred composition (see FIG. 1) containing only ammonium hydroxide as a source of hydroxyl ions.

Briefly, then, my invention is employed by preparing an electroless plating bath comprising (i) a nickel salt, (ii) a source of hypophosphite ions, (iii) a nickel ion complexing agent such as a pyrophosphate anion, and (iv) a concentration of ammonium hydroxide sufficient to adjust the pH of the plating bath to an initial value corresponding to the desired plating rate. The initial value of pH corresponding to a particular plating rate may be ascertained by reference to a curve such as that of FIG. 1.

The plating bath, having been set to an initial pH value, is then stabilized against variation of plating rate with pH by adding a (preferably strong) base (not containing ammonium $(\text{NH}_4)^+$ ions) to the plating solution. The strong base increases the pH of the solution without substantially affecting the plating rate. The net result is that the plating rate is substantially insensitive to any subsequent reduction in pH which takes place while the layer of electroless nickel-phosphorus is being deposited onto a substrate from the plating solution.

While the examples I have given are directed to the use of lithium hydroxide, sodium hydroxide, potassium hydroxide and tetraethylammonium hydroxide as the strong bases, other bases may be used. In particular, I prefer to employ alkali metal hydroxides.

I prefer to maintain both the initial (as set by the concentration of ammonium hydroxide) and final (as set by the concentration of base added to the plating solution after the initial setting) values of pH in the range of 9.0 to 11.5. Substantially lower values of pH than 9.0 tend to cause the formation of undesirable precipitates, while higher values of pH than 11.5 tend to introduce other undesirable side reactions.

A particular advantage of my process is that the electroless plating process may be carried out at room temperature, thus alleviating a number of problems inherent in prior art plating processes. In particular, my room temperature process alleviates the necessity for accurate temperature control (since room temperature is normally stable within 2° or 3° C.), reduces the ammonia loss to a negligible value, and decreases the percentage of phosphorus in the deposited nickel-phosphorus layer. The percentage of phosphorus (by weight) in the layers deposited by my process, using the aforementioned preferred composition, is approximately 2 to 3 percent, as compared with 5 to 15 percent for the elevated temperature processes heretofore known.

Where my process is employed to deposit a nickel-phosphorus layer on a non-metallic or non-catalytic substrate, it is necessary to first activate the substrate by forming a film of a catalytic material thereon.

For example, I have successfully employed the process of my invention to electrolessly plate, at room temperature, a nickel-phosphorus layer on a high alumina content ceramic substrate by first immersing the substrate in an aqueous sensitizing solution comprising (i) 70 grams per liter of stannous chloride, having the formula $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ and (ii) 40 cc. per liter of 37% (by weight) hydrochloric acid.

After immersion in the sensitizing solution, I carefully rinsed the substrate in water and immersed it in an aqueous activating solution comprising (i) 1 gram per liter of palladium chloride having the formula PdCl_2 and (ii) 1 cc. per liter of 37% (by weight) hydrochloric acid. The substrate was again carefully rinsed in water and then dried for several minutes at 40° to 50° C. in a vacuum. The substrate was immersed in each of the (sensitizing and activating) solutions for a non-critical period of about one minute.

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The resultant processed substrate was readily susceptible to room temperature electroless nickel deposition according to my process.

I have also discovered that at room temperature the high concentrations of sulfate (or chloride), sodium and phosphite ions introduced by regenerating the plating bath (i.e., by the addition of nickel sulfate or nickel chloride, and sodium hypophosphite) are not detrimental, and in fact, result in a slight increase in plating rate.

This phenomenon appears to be due at least in part to the inverse solubility characteristic of nickel phosphite (NiHPO_3). That is, nickel phosphite, which forms an undesirable precipitate, has higher solubility at room temperature than at the elevated temperatures employed in the electroless deposition processes heretofore known.

It will be appreciated that although my invention is primarily adapted for use at room temperature, it may also be employed to render electroless nickel plating baths of the type I have described relatively insensitive to variations in pH at elevated temperatures.

As long as the nickel and hypophosphite ion concentrations in the electroless plating bath are maintained constant, my invention provides a substantially fixed plating rate for electroless deposition of a nickel-phosphorous layer, even though the pH of the bath drops as the deposition progresses.

What is claimed is:

1. A process for electrolessly depositing a nickel-phosphorus layer on a substrate surface, said process normally involving a decrease in pH of the plating bath as deposition progresses and comprising the steps of:

preparing an aqueous plating bath consisting essentially of (i) 10 to 50 gms./liter of a nickel salt, (ii) 10 to 50 gms./liter of a source of hypophosphite ions, (iii) 10 to 100 gms./liter of sodium pyrophosphate, and (iv) 5 to 40 cc./liter of 58% by weight ammonium hydroxide to adjust the pH of the bath to a predetermined value;

adding to said bath a quantity of a base selected from the class consisting of sodium hydroxide, potassium hydroxide, lithium hydroxide and tetraethylammonium hydroxide to increase said pH, said predetermined and increased values of pH being in the range of 9.0 to 11.5, and

immersing said substrate in said bath to deposit said layer on said surface, so that said plating rate remains relatively unaffected by the decrease in pH of said bath as said layer deposition progresses.

2. A process according to claim 1, wherein said layer is deposited from said solution in the presence of a catalyst, comprising the additional step of, prior to said immersing step, forming a film comprising said catalyst on said substrate surface.

3. A process according to claim 2, wherein said film forming step and said immersing step are performed at room temperature, and said forming step comprises:

immersing said surface in an aqueous sensitizing solution comprising (i) stannous chloride, having the formula $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and (ii) hydrochloric acid; and subsequently immersing said surface in an aqueous activating solution comprising (i) palladium chloride, having the formula PdCl_2 and (ii) hydrochloric acid.

4. A process according to claim 1, wherein said immersing step is performed at room temperature.

5. A process according to claim 4, wherein:

said nickel salt is selected from the group consisting of (i) nickel chloride, having the formula $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and (ii) nickel sulfate, having the formula $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;

said source comprises sodium hypophosphite, having the formula $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and

said complexing agent comprises sodium pyrophosphate having the formula $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$.

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6. A process according to claim 5, wherein said sodium hypophosphite, sodium pyrophosphate and nickel salt concentrations are 25 grams/liter of bath, 50 grams/liter of bath and 25 grams/liter of bath respectively.

7. A process according to claim 5, comprising the additional step of:

after said immersing step, regenerating the bath by adding additional quantities of said nickel salt and said sodium hypophosphite to maintain said bath substantially at said specified plating rate without precipitating any undesired phosphite compound.

8. An aqueous electroless nickel plating bath, each liter of bath consisting essentially of:

10 to 50 grams of a nickel salt selected from the group consisting of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$;
10 to 50 grams of $\text{NaH}_2\text{PO}_3 \cdot \text{H}_2\text{O}$;
10 to 100 grams of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$;
5 to 40 cc. of concentrated ammonium hydroxide; and
a base selected from the group consisting of an alkali

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metal hydroxide and $(\text{C}_2\text{H}_5)_4\text{NOH}$, in sufficient quantity so that the bath initially exhibits a pH between about 9.0 and 11.5.

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