

**METHOD AND COMPOSITION FOR BRIGHT ELECTROLESS NICKEL
DEPOSITION**

THE PRESENT INVENTION relates to an improved method and plating solution for carrying out the electroless or chemical deposition of a nickel alloy on a metallic or non-metallic substrate.

Electroless nickel plating is a process involving the controlled autocatalytic reduction of nickel ions by hydrogen atoms adsorbed on the surface of a substrate. The resulting deposit is essentially an alloy of nickel and phosphorus (as hypophosphite salt is normally used as a reducing agent). In addition, trace amount of other elements may be brought into the deposits if compounds thereof are added as stabilisers or brighteners.

Electroless nickel-phosphorus deposits display excellent corrosion and wear resistance. No electrical current is applied in this plating process, and so nickel-phosphorus can be deposited uniformly on metallic or non-metallic surfaces of complex shape. Because of this, electroless nickel-phosphorus coatings have found widespread applications in many fields such as the aerospace, automobile, microelectronics, chemical, petrochemical, food, and precision engineering industries.

The essential principles and applications of electroless nickel-phosphorus depositions are known in the art, and may be found in, for example, 'Electroless Nickel Plating' by W. Riedel or 'Electroless Plating: Fundamentals and Applications' by G.O. Mallory and J.B. Hajdu.

One of the problems typically associated with electroless nickel-phosphorus plating is micropitting of the nickel deposited on a very smooth surface as a result of hydrogen evolution during the plating process. Despite measures to avoid this, which may include agitation of the plating solution, movement of a part being plated, addition of surfactants and so on, micropitting is in many cases the limiting factor for special engineering applications of electroless nickel-phosphorus coatings that demand a deposit with a smooth and bright surface finish.

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The most effective remedy for this problem has been found to be to reduce the surface tension of the plating solution by the addition of carefully selected surfactants to it. The lowering of the surface tension of the plating solution leads to the rapid discharge of hydrogen bubbles. Surfactants known in the art include alkyl or aryl sulphonates, and fluorocarbons. However, even with the use of such surfactants, micropitting can still occur.

It is an object of the present invention to provide a plating solution and method for electroless nickel deposition which results in reduced micropitting and a brighter finish than existing solutions and methods.

Accordingly, in one aspect, the present invention provides an aqueous plating solution for use in depositing an electroless nickel coating on a substrate, which solution contains: a source of nickel ions; a reducing agent; and an anti-pitting agent in the form of a water-soluble styrenic compound.

The source of nickel ions may be a soluble nickel salt, such as a nickel sulphate.

Preferably, the concentration of the source of nickel ions is from 5.2 g/l to 6.8 g/l.

Advantageously, the concentration of the source of nickel ions is substantially 6.0 g/l.

The reducing agent may be an alkali metal hypophosphite, such as sodium hypophosphite.

Preferably, the concentration of the reducing agent is from 20 g/l to 40 g/l and, advantageously, is about 28 g/l.

The water-soluble styrenic compound corresponds to the general formula:



where Z is a hydrophilic group.

In preferred embodiments of the invention, Z is one of the polar chemical groups consisting of: sulphonate; ethylene glycol oligomer; carboxylate; quaternary ammonium; primary amide; or phosphate.

The concentration of the water-soluble styrenic compound is preferably from 0.1 to 10 micro mol/l.

Desirably, the solution contains a metal complexing agent which may, for example, be selected from the group consisting of lactic acid, malic acid and mixtures thereof. Suitably, the metal complexing agent is present in stoichiometric excess over the level of nickel in the solution.

The solution may contain a pH adjusting agent which may, for example, be selected from the group consisting of borax, adipic acid and mixtures thereof.

The solution may contain a stabilising agent selected, for example, from the group consisting of ions of lead, cadmium, zinc, silver, IO_3^- ; and SCN^- , and combinations thereof.

Advantageously, the concentration of the stabilising agent is between 1 and 50 ppm.

In another aspect, the invention provides a method of depositing an electroless nickel coating on a substrate surface, which method comprises the step of at least partially immersing the substrate in a plating solution according to the present invention.

Advantageously, the method further comprises the step of maintaining the plating solution at a temperature of from 85°C to 95°C.

The method may further comprise the step of maintaining the plating solution at a pH of from 4.5 to 5.5. Preferably, the pH is maintained at substantially 5.

Conveniently, the pH of the plating solution is controlled by adding to the solution at least one acid or at least one base or a combination thereof.

Preferably, the pH of the plating solution is controlled by adding sulphuric acid or ammonium hydroxide or a combination thereof.

Desirably, the method further comprises the step of cleaning the surface of the substrate prior to at least partial immersion of the substrate in the plating solution.

Advantageously, where the substrate is an aluminium substrate, the method further comprises the step of zincation treatment of the substrate prior to at least partial immersion of the substrate in the plating solution.

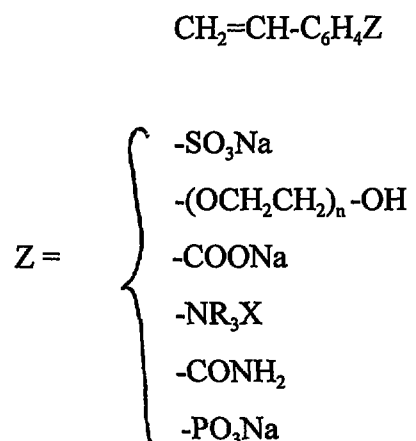
In order that the invention may be more readily understood, an Example of nickel plating using a conventional plating solution will be compared with Examples of nickel plating using plating solutions which embody the present invention and which are described in more detail hereinafter.

In general, an electroless nickel plating bath embodying the present invention contains the following constituents dissolved in distilled water:

- (a) a soluble source of nickel ions, such as nickel sulphate which is readily available or any other soluble nickel salt. The concentration of nickel ions can range from 5.2 to 6.8 g/l.
- (b) a soluble source of a reducing agent which may be an alkali metal hypophosphite, such as sodium hypophosphite with a concentration of from 20 to 40 g/l.
- (c) a complexing agent for nickel ions which may be selected from lactic acid, malic acid or a mixture of these.
- (d) a pH adjusting agent, such as borax and adipic acid which can be used as buffers to prevent rapid pH changes.

- (e) a stabilising agent which may be selected from ions of lead, cadmium, zinc, silver, IO_3^- and SCN^- or combinations of these at concentration levels of from 1 to 50 ppm.
- (f) a water-soluble styrenic compound which serves as an anti-pitter with a concentration between 0.1 to 10 micro mol/l.

The water-soluble styrenic compound corresponds to the general structure



Where Z is a hydrophilic head which can be one of the polar chemical groups consisting of sulphonate, ethylene glycol oligomer, carboxylate, quaternary ammonium, primary amide and phosphate.

The basic structure of the water-soluble styrenic compounds has a hydrophobic styrenyl group that links with a water-soluble group. Although the styrenyl group has only eight carbon atoms, its conjugated structure (the double bond and the benzene ring are coplanar) endows it with much stronger hydrophobicity than other C-8 CHAINS. Since surface or interfacial tension reduction depends upon the replacement of solvent molecules at the interface by surfactant molecules, the efficiency of a surfactant in reducing surface tension should reflect the concentration of the surfactant at the interface relative to that in the bulk liquid phase. For surfactants in aqueous solution, the efficiency increases with increase in the hydrophobic character of the surfactant. Hence, the styrenic compounds have a higher surface-adsorption concentration than other surfactants having a C-8 chain as their longest chain. Whilst a comparable surface adsorption could be achieved by the use of a surfactant with a long enough carbon chain, such a surfactant would also have a high foaming ability,

which is a drawback as far as electroless plating is concerned. Thus, it has been found that water soluble styrenyl surfactants in an electroless nickel plating solution can achieve a high surface-adsorption concentration without producing undesirable foam, resulting in a bright electroless nickel-phosphorus deposit on the substrate surface.

The plating solution is maintained at a temperature of from 85 to 95°C and at a pH of from 4.5 to 5.5.

For catalytic metallic substrates, the deposition can be carried out by immersing the part, after proper cleaning procedure, in the solution under the specified operating conditions. For an aluminium substrate, such as the aluminium bond pad on silicon wafers, zincation treatment is performed prior to the electroless nickel plating to ensure good adhesion between the substrate and the nickel-phosphorus deposit. For non-conductive and/or non-catalytic metallic substrates, activation is required before the plating process, as known to those skilled in the art.

Example 1. - Plating in accordance with a conventional plating solution and method.

A 500 millilitre electroless plating bath was prepared, containing an aqueous plating solution with: 26 g/l of nickel sulphate hexahydrate; 28 g/l of sodium hypophosphite monohydrate; 15 g/l of lactic acid; 14 g/l of malic acid; 6 g/l of borax; 10 g/l of sodium acetate; 2 mg/l of cadmium acetate and 2 mg/l of lead acetate. The pH of the solution was adjusted to 5.0 using ammonium hydroxide. The temperature of the plating bath was controlled to 90 +/- 1°C. The bath was agitated using a magnetic stirrer. A sample in the form of a polished and cleaned brass sheet with a total surface area of 0.75 dm² was immersed in the said plating bath and subjected to electroless nickel-phosphorus deposition for 1 hour. The surface of the resulting electroless nickel-phosphorus deposit on the brass sheet was examined visually as well as under a scanning electron microscope (SEM). Micropits were observed with an average density of greater than 40 pits/mm², and the sizes of the micropits were as large as a few micron-meters observed under SEM.

Example 2. - Plating in accordance with a first embodiment of the present invention.

A series of 500 millilitre electroless nickel plating baths were prepared, each with the same composition as that given in Example 1 but with the addition of 4-styrenesulphonic acid-sodium salt at various concentrations. Polished brass samples were plated using these baths under identical conditions to those described in Example 1 and the resultant surface finish of the electroless nickel-phosphorus deposit was examined. It was found that the number of micropits in a given surface area was greatly reduced by the addition of 4-styrenesulphonic acid - sodium salt with concentration in the range of 0.1 to 10 micro mol/l. When the concentration of 4-styrenesulphonic acid - sodium salt is at 1 micro mol/l, a visually pit-free bright electroless nickel-phosphorus deposit is obtained. The density of micropits under SEM was 5 pits/mm² and the pit size was typically in the sub-micron range.

Example 3. - Plating according to a second embodiment of the present invention

(1) Synthesis of 4-vinylbenzyltriethyl ammonium chloride (VBTEAC) - a styrenic cationic surfactant.

In a 100-ml flask, equimolar amounts of 4-vinylbenzyl chloride and triethylamine were allowed to react in N,N'-dimethylformamide under stirring at ambient temperature for 24 hours. The formed VBTEAC solid was then precipitated by introducing a large excess of ether into the flask. After being washed several times in ether, the solid was filtered and dried.

(2) Testing

A series of 500 millilitre electroless nickel plating baths were prepared, each containing plating solution with the same composition as that given in Example 1 but with the addition of the synthesised VBTEAC in various concentrations. Polished and cleaned brass sheets were plated using these baths under conditions identical to those described in Example 1 and the resultant surface finish of the electroless nickel-phosphorus deposit was examined. It was found that the number of micropits in a given surface area was also largely reduced by the addition of the VBTEAC with concentration in the range of 0.1 to 10 micro mol/l. When the

concentration of the VBTEAC was at 1 micro mol/l, micropits were observed with an average density of less than 17 pits/mm². The sizes of the pits were within the sub-micron range.

Example 4. - Plating in accordance with a third embodiment of the present invention

(1) Synthesis of dimethylhydroxyethyl(4-vinylbenzyl)-ammonium chloride (DMEVBAC)
- a styrenic cationic surfactant.

N,N-Dimethylethanol amine (3.56 g, 40 mmol) was dissolved in 15 ml of DMF (dimethyl formamide). After this the solution was cooled to about 5°C in an ice-water bath, 4-vinylbenzyl chloride (6.24g, 41 mmol) was added dropwise with magnetic stirring and the system was kept, under stirring, at the same temperature for about 30 min or longer. White crystals precipitated and were washed with stirring in 30 ml of ethyl ether and filtered in a Buchner funnel. This operation was repeated three times. After vacuum drying, 6.5 g of white powder was obtained.

(2) Testing

A series of 500 millilitre electroless nickel plating baths were prepared, each containing a plating solution with the same composition as that given in Example 1 but with synthesised DMEVBAC added in various concentrations. Polished brass samples were plated using these baths under identical conditions to those described in Example 1 and the resultant surface finish of the electroless nickel-phosphorus deposits was examined. It was found that the number of micropits in a given surface area was also largely reduced by the addition of the DMEVBAC at a concentration in the range of 0.1 to 10 micro mol/l. When the concentration of the DMEVBAC was at 1 micro mol/l, micropits were observed with an average density of less than 10 pits/mm². The sizes of the pits were within the sub-micron range.

Example 5. - Plating in accordance with a further embodiment of the invention.

(1) Synthesis of 4-vinylbenzylpolyoxyethylene (VBPEG) - a styrenic non-ionic surfactant.

Poly(ethylene glycol), with $\bar{M} = 600$, (6g) was dissolved in 20 ml of anhydrous THF (tetrahydrofuran). Sodium hydride (0.7g) was then introduced into the solution under magnetic stirring. When the bubbling of H_2 ceased, 4-vinylbenzyl chloride (1.52g, 10 mmol) was added into the reaction mixture very slowly. After addition, the system was allowed to reflux for two hours under stirring. Then the NaCl precipitate was filtered and the THF solvent was evaporated. An oil-like product VBPEG was obtained.

(2) Testing

A series of 500 millilitre electroless nickel plating baths were prepared, each containing a plating solution with the same composition as that given in Example 1, but with the VBPEG added in various concentrations. Polished and cleaned brass samples were plated using these baths under identical conditions to those described in Example 1 and the resultant surface finish of the electroless nickel-phosphorus deposit was examined. It was found that the number of micropits in a given surface area was significantly reduced by the addition of the VBPEG at a concentration in the range of 0.1 to 10 micro mol/l.

When the concentration of the VBPEG was at 0.5 micro mol/l, micropits were observed with an average density lower than 20 pits/mm². The sizes of the pits were within the sub-micron range.

Example 6. - Plating in accordance with a fifth embodiment of the present invention

A 500 millilitre electroless nickel bath was prepared, containing an aqueous plating solution with 26 g/l nickel sulphate hexahydrate; 28 g/l sodium hypophosphite monohydrate; 20 g/l lactic acid; 14 g/l malic acid; 6 g/l of borax; 10 g/l of sodium acetate; 4 g/l of glycine; 1 g/l of adipic acid; 2 mg/l of cadmium acetate; 2 mg/l of lead acetate; 1 mg/l of potassium thiocyanate; and 20 mg/l potassium iodate; in further combination with 1 micro mol/l of 4-styrenesulphonic acid - sodium salt. The bath was adjusted and maintained at a pH of 4.8 to 5.2 with ammonium hydroxide or 25% sulphuric acid and at a temperature in the range of 89 to 91°C for a prolonged test. The bath was periodically replenished to maintain constant concentrations of nickel and hypophosphite ions for more than 10 metal turnovers. By "metal turnover" is meant a plating cycle when all of the original nickel metal content in the bath has

been consumed and has been replenished. At various times during the operating life of the bath, polished and cleaned brass sheets were plated in the bath in accordance with the procedure set forth in Example 1 and the resultant surface finish of the deposit was visually examined. Deposits of electroless nickel-phosphorus with bright surfaces and few or no micropits were obtained throughout the entire bath life tests. The deposition speed of the bath was in the range of 18-25 $\mu\text{m/hr}$. This example demonstrated that the 4-styrenesulphonic acid - sodium salt served as an anti-pitting agent without any detrimental effects on the bath life of the electroless nickel plating bath.

It is envisaged that plating solutions and methods embodying the present invention will be particularly useful in producing bright electroless nickel coatings with smooth surfaces for decorative applications or technological applications such as silicon wafer underbump metalisation.



CLAIMS:

1. An aqueous plating solution for use in depositing an electroless nickel coating on a substrate, which solution contains: a source of nickel ions; a reducing agent; and an anti-pitting agent in the form of a water-soluble styrenic compound.
2. A solution according to Claim 1, wherein the source of nickel ions is a soluble nickel salt.
3. A solution according to Claim 2, wherein the nickel salt is a nickel sulphate.
4. A solution according to any preceding Claim, wherein the concentration of the source of nickel ions is from 5.2 g/l to 6.8 g/l
5. A solution according to Claim 4, wherein the concentration of the source of nickel ions is substantially 6.0 g/l.
6. A solution according to any preceding Claim, wherein the reducing agent is an alkali metal hypophosphite.
7. A solution according to Claim 6, wherein the alkali metal hypophosphite is sodium hypophosphite.
8. A solution according to any preceding Claim, wherein the concentration of the reducing agent is from 20 g/l to 40 g/l.
9. A solution according to Claim 8, wherein the concentration of the reducing agent is about 28 g/l.
10. A solution according to any preceding Claim, wherein the concentration of the water-soluble styrenic compound is from 0.1 to 10 micro mol/l.

11. A solution according to any preceding Claim, wherein the water-soluble styrenic compound corresponds to the general formula:



where Z is a hydrophilic group.

12. A solution according to Claim 11, wherein Z is one of the polar chemical groups consisting of: sulphonate; ethylene glycol oligomer; carboxylate; quaternary ammonium; primary amide; or phosphate.
13. A solution according to Claim 12, wherein the water-soluble styrenic compound is 4-styrenesulphonate sodium salt.
14. A solution according to Claim 12, wherein the water-soluble styrenic compound is 4-vinylbenzyltriethyl ammonium chloride.
15. A solution according to Claim 12, wherein the water-soluble styrenic compound is dimethylhydroxyethyl(4-vinylbenzyl)-ammonium chloride.
16. A solution according to Claim 12, wherein the water-soluble styrenic compound is 4-vinylbenzylpolyoxyethylene.
17. A solution according to any one of Claims 13 to 15, wherein the 4-styrenesulphonate sodium salt, 4-vinylbenzyltriethyl ammonium chloride, or dimethylhydroxyethyl(4-vinylbenzyl)-ammonium chloride is present at a concentration of about 1 micro mol/l.
18. A solution according to Claim 16, wherein the 4-vinylbenzylpolyoxyethylene is present at a concentration of about 0.5 micro mol/l.



19. A solution according to any preceding Claim, containing a metal complexing agent.
20. A solution according to Claim 19, wherein the metal complexing agent is selected from the group consisting of lactic acid, malic acid and mixtures thereof.
21. A solution according to Claim 19 or 20, wherein the metal complexing agent is present in stoichiometric excess over the level of nickel in the solution.
22. A solution according to any preceding Claim, containing a pH adjusting agent.
23. A solution according to Claim 22, wherein the pH adjusting agent is selected from the group consisting of borax, adipic acid and mixtures thereof.
24. A solution according to any preceding Claim, containing a stabilising agent.
25. A solution according to Claim 24, wherein the stabilising agent is selected from the group consisting of ions of lead, cadmium, zinc, silver, IO_3^- and SCN^- and combinations thereof.
26. A solution according to Claim 24 or 25, wherein the concentration of the stabilising agent is from 1ppm to 50ppm.
27. A method of depositing an electroless nickel coating on a substrate surface, which method comprises the step of at least partially immersing the substrate in a plating solution according to any preceding Claim.
28. A method according to Claim 27, further comprising the step of maintaining the plating solution at a temperature of from 85°C to 95°C.
29. A method according to Claim 27 or 28, further comprising the step of maintaining the solution at a pH of from 4.5 to 5.5.



30. A method according to Claim 29, comprising maintaining the pH of the solution in the bath at substantially 5.
31. A method according to Claim 29 or 30, wherein the step of controlling the pH of the solution in the bath is performed by adding to the solution at least one acid or at least one base or a combination thereof.
32. A method according to Claim 31, wherein the step of controlling the pH of the solution in the bath is performed by adding to the solution sulphuric acid or ammonium hydroxide or a combination thereof.
33. A method according to any one of Claims 27 to 32, further comprising the step of cleaning the surface of the substrate prior to at least partial immersion of the substrate in the plating solution.
34. A method according to any one of claims 27 to 33, wherein the substrate is metallic.
35. A method according to any one of Claim 34, wherein the substrate is an aluminium substrate and the method further includes the step of zincation treatment of the substrate prior to immersion in the plating solution.
36. A method according to any one of Claims 27 to 33, wherein the substrate is non-metallic.
37. A substrate having an electroless nickel coating produced by the method of any one of Claims 27 to 36.