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3,738,849

CHEMICAL PLATING SOLUTIONS

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16 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous chemical plating solution for depositing a metal such as nickel, cobalt, copper or iron on a catalytic substrate, using a reducing agent such as formaldehyde, sodium hypophosphite or a borane, particularly an alkali metal borohydride, is stabilized against decomposition by containing therein an alkali metal cyanoborohydride.

BACKGROUND OF THE INVENTION

Field of invention

This invention relates to chemical plating solutions and processes and, more particularly, to stabilized aqueous chemical plating solutions and processes for chemical plating using such solutions.

Prior art

The electroless plating or deposition of metals or alloys by the chemical reduction of metal ions on the metal or plastic article to be plated has been known for some time. As coating metals, nickel and cobalt deposits are frequently mentioned, but other metals such as copper, iron, zinc, molybdenum and others can also be deposited either solely or as alloys. Known reducing agents are, besides formaldehyde and alkali metal hypophosphites, boron compounds such as the alkylamine boranes described in U.S. Pat. 3,338,726 issued to Talivaldis Berzins on Aug. 29, 1967, and alkali metal borohydrides described in U.S. Pat. 3,096,182 issued to Talivaldis Berzins on July 2, 1963.

To overcome the problem of plating bath stability in baths using amine boranes and borohydrides as reducing agents, the prior art describes the use of bath stabilizers, U.S. Pat. 3,234,031 issued to Eberhard Zirngiebl and Heinz Gunter on Feb. 8, 1966, describes the use of various organic sulfur compounds as stabilizers, U.S. Pat. 3,062,666 issued to Henry G. McLeod on Nov. 6, 1962, describes the use of glycolates as stabilizers and lead salts as auxiliary stabilizers and U.S. Pat. 3,295,999 issued to Heinz Gunter Klein and Eberhard Zirngiebl on Jan. 3, 1967, describes the use of various metal salts, particularly thallium nitrate and arsenate, as stabilizers. While these materials are effective stabilizers, the coating is adversely affected by codeposition of sulfur, and lead and thallium tend to pose toxicity problems in handling baths and in some final coatings.

SUMMARY OF THE INVENTION

According to the present invention there is provided an aqueous chemical plating solution comprising water, reducible metal ions, a complexing agent for the metal ions and a reducing agent for said metal ions and having the improvement in which the solution contains an alkali metal cyanoborohydride in an amount effective to stabilize the solution against decomposition, said solution being at a pH greater than about 4.5.

There is also provided a process for depositing a metal on a substrate by contacting a catalytic substrate with the above aqueous plating solution.

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DETAILED DESCRIPTION OF THE INVENTION

The plating of a metal on a catalytic surface using various chemical plating solutions is well known in the art. For instance, the aforesaid U.S. Pats. 3,338,726 and 3,096,182 describe in detail the use of various borane compounds such as alkali metal borohydrides and alkylamine boranes as reducing agents in the chemical plating of catalytic substrates with nickel and cobalt. The contents of these patents are hereby incorporated by reference. Other reducible metal ions can be reductively plated either alone or as alloys by these reducing agents including iron, molybdenum, zinc and precious metals such as gold and platinum. Typical of well-known copper and other metal reducing agents are the alkali metal hypophosphites and formaldehyde. Chemical plating solutions using formaldehyde and sodium hypophosphite have been used commercially for a number of years.

It has now been found that such plating solutions can be stabilized against decomposition by having present in the solution an alkali metal cyanoborohydride in an amount effective to stabilize the solution against decomposition. It has been found that such a compound exerts such a stabilizing effect on the solution that the process of chemical plating can be executed continuously while minimizing the adverse effects of stabilizers known in the art. For example, the alkali metal cyanoborohydride does not form significant by-products which co-deposit with the plated metal. It is preferred to use the cyanoborohydride at a concentration of about 0.01 to 1 gram per liter, depending upon the bath used. A most preferred concentration is 0.02 to 0.5 gram per liter. Since sodium cyanoborohydride is commercially available, it is preferred; however, potassium cyanoborohydride is also suitable. The pH of the solution should be greater than about 4.5 since at a lower pH the sodium cyanoborohydride tends to decompose.

A particularly preferred chemical plating solution consists essentially of an aqueous solution of about 10 to 100 grams per liter of a water-soluble nickel or cobalt salt, about 25 to 100 grams per liter of the complexing agent, about 0.1 to 1 gram per liter of sodium borohydride, an amount of alkali metal hydroxide, particularly sodium hydroxide, to a pH over 4.5, preferably in the range of about 10 to 14, and about 0.05 to 0.5 gram per liter of alkali metal cyanoborohydride.

The invention can be further understood by the following examples in which parts and percentages are by weight unless otherwise indicated:

EXAMPLE 1

A series of aqueous plating baths (pH 14) comprising 30 g./l. nickel chloride.6H₂O, 40 g./l. sodium hydroxide, 60 g./l. ethylene diamine and 0.5 g./l. sodium borohydride (SBH) was brought to 92° C. with varying amounts of sodium cyanoborohydride (SCB) added. Observations were made on bath stability by measuring plating efficiency as a function of plating time. No additional SCB was added except for the initial charge.

Test No.	SCB, g./l.	Plating efficiency, g. Ni/g. SBH			Plating rate, mls./hour, last hour
		1st hr.	2d hr.	6th hr.	
1	0.10	1.06	1.02	1.01	0.29
2	0.04	1.44	1.02	-----	0.18
3	0.13	1.13	-----	-----	0.35
4	-----	0.22	0.26	0.10	0.10

A 0.5 g. coating was prepared on a stainless steel coupon from the bath of Example 1 bath stabilized with 0.15 g./l. sodium cyanoborohydride. The coating was stripped

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in concentrated nitric acid and analyzed for carbon and nitrogen content. The result was 112 p.p.m. carbon and 64 p.p.m. nitrogen in the nitric acid solution.

EXAMPLE 3

An aqueous plating bath comprising 79 g./l. copper sulphate.6H₂O, 10 g./l. citric acid.H₂O, aqueous ammonia to pH 6.5, 2.5 g./l. dimethyl amine borane was divided into 2 equal portions. One portion received 0.10 g. sodium cyanoborohydride as stabilizer. The unstabilized portion decomposed spontaneously at 75° C. within 2 hours of coating steel panels. The portion containing SCB was still operative after 6 hours with only minor reductions in plating efficiency and plating rate.

EXAMPLE 4

An aqueous plating bath comprising 79 g./l. copper sulfate.5H₂O, 395 g./l. potassium sodium tartrate, 74 g./l. sodium hydroxide and 10 g./l. formaldehyde was divided into 2 equal portions. One portion received 0.04 g./l. sodium cyanoborohydride (SCB) as stabilizer. Formaldehyde was added over a 6 hr. period in amounts sufficient to exhaust completely the copper content of each bath. Baths were operated at 30° C. and pH greater than 14. The unstabilized bath portion deposited 7.1 grams copper on steel panels but produced another 13.5 grams of nonuseful copper powder. Further, the coating was both rough and nonadherent. The bath portion containing SCB deposited 18.8 grams copper on steel and only 1.3 grams of copper powder. The coating was adherent and smoother than that from the control bath. This example shows that SCB is effective in stabilizing typical electroless copper baths against spontaneous decomposition.

EXAMPLE 5

An aqueous plating bath comprising 30 g./l. nickel chloride.6H₂O, 100 g./l. sodium citrate, 50 g./l. ammonium chloride, and 10 g./l. sodium hypophosphite was divided into 2 equal portions. One portion received 0.02 g./l. sodium cyanoborohydride (SCB) as stabilizer. Sodium hypophosphite was added over a 4 hr. period in amounts sufficient to exhaust completely the nickel content of each bath. The baths were operated at 90° C. and pH 9.0. The unstabilized bath portion deposited 6.0 grams nickel on steel panels while producing another 1.9 grams of non-useful nickel powder. The bath portion containing SCB deposited 7.7 grams nickel on steel and produced only 0.2 gram nickel powder. The coating was smoother and brighter than that from the control bath. This example shows that SCB is effective in stabilizing typical electroless nickel-phosphorus baths against spontaneous decomposition.

What is claimed is:

1. In an aqueous chemical plating solution comprising water, reducible metal ions selected from the group consisting of nickel, cobalt and copper ions, a complexing agent for the metal ions and a reducing agent for said metal ions selected from the group consisting of a borane compound, alkali metal hypophosphite and formaldehyde; the improvement in which the solution contains an alkali metal cyanoborohydride in an amount effective to stabilize the solution against decomposition within the range of

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0.01–0.5 gram per liter of said solution, said solution being at a pH greater than about 4.5.

2. The plating solution of claim 1 wherein the reducing agent is a borane compound selected from the group consisting of an alkali metal borohydride and an alkylamine borane.

3. The plating solution of claim 2 wherein the concentration of the alkali metal cyanoborohydride is within the range of 0.02 to 0.5 gram per liter.

4. The plating solution of claim 3 wherein the metal ions are nickel or cobalt, and the borane compound is sodium borohydride.

5. The plating solution of claim 3 wherein the metal ions are nickel or cobalt and the borane compound is dimethylamine borane.

6. The plating solution of claim 1 wherein the reducing agent is an alkali metal hypophosphite and the metal ions are nickel.

7. The plating solution of claim 1 wherein the reducing agent is formaldehyde and the metal ions are copper.

8. In a process for depositing a metal on a substrate, the improvement which comprises contacting a catalytic substrate with the aqueous plating solution of claim 1.

9. The process of claim 8 wherein the reducing agent is a borane compound selected from the group consisting of an alkali metal borohydride and an alkylamine borane.

10. The process of claim 8 wherein the concentration of the alkali metal cyanoborohydride is within the range of 0.02 to 0.5 gram per liter.

11. The process of claim 10 wherein the metal ions are nickel or cobalt and the borane compound is sodium borohydride.

12. The process of claim 10 wherein the metal ions are nickel or cobalt and the borane compound is dimethylamine borane.

13. The process of claim 8 wherein the reducing agent is an alkali metal hypophosphite and the metal ions are nickel.

14. The process of claim 8 wherein the reducing agent is formaldehyde and the metal ions are copper.

15. A process for stabilizing an aqueous nickel or cobalt chemical plating solution against decomposition, said solution containing an alkali metal borohydride as the reducing agent which comprises maintaining in the solution an alkali metal cyanoborohydride in an amount effective to stabilize the solution against decomposition.

16. The plating solution of claim 1 consisting essentially of about 10 to 100 grams per liter of a water-soluble nickel or cobalt salt, about 25 to 100 grams per liter of the complexing agent, about 0.1 to 1 gram per liter of sodium borohydride, an amount of alkali metal hydroxide to give a pH in the range of 10 to 14 and about 0.05 to 0.5 gram per liter of alkali metal cyanoborohydride.

References Cited

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