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[54] **GOLD ALLOY ELECTROPLATING BATH**

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[58] **Field of Search** ..... 204/43 G, 46 G, 44

[56] **References Cited**

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[57] **ABSTRACT**

An improved bath for the electrolytic deposition of gold or gold alloys on electrically conductive objects contains an alkali metal gold sulfite, a gold alloy metal, an electrically conductive salt, a chelating agent, a water soluble salt of cadmium, a water soluble salt of copper, a water soluble salt of nickel, and a specified organic phosphorus compound. The bath is useful for depositing white gold on conductive objects.

28 Claims, No Drawings

GOLD ALLOY ELECTROPLATING BATH

This invention relates to an improved bath for the electrolytic deposition of gold or gold alloys on electrically conductive objects. More particularly, the improvement comprises employing a water soluble salt of cadmium, a water soluble salt of copper, a water soluble salt of nickel, and an organic phosphorus compound in an aqueous galvanic bath containing an alkali metal gold sulfite, a gold alloy metal, an electrically conductive salt, and a chelating or complexing agent.

Aqueous alkaline electrolytic baths for depositing gold or gold alloys on objects are known. Such baths typically contain the gold as an alkali metal gold sulfite. Arsenic compounds can be added to the bath to improve luster characteristics. Furthermore, such baths can contain a chelating agent, alloying metals and conducting salts (German published application No. 2 042 127). It is not possible with these baths, however, to deposit white gold on objects.

Accordingly, this invention provides an aqueous bath for the electrolytic deposition of gold or gold alloys on electrically conductive objects. More particularly, this invention provides an improvement in such a bath which makes possible the deposition of white gold alloys. The improvement comprises incorporating in the plating bath at least one water soluble salt of cadmium, at least one water soluble salt of copper, at least one water soluble salt of nickel, and at least one chelating or complexing agent. Additionally, the plating bath contains an organic phosphorus compound of either

a. a compound of the formula

$$R^1_{(3-n)} - N[-R - \overset{O}{\overset{\|}{P}} - (OH)_2]_n$$

in which R^1 is a hydrogen atom or about C_1 — C_6 lower alkyl radical, R is about a C_1 — C_6 alkylene radical and n is a whole number of about 1 – 3; or

b. an alkylene diamino tetra-(methyl phosphonic acid), or especially a 1-hydroxyalkylidene-1,1-diphosphonic acid, the alkylene and alkylidene groups of which contain about 1 – 12 carbon atoms, especially about 1 – 6 carbon atoms; or

c. a water soluble salt of the compounds a or b.

Particularly preferred is 1-hydroxy ethylidene-1,1-diphosphonic acid which has the formula

$$CH_3 - \overset{H_2PO_3}{\overset{|}{C}}\overset{H_2PO_3}{} - OH$$

The electroplating bath of this invention has a pH of about 8.5 – 11.

Typical of the alkylene diamino tetra -(methylphosphonic acids) are: ethylene diamino tetra-(methylphosphonic acid) and hexamethylene diamino tetra-(methyl phosphonic acid). Other suitable compounds will be apparent to persons skilled in the art.

The phosphorus compounds employed in the plating bath are typically in quantities of about 0.01 – 10 g/l, preferably about 0.5 – 2 g/l.

The alloying metals contained in the plating bath are well known in the art. These are soluble salts of cadmium, copper and nickel. Preferably, the alloying metals are employed in the form of their sulfates. Besides these metals, the bath can also contain the water soluble salts of indium, cobalt and iron.

The bath typically contains the gold in a quantity of about 1 – 8 g/l, preferably about 3 – 5 g/l, in the form of an alkali metal gold sulfite. The preferred compound is sodium gold sulfite.

Typically, the cadmium is employed in an amount of about 0.1 – 30 g/l, preferably about 8 – 14 g/l. The copper is generally employed in an amount of about 0.001 – 0.5 g/l, preferably about 0.01 – 0.08 g/l. The nickel is typically present in an amount of about 0.001 – 10 g/l, preferably about 4 – 6 g/l. All other alloying metals which might be present are typically employed in amounts of about 0.01 – 10 g/l. The aforementioned quantities are calculated on the basis of the metal in the plating bath.

The chelating and complexing agents present in the plating bath of this invention are well known in the art. Their use in galvanic baths is well known in the art and are described in German published application No. 2 042 127, the entire disclosure of which is incorporated herein by reference. Persons skilled in the art will recognize that the chelating and complexing agents are employed in quantities which will result in the substantially complete complexing of all metals present. While the amount generally employed is typically about 20 – 30 g/l, it is recommended to use an excess. A particularly preferred agent for use in the bath of this invention is ethylene diamino tetra acetate.

The pH of the plating bath of this invention is about 8.5 – 11, preferably about 9.5 – 10.2

Additionally, the bath of this invention can contain conventional conductive salts or free sulfite in quantities of, for example, about 0.5 – 100 g/l. Alkali metal sulfates and alkali metal sulfites are preferred for this purpose.

The electroplating bath of this invention can be operated at temperatures of about 50° – 70° C., preferably about 60° – 65° C. It is advantageous to employ current densities of about 0.1 – 1.0 A/100 cm^2, preferably about 0.5 – 0.8 A/100 cm^2.

The use of conventional wetting agents in the bath of this invention is optional. Such wetting agents, however, are particularly effective when coatings of more than about 5 microns are desired on the object being coated. All of the wetting agents known in the art to be useful in alkaline galvanic baths, and which are stable in such baths can be used. Preferred wetting agents are the fatty alcohol polyglycol ether phosphates and their sodium salts.

This invention will be more clearly understood by reference to the following example in which all parts, proportions, percentages and ratios are by weight unless otherwise specified.

EXAMPLE 1

In one liter of water are dissolved:

5 g gold as sodium gold sulfite
15 g cadmium as cadmium sulfate
2.5 g nickel as nickel sulfate
0.01 g copper as copper sulfate
130 g ethylene diaminotetraacetate as sodium salt and

100 g sodium sulfite.

The pH value is adjusted to 10.0 by addition of a diluted aqueous solution of sodium hydroxide or sulfuric acid. To this solution are added:

2.5 g 1-hydroxyethylidene-1,1-diphosphonic acid, and 0.5 ml of a 10% solution of the sodium salt of a coconut fatty alcohol polyglycolether phosphate (commercial product FORLANON of Henkel).

The bath is operated at a temperature of 58° C. and a current density of 0.5 to 0.7 amperes/100 cm^2 with vigorous agitation of the bath. There is obtained a lustrous deposit of white gold on an object being coated.

As used herein, the term "alkali metal" refers to a metal selected from Group I A of the Periodic Table of Elements.

What is claimed is:

1. In an improved aqueous bath for the electrolytic deposition of gold or gold alloys on electrically conductive objects, said bath containing at least one chelating agent, an alkali metal gold sulfite, at least one gold alloying metal, and about 0.5–100 g/l of at least one electrically conductive salt other than said alkali metal gold sulfite, said gold alloying metal and said chelating agent, the improvement wherein white gold is deposited on said object and wherein said at least one gold alloying metal is at least one water soluble salt of cadmium, at least one water soluble salt of copper, at least water soluble salt of nickel, and additionally there is incorporated in said bath an organic phosphorus compound of either

a. a compound of the formula

$$R^1_{(3-n)} - N\left[-R - \overset{O}{\overset{\|}{P}} - (OH)_2 \right]_n$$

in which R^1 is a hydrogen atom or about a $C_1 - C_6$ lower alkyl radical, R is about a $C_1 - C_6$ alkylene radical, and n is a whole number of about 1 – 3; or

b. an alkylene diamino tetra-(methylphosphonic acid) or a 1-hydroxyalkylidene-1,1-diphosphonic acid, the alkylene and alkylidene groups of which contain about 1–12 carbon atoms, or

c. a water soluble salt of compounds of a or b;

said bath having a pH of about 8.5 – 11, and further wherein said bath contains gold in an amount of about 1 – 8 g/l, cadmium in an amount of about 0.1 – 30 g/l, copper in an amount of about 0.001 – 0.5 g/l, nickel in an amount of about 0.001 – 10 g/l and the organic phosphorous compounds in an amount of about 0.01 – 10 g/l; wherein said at least one chelating agent is other than a, b and c and is present in an amount sufficient to substantially completely complex all of the metals present in the plating bath.

2. Improved bath according to claim **1** in which the organic phosphorus compound is in an amount of about 0.5 – 2 g/l.

3. Improved bath according to claim **2** in which the pH is about 9.5 – 10.2.

4. Improved bath according to claim **2** in which the amount of gold is about 3 – 5 g/l, the amount of cadmium is about 8 – 14 g/l, the amount of copper is about 0.01 – 0.08 g/l and the amount of nickel is about 4 – 6 g/l.

5. Improved bath according to claim **1** in which the water soluble gold alloying metal salts are metal sulfates.

6. Improved bath according to claim **5** in which the alkali metal gold sulfite is sodium gold sulfite.

7. Improved bath according to claim **1** in which the organic phosphorus compound is an alkylene diamino tetra-(methylphosphonic acid) in which the alkylene group has about 1 – 6 carbon atoms.

8. Improved bath according to claim **1** in which the organic phosphorus compound is a 1-hydroxyalkylidene-1,1-diphosphonic acid the alkylidene group of which contains about 1 – 6 carbon atoms.

9. Improved bath according to claim **1** in which the organic phosphorus compound is 1-hydroxyethylidene-1,1-diphosphonic acid.

10. Improved bath according to claim **1** in which the pH is about 9.5 – 10.2.

11. Improved bath according to claim **1** in which the bath contains a wetting agent in an amount sufficient to reduce the surface tension of the plating bath.

12. Improved bath according to claim **1** in which the amount of gold is about 3 – 5 g/l.

13. Improved bath according to claim **1** in which the amount of cadmium is about 8 – 14 g/l.

14. Improved bath according to claim **1** in which the amount of copper is about 0.01 – 0.08 g/l.

15. Improved bath according to claim **1** in which the amount of nickel is about 4 – 6 g/l.

16. Improved bath according to claim **1** wherein said bath contains about 0.01 – 10 g/l of a water soluble salt of indium.

17. Improved bath according to claim **1** wherein said bath contains about 0.01 – 10 g/l of a water soluble salt of cobalt.

18. Improved bath according to claim **1** wherein said bath contains about 0.01 – 10 g/l of a water soluble salt of iron.

19. Improved bath according to claim **1** wherein said bath contains a water soluble salt of indium, cobalt and iron in an amount of about 0.01 – 10 g/l calculated on the basis of metal in the bath.

20. Improved bath according to claim **1** in which the organic phosphorous compound is ethylene diamino tetra-(methylphosphonic acid) or hexamethylene diamino tetra-(methyl phosphonic acid).

21. In an improved aqueous bath for the electrolytic deposition of gold or gold alloys on electrically conductive objects, said bath containing at least one chelating agent, an alkali metal gold sulfite, at least one gold alloying metal, and about 0.5 – 100 g/l of at least one electrically conductive salt other than said alkali metal gold sulfite, said gold alloying metal and said chelating agent, the improvement wherein there is incorporated in said bath at least one water soluble salt of cadmium, at least one water soluble salt of copper, at least one water soluble salt of nickel, and additionally a 1-hydroxyalkylidene-1,1-diphosphonic acid, the alkylidene group of which contains 1 – 12 carbon atoms, or a water soluble salt of the diphosphonic acid; said bath having a pH of about 8.5 – 11, and further wherein said bath contains gold in an amount of about 1 – 8 g/l, cadmium in an amount of about 0.1 – 30 g/l, copper in an amount of about 0.001 – 0.5 g/l, nickel in an amount of about 0.001 – **10** g/l and the organic phosphorous compounds in an amount of about 0.01 – 10 g/l; said

at least one chelating agent being other than said diphosphonic compound and present in an amount sufficient to substantially completely complex all of the metals in the plating bath.

22. Improved bath according to claim **21** in which the organic phosphorus compound is in an amount of about 0.01 – 10 g/l.

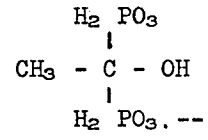
23. Improved bath according to claim **22** in which the pH is about 9.5 – 10.2.

24. Improved bath according to claim **23** in which the amount of gold is about 3 – 5 g/l, the amount of cadmium is about 8 – 14 g/l, the amount of copper is about 0.01 – 0.08 g/l and the amount of nickel is about 4 – 6 g/l.

25. Improved bath according to claim **24** in which the water soluble gold alloying metal salts are metal sulfates and the alkali metal gold sulfite is sodium gold sulfite.

26. Improved bath according to claim **25** in which the alkylidene group contains 1 – 6 carbon atoms.

27. Improved bath according to claim **26** in which the phosphorous compound has the formula:



28. Improved bath according to claim **24** wherein said bath contains a water soluble salt of indium, cobalt and iron in an amount of about 0.01 – 10 g/l calculated on the basis of metal in the bath.

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