United States Patent
Nobel et al.

[15] **3,642,589**
[45] **Feb. 15, 1972**

[54] GOLD ALLOY ELECTROPLATING BATHS

[72] Inventors: **Fred I. Nobel**, 75 Fern Drive; **Barnet D. Ostrow**, 125 Redwood Drive, both of Roslyn, N.Y. 11576

[22] Filed: **Sept. 29, 1969**

[21] Appl. No.: **861,985**

[52] **U.S. Cl.** **204/44,** 204/43, 204/46
[51] **Int. Cl.** **C23b 5/42**
[58] **Field of Search** ....204/46, 43, 44, 123; 106/1; 117/130 E

[56] **References Cited**

UNITED STATES PATENTS

Re24,582	12/1958	Rinker	204/43
3,227,638	1/1966	Burnson	204/46 X
2,660,554	11/1953	Ostrow	204/43
2,967,135	1/1961	Ostrow et al.	204/43

OTHER PUBLICATIONS

A. G. Gray, Modern Electroplating, pp. 8–10 (1953) TS 670 E 46 1953

Primary Examiner—G. L. Kaplan
Attorney—E. J. Berry and L. Rosen

[57] ABSTRACT

An electroplating bath solution for depositing gold-base alloys containing soluble gold and silver salts as well as a soluble polymeric condensate of an epihalohydrin and an alkylene polyamine. The solution also contains free alkali metal cyanide. Optional components include a different metal salt, such as nickel or cobalt salts; a wetting agent; buffers or conductive salts; and alkylene-, alkanol-, and alkylol-amines, polymers thereof, or mixtures thereof.

9 Claims, No Drawings

GOLD ALLOY ELECTROPLATING BATHS

The present invention relates to improved gold alloy electroplating baths. More particularly, the invention pertains to electroplating bath solutions for plating gold alloys of silver with or without other alloying metals.

It has been customary for many years to deposit gold-base alloys from aqueous solutions containing gold metal as a soluble cyanide plus other metal salts. Various materials such as sulfites, thiosulfates, certain amines, phosphates, glues, and the like have been added to these solutions in an effort to obtain improved results. Under the requirements of present day industry it is important to have available electroplating baths capable of plating heavy gold alloy deposits to thicknesses as high as 20 microns or more with good brightness and ductility. Previous electroplating baths were not able to fulfill these requirements.

U.S. Pat. No. 2,660,554 describes a composition which is intended to produce a heavy plate from a bath containing aurous cyanide, an alkylene-, alkylol- or alkanol-amine at a pH of 8.0 to 11.5, together with a theoretical free alkali metal cyanide of 1.2 to 2.0 grams per liter. While this bath was satisfactory for commercial operation, there were some defects which lessened its applicability. The pH of the solution tended to rise and as such pH increase occurred, it became more difficult to secure a wide, bright plating range, particularly with baths which had been in operation for some time. Another difficulty was in maintaining the life of this bath. When the amount of gold replenished and deposited was three or four times the amount used in making a fresh bath, harmful breakdown products reduced the overall bright plating range. This made it necessary to discard the solution and make up a new bath, which obviously increased the cost of operation.

The use of these particular amines is also described in U.S. Pat. No. 2,967,135 in the formulation of gold-base alloy electroplating baths further characterized as having a pH within the range of 2.5 to 6.5 and by the absence of free alkali metal cyanides. While these electroplating solutions were definitely superior to those previously available, it was found that they were not capable of producing ductile deposits greater than about 10 microns. At greater thicknesses the deposits tended to crack due to very high internal stresses which rendered them unsuitable for commercial use. It was further found that the electroplating baths of U.S. Pat. No. 2,967,135 could not be effectively employed for very low karat deposits, e.g., 5 to 14 kt.

One object of the present invention is to provide gold-alloy electroplating baths which avoid the disadvantages and limitations of the prior art plating baths.

Another object of the present invention is to provide stable gold-alloy electroplating baths capable of giving ductile deposits over a wide range of karats.

A further object of the present invention is to provide improved gold-silver alloy electroplating baths.

A still further object of the present invention is to provide an aqueous electroplating bath solution for depositing an alloy of gold, silver and one other metal.

These and other objects will become apparent from the ensuing description of the present invention.

In accordance with this invention, it has now been found that improved gold-base alloy electroplating bath composition can be attained by the incorporation of a soluble polymeric condensate of an epihalohydrin and an alkylene polyamine or the quaternaries thereof. Such materials and similar materials as well as their method of preparation are described in British Pat. No. 1,083,681. The resulting compositions have an increased stability and can plate semibright to brilliant gold-base alloys for long periods of time. Both low and high karat deposits can be achieved. Moreover, heavy or thick deposits of the gold-base alloys will not be subject to the cracking problem encountered when utilizing prior art plating baths.

Epichlorohydrin and epibromohydrin are the preferred epihalohydrins used in the preparation of the soluble polymeric condensate. Preferred alkylene polyamines are those having at least one secondary amino group and at least one primary amino group such as polyalkylene polyamine. When tertiary amino groups are present they are desirably dialkylamino groups, preferably those containing up to 10 carbon atoms in the alkyl radicals.

Illustrative materials include lower polyalkylene polyamines, such as polyethylene polyamine, diethylenetriamine, triethylene-tetramine, and tetraethylenepentamine; polypropylenepolyamines, such as imino-bis-propylamine; dimethylaminopropylamine, (N,N-dimethylpropylenediamine); diethylaminopropylamine, (N,N-diethylpropylenediamine); N-morpholinopropylamine; N,N-dimethylaminoethylamine and N,N-diethylaminoethylamine. Other alkylenepolyamines containing at least one tertiary amino group and at least one secondary amino group may also be employed, such as N,N-dimethyl-N'-methylpropylenediamine, N,N-dimethyl-N'-methylethylenediamine and N,N-diethyl-N'-ethylethylenediamine.

In general, the molar ratio of the epihalohydrin to the alkylene polyamine or mixture of alkylene and polyalkylene polyamines employed to prepare the unquaternized water soluble condensate or resin should preferably range from about 0.8–1.15 to 1, although a somewhat broader range of from about 0.5–1.75 to 1 is also suitable.

Quaternization can be carried out either in a separate step or in situ at temperatures up to 100° C. under atmospheric or elevated pressures. Suitable quaternizing agents are the alkyl halides such as methyl chloride, bromide and iodide, and ethyl chloride, bromide and iodide, dialkyl sulphates, such as dimethyl, diethyl, dipropyl and dibutyl sulphates, allyl halides such as allyl chloride, propargyl chloride, epihalohydrins, such as epichlorohydrin, and alkyl esters of aryl sulphonates, such as methyl toluene sulphonate and methyl benzene sulphonate.

The quaternized or unquaternized polymeric condensate is further characterized by being substantially free from cross-linking.

Only minor amounts of the above-described polymeric condensate need be employed in formulating the plating baths of this invention. However, a sufficient amount should be present to attain the requisite brightness, and the maximum amount is limited only by practical or economic considerations. For most purposes, at least 0.1 grams per liter of the polymeric condensate can be employed, and a suitable range covers from about 0.1 to 100 grams per liter of the plating solution.

In accordance with another feature of this invention it has been found advantageous to have some alkali metal cyanide in the bath. The preferred cyanides are potassium and sodium cyanides. The amount of free alkali metal cyanide will generally range from about 2 to 60, and preferably from about 7 to 35 grams per liter.

The metal components of the electroplating bath of the present invention comprise (a) gold metal added as a soluble gold cyanide salt, and preferably as the double alkali metal cyanide; and (b) a soluble silver salt, complex, or chelate such as the double alkali metal cyanide, the amine cyanide, hydrocyanide, nitrate, chloride and the like. Other metals which may be present in the bath include nickel, cobalt, cadmium, indium, copper, etc., in the form their salts, complexes, or chelates such as nickel sulfate, alkali metal nickel cyanide, nickel amine, cobalt sulfate, alkali metal cobalt cyanide, cobalt amine, indium sulfamate, cadmium sulfate, copper sulfate, alkali metal copper cyanide, and the like. For many commercial applications, the aforementioned metals are used in the form of their double alkali metal cyanide salts, and preferably where the alkali metal is sodium or potassium.

The amounts of metals employed in the plating baths may vary widely, and the following ranges have been found suitable:

Metal	Grams per Liter (g./l.)
Gold	4 to 12
Silver	1 to 8
Nickel	1 to 10
Cobalt	1 to 10
Indium	0.1 to 5
Cadmium	1 to 10

Copper	1 to 15

The pH of the solution may range from about 8 to 11.5 with a pH of from about 9.5 to 11 being preferred. Materials such as sulfamic acid, boric acid, phosphoric acid, sulfuric acid, nitric acid, citric acid, etc., may be employed to adjust the pH of the electroplating bath. As the operation with the baths of the present invention proceeds, in some cases there may be a tendency for the pH to change. To overcome this, some form of buffering compounds are added to the bath, whereby this tendency is minimized and the pH is maintained more closely within the optimum operating ranges. Among such compounds are water soluble citrates, borates, phosphates, carbonates, and the like. The amount of buffering salt employed is not critical.

In some instances wetting agents, which are compatible with the gold-base bath, can also be added to assist in preventing pitting in the gold alloy deposits. The wetting agent must be capable of reducing the surface tension of the aqueous plating solution without adversely affecting either the solution or the metal deposit. Examples of such materials include organic phosphates, ethylene oxide condensates of organic phosphates, and the like. Generally, the amount of wetting agent will range from about 0.5 to 1 gram per liter or more. The amount need only be sufficient to permit the metal plating without pitting.

The electroplating baths of this invention may also contain water soluble titanium, selenium or tellurium compounds as brightener additives. Titanium compounds such as ethanolamine titanate, triethanolamine titanate, etc., may be employed in amounts ranging from about 0.05 to 5 grams per liter. Illustrative water soluble selenium and tellurium compounds are sodium selenite and sodium tellurite; and they may be employed in amounts ranging from about 0.001 to 0.1 gram per liter.

Another feature of the present invention resides in the optional addition to the electroplating; bath of alkylol-, alkylene- or alkanol-amines having from one to 12 carbon atoms as well as polymers thereof having molecular weights of up to 2,500 or higher, preferably from about 100 to 2,500. Examples of such amines and their polymers are:

Ethylene diamine
Diethylene triamine
Tetraethylene pentamine
Hydroxyethyl ethylene diamine
Aminoethyl ethanolamine
Monoethanolamine
Triethanolamine
Triisopropanolamine
Polymerized tetraethylene pentamine (average mol. wt. 1,800)
Polymerized tetraethylene pentamine (average mol. wt. 1,200), etc. Mixtures of the amines and/or polymeric amines may also be employed. These amines may also be present in minor amounts, and generally are used in the range of about 1 to 100 grams per liter. These amines must be used in conjunction with the epihalohydrin-alkylene polyamine condensation products, since they are unsatisfactory when used alone.

The invention will be more fully understood by reference to the following illustrative embodiments.

EXAMPLE 1

An aqueous electroplating bath solution is prepared from the following formulation:

	Grams/Liter
Gold—in the form of $KAu(CN)_2$	8
Silver—in the form of $KAg(CN)_2$	2
Reaction product of epichlorohydrin and tetraethylene pentamine	10
Free potassium cyanide	30
Organic phosphate wetting agent	1
Water	Make up to 1 liter

The pH is adjusted with boric acid to a value of 10. The solution is agitated during plating at a temperature of 80° F. and a current density 5 amperes per square foot. Resulting deposits are bright and crack free even up to 20 microns. The karat is approximately 16 to 18 kt.

EXAMPLE 2

An aqueous electroplating bath solution is prepared from the following formulation:

	Grams/Liter
Gold—in the form of $KAu(CN)_2$	10
Silver—in the form of $KAg(CN)_2$	2
Nickel—in the form of $KNi(CN)_2$	2
Reaction product of epichlorohydrin and triethylene tetramine	8
Tetraethylene pentamine	30
Free potassium cyanide	25
Organic phosphate wetting agent	25
Water	Make up to 1 liter

The pH is adjusted with sulfamic acid to a value of 10.5. Plating conditions were the same as in Example 1 except for a current density of 4 amperes per square foot. Resulting deposits were bright and crack-free even up to 20 microns. The karat is approximately 16 to 18 kt.

EXAMPLE 3

An aqueous electroplating bath solution is prepared from the following formulation:

	Grams/Liter
Gold—in the form of $NaAu(CN)_2$	8
Silver—in the form of $NaAg(CN)_2$	1.5
Cobalt—in the form of $NaCo(CN)_2$	1
Reaction product of epichlorohydrin with tetraethylene Pentamine—quaternized with methyl chloride	10
Tetraethylene pentamine	50
Free sodium cyanide	25
Organic ethophosphate wetting agent	0.5
Water	Make up to 1 liter

The pH is adjusted with phosphoric acid to a value of 11. At a current density of 3 amperes per square and under the same plating conditions of Example I, bright metal deposits were obtained and are crack-free even up to 20 microns. The karat is approximately 16 to 18 kt.

EXAMPLE 4

An aqueous electroplating bath solution is prepared from the following formulation:

	Grams/Liter
Gold—in the form of $KAu(CN)_2$	8
Silver—in the form of $KAg(CN)_2$	6
Reaction product of epichlorohydrin and diethylene triamine—quaternized with diethyl sulfate	5
Aminoethyl ethanolamine	20
Tetraethylene pentamine	50
Potassium carbonate	20
Free potassium cyanide	20
Water	Make up to 1 liter

The pH is adjusted with sulfamic acid to a value of 9.5. At a current density of 7 amperes per square foot and with good agitation, the solution plated bright, crack-free 10-karat deposits in heavy thicknesses.

The above data show that electroplating bath solutions of this invention can be effectively employed for the deposition of gold-base alloys. The metal deposits are characterized by the desired brightness, ductility and variety of karat values.

Although the invention has been illustrated in conjunction with above embodiments, it will be understood that the invention is subject to variations and modifications without departing from its broader aspects.

What is claimed is:

1. An electroplating bath for producing gold-base alloy deposits comprising an aqueous, alkaline solution of a soluble gold salt, a soluble silver salt, a free alkali metal cyanide content of at least about 2 grams per liter and up to about 60 grams per liter of solution, and a minor amount of a soluble polymeric condensate of an epihalohydrin and an alkylene polyamine, the molar ratio of the epihalohydrin to alkylene polyamine being in the range of 0.5–1.75 to 1, and the soluble polymeric condensate being present in concentration of from about 0.1 to 100 grams per liter of solution.

2. The electroplating bath of claim **1** wherein said polymeric condensate is quaternized.

3. The electroplating bath of claim **2** wherein said polymeric condensate is quaternized with methyl chloride.

4. The electroplating bath of claim **2** wherein said polymeric condensate is quaternized with diethyl sulfate.

5. The electroplating bath of claim **1** wherein the aqueous solution also contains a soluble form of a metal selected from the group consisting of nickel, cobalt, indium, cadmium, and copper.

6. The electroplating bath of claim **1** wherein the pH of the aqueous solution ranges from about 8 to 11.5.

7. The electroplating bath of claim **1** wherein the soluble gold salt is gold-alkali metal cyanide, and the soluble silver salt is silver-alkali metal cyanide.

8. The electroplating bath of claim **1** wherein the aqueous solution also contains an amine selected from the group consisting alkylol-, alkylene- and alkanol-amines having from one to 12 carbon atoms and polymers thereof.

9. The electroplating bath of claim **1** wherein the molar ratio is within the range of about 0.8–1.15 to to 1.

* * * * *