

1

3,666,640

GOLD PLATING BATH AND PROCESS

Paul T. Smith, Pascoag, R.I., assignor to Sel-Rex Corporation, Nutley, N.J.

No Drawing. Continuation of abandoned application Ser. No. 851,495, Aug. 19, 1969, which is a continuation-in-part of application Ser. No. 486,553, Sept. 10, 1965. This application Apr. 23, 1971, Ser. No. 137,014 Int. Cl. C23b 5/28, 5/42

U.S. Cl. 204—44

6 Claims

ABSTRACT OF THE DISCLOSURE

An electroplating bath and process for obtaining non-hazy, hard, brilliant gold deposits by the addition of a small quantity of a soluble arsenic, a soluble antimony or a soluble selenium compound to the plating solution, optionally including the addition of soluble base metal salts and chelating agents to further improve the properties of the deposit.

This application is a continuation of U.S. application Ser. No. 851,495 filed Aug. 19, 1969 which in turn is a continuation-in-part of U.S. application Ser. No. 486,553 filed Sept. 10, 1965, both now abandoned.

This invention relates to a composition and bath for gold plating and more particularly it relates to a process for gold plating from a bath containing a gold sulfite complex, and to the bath per se.

In my U.S. Pat. No. 3,057,789 there is disclosed a process of gold plating from a bath containing alkali gold sulfite. According to the disclosure of said patent, the bath may also contain a chelating agent such as sodium pyrophosphate, ethylenediamine tetraacetic acid (EDTA) and salts thereof, and hexamethylenamine. In addition, salts of other metals which may be codeposited with the gold (specifically the copper complex of disodium EDTA) are disclosed as a satisfactory addition to the bath.

Such baths have the advantages in being free of cyanide and in that relatively thick gold deposits which are smooth, fine grained, non-porous and bright are obtained.

Among the objects of the present invention is to provide an improvement over the process of said patent.

Among other objects of the invention is to provide a process and composition for obtaining gold deposits of improved hardness and brightness.

Whereas the composition and process of said prior patent produce gold deposits of good brightness, such deposits are frequently hazy and do not have the full brightness attainable in gold deposits.

Among further objects of this invention is to provide a composition and process for obtaining non-hazy brilliant gold deposits.

I have discovered that the addition of small amounts of arsenic or antimony or selenium can overcome the problem of haziness and give rise to a brilliant gold deposit. Indeed, the deposit is hard, bright, as well as being fine grained, smooth and non-porous. The amount of arsenic or antimony, selenium, to be added to the bath ranges from about 15 to about 1500 milligrams per liter.

The term "alkali gold sulfite" as used herein is intended to mean the sodium, potassium, lithium, ammonium or cesium gold sulfites. Thus, it shall be understood for the purposes of this application, that by the term "alkali" is meant the conventional alkali metals and ammonium.

2

Additional sulfite ion may be added to the composition or bath as alkali sulfite.

Alkali sulfates or other alkali salts which are compatible with the alkali gold sulfite may be added to said baths. The following are illustrative: soluble phosphate, carbonate, acetate, citrate, and tartrate salts including, for example, dipotassium phosphate, disodium phosphate, ethylenediamine diacetate, disodium ethylenediamine, diacetate, disodium ethylenediamine tetraacetate, dipotassium ethylenediamine tetraacetate, tripotassium phosphate, trisodium phosphate, sodium tetraphosphate, potassium tetraphosphate, sodium metaphosphate, potassium metaphosphate, sodium or potassium bicarbonate, sodium or potassium carbonate, sodium or potassium acetate, sodium or potassium citrate, sodium or potassium tartrate, sodium or potassium hexametaphosphate. Other examples include the use of chlorides, nitrates, bromides, borates, borofluorides, sulfonates, acetates, oxylates, formates, and other weak organic acids.

Chelating agents such as the disodium EDTA compounds illustrated above may be added to the bath or composition. Other chelating compounds that may be added include nitrilo-, imino- and amino polycarboxylic acids such as nitrilo triacetic acid, ethylenediamine tetraacetic acid, hydroxy ethylenediaminetetraacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid and aminodiacetic acid. Other chelating agents include acetylacetones, hydroxy organic acids, such as citric acid, lactic acid, and tartaric acid. In general, any chelating agent having a pK value of about 12 to about 22 may be employed.

Base metals which co-deposit with the gold such as cadmium, copper, nickel, zinc, cobalt, manganese, etc. may be added to the composition or bath. They are usually added in the form of a salt and can be added in the form of any one of the salts above mentioned such as the sulfates, chlorides, nitrates, borates, sulfonates, acetates, oxylates, etc.

The bath operates satisfactorily at a current density of about 1–20 or more amperes per square foot (a.s.f.) or about 0.1 to 2 amperes per square decimeter (a./dm.²), and at temperatures of about 35–60° C.

Thus, the overall proportions of the bath may be summarized as follows:

Gold (as alkali gold sulfite)—2 to 82 g./l.

Alkali sulfite (excess)—0 to saturation

Additional alkali salts—0 to saturation

Chelating agent—0 to 200 g./l.

Soluble base metal compound—0 to about 50 g./l.

at least one of the following

Arsenic (added as soluble compound)—0.5 to 1500 mg./l. or,

Antimony (added as soluble compound)—5 to 400 mg./l.

The addition of as little as 5 mg./l. of a soluble base metal compound is effective to improve the brightness or hardness of the plated layer and when such base metal compound is added at least 10 mg./liter of the chelating agent should also be added, the proportion of chelating agent increasing with the proportion of base metal compound.

The following examples illustrate in detail how the process is carried out:

EXAMPLES 1A–1C

A master bath is made up of the following composition:

Gold (as alkali gold sulfite)—8.2 g./l.

Sodium sulfite—20 g./l.

3

Sodium sulfate—30 g./l.
Disodium EDTA—40 ml./l.
Cadmium (as CdSO_4)—0.25 g./l.

Three aliquot parts of the master bath were selected and to these baths there were added: (A) 75 mg./l. of arsenic (as arsenite), (B) 300 mg./l. or arsenic (as arsenite); and (C) 1100 mg./l. or arsenic (as arsenite).

The pH of the bath was held at 8.5 and the temperature at about 50° C. and panels were plated at a c.d. of 0.3 a./dm.².

The following results were obtained:

	Appearance of panel
A -----	Perfect.
B -----	Slight overall haze.
C -----	Increased haze.

To check the effect of pH and temperature these conditions were both raised to about 13 and 85° C., respectively, to see if this would improve the hazy panels or harm Panel A. No substantial effect within these ranges was noted.

EXAMPLES 2A TO 2C

The processes of Examples 1A to 1C were repeated without the cadmium addition and with the following addition of As:

	Appearance of panel
(A) (60 mg./l. As) -----	Perfect.
(B) (225 mg./l. As) -----	Almost perfect (slight haze).
(C) (600 mg./l. As) -----	A high current density base (or burn). Plating at a lower c.d. of 0.15 amp. dm. ² produced an improved deposit. Also adding Cd and plating at a c.d. of 0.3 amp./dm. ² relieved the burning but produced a plating of reduced brightness.

EXAMPLES 3A TO 3C

The process was conducted as in Examples 1A to 1C (with the cadmium addition) but with the additions of antimony (added as antimony tartrate) in place of arsenic in the amounts set forth:

- (A) Up to 5 mg./l. of Sb (as stibnite)—Bad-brown streaks panel—dull.
(B) 200 mg./l. of Sb—Bright, not quite as brilliant as with As.
(C) Over 200 to 425 mg./l. of Sb—Precipitation of the tartrate in this range.

EXAMPLE 4

The process conducted as in Example 3 but without the addition of the cadmium. The results were substantially the same as in Examples 3A to 3C.

Similar results are obtained from the addition of the ionic compounds of other base metals such as copper, zinc, indium, iron, nickel, cobalt, etc. In the above examples cadmium has been added in Examples 1(A-C) and 3 to provide a better comparison.

4

The features and principles underlying the invention described above in connection with specific exemplifications will suggest to those skilled in the art many other modifications thereof.

I claim:

1. An aqueous bath for electroplating gold, which comprises:

- between 2 and 82 grams per liter of gold as an alkali gold sulfite;
- an alkali sulfite in an amount of from 0 gram per liter up to saturation;
- an alkali sulfate in an amount of from 0 gram per liter to saturation;
- a soluble compound of cadmium, copper or nickel in an amount of from 0 to 50 grams per liter;
- a soluble compound of arsenic in an amount of from 0.5 to 1500 milligrams per liter; and
- an organic acid chelating agent having a pK value of from 12 to 22 in an amount of from 0 to 200 grams per liter;

the bath containing sufficient acid or alkali to adjust its pH to between 8.5 and 13.

2. The plating bath of claim 1, incorporating at least 20 grams per liter of the alkali sulfite.

3. The plating bath of claim 1, wherein the chelating agent is nitrilo triacetic acid, ethylenediamine tetraacetic acid, diethylenetriamine pentaacetic acid or citric acid.

4. The plating bath of claim 1, wherein:

- the alkali gold sulfite is potassium gold sulfite or sodium gold sulfite,
- the alkali sulfite is sodium sulfite,
- the alkali sulfate is sodium sulfate,
- the soluble arsenic compound is an arsenite, and
- the organic acid chelating agent is ethylenediamine tetraacetic acid.

5. The process of plating gold comprising electro-depositing gold on a cathode from the aqueous bath of claim 1 at a temperature between 35° and 60° C.

6. The process of plating gold comprising electro-depositing gold on a cathode from the aqueous bath of claim 2 at a temperature between 35° and 60° C.

References Cited

UNITED STATES PATENTS

3,057,789	10/1962	Smith	204—46
3,380,814	4/1968	Cathrein et al.	204—43 X
3,380,898	4/1968	Danemark et al.	204—44
3,475,292	10/1969	Shoushanian	204—44

FOREIGN PATENTS

1,027,637	5/1953	France	204—46
-----------	--------	--------	--------

OTHER REFERENCES

Francis C. Frary: Trans. of the Electrochemical Soc., vol. 23, pp. 55-59 (1913).

GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

204—43, 46