

1

2

3,475,292

**GOLD PLATING BATH AND PROCESS**

Hrant H. Shoushanian, Cranston, R.I., assignor to  
Technic, Inc., Cranston, R.I.

No Drawing, Filed Feb. 10, 1966, Ser. No. 526,385

Int. Cl. C23b 5/46, 5/42, 5/28

U.S. Cl. 204-44

15 Claims

**ABSTRACT OF THE DISCLOSURE**

Alkaline aqueous baths for electroplating gold and gold alloys which contain therein: (1) gold as the sulphite; (2) an alkali metal sulphite; (3) a buffering and conducting salt; and (4) an additive selected from the group consisting of soluble salts or soluble complexes of a brightening metal additive, soluble salts or soluble complexes of a brightening semimetallic additive, and soluble salts or soluble complexes of an alloying element; said aqueous baths having pH levels in excess of 8.

The present invention is directed to a process for electrodepositing gold and gold alloys and to improved complex gold sulfite baths used in such processes.

Gold has been reported electrodeposited from sodium gold sulfite solutions as early as 1842, Dingler's Journal 97, pp. 429-446 (1845), and British Patent No. 9,431, issued Aug. 1, 1842. Such solutions were apparently used for a period of approximately ten years. The gold deposits produced were porous and the physical properties were inferior to deposits obtained from cyanide-containing gold plating baths, resulting in the abandonment of the sulfite baths in favor of the cyanide baths.

It is an object of the present invention to provide improved processes for preparing gold electrodeposits, including 24 karat gold, having superior physical properties including high luster and specular reflection.

It is another object of the present invention to provide improved sulfite electroplating baths suitable for use in said processes.

It is a further object of the invention to provide improved processes for electrodepositing superior alloy gold deposits having improved brightness and hardness; said processes being capable of yielding deposits of various shades of yellow.

It is also an object of this invention to provide improved sulfite electroplating baths for plating gold alloy deposits.

Other objects and advantages of this invention will in part be obvious and will in part become apparent from the following specification.

One aspect of the present invention contemplates electrodepositing gold and gold alloys from an alkaline aqueous bath containing

(i) Between 1 and 30 grams per liter and preferably between 5 and 15 grams per liter of gold as sulfite selected from the group consisting of potassium gold sulfite and sodium gold sulfite;

(ii) Potassium sulfite or sodium sulfite in an amount between 40 and 150 grams per liter and preferably between 40 and 120 grams per liter;

(iii) A buffering and conducting salt selected from soluble phosphate, sulfate, acetate, and citrate salts of the alkali metals and the alkaline earth metals, in an amount between 5 and 150 grams per liter and preferably between 10 and 100 grams per liter;

(iv) At least one brightening and/or alloying additive selected from

(a) Between about 5 and 500 milligrams per liter of a base metal in the form of a soluble salt or a soluble complex,

(b) Between 1 and 400 milligrams per liter of a semimetal in the form of a soluble salt complex, and

(c) An alloying metal or semimetal in the form of a soluble salt or soluble complex, when in the form of a salt in the amount between 0.5 and 5 grams per liter, and when in the form of a complex in an amount between 0.5 and 10 grams per liter; and

(v) Sufficient of an acid or alkali to adjust the pH to a value in excess of 8 and preferably between about 9 and 11.

The base metals effective as brighteners are cadmium, titanium, molybdenum, tungsten, lead, zinc, iron, nickel, cobalt, tin, indium, copper, manganese, and vanadium.

The semimetals effective as brighteners are arsenic, antimony, selenium, and tellurium. Lead, copper, arsenic and cobalt are the preferred brighteners.

The base metals and semimetals effective as alloying agents are cadmium, lead, zinc, iron, nickel, cobalt, tin, indium, copper, manganese and antimony. Cobalt, antimony and nickel are the preferred alloying agents.

The soluble salts may vary widely in their degree of solubility in the electrolyte. With the relatively small amounts of the metals required, salts having even limited solubility may be utilized. Advantage may be taken of this limited solubility to provide control of the additive level by maintaining an undissolved excess of the salt in the bath. The following list of specific salts that may be used is illustrative of the many salts of the metals and semimetals which are suitable sources of the metal or semimetal respectively: cadmium sulfate, cadmium acetate, lead acetate, lead nitrate, zinc sulfate, zinc acetate, iron sulfate, iron acetate, nickel sulfate, nickel nitrate, cobalt sulfate, cobalt acetate, indium sulfate, indium nitrate, copper sulfate, copper acetate, manganese sulfate, and manganese acetate. The foregoing cations could also be introduced into solution in the form of any soluble salt with the following anionic moieties: acetates, sulfates, chlorides, nitrates, bromides, borates, borofluorides, oxalates, formates, sulfamates, and similar weak organic acids. Compounds in which the metal or semimetal is in the anionic moiety may also be used, e.g., potassium titanate, ammonium titanate, sodium molybdate, potassium molybdate, sodium tungstate, potassium tungstate, sodium stannate, potassium stannate, sodium vanadate, ammonium vanadate, potassium arsenite, ammonium arsenite, potassium antimony tartrate, sodium antimonite, sodium selenate, potassium selenate, potassium tellurate, and sodium tellurate. The foregoing anions could also be introduced into solution in the form of any soluble salt with the following cationic moieties: cesium, lithium, quaternary ammonium salts and other organic cationic moieties.

The base metals and semimetals may also be added to the bath in the form of a soluble complex, sometimes also referred to as a chelate, with a compound selected from the group consisting of aminopolycarboxylic acids such as nitrilotriacetic acid, ethylenediaminetetraacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid, cyclohexanediaminetetraacetic acid, diethylenetriaminepentaacetic acid, iminodiacetic acid, etc.; acetylacetonates; and hydroxyorganic acid moieties such as citric acid, lactic acid, and tartaric acid.

The buffering and conducting salts are selected from the soluble phosphate, sulfate, carbonate, acetate, citrate, and tartrate salts of the alkali metals and the alkaline earth metals. Such salts as dipotassium phosphate, disodium phosphate, dipotassium ethylenediaminediacetate, disodium ethylenediamine diacetate, disodium ethylenediamine tetraacetate, dipotassium ethylenediaminetetraacetate, tripotassium phosphate, trisodium phosphate, sodium tetraphosphate, potassium tetraphosphate, sodium metaphosphate, potassium metaphosphate, sodium bicar-

bonate, potassium bicarbonate, sodium carbonate, potassium carbonate, sodium acetate, potassium acetate, sodium citrate, potassium citrate, sodium tartrate, potassium tartrate, sodium hexametaphosphate, and potassium hexametaphosphate are illustrative of operative buffering and conducting salts.

The bath is operated at a pH more alkaline than 8, to an alkalinity in excess of 12. The preferred operating range is between 9 and 11. The bath is generally adjusted to the desired pH range by the addition of an alkali metal or alkaline earth metal hydroxide, preferably sodium or potassium hydroxide. If by chance the pH of the bath is above the desired operating range, the necessary adjustment may be made by addition of an acid, preferably a sulfuric acid such as sulphuric acid.

The baths may be operated, dependent on the desired rate of electrodeposition and the amount of agitation, over a wide range of current densities. A range of between about 1 and 50 amperes per square foot is preferred with moderate agitation. Agitation enhances brightness and uniformity of the deposit, and also permits a wider current density operating range. The bath may be operated from about room temperature up to about 180° F., with a preferred range between about 110° F. and 140° F.

The following examples further illustrate the invention to those skilled in the art. All parts and percentages are by weight. The baths were adjusted to the specified pH by addition of sodium or potassium hydroxide.

#### EXAMPLE 1.—24 KARAT GOLD DEPOSITION

Into an amount of water sufficient to form one liter of solution is dissolved:

6 grams of gold in the form of potassium gold sulfite,  
90 grams of potassium sulfite,  
15 grams of dipotassium phosphate, and  
200 milligrams of cobalt as cobalt ethylenediaminetetraacetic acid.

At a pH of 9.5, 120° F. and about 6 amperes per square foot, smooth, pore-free deposits of about 96 Knoop hardness number are obtained.

#### EXAMPLE II.—24 GARAT GOLD DEPOSITION

Into an amount of water sufficient to form one liter of solution is dissolved:

12 grams of gold in the form of potassium gold sulfite,  
120 grams of sodium sulfite,  
30 grams of dipotassium ethylenediaminediacetate, and  
15 milligrams of lead as lead acetate.

At a pH of 10.0, 140° F. and 10 amperes per square foot, bright deposits are obtained.

#### EXAMPLE III.—HARD ALLOY GOLD DEPOSITION

Into an amount of water sufficient to form one liter of solution is dissolved:

10 grams of gold in the form of sodium gold sulfite,  
90 grams of sodium sulfite,  
30 grams of dipotassium phosphate, and  
0.50 gram of nickel as nickel imminodiacetate.

At a pH of 10.0, 120° F. and 6 amperes per square foot, bright deposits are obtained. Hardness is 320 Knoop hardness number.

#### EXAMPLE IV.—24 KARAT GOLD DEPOSITION

Into an amount of water sufficient to form one liter of solution is dissolved:

10 grams of gold in the form of sodium gold sulfite,  
90 grams of sodium sulfite,  
30 grams of disodium ethylenediaminetetraacetate,  
4 milligrams of arsenic as arsenic trioxide.

At a pH of 10.0, 130° F. and 8 amperes per square foot, bright deposits are obtained.

#### EXAMPLE V.—HARD ALLOY GOLD DEPOSITION

Into an amount of water sufficient to form one liter of solution is dissolved:

6 grams of gold in the form of potassium gold sulfite,  
75 grams of potassium sulfite,  
30 grams of ethylenediaminetetraacetic acid, and  
6 grams of nickel as nickel nitrilotriacetate.

At a pH of 10.0, 140° F. and 5 amperes per square foot, bright deposits are obtained.

#### EXAMPLE VI.—HARD ALLOY GOLD DEPOSITION

Into an amount of water sufficient to form one liter of solution is dissolved:

10 grams of gold in the form of sodium gold sulfite,  
90 grams of sodium sulfite,  
30 grams of dipotassium phosphate, and  
1.0 gram of antimony in the form of potassium antimony tartrate.

At a pH of 10, 120° F. and about 7 amperes per square foot, bright deposits are obtained having a very pale yellow color. The hardness of the deposit is 200 Knoop hardness number.

Similar sound gold and gold alloy deposits are obtained following the procedure of the examples and utilizing baths having compositions within the ranges specified and containing cadmium, iron, zinc, titanium, tin, antimony, selenium, or tellurium, as the metal or semimetal additive. The deposits have a Knoop hardness of between about 85 and 350. The use of other salts and complexes within the definition of the specification in place of those exemplified, similarly results in the production of sound gold and gold alloy electrodeposits.

The deposits of the present invention may be electrodeposited on a variety of basis metals. As is usual in electroplating metals, the basis metal should be a conductor and preferably a metal having a clean, smooth surface. The gold and gold alloy electrodeposits may be obtained on the wide variety of basis metals which are known as conductors and may also be obtained on nonconducting materials by first making the surface conductive, utilizing the techniques conventional for this purpose.

The gold electrodeposits and gold alloy electrodeposits obtained using the baths and processes of this invention are sound deposits which may be formed in relatively thick deposits. The deposits have good physical properties. They are hard and have superior wearing characteristics. They are also bright, being categorized as "bright" deposits on two grounds: they are visually bright and they are brighter than the surface upon which they are deposited. They have high luster and specular reflection. Alloy deposits of various shades of yellow having a pleasing appearance may be obtained using metal alloying additives. The baths have excellent characteristics for electroplating purposes permitting electrodeposition over a relatively wide range of process conditions. Good throwing power is obtained. An important economic advantage of utilizing the baths of the present invention rather than the currently widely used gold cyanide electroplating baths results from the savings in not having to construct and operate elaborate facilities for processing waste cyanide solutions.

What is claimed is:

1. An alkaline aqueous bath for electroplating gold and gold alloys consisting essentially of

(i) between 1 and 30 grams per liter of gold as sulfite selected from the group consisting of potassium gold sulfite and sodium gold sulfite;

(ii) between 40 and 150 grams per liter of an alkali metal sulfite selected from the group consisting of sodium sulfite and potassium sulfite;

(iii) between 5 and 150 grams per liter of a buffering and conducting salt selected from the group consisting of the soluble phosphate, sulfate, carbonate, acetate, citrate, and tartrate salts of the alkali metals and the alkaline earth metals;

(iv) at least one additive selected from the group consisting of

(a) a brightening metal additive selected from the

5

group consisting of cadmium, titanium, molybdenum, tungsten, lead, zinc, iron, nickel, cobalt, tin, indium, copper, manganese, and vanadium, in an amount between 5 and 500 milligrams per liter, as a soluble salt of said meal or as a soluble complex of said metal,

(b) a brightening semimetallic additive selected from the group consisting of antimony, arsenic, selenium and tellurium in an amount between 1 and 400 milligrams per liter as a soluble salt or a soluble complex of said semimetal, and

(c) an alloying element selected from the group consisting of cadmium, lead, zinc, iron, nickel, cobalt, tin, indium, copper, manganese, and antimony as a soluble salt or soluble complex, when in the form of a salt in an amount between 0.5 and 5 grams per liter, and when in the form of a complex in an amount between 0.5 and 10 grams per liter; and

(v) sufficient of an acid or alkali to adjust the pH to a value in excess of 8.

2. The bath of claim 1 having a pH between 9 and 11, and containing between about 5 grams per liter and 15 grams per liter of gold, between about 40 grams per liter and 120 grams per liter of said alkali metal sulfites, and between about 10 grams per liter and 100 grams per liter of said buffering and conducting salt.

3. The bath of claim 2 wherein said additive is at least one of said brightening metal additives.

4. The bath of claim 2 wherein said additive is at least one of said brightening semimetallic additives.

5. The bath of claim 2 wherein said additive is at least one of said alloying elements.

6. The bath of claim 2 wherein said buffering and conducting salt is selected from the group consisting of dipotassium phosphate, disodium phosphate, disodium ethylenediaminetetraacetate, dipotassium ethylenediaminetetraacetate, disodium ethylenediaminediacetate, and dipotassium ethylenediamine diacetate.

7. The bath of claim 6 wherein said brightening additive is selected from the group consisting of cobalt, lead, copper, and arsenic.

8. The bath of claim 6 wherein said alloying additive is selected from the group consisting of cobalt and nickel.

9. The bath of claim 1 containing 6 grams per liter of gold as potassium gold sulfite, 90 grams per liter of potassium sulfite, 15 grams per liter of dipotassium phosphate, and 200 milligrams per liter of cobalt as cobalt ethylenediaminetetraacetic acid.

10. The bath of claim 1 containing 12 grams per liter of gold as potassium gold sulfite, 120 grams per liter of sodium sulfite, 30 grams per liter of dipotassium ethylenediamineacetate, and 15 milligrams per liter of lead as lead acetate.

6

11. The bath of claim 1 containing 10 grams per liter of gold as sodium gold sulfite, 90 grams per liter of sodium sulfite, 30 grams per liter of dipotassium phosphate, 0.5 gram per liter of nickel as nickel imminodiacetate.

12. The bath of claim 1 containing 10 grams per liter of gold as sodium gold sulfite, 90 grams per liter of sodium sulfite, 30 grams per liter of disodium ethylenediaminetetraacetate,

4 milligrams per liter of arsenic as arsenic trioxide.

13. The bath of claim 1 containing 6 grams per liter of gold as potassium gold sulfite, 75 grams per liter of potassium sulfite, 30 grams per liter of ethylenediaminetetraacetic acid, 6 grams per liter of nickel as nickel nitrilotriacetate.

14. The bath of claim 1 containing 10 grams per liter of gold as sodium gold sulfite, 90 grams per liter of sodium sulfite, 30 grams per liter of dipotassium phosphate, 1.0 gram per liter of antimony as potassium antimony tartrate.

15. The process of plating gold comprising electrodepositing gold on a cathode from the aqueous bath of claim 1 at a temperature between room temperature and 180° F.

## References Cited

## UNITED STATES PATENTS

2,800,439	7/1957	Fischer et al.	204—46 XR
923,864	6/1909	Levy	204—46 XR
2,812,299	11/1957	Volk	204—46 XR
2,905,601	9/1959	Rinker et al.	204—46 XR
2,967,135	1/1961	Ostrow et al.	204—46 XR
3,020,217	2/1962	Rinker	204—43
3,057,789	10/1962	Smith	204—46
3,149,057	9/1964	Parker	204—43 XR

## FOREIGN PATENTS

78,438	11/1954	Denmark.
9,431	1842	Great Britain.

## OTHER REFERENCES

- Brenner, Abner, "Electrodeposition of Alloys," vol. 2, pp. 496-497, 1963.
- Frary, Francis C., "Electrodeposition of Gold and Silver," Transactions of the Electrochemical Soc., vol. 23, pp. 49-59, 1913.
- Fischer, Johannes, et al., "Precious Metal Plating," pp. 110-111, 1964.

JOHN H. MACK, Primary Examiner

G. L. KAPLAN, Assistant Examiner

U.S. Cl. X.R.

204—43, 46