

1

3,380,898

ELECTROLYTE AND METHOD FOR ELECTRO-DEPOSITING A PINK GOLD ALLOY

Marius Danemark and René Cathrein, Geneva, Switzerland, and Atkin Y. Simonian, Fort Lee, N.J., assignors to Sel-Rex Corporation, Nutley, N.J., a corporation of New Jersey

No Drawing. Filed June 18, 1965, Ser. No. 465,201
4 Claims. (Cl. 204—44)

This invention relates to an electroplating process and bath for the production of pink gold deposits consisting essentially of a copper-gold-antimony alloy.

Among the objects of the invention is to provide an improved electroplating bath and process for the production of bright pink gold deposits.

Acid gold plating baths for the deposition of gold operating at a pH of between 3 and 5 or 6.5 are known. It is also known that bright, hard gold deposits obtained when base metal ions capable of codepositing with the gold are added to such baths. See, for example, U.S. 2,905,601.

One of the most difficult colors to obtain by the acid gold plating process is a bright gold deposit with a pink coloration. This is difficult because copper is the main metal ion producing pink coloration and with copper ions the bath is sensitive to changes in concentration, etc., so that uniformly-reproducible, copper-gold alloy deposits can be obtained only by careful regulation of the bath components and of the conditions of operation. Also, after a time, a slight haze develops in deposits obtained from such baths, the haze becoming more important as the bath or solution ages.

Among the objects of this invention is to provide a uniformly reproducible bright, hard, copper-gold alloy deposit with a pinkish coloration.

In copending application Ser. No. 465,181, filed on even date herewith, there is disclosed a process of preparing such rose or pinkish gold by providing an acid type of gold alloy electroplating bath having the following ingredients and conditions of operation:

	Range	Preferred
Gold (added as alkali metal gold cyanide), g./l.	1-8	4
Copper (as a copper complex), g./l.	2-10	5
Antimony (added as Sb salt such as the tartrate), g./l.	0.5-10	1.5
Additional chelating agent, g./l.	5-60	20
Weak Acid and salt thereof, g./l.	20-120	60
pH, adjust to	4.5-6	5.3
Current density, amp./dm. ²	.5-2.0	1.5
Temperature, °C.	40-60	50

The copper complex is a copper salt of any suitable chelating or complexing agent having a negative logarithm of stability constant for copper of about 17 or less. Such complexing agents include ethylenediamine tetracetic acid (EDTA), diethylenetriamino pentaacetic acid, N-hydroxyethylethylenediamine triacetic acids or the sodium or other alkali metal salts thereof. The excess chelating agent is the same type of compound.

Specular bright deposits are obtained from such baths at thicknesses of 25 microns and over so that the gold layer is thick enough to provide corrosion resistance as well as the pink decoration.

The weak acid is one, as defined in the literature, which has a pK value of over about 3 and such weak acids include the organic acids and phosphoric acid. Where the acid employed is polybasic, the partially

2

neutralized acid salts or mixtures thereof may be employed in place of the acid and salt. Thus KH_2PO_4 , or corresponding salt of sodium, lithium or ammonium, may be employed in the above bath as the weak acid and salt. Similarly the mono-potassium salt of citric acid may be employed as the acid and salt combination.

Although it is preferred to add the antimony as the tartrate, it can also be added as other salts which are soluble in the bath.

Although copper is an essential alloying metal for obtaining a pink coloration in alkali gold cyanide baths, and is sufficient by itself for the production of pink coloration in such baths, the antimony, as disclosed in this specification, is also essential for the production of pink coloration and specular effects with the acid gold baths disclosed herein. The alloy deposits obtained from baths as described above consists essentially of 75 to 85% gold, 14 to 24% copper and 0.5 to 1.5% antimony. The alloy has a Knoop hardness of about 230-280 kg./mm.² with a 25 g. load.

The present invention is based on the discovery that minute additions of lead to such baths decrease a tendency which such baths have to form haze when the agitation and current density are not controlled properly. Thus the bath contains the ingredients sets forth above and in addition the following:

Lead (added as soluble lead salt as lead acetate) 15-200 mg./l. preferably 15 mg./l.

The exact mechanism of this phenomenon is not understood, but in view of the small amounts needed, the effect would appear to be diffusion-controlled. It is preferred to add the lead as the acetate, a common water soluble lead salt, but any lead compound soluble in the bath, such as lead ethylenediamine-tetra-acetate, may be used.

The following example is given to illustrate in detail a preferred bath and method of operating the same. It is to be understood that the specific details given in the example is not to be considered as limiting the scope of the invention.

EXAMPLE

	Grams/liters
Gold [as $\text{KAu}(\text{CN})_2$], as metal	3
Copper (as salt of Na_2EDTA), as metal	4
Antimony tartrate, as metal	3
Na_2EDTA	20
KH_2PO_4	60
Lead [as $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, 63%], as metal	.015
pH, adjusted to 5.0.	

Brass panels plated to a thickness of 25 microns with the bath at a temperature of 50° C. and at a density of about 10 amp./dm.² (amperes per square decimeter) are full bright and pink in color.

The lead content was increased to 200 mg./l., the only effect being an increase in brightness and levelling action.

Substitution of tetrasodium polyphosphate or the potassium salt of polyphosphate for the orthophosphate gave similar results.

Baths made up with citric acid neutralized to a pH of 5.0 gave results slightly less satisfactory than the inorganic acids, but the panels so plated were quite attractive. Baths prepared from tartaric acid did develop a precipitation due the formation of potassium bitartrate when potassium gold cyanide was used. Acetic acid-potassium acetate tended to precipitate out some of the antimony but gave satisfactory deposits.

3

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. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

We claim:

1. Process for electrodepositing bright, hard gold-copper alloys having a pink coloration which comprises electrolyzing an aqueous solution comprising the following ingredients:

Gold (added as alkali metal gold cyanide) _____g./l._	1-8
Copper (added as a copper complex) _____g./l._	2-10
Antimony (added as a salt) _____g./l._	0.5-10
Chelating agent (in addition to that complexed with the copper) _____g./l._	5-60
Weak acid and salt thereof, and in proportion to provide a pH of _____	4.5-6
Lead (added as soluble salt) _____g./l._	15-200

maintaining said bath at a temperature of 40 to 60° C. and regulating the current density to a value of 0.5 to 2.0 amp./dm.².

2. The process as set forth in claim 1 wherein the bath contains the following ingredients:

Gold (added as alkali metal gold cyanide) _____g./l._	about 4.8
Copper salt of Na ₂ EDTA (calc. as Cu) _____g./l._	about 5
Antimony tartrate (calc. as Sb) _____g./l._	about 1.5
Na ₂ EDTA _____g./l._	about 1.5
KH ₂ PO ₄ _____g./l._	about 60
Lead (added as lead acetate) _____m.g./l._	about 15

said bath being operated at a pH of about 5.3, a temperature of about 50° C. and a current density of about 1.5 amp./dm.².

4

3. An aqueous bath for plating hard, specularly bright copper-gold alloy consisting essentially of the following:

Gold (added as potassium gold cyanide) _____g./l._	1-8
Copper (added as copper complex) _____g./l._	2-10
Antimony (added as a salt) _____g./l._	0.5-10
Chelating agent in addition to that combined to form the copper complex _____g./l._	5-60
Lead (added as soluble salt) _____mg./l._	15-200
Weak acid and salt thereof _____g./l._	20-120

10 In proportion to provide a pH of 4.5-6.

4. An aqueous bath for plating hard, specularly bright copper-gold alloy consisting essentially of the following:

Gold (added as potassium gold cyanide) _____g./l._	about 4
Copper salt of Na ₂ EDTA (calc. as Cu) _____g./l._	about 5
Antimony tartrate (calc. as Sb) _____g./l._	about 1.5
Lead (added as lead acetate) _____mg./l._	about 15
Na ₂ EDTA _____g./l._	about 20
KH ₂ PO ₄ _____g./l._	about 60

20 Adjusted to pH of 5.3.

References Cited

UNITED STATES PATENTS

2,724,687	11/1955	Spreter et al. _____	204-43
2,905,601	9/1959	Rinker et al. _____	204-44 XR
2,967,135	1/1961	Ostrow et al. _____	204-46 XR
3,020,217	2/1962	Rinker _____	204-46 XR

OTHER REFERENCES

30	Thews, Edmund R., "The Production of Colored Gold Finishes," Metal Finishing, pp. 80-85, September 1951.
	Pritchard, Alfred K., Jr., "Deposition of Pink Gold," Metal Industry, vol. 31, No. 12, p. 408, 1933.
35	HOWARD S. WILLIAMS, <i>Primary Examiner</i> .
	G. KAPLAN, <i>Assistant Examiner</i> .

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,380,898

April 30, 1968

Marius Danemark et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 53, "10" should read -- 1.0 --.

Signed and sealed this 11th day of November 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents