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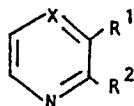
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(54) **Gold electroplating bath.**

(57) An acid gold electroplating bath contains gold in an electrodepositable form, such as potassium gold cyanide, together with a metallic additive and an organic additive.

The organic additive is a compound of the formula



wherein X is $-N=$ or $-CR^3=$, and R^1 , R^2 and R^3 are each hydrogen, or an amino-, amido, thioamido- or cyano- group provided that one (and no more than one) of R^1 , R^2 and R^3 is not hydrogen.

The metallic additive is preferably a cobalt, nickel or iron salt.

GOLD ELECTROPLATING BATH

This invention relates to a gold electroplating bath and more particularly to a gold electroplating bath which includes an organic additive. The invention also relates
5 to a process for the electrodeposition of gold using the bath.

Gold is widely used as a contact material in the electronics industry, most usually in the form of a thin coating obtained by an electroplating process. The more
10 important properties required of such a coating are low contact resistance, high corrosion resistance and good wear resistance.

Pure gold electroplating baths have been found to give coatings which are inadequate for use in contact
15 applications in the electronics industry, principally because such coatings show insufficient resistance to abrasion. However, the quality of electrodeposited gold coatings can be improved by adding other materials to the gold plating bath. Such additives are often called
20 "brighteners", because they increase the brightness of gold deposits obtained at a given current density. Of course, the brightness of a gold deposit is not itself of importance in most industrial applications. However, it has been found that the brightness of a gold coating is
25 often a good guide to one or more other aspects of coating quality, such as wear resistance and deposit structure.

Transition metal salts, such as cobalt, nickel and iron salts, form one group of widely-used additives for
30 acid gold baths. Gold electroplating baths which include these compounds have been found to give gold coatings of greatly improved wear resistance. For this reason, cobalt and nickel-containing acid gold electrolytes are widely used in the electronics industry. However, with
35 the introduction of machines for the high speed selective plating of printed circuit boards and connectors, even

cobalt and nickel brightened plating baths have been found to be lacking, because the maximum current density at which hard deposits can be obtained is relatively low. Attempts have been made to overcome this disadvantage by using higher
5 concentrations of gold (typically 15 g/l instead of 8 g/l), but this substantially increases the cost of the process and the improvement obtained is only slight.

Certain organic compounds have also been used as additives in gold electroplating baths. One such compound
10 is polyethyleneimine, as described in British Patent Specification No. 1453212. The effect of using this compound is to increase the maximum current density which can be employed, but the resultant coating is generally found to give poor wear resistance.

15 Unfortunately, attempts to combine the hardening effects of transition metal additives with the benefits of organic additives have generally met with little success. However, British Patent Specification No. 1426849 discloses an electroplating bath which contains a metallic as well as
20 an organic additive. The organic additives used are chemical compounds of sulphonic acids or sulphonic acid salts with heterocyclic nitrogen-containing hydrocarbons, such as pyridine sulphonic acid, quinoline sulphonic acid and picoline sulphonic acid.

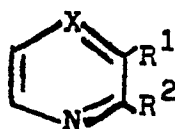
25 We have now identified a further group of organic compounds which are especially effective additives for acid gold baths. These compounds are found to give bright coatings at substantially increased current densities. Two-fold increases in maximum current density are typically
30 achieved with the electroplating bath of the invention. Such increased current densities can be employed to increase the rate of deposition of gold, or to allow a reduction in the concentration of gold in the bath, or both, according to preferred practice.

35 When the plating baths of the present invention are

used in high speed reel-to-reel plating equipment, line speed increases of up to four-fold are achievable, for example from 2 m/min to 8 m/min.

Moreover, the organic additives of the present invention are found to be particularly compatible with transition metal additives, so that highly wear-resistant coatings can be obtained.

According to the present invention there is provided an acid gold electroplating bath comprising gold in electrodepositable form, together with a minor amount of an organic additive of the general formula



wherein X is -N= or -CR³=, and R¹, R² and R³ are each hydrogen, or an amino-, amido-, thioamido-, or cyano-group, provided that one (and no more than one) of R¹, R² and R³, when present, is other than hydrogen.

The bath of the present invention may be used for obtaining very bright gold deposits, such as are required, for example, in the jewellery industry. When a particularly hard bright deposit is required, for example in the electronics industry, a metallic brightener will also be included in the baths.

Particularly effective organic additive are those of the above formula in which R¹ is an amino- or thioamido-group.

Examples of organic additives according to the invention are 3-aminopyridine, 4-aminopyridine, 2-aminopyridine, 3-cyanopyridine, 4-cyanopyridine, 2-cyanopyridine, 3-amidopyridine (nicotinamide), 4-amidopyridine, 2-amidopyridine, 3-thioamidopyridine (thionicotinamide), 4-thioamidopyridine, 2-thioamidopyridine, aminopyrazine,

cyanopyrazine, amidopyrazine and thioamidopyrazine. 3-Aminopyridine, thionicotinamide, aminopyrazine and thioamidopyrazine are especially preferred.

5 The concentration of organic additives used will depend on the particular electroplating conditions contemplated. If the concentration of organic additive is too low, a negligible brightening affect may be obtained. On the other hand, if the concentration of additive is too high, the cathodic efficiency may become unacceptably low. The
10 particular range of concentration appropriate for any given set of electroplating conditions will be readily determinable by the person skilled in the art. Generally speaking, a concentration of organic additive in the range 0.01 g/l to 5 g/l will be found to be appropriate. A concentration
15 of from 0.05 g/l to 1.0 g/l is preferred, and a concentration of from 0.2 g/l to 0.75 g/l is particularly preferred.

The metallic brightener can be any base metal or mixture of base metals which are known to be appropriate for use in acid gold electroplating baths. Included in
20 such metals are cobalt, nickel, iron, chromium, cadmium, copper, zinc, tin, indium, manganese and antimony. Cobalt, nickel and iron are particularly preferred.

The metallic brightener is generally used in the form of a water-soluble salt, such as the sulphate, or citrate or
25 acetate or the like, and may be used at a concentration of from 10 mg to 10 g/l. Alternatively one could use metal complexes with chelating agents such as ethylene diamine tetracetic acid. More preferably, the concentration of metallic brightener is from 100 mg/l to 5 g/l, for example
30 from 250 mg/l to 2 g/l.

The gold of the electroplating bath of the invention is in the form of a water-soluble complex, such complexes being well known in the art. Examples of such complexes include ammonium and alkali metal gold cyanides. Potassium
35 gold cyanide is especially preferred.

The gold complex will generally be present in the

electroplating bath at a concentration of from 1 to 100 g/l, and more preferably at a concentration of from 2 to 20 g/l, for example 4 or 8 g/l.

5 The usual acid buffering systems may be used in the electroplating bath of the invention, to obtain a pH which is preferably in the range 3.0 to 5.5. For example, a citrate oxalate buffer may be used to obtain a pH in the range 4 to 5, for example a pH of 4.5.

10 In addition, other conventional plating bath additives such as wetting agents, can be used.

The electroplating bath of the present invention, and a process for its use, are now illustrated further by the following examples.

EXAMPLE 1

15 Aqueous gold electroplating baths having the following compositions were prepared. (In this and the following Examples, all compositions were buffered to pH 4.5 to 5.0 using tripotassium citrate/citric acid buffer.)

	A	B	C
20 Gold (as potassium cyanide complex, g/l)	17	10	18
Cobalt sulphate, g/l	0.9	0.6	0.6
3-Aminopyridine, g/l	-	0.4	0.4

25 The three compositions were tested in turn in a high speed reel-to-reel plating apparatus at 30°C, in order to determine the maximum usable current density. In this and the following Examples, the expression "maximum current density" is used to indicate the highest D.C. current which can be employed, while still obtaining a bright
30 coating. Maximum line speed and maximum deposition rate were also determined on the same basis, as well as the efficiency (i.e. the proportion of applied current which results in the deposition of gold). The results were as follows:-

	A	B	C
Maximum current density (A/ft ²)	200	325	325
Maximum line speed (ft/min)	4	6.5	10
Maximum deposition rate (microns/min)	3.5	4.2	11.0
Efficiency (%)	31	27	46

It will be seen that the baths according to the invention (B and C) gave substantially improved line speeds and deposition rates, even at a reduced gold concentration (bath B). Moreover, in subsequent tests, improved synchronisation between the test piece and the electrolyte flow gave deposition rates for bath C of up to 22.5 microns/minute, which is almost 7 times the rate for conventional bath A.

EXAMPLE 2

Laminates for use in printed circuit boards were plated at 35°C in a Kentucky Tab Plater using baths of the following compositions, and with the following results:-

	A	B
Gold (as potassium cyanide complex, g/l)	16	16
Cobalt sulphate, g/l	0.8	0.8
3-Aminopyridine, g/l	-	0.5
Maximum current density (A/ft ²)	50	100
Maximum deposition rate (microns/min)	1.0	1.6

EXAMPLE 3

Printed circuit boards were plated in a Robins-Craig laboratory plater, first at 35°C and then at 60°C, using the following electrolyte compositions:-

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	A	B
Gold (as potassium cyanide complex, g/l)	8	8
Cobalt sulphate, g/l	0.8	0.8
5 3-Aminopyridine, g/l	-	0.5

The results were as follows:

	A(35°C)	B(35°C)	A(60°C)	B(60°C)
Maximum current density (A/ft ²)	110	200	-	300
10			(matte deposit obtained)	
Maximum deposition rate (microns/min)	1	2.5	-	6.0

It will be seen that the use of 3-aminopyridine allows higher temperatures to be used with great success.

15 EXAMPLE 4

Printed circuit boards were vat plated at 35°C with cathode rod agitation as follows:

	A	B
Gold (as potassium cyanide complex, g/l)	4	4
20 Nickel sulphate, g/l	1.25	1.25
3-Aminopyridine, g/l	-	0.25
Maximum current density (A/ft ²)	10	40
25 Maximum deposition rate (microns/min)	0.29	0.5

Substituting cobalt or iron for nickel gave comparable results.

EXAMPLE 5

Sheets of copper were plated at 40°C mounted on a rotating cathode to simulate high speed conditions as follows:-

5		A	B
	Gold (as potassium cyanide complex, g/l)	4	4
	Nickel sulphate, g/l	1.25	1.25
	3-Aminopyridine, g/l	-	0.25
10	Maximum current density (A/ft ²)	20	45
	Maximum deposition rate (microns/min)	0.4	0.6

In this Example, a 50% increase in deposition rate is obtained through the use of 3-aminopyridine, and the maximum current density is considerably increased. This occurred at relatively low gold concentrations, where the efficiency is known to fall rapidly as the current density increases.

20 EXAMPLE 6

Flat polished brass plaques were plated to a thickness of $2.5 \pm 0.5 \mu$ at 45°C and at 10 A/ft² in electrolyte baths of the following compositions (all at pH 4.7):-

		A	B	C
25	Citric acid, g/l	100	100	100
	Oxalic acid, g/l	-	-	10
	Gold (as potassium cyanide complex, g/l)	10	10	10
	3-Aminopyridine, g/l	0.5	0.5	0.5
30	Nickel sulphate, g/l	-	0.2	-
	Cobalt sulphate, g/l	-	-	0.5

The coated plaques were tested for wear resistance using hemispherically ended brass probes (5 mm diameter) which had been similarly plated. The probe was loaded to

150 gf and moved in a reciprocating manner across the plaque surface at a linear velocity not exceeding 2.5 mm/sec over a path length of between 7 and 10 mm.

5 Microscopic examination of the plaque and probe which had been coated using bath A revealed failure of the coating after only 20 reciprocations of the probe. The addition to the electrolyte bath of 0.2 g/l nickel sulphate (bath B) increased the failure point to 200 reciprocations, while the addition of 0.5 g/l cobalt
10 sulphate (bath C) gave a coating which had not failed even after 500 reciprocations.

This Example shows that the hardening effects of transition metal salts are retained in the baths of the present invention.

15 EXAMPLE 7

In this Example, the brightening ability of a number of different organic additives was tested. Flat polished brass plaques were plated at 35°C and 93 A/ft² using baths of the following composition:-

20 Potassium oxalate 25 g/l
Citric acid 100 g/l
Organic additive 0.5 g/l
Cobalt sulphate 0.5 g/l
Gold potassium cyanide 8 g/l
25 pH 4.5

The brightness of the resulting deposit was assessed visually on an arbitrary scale from 0 to 10 and also by the following procedure:-

A PYE Unicam SP8-100 twin-beam spectrophotometer
30 operating at 760 nm was adjusted to give a zero reading with the sample cell empty. The aluminium mirror from the sample beam path was then replaced with the experimentally plated plaque. The "optical density" reading given was thus a measure of the amount of light absorbed

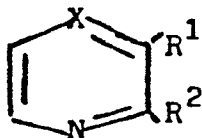
or scattered by the plaque.

The results obtained are set out in the Table
(a "bright" coating, as referred to in Example 1, corresponds to an "optical density" reading of from 0-0.25, or
5 from 8 to 10 on the arbitrary visual scale).

TABLE			
Additive	Brightening Ability (visual)	"O.D."	
10	3-aminopyridine	9	0.1
	2-aminopyridine	7	0.3
	4-aminopyridine	7	0.3
	aminopyrazine	10	0.03
	3-cyanopyridine	5	0.9
15	4-cyanopyridine	5	0.9
	thionicotinamide	10	0.02
	2,3-diaminopyridine (comparative)	3	1.6
	3,4-diaminopyridine (comparative)	0	>2
	3-aminoquinoline (comparative)	2	>2
20	4,5-diaminopyrimidine (comparative)	1	>2
	3-aminopyrazine-2-carboxylic acid (comparative)	1	>2
	pyridine-3-sulphonic acid (comparative)	1	>2

CLAIMS

1. An acid gold electroplating bath comprising gold in electrodepositable form, together with an organic additive of the general formula:-



- 5 wherein X is -N= or -CR³=, and R¹, R² and R³ are each hydrogen, or an amino-, amido, thioamido, or cyano- group provided that one (and no more than one) of R¹, R² and R³, when present, is not hydrogen.
2. An acid gold electroplating bath according to claim
- 10 1 which also contains a metallic additive.
3. An acid gold electroplating bath according to claim 1 or claim 2 wherein R¹ is an amino group.
4. An acid gold electroplating bath according to claim 1
- 15 wherein the organic additive is 3-aminopyridine, thionicotinamide, aminopyrazine or thioamidopyrazine.
5. An acid gold electroplating bath according to any preceding claim wherein the organic additive is present in a concentration of from 0.1 to 1.0 g/l.
6. An acid gold electroplating bath according to any
- 20 preceding claim wherein the metallic additive is a cobalt, nickel or iron salt.
7. An acid gold electroplating bath according to any preceding claim wherein said gold is present as a water-soluble complex at a concentration of from 1 to 20 g/l.
- 25 8. A process for forming a gold deposit on a metallic article, comprising electroplating said article in a bath as claimed in any preceding claim.