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ELECTRODEPOSITION OF COPPER AND COPPER ALLOYS

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The present invention relates to the electrodeposition of decorative and protective copper and copper alloys and more particularly to the electrodeposition of copper and copper alloys from improved alkaline-cyanide type baths.

Copper and copper alloy electrodeposits are used as protective and/or decorative finishes. They are also used as undercoats for subsequent electrodeposits, usually nickel and chromium. Alkaline-cyanide type baths are widely used for copper and copper alloy plating because of their relatively high plating speed, excellent throwing power and ease of maintenance. When plating from these baths, it has been found that anode current efficiencies are markedly lowered by anode polarization. Effective use has been made of relatively high anode current densities, e.g., current densities in the range up to about 20 amps. per square foot (a.s.f.), by adding tartrates and/or citrates to the bath. Although the anode current efficiencies of these baths have been improved by the foregoing addition agents, they still tend to fall off rapidly as the current density is raised. The use of still higher current densities is desirable provided the appreciable anode polarization is obviated, because the copper metal concentration of the bath can be better maintained without rapid fluctuation; there is decreased tendency toward anodic oxidation of cyanide resulting in decreased cyanide consumption; and fewer copper anodes are required for a given installation. Effective plating utilizing these higher anode current densities has not been generally feasible because of the anode polarization and low current efficiencies obtained at the higher current densities when plating from conventional cyanide baths, even those containing citrate or tartrate additions.

I have now discovered improved alkaline-cyanide type baths from which copper and copper alloys are electrodeposited at improved anode and cathode current efficiencies in the lower current density range and at greatly improved current efficiencies in the higher current density range.

It is an object of the present invention to provide an efficient and economical process for electrodepositing copper and copper alloy plates.

It is a further object of the present invention to provide improved baths for the electrodeposition of copper and copper alloys.

The invention also contemplates providing improved baths for the electrodeposition of copper.

Still another object of the invention is to provide improved baths for the electrodeposition of bronze.

The invention also contemplates providing improved baths for the electrodeposition of brass.

Other objects and advantages of the invention will become apparent from the following description.

The present invention contemplates electrodepositing decorative and/or protective copper or copper alloy plates from alkaline-cyanide baths containing at least 0.06 mole per liter of saccharate ion, $—OOC(CHOH)_4COO—$. The saccharate ion may be incorporated by the addition to the bath of a soluble saccharate compound. The cation

of the soluble saccharate compound should be one that does not adversely affect the properties or plating characteristics of the bath. Preferred saccharate compounds are the alkali metal saccharates, the alkali metal acid saccharates, copper saccharate and ammonium saccharate. The saccharate addition in the form of the potassium and/or sodium salts or their acid salts, or mixtures thereof, is especially preferred. The saccharate addition may also be made in the form of the mixed salts and particularly mixed sodium and potassium saccharate. Saccharic acid, $HOOC(CHOH)_4COOH$, when added to cyanide baths may generate HCN, dependent on the alkalinity of the bath. The acid addition may be safely made to highly alkaline baths. The generation of some HCN by the acid addition to less alkaline baths may be tolerated if the addition is made under controlled conditions (slowly) and with good ventilation. To a lesser degree, the use of the acid salts involves the same considerations.

Alkaline-cyanide baths containing as little as 0.06 mole per liter of a saccharate have improved anode current efficiencies, particularly at higher current densities, as well as improved cathode current efficiencies. It is preferred that the baths contain between about 0.09 mole per liter and 0.24 mole per liter of the saccharate additive. In amounts greater than 0.24 mole per liter, the improved characteristics obtained do not usually justify the additional cost.

The plates electrodeposited from these baths are sound and generally smooth and fine-grained. The addition of saccharate to alkaline-cyanide plating baths improves the operating characteristics and deposits for all alkaline-cyanide type copper and copper alloy plating baths. These generally include the following types of baths:

(1) Copper "strike" baths:

Copper	g./l.—About 15
Free potassium or sodium cyanide	g./l.—11–15
Temperature	°F.—120–140
Agitation	Little or none
Current density	a.s.f.—10–50

(2) Intermediate speed baths:

Copper	g./l.—30–38
Free potassium or sodium cyanide	g./l.—7.5–15
Potassium or sodium hydroxide	g./l.—15–30
Potassium or sodium carbonate (optional)	g./l.—About 15
Temperature	°F.—Generally 150–180
Agitation	Yes
Current density	a.s.f.—10–80

(3) Bright copper baths:

Copper	g./l.—37–75
Free potassium or sodium cyanide	g./l.—3.7–15
Potassium or sodium hydroxide	g./l.—15–30
Brightener, e.g., selenium bis diethyl-dithiocarbamate	g./l.—About 0.004
Temperature	°F.—Generally 150–180
Agitation	Yes
Current density	a.s.f.—5–50

(4) Brass plating baths:

CuCN	g./l.—30–225
$Zn(CN)_2$	g./l.—9.4–71
Total NaCN	g./l.—56–425
Na_2CO_3	g./l.—30–123
Free NaCN	g./l.—30–225
Temperature	°F.—70–100
C.D. (cathode)	a.s.f.—2–20

(5) Bronze plating baths:

Tin (as stannate)	g./l.—11–16
Copper	g./l.—18–30
Free KCN or NaCN	g./l.—20–25

Free KOH or NaOH	g./l.	6–10.5
Temperature	° F.	145–160
C.D. (cathode)	a.s.f.	20–100

Equivalent amounts of potassium or sodium salts may be used. These baths and operating conditions are merely illustrative of plating from alkaline-cyanide type copper and copper alloy baths. Alkaline-cyanide baths and processes are described in "Modern Electroplating," edited by A. G. Gray, pages 98–114 and 194–225 (1953). Electroplating from the bronze and brass plating baths illustrated may utilize the respective alloy anodes or copper anodes with periodic additions of the tin or zinc salts as they are deplenished.

The alkaline-cyanide bath may contain such primary brightening agents as the selenium and tellurium dithiocarbamates, e.g., selenium bis diethyldithiocarbamate; rhodanine; pseudothiohydantoin; 2,4 dioxothiazolidine; etc., alone or in conjunction with such secondary brighteners such as lead, zinc, bismuth, antimony salts, etc.

Conventional wetting agents of the kind generally used in alkaline-cyanide baths are also preferably incorporated in the bath. These include quaternary amine wetting agents such as C-decylbetaine, trimethylbenzylammonium chloride, or compounds such as alkyl β-aminopropionates, alkyl β-iminodipropionates, alkyl polyoxyethylene glycol ethers, etc.

Best results are achieved when utilizing in the electrodeposition process a method of preventing the thin film immediately adjacent to the cathode from becoming depleted in metal ion content. This is conventionally accomplished by agitation e.g., solution pumping, cathode movement, air agitation etc., or by diffusion effects, e.g., current interruption, periodic current reversal etc., or by combinations thereof. Superior results have been achieved by utilizing current interruption in conjunction with cathode movement. Anodes are conventionally not agitated.

For the purpose of providing a better understanding of the invention and a better appreciation of the advantages of the invention, the following illustrative examples are given.

EXAMPLE NO. 1

CuCN	60 g./l.
KCN	90 g./l.
KOH	22.5 g./l.
Potassium acid saccharate	22.5 g./l. (0.078 mole/l.).

EXAMPLE NO. 2

The bath of Example No. 1, using 22.5 g./l. Rochelle salts (potassium sodium tartrate) in place of the potassium acid saccharate.

Sound copper was electrodeposited from the baths of Example Nos. 1 and 2. The operative conditions and resultant current efficiencies are given in Table I.

Table I

	Percent Current Efficiency			
	Anode		Cathode	
	Bath No. 1	Bath No. 2	Bath No. 1	Bath No. 2
Room temp. (about 70° F.):				
50 a.s.f.	44	33.1	28.5	13.6
25 a.s.f.	25.1	1.0	39.9	35.2
12.5 a.s.f.	52.9	35.4	56.5	38.5
130° F.:				
50 a.s.f.	48.2	31.5	42.6	30.6
25 a.s.f.	49.5	37.7	78.7	82.1
12.5 a.s.f.	92	98.1	83.1	80.8
150° F.:				
50 a.s.f.	22	8.4	56.1	59.1
25 a.s.f.	93	68.9	73.3	78.9
12.5 a.s.f.	103	103	96	96

EXAMPLE NO. 3

CuCN	g./l.	60
Free KCN	g./l.	11.2
KOH	g./l.	22.5
Temp.	° F.	150
(*a*) Potassium saccharate	g./l.	15
(*b*) Potassium sodium tartrate	g./l.	15
(*c*) No additive		Control

The bath of Example No. 3 was run with additives (*a*) and (*b*) as well as without additives. The results of the tests are given in Table II below.

Table II

C.D., a.s.f.	Percent Anode Current Efficiencies		
	control (*c*)	tartrate (*b*)	saccharate (*a*)
5	100	99.6	99.6
10	93.1	93.2	92.8
20	12.8	16.3	74.5
40	3.0	2.9	25.5
50	1.1	11.4	20.2

This bath was also run with 60 g./l. additions of the above noted compounds (*a*) and (*b*).

EXAMPLE NO. 4

CuCN	g./l.	30
KCN (free)	g./l.	7.5
KOH	g./l.	11.2
$K_2SnO_3 \cdot 2H_2O$	g./l.	37.5
(*a*) Potassium acid saccharate	g./l.	22.5
(*b*) Sodium acid saccharate	g./l.	22.5
(*c*) Sodium saccharate	g./l.	22.5
Anodes		Copper

The bath using additives (*a*), (*b*), or (*c*) and operated at 130° F., and 150° F. with current densities of 10, 30 and 50 a.s.f., yields lustrous bronze deposits. The current efficiencies are high. The deposits are somewhat "redder" than deposits from baths of the same composition utilizing tartrates in place of saccharates, signifying a deposit containing more copper and less tin. This results from the greater copper current efficiency characteristics of the bath.

The excellent plating characteristics and the wide applicability of alkaline-cyanide copper-containing baths with saccharate additions is illustrated in these examples. Examples 1, 2 and 3 are furnished for comparative purposes. A study of the results in Tables I and II brings out the markedly improved anode and cathode current efficiencies achieved with baths containing the saccharate salt.

Additions of copper saccharate, ammonium saccharate, the other alkali metal (Li, Rb, Cs) saccharates, the alkali metal acid saccharates, and saccharic acid, when used in the foregoing baths, provide equally good electrodeposits with similarly improved current efficiencies as do the potasssium and sodium salts.

The sound copper and copper alloy electrodeposits obtained from alkaline-cyanide type baths of the present invention are obtained on such conventional basis metals as iron, steel, nickel, zinc, lead, copper, etc., and alloys thereof. On certain basis metals such as iron or steel and zinc-base die-castings the basis metal is first given an initial thin flash of copper from a low efficiency cyanide copper bath.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. An improved alkaline-cyanide bath for plating a metal selected from the class consisting of copper and

copper base alloys which comprises copper cyanide, free cyanide and a small but effective amount not less than about 0.06 mole per liter of saccharate ion, said amount being sufficient to improve the anode current efficiency.

2. A bath as claimed in claim 1, said amount being between about 0.09 and about 0.24 mole per liter.

3. An improved alkaline-cyanide bath for plating a metal selected from the class consisting of copper and copper base alloys which comprises copper cyanide, free cyanide and a small but effective amount not less than about 0.06 mole per liter of at least one saccharate selected from the class consisting of alkali metal saccharates, alkali metal acid saccharates, copper saccharate, ammonium saccharate and saccharic acid, said amount being sufficient to improve the anode current efficiency.

4. A bath as claimed in claim 3, said saccharate being potassium saccharate.

5. A bath as claimed in claim 3, said saccharate being ammonium saccharate.

6. A bath as claimed in claim 3, said saccharate being sodium saccharate.

7. A bath as claimed in claim 3, said saccharate being lithium saccharate.

8. A bath as claimed in claim 3, said saccharate being copper saccharate.

9. In a method of electrodepositing a metal selected from the class consisting of copper and copper base alloys, the step of depositing said metal from an alkaline-cyanide bath comprising copper cyanide, free cyanide and a small but effective amount not less than about 0.06 mole per liter of saccharate ion, said amount being sufficient to improve the anode current efficiency.

10. A method as claimed in claim 9, said amount being between about 0.09 and about 0.24 mole per liter.

11. In a method of electrodepositing a metal selected from the class consisting of copper and copper base alloys, the step of depositing said metal from an alkaline-cyanide bath comprising copper cyanide, free cyanide and a small but effective amount not less than about 0.06 mole per liter of at least one saccharate selected from the class consisting of alkali metal saccharates, alkali metal acid saccharates, copper saccharate, ammonium saccharate and saccharic acid, said amount being sufficient to improve the anode current efficiency.

12. A method as claimed in claim 11, said saccharate being potassium saccharate.

13. A method as claimed in claim 11, said saccharate being ammonium saccharate.

14. A method as claimed in claim 11, said saccharate being sodium saccharate.

15. A method as claimed in claim 11, said saccharate being lithium saccharate.

16. A method as claimed in claim 11, said saccharate being copper saccharate.

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