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BRIGHT COPPER PLATING

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9 Claims. (Cl. 204—52)

This invention relates to electroplating copper from cyanide baths, more particularly to a method for directly electroplating bright copper electrodeposits over a relatively wide current density range.

The copending patent application by C. J. Wernlund et al., Serial No. 206,002, filed May 4, 1938 now Patent No. 2,287,654, describes and claims a process for electroplating bright copper deposits. In this process the electrolyte is a solution of sodium copper double cyanide and the solution contains at least 1 oz. per gallon of sodium hydroxide, a limited amount of sodium cyanide beyond that required to form the double cyanide, and 1 to 8 ozs. per gallon of sodium sulfocyanide. This solution has been operated successfully in a large number of commercial installations to produce excellent bright copper plate. However, to obtain uniform bright copper deposits by this method it has often been found necessary to carefully control the cathode current density. It has been found that if the current density is permitted to become either too low or too high, dull deposits result. In some cases this has caused difficulty in electroplating articles when the electroplating conditions are such that the current density varies at different parts of the cathode. For example, the current density is usually higher on the edges of the cathode than at other parts under the usual commercial electroplating conditions. Also in electroplating recessed articles, the current density is usually lower in the recesses because these are at greater distance from the anodes. Such difficulties can of course be overcome by using anodes so shaped that all parts of the cathode surface will be equidistant from anode surface, but such mode of operation is uneconomical and not suited for commercial production except in relatively few instances.

An object of the present invention is to improve the bright copper plating process which is described and claimed in the aforesaid patent application. A further object is to provide a means for electroplating bright copper over a relatively wide current density range. Other objects will be apparent from the following description of the invention.

It has been discovered that if bright copper plating solutions of the type described in the aforesaid patent application are made up so as to contain both sodium and potassium ions in certain definite proportions, the current density bright range of the solution is markedly increased. For example, it has been found that if a certain proportion of one of the sodium compounds in the aforesaid solution is replaced by an equivalent amount of the corresponding potassium compound, excellent bright copper deposits can be obtained over a distinctly wider current density range of current densities. The following example is illustrative of this effect:

Example I

Two electroplating baths were prepared as follows:

	Bath 1	Bath 2
NaCN.....oz./gal.	18	18
CuCN.....oz./gal.	16	16
NaCNS.....oz./gal.	2	1
NaOH.....oz./gal.	4	None
KOH.....oz./gal.	None	5
Molar ratio: Na/K		4/1

To each bath was also added 4 cc. per gal. of a high molecular weight betaine as anti-pitting agent. Both baths were operated at 82–83° C., while stirring to cause flow of electrolyte past the cathode. Each bath was operated over a wide range of current densities to determine the maximum and minimum current densities at which bright copper deposits could be obtained. The following results were obtained:

Bath	Bright plating C. D. range
1	From 15 to 45 amp./sq. ft., or 30 amp./sq. ft.
2	From 20 to 63 amp./sq. ft., or 43 amp./sq. ft.

It has further been discovered that by the addition of potassium ions to the sulfocyanide type of copper cyanide plating baths, the minimum amount of sulfocyanide required to produce an excellent bright plate is markedly reduced. Thus, while it is usually necesary to maintain an alkali sulfocyanide concentration of at least 1 oz. per gal. to obtain bright deposits, if part of the sodium ions are replaced by potassium ions as herein described, equally good results may be obtained with an alkali sulfocyanide concentration as low as 0.25 oz. per gallon. In fact, if the sulfocyanide is omitted from the bath, it will be found that the presence of the potassium ions still has a certain brightening effect, although the resulting deposit does not have the high degree of brightness obtainable from the sulfocyanide baths. The following example illustrates the brightening effect of the potassion ions in a copper plating bath containing no sulfocyanide:

Example II

Two copper plating baths were prepared as follows:

Ingredients	Bath 1	Bath 2
CuCN.....oz./gal..	16	16
NaCN.....oz./gal..	18	18
NaOH.....oz./gal..	4	None
KOH.....oz./gal..	None	6
Molar ratio: Na/K.....	.....	3/1

Each bath was operated at a temperature of about 80° C. to electroplate steel cathodes at various current densities. The following results were obtained:

Current density	Appearance of electrodeposits	
	Bath 1	Bath 2
20 amp./sq. ft.....	Dull to semi-bright....	Semi-bright.
30 amp./sq. ft.....	Bright and dull areas..	Fairly bright, uniform.
45 amp./sq. ft.....	....do.....	Do.
45–75 amp./sq. ft.....	Dull.....	Do.

In order to obtain bright copper plate in accordance with the present invention it has been found necessary (1) to maintain a relatively high concentration of the copper double cyanide, i. e., that equivalent to at least 8 oz. per gallon of copper cyanide (CuCN), (2) to make the bath alkaline by the addition of at least 1 oz. per gallon of alkali metal hydroxide and (3) to avoid any large excess of free cyanide. Preferably, the copper cyanide concentration should lie between 8 and 22 oz. per gallon. The total alkali metal cyanide should not exceed that which is equivalent to a weight ratio of sodium cyanide to copper cyanide equal to 1.25 to 1; preferably this ratio should be about 1.1 to 1. The total alkali metal hydroxide concentration preferably should be about 3–8 oz. per gallon. The concentration of alkali metal sulfocyanide should lie between 0.25 and 8 oz. per gallon. Finally in order to obtain the improvements in brightness and in the current density bright range, it is essential that the electrolyte contains sodium and potassium compounds in such proportions that there is from 1 to 6 moles of sodium ions for each mole of potassium ions in the bath.

Preferably the potassium compound is added as potassium hydroxide, and usually it will not be necessary to add any other potassium compound in order to obtain the desired concentration of potassium in the bath. For example, excellent bright copper deposits may be obtained from electroplating baths having the following composition:

Copper cyanide (CuCN).....	oz. per gal..	8	to 22
Sodium cyanide.....	oz. per gal..	8	to 27.5
Sodium sulfocyanide.....	oz. per gal..	0.25	to 8
Potassium hydroxide.....	oz. per gal..	3	to 8
Ratio: moles Na ions/moles K ions.....		1/1	to 6/1

In baths made according to the above formulae, the sodium cyanide concentration must be from 1.0 to 1.25 times the concentration of the copper cyanide.

The various addition agents which are suitable for use in bright copper cyanide plating solutions may be utilized with equal effectiveness in the bath of the present invention. For example, carbohydrates, such as starch, gum arabic or various sugars may be added. Likewise, the high molecular betaines, such as those claimed and described in Holt, U. S. patent application, Serial No. 297,433, filed October 2, 1937, now Patent No. 2,255,057, may be used effectively in the present plating bath.

To obtain the best results it is preferable to operate the plating bath hot, e. g., from 60° C. up to the boiling point. In most cases the optimum operating temperature will be about 75 to 85° C. It is also preferable to keep the cathode in motion, or alternatively to keep the bath in motion past the cathode. Known methods for moving the cathode or stirring the bath may be used for this purpose, for example, as described in the above mentioned patent application by C. J. Wernlund, et al. The effect of the partial replacement of sodium by potassium in the copper plating bath is to brighten the deposit, to widen the current density range at which the bright copper deposit can be obtained and to decrease the minimum amount of sulfocyanide. It has been found that this effect is not appreciable until sufficient potassium has been added to the bath so that the molar ratio of sodium ions to potassium ions in the bath is equal to 6 to 1. In general, as the proportion of potassium is increased in the bath within these limits, the bright current density range is widened correspondingly. However, if the amount of potassium is increased so that it is in excess of that represented by a molar ratio of sodium to potassium ions of 1 to 1, the resulting plate tends to be dull at the lower current densities. Such high proportions of potassium ions in the plating bath therefore are not desirable because they do not permit the deposition of sufficiently bright and uniform plate. Therefore, in operating the present invention, the concentration of potassium compounds is limited so that the molar ratio of sodium ions to potassium ions is kept between the limits of 1:1 to 6:1 and preferably at about 2:1 to 4:1.

I claim:

1. A process for the electrodeposition of bright copper which comprises electrolyzing a solution containing 8 to 22 oz. per gallon of copper cyanide, 3 to 8 oz. per gallon of alkali metal hydroxide, 0.25 to 8 oz. per gallon of alkali metal sulfocyanide and an amount of alkali metal cyanide equivalent to a sodium cyanide to copper cyanide weight ratio of from 1:1 to 1.25:1, the alkali metal constituents of said solution being sodium and potassium present in the proportion of 1 to 6 moles of sodium ions for each mole of potassium ions.

2. A process for the electrodeposition of bright copper which comprises electrolyzing a solution containing 8 to 22 oz. per gallon of copper cyanide, an amount of alkali metal cyanide sufficient to dissolve said copper cyanide and equivalent to a concentration of sodium cyanide which is 1 to 1.25 times the concentration of said copper cyanide, 3 to 8 oz. per gallon of alkali metal hydroxide and 0.25 to 8 oz. per gallon of alkali metal sulfocyanide, the alkali metal constituents of said solution being sodium and potassium present in the proportion of 1 to 6 moles of sodium ions for each mole of potassium ions.

3. A process for the electrodeposition of bright copper which comprises electrolyzing a solution containing 8 to 22 oz. per gallon of copper cyanide, 1 to 1.25 parts by weight of sodium cyanide for each part by weight of copper cyanide, 0.25 to 8 oz. per gallon of sodium sulfocyanide and an amount of potassium hydroxide, within 3 to 8 oz. per gallon, such that the molar ratio of

sodium ions to potassium ions in said bath is from 1:1 to 6:1.

4. A process for the electrodeposition of bright copper which comprises electrolyzing a solution containing 8 to 22 oz. per gallon of copper cyanide, an amount of alkali metal cyanide which is equivalent to a concentration of sodium cyanide equal to 1 to 1.25 times the concentration of said copper cyanide, and 3 to 8 oz. per gallon of alkali metal hydroxide, the alkali metal constituents of said bath being sodium and potassium present in the proportion of 1 to 6 moles of sodium ions for each mole of potassium ions.

5. A process for the electrodeposition of bright copper which comprises electrolyzing a solution containing 8 to 22 oz. per gallon of copper cyanide, an amount of sodium cyanide equal to 1 to 1.25 times the concentration of said copper cyanide and an amount of potassium hydroxide, within 3 to 8 oz. per gallon, such that the molar ratio of sodium ions to potassium ions in said bath is from 1:1 to 6:1.

6. A plating bath for the electrodeposition of bright copper comprising a solution containing 8 to 22 oz. per gallon of copper cyanide, an amount of alkali metal cyanide which is equivalent to a concentration of sodium cyanide equal to 1 to 1.25 times the concentration of said copper cyanide, and 3 to 8 oz. per gallon of alkali metal hydroxide, the alkali metal constituents of said bath being sodium and potassium present in the proportion of 1 to 6 moles of sodium ions for each mole fo potassium ions.

7. A plating bath for the electrodeposition of bright copper comprising a solution containing 8 to 22 oz. per gallon of copper cyanide, an amount of sodium cyanide equal to 1 to 1.25 times the concentration of said copper cyanide and an amount of potassium hydroxide, within 3 to 8 oz. per gallon, such that the molar ratio of sodium ions to potassium ions in said bath is from 1:1 to 6:1.

8. A plating bath for the electrodeposition of bright copper comprising a solution containing 8 to 22 oz. per gallon of copper cyanide, 3 to 8 oz. per gallon of alkali metal hydroxide, 0.25 to 8 oz. per gallon of alkali metal sulfocyanide and an amount of alkali metal cyanide equivalent to a sodium cyanide to copper cyanide weight ratio of from 1:1 to 1.25:1, the alkali metal constituents of said solution being sodium and potassium present in the proportion of 1 to 6 moles of sodium ions for each mole of potassium ions.

9. A plating bath for the electrodeposition of bright copper comprising a solution containing 8 to 22 oz. per gallon of copper cyanide, 1 to 1.25 parts by weight of sodium cyanide for each part by weight of copper cyanide, 0.25 to 8 oz. per gallon of sodium sulfocyanide and an amount of potassium hydroxide, within 3 to 8 oz. per gallon, such that the molar ratio of sodium ions to potassium ions in said bath is from 1:1 to 6:1.

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