United States Patent Office

2,970,951

Patented Feb. 7, 1961

2,970,951

COPPER COMPOSITIONS AND METHOD FOR MAKING THE SAME

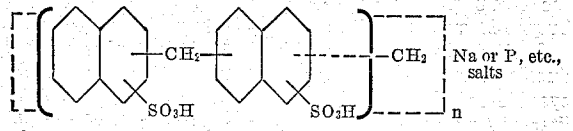
John W. Manquen, Berkley, and Henry Brown, Huntington Woods, Mich., assignors to The Udylite Research Corporation, Detroit, Mich., a corporation of Michigan

No Drawing. Filed Dec. 4, 1958, Ser. No. 778,067

18 Claims. (Cl. 204—52)

This invention relates to the electrodeposition of copper from aqueous alkaline cyanide solutions. More particularly, this invention relates to the use of certain new organic addition agents for cyanide copper plating baths, and especially to the use of a new combination of addition agents to achieve bright, very fine-grained, ductile copper electrodeposits over a very wide range of cathode current densities.

It has been found that the addition of certain acetylenic ether nitriles (illustrated in Table I) to aqueous alkaline copper cyanide plating baths as the sole brightening agent increases the luster of the copper electrodeposits. When these compounds of Table I are used in conjunction with water soluble salts (e.g. Na or K salts) of methylene bis-(naphthalene sulfonic acids) as exaemplified by the formula



where *n* is a whole number, and especially the methylene bis-(alpha naphthalene sulfonic acids), in an amount of 0.1 to 10 grams/liter an enhanced brightness occurs in the medium current density range plate down to the very low current density range plate.

TABLE I

	Useful Concentration Range grams/liter
(1) HO-CH_2-C≡C-$CH_2O C_2H_4$C≡N (1-Hydroxy-4-(beta cyanoethoxy) butyne-2).	0.02–1.0 (0.1–0.3 average).
(2) N≡C-$C_2H_4OCH_2$-C≡C-$CH_2O C_2H_4$C≡N (1,4-Di-(beta cyanoethoxy) butyne-2).	0.02–1.0 (0.2 average).

It was further found that the above combination of brighteners give even further improvement when tellurium is also dissolved in the bath. The dissolution of tellurium in the bath is most readily accomplished by preliminarily dissolving tellurium dioxide in sodium or potassium hydroxide solution or by dissolving tellurium dioxide directly in the bath. When tellurium is present in the bath in a concentration of about 0.0002–0.006 grams/liter, preferably about 2 mg./liter in conjunction with a compound from Table I or 2-butyne-1,4-diol at a concentration of about 0.1–0.3 grams/liter, and methylene bis-(naphthalene sulfonic acids) at a concentration of about 3 grams/liter, with the conjunctive use of these three types of brighteners, the tendency for formation of cloudy plate at the high current density areas is minimized and the brightness of the plate is greatly enhanced uniformly from the highest current density ranges down to the lowest current density ranges. Moreover the presence of tellurium greatly decreases the tendency of the plate to stain, particularly from humidity and fingerprints.

The copper cyanide baths can be made up of copper cyanide and an alkali metal cyanide with or without the addition of an alkali metal hydroxide or carbonate, and with or without the addition of tartrates, glycolates, or gluconates, citrates, malates or other similar organic acids or their salts such as the sodium, potassium or ammonium salts. In general, the preferred baths contain salts of these organic acids. Preferably the baths should contain both sodium and potassium ions, through the alkali metal ions may be exclusively sodium or potassium. Satisfactory results are obtained when the copper cyanide varies between about 3 to about 12 ounces per gallon, the alkali metal cyanide varies between about 4.5 to about 20 ounces per gallon, and the alkali metal hydroxide varies between about 0.5 and about 4 ounces per gallon. The copper cyanide baths are preferred to be operated warm, with optimum results at temperatures of 50° C.–95° C., though cooler or warmer baths may be used with excellent results. It is preferred to use the baths of composition similar to the examples given below, operated at the maximum current densities which can be used under the given conditions of temperature and agitation. Under the usual conditions of commercial operation, cathode current densities of 10–60 amperes per square foot are used with the normal cathode rod type agitation, or solution agitation. On articles of simple shape, current densities of 100 amps./sq. ft. can be used when vigorous agitation is used. The following three examples are intended to illustrate typical copper baths which produce copper plate of good luster and color but not of the highest brightness.

Example I

	Ounces/gal.	Grams/liter
Copper cyanide	6.0	45.
Potassium cyanide	9.7	72.75.
Potassium hydroxide	2.0	15.
Rochelle salts	6.0	45.
1-hydroxy-4-(beta cyanoethoxy) butyne-2 (Compound I, Table I).		0.02–1.0 (average 0.1–0.3).

Example II

	Oz./gal.	Grams/liter
Copper cyanide	4.0	30.
Sodium cyanide	5.0	37.5.
Sodium hydroxide	2.5	18.75.
Rochelle salts	4.0	30.
1,4-Di-(beta cyanoethoxy) butyne-2 (Compound 2 of Table I).		0.02–1.0 (average 0.2 g./l.).

Example III

	Oz./gal	Grams/liter
Copper cyanide	6	45.
Sodium cyanide	7.5	56.2b.
Potassium hydroxide	2.5	18.75.
Rochelle salts	4	30.
1-hydroxy-4-(beta cyanoethoxy) butyne-2 (Compound I of Table I).		0.02–1.0 (average 0.1–0.3).

The addition of the above-described acetylenic derivatives or combinations thereof to cyanide copper electroplating baths also containing soluble salts of methylene bis-(naphthalene sulfonic acids) and tellurium as explained above, greatly increases the brightness and uniformity of the copper electrodeposit, enables the electrodeposition of bright very fine-grained copper electrodeposits over extended temperature ranges, and allows the operation of the electroplating baths over extended current density ranges. The plating of irregular objects having projections and recesses is consequently

greatly simplified. These improvements are obtained by using the baths of Examples V–VII which illustrate the brightest cyanide copper plating baths of this invention.

Example IV

	Grams/liter
Copper cyanide	45
Sodium cyanide	56.5
Potassium hydroxide	18.75
Rochelle salts	30
Na or K salts of methylene bis-(alpha naphthalene sulfonic acid)[1] (average 3 g./l.)	0.1–10.0
1-hydroxy-4-(beta cyanoethoxy) butyne-2 (compound 1 of Table I)	0.1–0.3

[1] Daxad No. 11 (Dewey and Almy Co.)

Example V

	Grams/liter
Copper cyanide	45
Sodium cyanide	56.5
Potassium hydroxide	18.75
Rochelle salts	30
Tellurium (dissolved as TeO_2)	0.0002–0.006
Na or K salt of methylene bis-(alpha naphthalene sulfonic acid [1]	3
1,4-di-(betacyanoethoxy) butyne-2 (compound 2 of Table I)	0.2

[1] Daxad No. 11 (Dewey and Almy Co.)

Example VI

	Grams/liter
Copper cyanide	45
Sodium cyanide	56.5
Potassium cyanide	18.75
Rochelle salts	30
Tellurium	0.002–0.006
Na or K salt of methylene bis-(alpha naphthalene sulfonic acids)	3
1-hydroxy-4-(beta cyanoethoxy)butyne-2	0.1–0.3

The baths of Examples IV–VI produce uniformly bright very fine-grained ductile copper deposits over current densities extending from the highest to the lowest normally encountered in commercially important electroplating operations.

In general, wetting agents are not needed especially with the less concentrated metal baths. Nevertheless, wetting agents may be employed, if desired. When cationic wetting agents are used, anionic wetting agents such as sodium lauryl sulfate or sodium dodecyl ether sulfate should not be used unless the cationic wetting agent is weakly cationic (short chain type). Non-ionic wetting agents may also be used.

Periodic current reversals or current interruption can be used with the above baths with some benefit. However, because of the very wide bright plating range of Examples V–VI, the need for the use of interrupted current or periodic current reversals is minimized. Sequestering or chelating agents, such as ethylene diamine tetraacetates or similar compounds may be used in the copper baths of this invention to sequester impurities such as trivalent chromium, without affecting the brightness of the deposits.

What is claimed is:

1. A bath for electrodepositing bright ductile copper comprising an aqueous alkaline copper cyanide solution containing dissolved therein an acetylenic ether nitrile selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2 and 1,4-di-(beta cyanoethoxy) butyne-2 in an amount of from about 0.02 gram/liter to about 1.0 gram per liter.

2. A bath for electrodepositing bright ductile copper comprising an aqueous alkaline copper cyanide solution containing the compound 1-hydroxy-4-(beta cyanoethoxy) butyne-2 dissolved therein in an amount from about 0.02 to about 1.0 gram per liter.

3. A bath for electrodepositing bright ductile copper comprising an aqueous alkaline copper cyanide solution containing the compound 1,4-di-(beta cyanoethoxy) butyne-2 dissolved therein in an amount from about 0.02 to about 1.0 gram per liter.

4. A bath for electrodepositing bright fine-grained ductile copper comprising an aqueous alkaline copper cyanide solution which contains about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and about 0.02 to about 1.0 gram per liter of at least one compound seletced from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

5. A bath for electrodepositing bright fine-grained ductile copper comprising an aqueous alkaline copper cyanide solution which contains about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and about 0.02 to about 1.0 gram per liter of 1-hydroxy-4-(beta cyanoethoxy) butyne-2.

6. A bath for electrodepositing bright fine-grained ductile copper comprising an aqueous alkaline copper cyanide solution which contains about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and about 0.02 to about 1.0 gram per liter of 1,4-di-(beta cynaoethoxy) butyne-2.

7. A bath for electrodepositing bright very fine-grained ductile copper comprising an aqueous alkaline copper cyanide solution containing an amount of tellurium dissolved therein in the range of about 0.0002 to about 0.006 gram per liter, about 0.1 to 10.0 grams/liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and in addition thereto about 0.02 to about 1.0 gram per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

8. A bath for electrodepositing bright fine-grained ductile copper comprising an aqueous alkaline copper cyanide solution containing about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(alpha naphthalene sulfonic acids), about 0.02 to about 1.0 gram per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

9. A bath for electrodepositing bright very fine-grained ductile copper comprising an aqueous alkaline copper cyanide solution containing an amount of tellurium dissolved therein in the range of about 0.0002 to about 0.006 gram per liter, about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(alpha naphthalene sulfonic acids), and in addition thereto about 0.02 to 1.0 grams per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

10. A method for electrodepositing bright ductile copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing dissolved therein an acetylenic ether nitrile selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2 and 1,4-di-(beta cyanoethoxy) butyne-2 in an amount of from about 0.02 gram/liter to about 1.0 gram per liter.

11. A method for electrodepositing bright ductile copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing the compound 1-hydroxy-4-(beta cyanoethoxy) butyne-2 dissolved therein in an amount from about 0.02 to about 1.0 gram per liter.

12. A method for electrodepositing bright ductile copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing the compound 1,4-di(beta cyanoethoxy) butyne-2 dissolved therein in an amount from about 0.02 to about 1.0 gram per liter.

13. A method for electrodepositing bright ductile fine-grained copper which comprises electrodepositing copper

from an aqueous alkaline copper cyanide solution containing about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-naphthalene sulfonic acids), and about 0.02 to about 1.0 gram per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

14. A method for electrodepositing bright ductile fine-grained copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and about 0.02 to about 1.0 gram/liter of 1-hydroxy-4-(beta cyanoethoxy) butyne-2.

15. A method for electrodepositing bright ductile fine-grained copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and about 0.02 to about 1.0 gram per liter of 1,4-di-(beta cyanoethoxy) butyne-2.

16. A method for electrodepositing bright ductile very fine-grained copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing an amount of tellurium dissolved therein in the range of about 0.0002 to about 0.006 gram/liter, about 0.1 to 10.0 grams/liter of a water soluble salt of methylene bis-(naphthalene sulfonic acids), and in addition thereto about 0.02 to about 1.0 gram per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

17. A method for electrodepositing bright ductile fine-grained copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis(alpha naphthalene sulfonic acids), and in addition thereto about 0.02 to about 1.0 gram per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

18. A method for electrodepositing bright ductile very fine-grained copper which comprises electrodepositing copper from an aqueous alkaline copper cyanide solution containing an amount of tellurium dissolved therein in the range of about 0.0002 to about 0.006 gram/liter, about 0.1 to 10.0 grams per liter of a water soluble salt of methylene bis-(alpha naphthalene sulfonic acids), and in addition thereto about .02 to 1.0 gram per liter of at least one compound selected from the group consisting of 1-hydroxy-4-(beta cyanoethoxy) butyne-2, and 1,4-di-(beta cyanoethoxy) butyne-2.

References Cited in the file of this patent

UNITED STATES PATENTS

2,841,542	Manquen	July 1, 1958
2,881,122	Foulke et al.	Apr. 7, 1959

FOREIGN PATENTS

874,100	Germany	Apr. 20, 1953

UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,970,951 February 7, 1961

John W. Manquen et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, extreme right-hand portion of the formula, for "Na or P, etc., salts" read -- Na or K, etc., salts --; column 2, line 9, for "through" read -- though --; column 4, line 5, for "10" read -- 1.0 --; column 5, line 3, for "bis-naphthalene sulfonic acids)" read -- bis-(naphthalene sulfonic acids) --.

Signed and sealed this 5th day of September 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents