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ELECTROPLATING

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This invention relates to copper plating and, more particularly, to electrodepositing copper from an aqueous alkaline cyanide copper plating bath. The invention provides an improved process based on our discovery that alkali-soluble tellurium compounds, when incorporated in a copper plating bath in conjunction with one or more water-soluble acetylenic compounds, are capable of promoting the formation of bright copper electroplates over a very wide current density range. The current density range over which bright deposits are formed, and the quality of the deposit, may be further improved by incorporating additional agents such as lead salts, chelating agents for copper, condensation products of naphthalene sulfonic acid with formaldehyde, selenium compounds, wetting agents, and other materials.

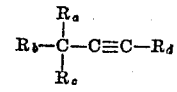
The process of our invention is carried out by using an alkaline cyanide copper plating bath in which both the concentration of copper and of cyanide, as well as the ratio of copper concentration to cyanide concentration, are most advantageously within the limits generally considered to be optimum for standard copper electroplating operations. Such plating baths usually contain from 20 to 75 grams per liter of copper and from 45 to 185 grams per liter of an alkali metal cyanide. With this plating bath, we generally prefer to employ from about 0.001 to about 1 millimole per liter of an alkali-soluble tellurium compound, and from about 1 to 250 millimoles per liter of a water-soluble acetylenic compound. Among the further addition agents which we preferably include in the bath are small quantities of alkali-soluble lead salts, polyamino polycarboxylic acid chelating agents, bis[sulfonaphthyl]methanes, and water-dispersible wetting agents.

Any tellurium compound capable of being dissolved in weakly alkaline media, may be successfully employed in preparing the plating bath. Selection of a suitable tellurium compound for inclusion in the plating bath may be made from either organotellurium compounds or tellurium salts, including the alkali-soluble tellurites and tellurates. Although these tellurium compounds may be used over a very wide range of concentrations, they are preferably employed in an amount in the range from 0.00015 to 0.15 gram per liter, or expressed in equivalent weights, from 0.001 to 1 millimole per liter. A particularly satisfactory concentration range for general use is from 0.01 to 0.1 millimole per liter.

The tellurium compound is employed in the plating bath with a water-soluble acetylenic compound. Our experiments indicate that any water-soluble acetylenic compound effectively cooperates to some degree with the tellurium compound for enhancing the brightness of the copper electroplate, though some acetylenic compounds are more effective than others. The common structural feature of these water-soluble acetylenic compounds is the presence of a highly nucleophilic triple bond which is neither sterically hindered nor impeded in approaching the cathode. Only relatively small quantities of the acetylenic compounds are required in the plating bath

when used in conjunction with a tellurium compound. Concentrations as low as ¼ millimole per liter, or even less, are effective in some cases, though in general it is preferable to employ at least 1 millimole per liter. There appears to be no critical upper limit on the concentration of the acetylenic compound save solubility, but there is no advantage in using more than about 250 millimoles per liter, and in most plating baths substantially the full benefit of its presence is achieved with 10 millimoles per liter or even less.

While any water-soluble acetylenic compound may be employed in the plating bath conjointly with a tellurium compound to produce bright copper deposits in accordance with the invention, we have obtained particularly satisfactory results using oxygen-containing acetylenic compounds (particularly acetylenic alcohols) and acetylenic amine compounds. Compounds from among the oxygen-containing acetylenic group which have been found to be very satisfactory are those which have the formula



in which R_a and R_b are substituents selected from the group consisting of hydrogen and alkyl and hydroxy-substituted alkyl radicals, R_c is a substituent selected from the group consisting of hydroxy, hydroxymethyl, methoxy, hydroxyethyl, ethoxy, and hydroxyethoxy radicals, and R_d is a substituent selected from the group consisting of hydrogen, halogen, diethylaminoethyl, morpholinomethyl, alkyl, alkenyl, alkynyl, and hydroxy-, methoxy-, and ethoxy-substituted alkyl, alkenyl, and alkynyl radicals.

The acetylenic amines appear to function most effectively at the higher current density areas of the cathode. As a general rule, the acetylenic amines are less soluble in alkaline media than the oxygen-containing acetylenic compounds. Nonetheless, various acetylenic amines have been used with notable success in conjunction with a tellurium compound, and include those water-soluble acetylenic amines which may be selected from the group consisting of monoacetylenic primary monoamines, monoacetylenic polyamines, polyacetylenic monoamines, polyacetylenic polyamines, acetylenic alkanolamines, and acetylenic ammonium compounds.

The compounds listed in Table I are examples of water-soluble acetylenic compounds which have been used successfully in plating baths containing tellurium compounds. As indicated previously, these compounds may be used in concentrations from 1 to 250 millimoles per liter.

The combined use of tellurium and selenium compounds, two brightening agents which normally would be expected to cooperatively function together in the plating bath, results suprisingly in deposits which are erratically bright over the low and median current density ranges. The selenium compounds apparently act merely as complementary brightening agents with the tellurium compounds. But when minute quantities of a water-soluble acetylenic compound are included in a plating bath containing both tellurium and selenium compounds, bright copper electrodeposits are produced over a wide current density range. Consequently, the selenium compounds may be employed effectively in conjunction with tellurium compounds in the presence of a water-soluble acetylenic compound. Any alkali-soluble selenium compound may be employed, including both organo-selenium compounds and selenium salts such as selenides, selenites, selenates, and selenocyanates. These selenium com-

TABLE I

Water-soluble acetylenic compounds for bright copper plating

Compound	Structure
2-Butyne-1,4-diol	$HO-CH_2-C\equiv C-CH_2OH$
Propargyl alcohol	$HC\equiv C-CH_2OH$
Dipotassium acetylenedicarboxylate	$KOOC-C\equiv C-COOK$
1,4-Dimethoxy-2-butyne	$CH_3OCH_2C\equiv CCH_2OCH_3$
2,4-Hexadiyne-1,6-diol	$HOCH_2-C\equiv C-C\equiv C-CH_2OH$
1-(N,N-diethylamino)-2-butyn-4-ol	$(CH_3CH_2)_2N-CH_2C\equiv CCH_2OH$
Dimethyl 3-hexyndioate	$CH_3OOCCH_2C\equiv CCH_2COOCH_3$
1-Butyn-4-ol	$HC\equiv C-CH_2CH_2OH$
3-Methyl-3-hydroxyethoxy-1-butyne	$H_3C-C(CH_3)(OC_2H_4OH)C\equiv CH$
3-Methyl-1-butyn-3-ol	$CH_3-C(CH_3)(OH)C\equiv CH$
Propargyl amine	$HC\equiv CCH_2NH_2$
1,4-(N,N-diethylamino)-2-butyne	$(CH_3CH_2)_2N-CH_2C\equiv CCH_2N(CH_3CH_3)_2$
3-Amino-3-methyl-1-butyne	$CH_3C(CH_3)(NH_2)C\equiv CH$
3-Amino-3-ethyl-1-butyne	$CH_3C(C_2H_5)(NH_2)C\equiv CH$

pounds may be used over a very wide range of concentrations, but preferably are used in an amount to yield selenium in the range from about 0.0001 to about 0.1 gram per liter, or expressed in equivalent weights, from about 0.001 to about 10 millimoles per liter. In most cases the selenium concentration is maintained advantageously within the narrower concentrations range from 0.01 to 1 millimole per liter.

The lustre and brilliance of the electroplate may be still further broadened by incorporating a small amount of certain auxiliary agents in the plating bath. These auxiliary agents include compounds which influence the brightness of the deposit by suppressing haze and cloud formation, as well as compounds which are incapable of promoting bright copper deposits by themselves but which have the capacity to alter the surface properties of the plating bath, or to sequester and render ineffective metallic impurities contained in the bath. Although a large number of auxiliary agents may be incorporated in the plating bath containing both tellurium and acetylenic compounds, it has been our experience that nitriles, chelating agents for copper, condensation products of naphthalene sulfonic acid with formaldehyde, alkali soluble lead compounds, and wetting agents such as polyethylene and polyoxyethylene glycols, as well as selenium compounds, are among the most advantageous.

Alkali - soluble nitriles, especially those containing the structural moiety —Z—C≡N in which Z is either an imino or methylene radical, are effective for extending the range over which bright deposits are formed. Some examples of such nitriles which have been used successfully in embodiments of this invention include succinonitrile, dicyandiamide, β,β'-oxydipropionitrile, potassium dicyanoguanidine, β-sulfopropionitrile, and sodium dicyandiamide. In general, from about 0.05 to about 0.5 gram per liter of the nitrile may be employed effectively. The nitrile, as well as other auxiliary agents, may be added at any time during the preparation of the bath.

The chelating agents which are advantageously incorporated in the plating bath are those which are capable of chelating with divalent copper in the presence of cyanide ions. The effect of these agents is to render operation of the bath less subject to variation due to small changes in concentration of other constituents, and they also minimize any tendency for haze to form. Among the chelating agents which may be used with particular success are the polyamino polycarboxylic acids and their salts, including especially dihydroxyethylglycine, diethylenetriaminopentaacetic acid, nitrilotriacetic acid, hydroxyethylethylene diaminotriacetic acid, ethylenediaminotetraacetic acid, and salts thereof (especially the alkali metal and ammonium salts). Commercially available alkali chelating agents of the general character, such as the product marketed by the Dow Chemical Company under the tradename of "Versene Fe–3 Specific," have been found to be very effective. The concentration range over which the chelating agent may be used in the plating bath is very wide. As little as 0.01 gram per liter is effective, and as much as 50 grams per liter may be present.

Other auxiliary agents which may be used to enhance the brightening capacity of the plating bath are the bis-[sulfonaphthyl]methanes. These compounds are prepared by condensing a naphthalene sulfonic acid with formaldehyde in the presence of a basic catalyst, and include products commercially available under the tradenames of "Tamol N," "Tanak SC," "Tanak AA," "Lomar," "Tanasol," "Daxad 11," and "Daxed 11–KLS." They are particularly effective for minimizing formation of cloudy deposits, especially in the middle current density range. They have been employed successfully in concentrations from 0.5 to 15 grams per liter.

Polyethylene glycols, polypropylene glycols, and polyoxyethylene glycols and amides are examples of wetting agents which are often advantageously present in the bath. They reduce the surface tension of the bath and minimize the adverse effect of gassing in the higher current density areas. They may be used over a wide range of concentrations, from 0.05 to 20 grams per liter.

These auxiliary addition agents may be used all together in the bath, or they may all be omitted, or they may be used in whatever combination is most advantageous for a particular plating operation. We have had particular success using all of them except the wetting agent, the latter being used optionally depending on conditions; but in some cases one or two of them may be used advantageously without the others.

A conventional alkali cyanide copper plating bath, to which the above-identified addition agents may be added for making up a plating bath in accordance with this invention, customarily has the following composition:

	Ounces per Gallon	Grams per Liter
Copper (as cuprous ion)	3 to 10	20 to 75
Potassium Cyanide	6 to 24	45 to 180
Potassium Hydroxide	1 to 5	7.5 to 40
Potassium Sodium Tartrate	2 to 6	15 to 45
Potassium Carbonate	0 to 15	0 to 110

The Rochelle salt (potassium sodium tartrate) and the carbonate are optional ingredients which often are present in modern cyanide copper plating baths, but which are not essential for purposes of this invention. Sodium salts may be used interchangeably for the potassium salts, but the use of the potassium plating bath has found increased favor in recent years. The addition agents described in the invention, however, are equally applicable to both sodium and potassium plating baths. Indeed, the brightening agents described above function particularly well in a sodium plating bath, especially at the

higher concentrations of copper and at higher temperatures.

To illustrate the effect exerted on the brightening capacity of both sodium and potassium plating baths of several different concentrations, Table II lists the compositions of several different plating baths which were employed in carrying out the examples of the invention that are summarized below.

TABLE II

Bath concentrations in grams per liter

	Bath A	Bath B	Bath C	Bath D
Cuprous cyanide	48.0	48.0	66.75	48.0
Potassium cyanide (free)	9.0	15.0	9.0	----------
Potassium hydroxide	30.0	30.0	30.0	----------
Rochelle salt	30.0	30.0	30.0	----------
Sodium cyanide (free)	----------	----------	----------	11.25
Sodium hydroxide	----------	----------	----------	24.0
Sodium tartrate	----------	----------	----------	24.0

In each of the following examples, plating operations were carried out in a Hull test cell on brass cathodes so that the effect of a wide range of current densities could be observed.

EXAMPLE I

Using a standard copper plating solution of the basic composition of Bath A of Table II, to which had been added 0.008 gram per liter of potassium tellurite and 1 gram per liter of 2-butyne-1,4-diol, copper was electrodeposited on a test panel. The bath temperature was maintained at 68° C., and no agitation was provided. Under these conditions, the deposit was very bright over the entire area of the test panel, corresponding to current densities from the lowest observable value to 50 amperes per square foot. By way of contrast, when the plating operation was duplicated under identical conditions, but using only the potassium tellurite as a brightening agent, the electrodeposit was only fairly bright, and that only over the current density range from 15 to 40 amperes per square foot.

The systematic substitution of other acetylenic compounds for the 2-butyne-1,4-diol also resulted in very bright deposits over the entire current density range of the test panel. Such acetylenic compounds as dimethyl 3-hexynedioate, 3-methyl-3-hydroxyethoxy-1-butyne, 3-methyl-1-butyn-3-ol and 1-butyne-3,4-diol yielded excellent bright deposits when used in conjunction with the potassium tellurite.

EXAMPLE II

Using a freshly prepared copper cyanide plating bath (Bath A) which contained 0.01 gram per liter of potassium tellurate, a fairly bright electroplate was deposited on the test panel of a Hull cell operated at 67° C. and without agitation. The brightness range was confined, however, to current densities between 15 and 40 amperes per square foot. When 0.37 gram per liter of propargyl alcohol was added to the bath, the brightness range was extended to virtually the entire area of the test panel, extending from the lowest observable current density to 50 amperes per square foot. Increasing the concentration of the propargyl to 3 grams per liter did not significantly alter these results.

EXAMPLE III

A brilliant copper electrodeposit was formed on a polished brass panel in a Hull cell, using a plating bath and plating conditions similar to those described in Example II, with the sole exception that 0.8 gram per liter of 1,4-dimethoxy-2-butyne was used in the bath in place of propargyl alcohol. In this example, the bright current density range extended from the lowest observable value to about 40 amperes per square foot.

EXAMPLE IV

When copper was electrodeposited in a Hull test cell at 60° to 68° C. without agitation, using a standard plating bath (Bath A) to which 0.01 gram per liter of potassium tellurate had been added, the resulting electroplate was fairly bright from 15 to about 40 amperes per square foot but marred by haze in the low current density range of the test panel. Upon the addition of 1.6 grams per liter of dipotassium acetylenedicarboxylate to the bath, a very bright deposit was formed over the entire current density range from 2 to 45 amperes per square foot.

EXAMPLE V

To a high copper content plating bath having the basic composition of Bath C described in Table II were added 0.003 gram per liter of potassium selenocyanate and 1 gram per liter of 2-butyne-1,4-diol, and copper was electrodeposited for 10 minutes on a Hull test panel at a bath temperature of 65° C., without agitation. The deposit was bright over only the low current density range up to about 12 amperes per square foot. Upon the addition of 0.012 gram per liter of potassium tellurite to this bath, the bright current density was extended to about 30 amperes per square foot.

EXAMPLE VI

When copper was electrodeposited in a Hull test cell without agitation and at 65° C., using a standard copper plating solution (Bath A) which contained 0.002 gram per liter of potassium selenocyanate and 0.42 gram per liter of 2-butyne-1,4-diol, the deposit was bright over the low current density range up to about 10 amperes per square foot. Upon adding 0.005 gram per liter of potassium tellurate to this bath, the bright deposit was formed over a current density range up to about 35 amperes per square foot.

EXAMPLE VII

Although the combined use of a tellurium compound and an acetylenic compound in an unagitated plating bath favors exceptionally bright deposits over a wide current density range, air or mechanical agitation of the bath frequently results in the formation of a dull "stripe" on the cathode. For example, when copper is electrodeposited from an agitated plating bath containing 0.0067 gram per liter of tellurium and 0.4 gram per liter of 2-butyne-1,4-diol, the electroplate is very bright in the current density ranges of 15 to 30 and from 40 to 100 amperes per square foot. At current densities between 30 and 40 amperes per square foot, however, a dull streak mars the deposit. When, however, certain auxiliary agents are added to this bath, the electrodeposit is uniformly brilliant over the entire current density range.

To a freshly prepared standard copper plating bath having the composition of Bath B of Table II, was added 0.008 gram per liter of potassium tellurate, 0.8 gram per liter of 2-butyne-1,4-diol, 2 grams per liter of a bis-[sulfonaphthyl]methane ("Tamol N"), 0.0022 gram per liter of dissolved lead added in the form of an alkali-soluble lead salt (e.g. lead tartrate), and 0.2 gram per liter of ethylenediaminotetraacetic acid ("Sequestrene AA"). With vigorous agitation, a brilliant copper electrodeposit was formed over the entire current density range from below 1 to above 100 amperes per square foot. The basic inorganic salt composition of this bath could be widely altered, with respect to copper, free potassium cyanide and potassium hydroxide, without noticeably affecting the character of the deposit. Similarly, the concentrations of addition agents could be increased as much as tenfold without altering either the uniformity or brilliance of the deposit.

EXAMPLE VIII

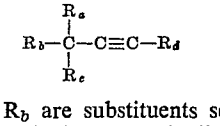
A sodium cyanide plating bath having the composition of Bath D of Table II was prepared, and to it was added 0.004 gram per liter of sodium tellurate, 0.004 gram per liter of lead tartrate, 0.5 gram per liter of a bis-[sulfonaphthyl]methane ("Tanak SC"), 0.4 gram per liter of 2-butyne-1,4-diol, and 0.5 gram per liter of sodium dihydroxyethylglycine (chelating agent). An electrodeposit of copper was formed from this bath on a bent panel of polished brass, using vigorous air agitation. The electrodeposit was brilliant over the entire current density range from below 10 to above 90 amperes per square foot. The electroplate throughout this current density range was completely free from clouds and haziness.

The tellurium content of the bath, and the concentration of lead, of bis-[sulfonaphthyl]methane, of butynediol, and of the chelating agent, could be greatly increased by factors of from 3 (in the case of the lead salt) to 60 (in the case of the chelating agent) without adversely affecting the brilliance of the deposit or the current density range over which it is formed, thus indicating the insensitiveness of this bath to variations in concentration of the addition agents.

We claim:

1. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, and from 1 to 250 millimoles per liter of a water-soluble acetylenic compound.

2. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, and from 1 to 250 millimoles per liter of a water-soluble acetylenic compound having the structure



in which R_a and R_b are substituents selected from the group consisting of hydrogen and alkyl and hydroxy-substituted alkyl radicals, R_c is a substituent selected from the group consisting of hydroxy, hydroxymethyl, methoxy, hydroxyethyl, ethoxy, and hydroxyethoxy radicals, and R_d is a substituent selected from the group consisting of hydrogen, halogen, diethylaminoethyl, morpholinomethyl, alkyl, alkenyl, alkynyl, and hydroxy-, methoxy-, and ethoxy-substituted alkyl, alkenyl, and alkynyl radicals.

3. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.01 to 0.1 millimole per liter of an alkali-soluble tellurium substance selected from the group consisting of tellurates and tellurites, and from 1 to 100 millimoles per liter of a water-soluble acetylenic compound.

4. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, and from 0.001 to 10 millimoles per liter of an alkali-soluble selenium compound.

5. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, and from about 0.05 to about 0.5 gram per liter of an alkali-soluble nitrile.

6. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, from 0.01 to 1 millimole per liter of an alkali-soluble selenium compound, and from about 0.05 to about 0.5 gram per liter of an alkali-soluble nitrile selected from the group consisting of succinonitrile, dicyandiamide, β,β'-oxydipropionitrile, β-sulfopropionitrile, potassium dicyanoguanidine, and sodium dicyanamide.

7. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, and from 0.5 to 15 grams per liter of a bis-[sulfonaphthyl]methane.

8. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, and from 0.01 to 50 grams per liter of a chelating agent capable of chelating with divalent copper in the presence of cyanide ions.

9. A process according to claim 8, in which the chelating agent is a polyamino polycarboxylic acid compound.

10. A process according to claim 8, in which the chelating agent is a polyamino polycarboxylic acid compound selected from the group consisting of dihydroxyethyl glycine, diethylenetriamino pentacetic acid, nitrilotriacetic acid, hydroxyethylethylene diaminotriacetic acid, ethylenediaminotetracetic acid, and salts thereof.

11. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, and from 0.001 to 0.1 millimole per liter of an alkali-soluble lead compound.

12. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, from 0.001 to 0.1 millimole per liter of dissolved lead, from 1 to 4 grams per liter of a bis-[sulfonaphthyl] methane, and from 0.01 to 50 grams per liter of a chelating agent capable of chelating with divalent copper in the presence of cyanide ions.

13. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of 2-butyne-1,4-diol, from 0.001 to 0.01 gram per liter of dissolved lead, from 0.5 to 10 grams per liter of a bis-[sulfonaphthyl]methane, and from 0.01 to 50 grams per liter of tetrasodium ethylenediaminetetraacetate.

14. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.01 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, from 0.5 to 15 grams per liter of a bis-[sulfonaphthyl]

methane, and from 0.01 to 50 grams per liter of a chelating compound capable of chelating with divalent copper in the presence of cyanide ions.

15. A process for producing a bright copper electroplate which comprises electrodepositing copper from an aqueous alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, from 0.001 to 0.01 gram per liter of dissolved lead, and from 0.01 to 50 grams per liter of a chelating agent capable of chelating with divalent copper in the presence of cyanide ions.

16. A process for producing a bright copper electroplate which comprises electrodepositing copper from an alkaline cyanide copper plating bath in which there is dissolved from 0.001 to 1 millimole per liter of an alkali-soluble tellurium compound, from 1 to 250 millimoles per liter of a water-soluble acetylenic compound, from 0.5 to 15 grams per liter of a bis-[sulfonaphthyl]methane, and from 0.001 to 0.01 gram per liter of dissolved lead.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,881,122 April 7, 1959

Donald Gardner Foulke et al.

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

Column 3, line 72, for "alkali" read -- able --; same line, for "the", first occurrence, read -- this --; column 4, line 30, for '"Daxed 11-KLS."' read -- "Daxad 11-KLS." --; column 10, line 19, for "(A.C.P.)" read -- (A.P.C.) --.

Signed and sealed this 21st day of July 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents