United States Patent Office 2,848,394 Patented Aug. 19, 1958

2,848,394

BRIGHT COPPER PLATING

Donald Gardner Foulke, Watchung, and Otto Kardos, Red Bank, N. J., assignors to Hanson-Van Winkle-Munning Company, a corporation of New Jersey

No Drawing. Application May 4, 1956 Serial No. 582,661

13 Claims. (Cl. 204—52)

This invention relates to bright copper plating and, more particularly, to electrodepositing copper from an alkali cyanide copper plating bath. The invention provides an improved process and improved copper plating bath for producing bright or brilliant copper electrodeposits over a wide current density range.

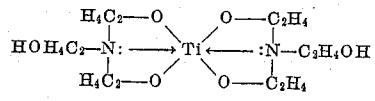
Using a conventional alkali cyanide copper plating bath, we have found that bright and even brilliant electrodeposits of copper may be formed by incorporating in such bath a fraction of a gram per liter of a stable alkali-soluble titanium compound. Accordingly, the process of this invention for producing bright copper deposits comprises electrodepositing copper from an aqueous alkaline solution containing from 10 to 90 grams per liter of copper, from 25 to 175 grams per liter of an alkali metal cyanide, and from about ¼ to about 100 millimols per liter of a stable alkali-soluble titanium compound. Exceptionally brilliant copper deposits are formed when the titanium compound is employed in conjunction with an alkali-soluble selenium compound. The brightness may also be extended when a small quantity of a water-dispersible wetting agent is added to the plating bath containing the titanium compound. Particularly brilliant copper deposits are obtained, however, when the plating bath contains both an alkali-soluble selenium compound and a water-dispersible wetting agent in addition to the titanium compound.

The process of our invention is accomplished most advantageously by using an alkali 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 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 125 grams per liter of an alkali metal cyanide. With this plating bath, we generally prefer to employ from about ½ to about 25 millimols per liter of the titanium compound, from about ½ to about 20 millimols per liter of an alkali-soluble selenium compound, and from about ⅒ to about 20 grams per liter of a water-dispersible wetting agent.

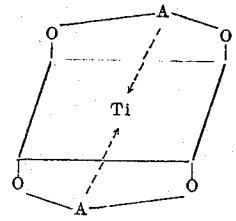
Any titanium compound capable of being dissolved in a weakly alkaline media may be successfully employed in the plating bath. Various titanium salts, such as potassium titanate, titanium lactate and potassium titanium oxalate, have been used successfully, thus indicating that the titanium moiety may be either in the cationic or anionic portion of the compound. We have obtained particularly satisfactory results, however, using a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines.

These latter titanium coordination compounds are soluble in water and generally stable in alkaline solution.

They may be prepared by condensing a titanium halide together with an alkoxide of the polyol or alkanolamine. Spatially, the coordination compound may be visualized as consisting of a central titanium nucleus covalently bonded to one or more clustering ligands through an oxygen atom. Since the adjacent oxygen or nitrogen atom is brought into close proximity to the titanium nucleus, the formation of coordinate linkages is facilitated. The structure of bis-[N-hydroxyethyldiethanolatoamine-O,O',N] titanium (IV), containing two triethanolamine ligands for each atom of titanium is illustrative of these unique titanium coordination compounds:



Where a particular titanium coordination compound contains two ligands, such as bis-[N-hydroxyethyldiethanolatoamine-O,O',N] titanium (IV), the spatial configuration of the molecule generally may be represented as having the structure



in which the ligand moieties A are coordinately bonded to the titanium nucleus.

In addition to bis-[N-hydroxyethyldiethanolatoamine-O,O',N]titanium (IV), we have found that those titanium coordination compounds containing sorbitol, or both sorbitol and triethanolamine, are unusually effective brightening agents. Thus, such compounds as [(N-hydroxyethyldiethanolateoamine - O,O',N) (sorbitolato-O,O',O'')] titanium (IV), containing one triethanolamine ligand and one sorbitol ligand for each atom of titanium, as well as tris-[sorbitolato-O,O',O''] titanium (IV), in which each atom of titanium possesses three sorbitol ligands, are particularly advantageous additives to the plating bath.

Plating baths which contain a titanium coordination compound together with an alkali-soluble solenium compound significantly extend the brightness of the copper deposits produced by electrodepositing copper from such baths. Any alkali-soluble selenium salt or organo-selenium compound may be used, including sodium selenate, sodium selenite, sodium selenosulfate, potassium selenocyanide and sodium selenoacetate.

We have found that it is generally possible to improve the brilliance of the electroplate, and particularly to broaden the current density range over which bright deposits are formed, by incorporating a small amount of a water-dispersible wetting agent in the plating bath. In general, from about ⅒ to about 20 grams per liter may be employed effectively. A vast number of wetting agents may be suitably incorporated into the plating bath, but we have consistently produced exceptionally

brilliant copper electroplates by adding to the plating bath a polyoxy compound having the formula

$$R_2\text{—}[CH_2CH(R_1)\text{—}O]_n\text{—}R_3$$

in which R_1 is a substituent selected from the group consisting of hydrogen and methyl, R_2 and R_3 are substituents selected from the group consisting of hydrogen, alkoxy, thioalkoxy, phenoxy, alkylphenoxy, thiophenoxy, alkylmercapto, and carbamido, and n is an integer from 6 to 60. These polyoxy compounds are, of course, polyoxyethylene or polyoxypropylene glycol and the condensation products of ethylene or propylene oxide together with alcohols, thioalcohols, phenols, thiophenols and amides. The polyoxy compound may be added at any time during the preparation of the plating bath.

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 metal)	3 to 10	20 to 75
Potassium Cyanide	6 to 16	45 to 120
Potassium Hydroxide	1 to 5	7.5 to 40
Potassium Sodium Tartarate	2 to 6	15 to 45
Potassium Carbonate	0 to 15	0 to 110

Although sodium salts may be used interchangeably for the potassium salts, 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 applicability of the different addition agents to both sodium and potassium plating baths under a variety of conditions, Table I lists the compositions of several types of plating baths which were employed in carrying out the examples of the invention that are summarized in Tables II to VI below.

TABLE I

Bath concentrations in ounces per gallon

	Bath A	Bath B	Bath C
Copper Cyanide	7.5	9.5	10
Potassium Cyanide	12.7	15.7	0.0
Potassium Hydroxide	1.0	1.0	0.0
Rochelle Salt	4	4	4
Sodium Cyanide	0.0	0.0	12.5
Sodium Hydroxide	0.0	0.0	1.0

In each of the following examples, of the invention, as set forth in Tables II to VI, the electrodeposit was formed in a Hull test cell on brass cathodes, using varying temperatures and current densities, with a plating time of ten minutes. Mild agitation of the bath was provided in each case by an electric stirrer.

Table II summarizes the results achieved when the electroplate was formed from different plating baths containing varying concentrations of a 1–M solution of [(N-hydroxyethyldiethanolatoamine - O,O',N) (sorbitolato-O,O',O'')] titanium (IV) and of a 4 percent solution of sodium selenite. The basic bath compositions used were there identified in Table I; and in addition to the titanium compound and sodium selenite each bath contained 0.05 gram per liter of nonylphenoxypolyoxyethylene glycol, formed by the reaction of 1 mol of nonylphenol with about 25 mols of ethylene oxide.

TABLE II

Temp. (° C.)	Bath Composition (Table I)	Titanium Coordination Compound (ml./l.)	Sodium Selenite Solution (ml./l.)	Current Density (amps./sq. ft.)	Results
70	A	0.5	3.2	20	Brilliant, slight haze.
65	A	2.2	3.2	25	Brilliant.
65	A	2.2	3.2	30	Bright.
65	A	3.2	3.2	30	Brilliant.
70	B	2.2	0.5	40	Brilliant, slight haze.
70	B	2.2	3.2	45	Bright overall.
70	B	25.2	6.4	35	Brilliant.
70	A	3.2	50.2	40	Do.
70	A	7.2	70.2	35	Do.
70	B	4.0	0.0	10	Bright with slight haze.
70	B	4.0	0.0	20	Brilliant.
70	B	4.0	0.0	30	Do.
70	B	4.0	0.0	40	Semibright.

Excellent results are also obtained when the electroplate is formed from a plating bath containing a different wetting agent in conjunction with the titanium coordination compound and sodium selenite. Each of the baths used in the examples summarized in Table III contained 0.04 gram per liter of dodecylmercaptopolyoxyethylene glycol, formed by the condensation of 1 mol of dodecylmercaptan with about 8 mols of ethylene oxide. Varying concentrations of 1–M [(N-hydroxyethyldiethanolatoamine-O,O',N) (sorbitolato-O,O',O'')] titanium (IV) and a 4 percent solution of sodium selenite were added as indicated.

TABLE III

Temp. (° C.)	Bath Composition (Table I)	Titanium Coordination Compound (ml./l.)	Sodium Selenite Solution (ml./l.)	Current Density (amps./sq. ft.)	Results
65	A	2.2	0.0	10	Semibright.
65	A	2.2	0.0	20	Brilliant spots, some burning.
65	A	2.2	3.2	25	Bright overall.
65	A	2.2	3.2	20	Brilliant overall.
65	B	3.2	3.2	30	Brilliant overall.
70	B	3.2	3.2	35	Bright, some burning.
70	B	3.2	3.2	15	Bright overall.

In each of the examples summarized in Tables II and III, potassium plating baths were employed to form the electroplates. It will be noted that the most brilliant deposits consistently appeared when the electroplate was formed at a temperature of 65°–70° C. using moderate current densities.

When sodium plating baths are employed, it has been our experience that slightly higher bath temperatures are required. Thus, the deposits formed from a sodium plating bath (bath C), containing 2 millimols per liter of [(N-hydroxyethyldiethanolatoamine - O,O',N) (sorbitolato-O,O',O'')] titanium (IV), 1 millimol per liter of sodium selenite, and 0.05 gram per liter of nonylphenoxypolyoxyethylene glycol, at 65° C. with a current density of 20 amperes per square foot were primarily dull and hazy. At 75° and 85° C., using a current density of 20 amperes per square foot, the electroplates produced were bright with a slight haze. Upon the addition of another 0.3 millimol per liter of sodium selenite to the plating bath, the deposits were consistently bright at 75° C. and a current density of 20 amperes per square foot.

Although our experience has indicated that any water-dispersible wetting agent may be used effectively in the bright copper plating baths prepared according to our invention, the ability of certain polyoxy compounds to extend the plating range of such baths is especially significant. Table IV sets forth several of these polyoxy

addition agents which have been used with particular success in the process of this invention. In each of the examples tabulated in Table IV, copper was electrodeposited from a potassium plating bath (bath B) containing 2.2 millimols per liter of [(N-hydroxyethyldiethanolatoamine-O,O',N)(sorbitolato-O,O',O'')] titanium (IV) and 1.0 millimol per liter of sodium selenite, at a temperature of 65°–70° C. over a wide current density range. The electroplates were uniformly bright and even brilliant.

TABLE IV

Bright copper plating with polyoxy addition agents

Polyoxy Compound—Name	Conc., ml./l.	Current Density Range (a. s. f.)	
		Low	High
Polyoxyethylene glycol Av. Mol. Wt. 600	4	15	35
Polyoxypropylene glycol Av. Mol. Wt. 400	4	15	35
Octoxypolyoxyethylene glycol, Av. Mol. Wt. 600	4	15	35
Oleylamidopolyoxy ethylene glycol, Av. Mol. Wt. 500	2	15	40
Octylphenoxypolyoxy ethylene glycol, Av. Mol. Wt. 600	4	15	35
Nonylphenoxypolyoxy ethylene glycol, Av. Mol. Wt. 1,350	4	15	45
Lauroxypolyoxy ethylene glycol, Av. Mol. Wt. 650	4	15	35
Thiododecoxypolyoxy ethylene glycol, Av. Mol. Wt. 700	4	15	40

The culmulative effect exerted by various selenium compounds in extending the plating range of the method of the invention is illustrated by the examples set forth in Table V below. Electroplates of copper, deposited from a potassium plating bath (bath B), increased in brilliance only when the selenium compound was used in conjunction with the titanium compound. As indicated in Table V, each selenium compound was tested in a solution free from titanium, and again in a solution to which 2 millimols per liter of [(N-hydroxyethyldiethanolatoamine-O,O',N) (sorbitolato-O,O',O'')] titanium (IV) and 0.05 gram per liter of nonylphenoxypolyoxyethylene glycol had been dissolved.

TABLE V

Effect of various selenium additives on bright copper plating

Selenium Compound—Name	Conc. (mmol./l.)	Titanium Conc. (mmol./l.)	Polyoxy Cmpd. (gm./l.)	Current Density (amps./ft.²)	Results
Sodium Selenate	1	0.0	0.0	20	Bright with smut.
	1	0.0	0.0	30–40	Hazy.
	1	2	0.05	20	Bright.
	1	2	0.05	30–40	Brilliant.
Sodium Selenide	2	0.0	0.0	20	Bright w. edge haze.
	2	0.0	0.0	30	Bright with haze.
	2	0.0	0.0	40	Burning.
	2	2	0.05	15	Bright w. slight haze.
	2	2	0.05	20–40	Brilliant.
Sodium Selenite	1	0.0	0.0	10	Semibright.
	1	0.0	0.0	20	Bright with haze.
	1	0.0	0.0	30	Dull.
	1.5	0.0	0.0	10–30	Semibright to dull.
	1.5	2	0.05	15–45	Brilliant.
Sodium Selenosulfate	1	0.0	0.0	40–50	Bright.
	1	2	0.05	30	Brilliant Spots.
	1	2	0.05	40–50	Brilliant.
Potassium Selenocyanide	1	0.0	0.0	40	Dull.
	1	0.0	0.0	50	Bright.
	1	2	0.05	30	Brilliant Spots.
	1	2	0.05	40–50	Brilliant.
Sodium Selenoacetate	1	0.0	0.0	30	Semibright.
	1	0.0	0.0	50	Bright.
	3.2	2	0.05	20–50	Brilliant.

Table V indicates that for optimum results, the plating bath should contain both the titanium and selenium additives, and preferably a wetting agent. At concentrations of about ½ to about 20 millimols per liter, all of the selenium compounds tested, including selenium salts and organoselenium compounds, broadened the plating ranges of baths containing various titanium additives.

To illustrate that any titanium compound capable of being dissolved in a weakly alkaline media may be successfully employed in the plating baths prepared in accordance with our invention, Table VI sets forth in detail the results achieved with a considerable number of titanium additives. Different concentrations of the respective titanium compounds were tested in a potassium plating bath (bath B) in the absence of selenium compound, and again in baths to which sodium selenite had been added. Further tests were performed, as indicated in Table VI, on solutions containing varying concentrations of a polyoxy compound, nonylphenoxypolyoxyethylene glycol, in addition to both the titanium and selenium compounds. Using a Hull test cell, the electroplates were deposited on bent brass cathodes at a bath temperature of 70° C. at varying current densities.

From an analysis of the results summarized in Table VI, it is apparent that any alkali-soluble titanium compound may be used in accordance with the method of this invention. Of the various titanium additives tested, we consider the titanium coordination compounds to be especially suitable for commercial use in bright copper plating. Excellent results are also obtained, as indicated by Table VI, using titanium salts.

It will also be seen that the current density range, over which bright copper deposits may be formed pursuant to this invention, is markedly extended by the introduction of an alkali-soluble selenium compound into the plating bath containing a titanium additive. Upon dissolving a wetting agent, such as a polyoxy compound, in the bath, the current density range is further extended.

The concentration of the wetting agent in the bath is not critical. As shown in Table VI, nonylphenoxypolyoxyethylene glycol was used in concentrations of 0.05 gram per liter and 20 grams per liter, yielding brilliant deposits in both instances. Although concentrations in excess of 20 grams per liter of a wetting agent may be employed, there is no particular advantage to be gained from the higher concentrations.

For optimum results, the current density from 20 to 60 amperes per square foot should be used. Although a current density as low as 10 amperes per square foot has given less satisfactory bright deposits than are obtained at the higher current density, a degree of brightness which is useful for many purposes can be obtained.

TABLE VI

Effect of various titanium additives on bright copper plating

Titanium Compound—Name	Conc. (mmol./l.)	Sodium Selenite (mmol./l.)	Polyoxy Compound (gm./l.)	Current Density (amp/ft²)	Results
[(N-hydroxyethyldiethanolatoamine) tris-(sorbitolato)]titanium (IV)	1	0.0	0.0	15–25	Bright.
	2	1	0.0	20–30	Do.
	2	1	0.0	40–50	Brilliant.
	2	1	0.05	30–50	Do.
Tris-[sorbitolato-O,O′,O″]titanium (IV)	1	0.0	0.0	15	Semibright.
	1	0.0	0.0	25	Bright.
	2	1	0.0	20–50	Do.
	2	1	0.05	20–50	Brilliant.
Bis-[N-hydroxyethyldiethanolatoamine-O,O′,N]titanium (IV)	1	0.0	0.0	10	Bright with slight haze.
	1	0.0	0.0	25	Bright.
	1	0.67	0.0	20–40	Do.
	1	0.67	0.05	20–45	Brilliant.
	2	0.0	0.0	20	Bright.
	2	1	0.0	20–30	Brilliant.
	2	1	0.05	20	Bright.
Titanium Lactate	2	0.0	0.0	20–30	Do.
	4	1	0.05	20	Do.
	4	1	0.05	30–40	Brilliant.
Potassium Titanate	2.3	0.0	0.0	20–30	Bright with some smut.
	2.3	0.0	0.0	40	Dull.
	2.3	1	0.05	20	Bright with slight smut.
	2.3	1	0.05	30	Bright.
	2.3	1	0.05	40	Brilliant.
Potassium titanium oxalate	1	0.0	0.0	10	Dull.
	1	0.0	0.0	20	Bright.
	1	0.0	0.0	30	Less Bright.
	1	1	0.05	20–30	Brilliant.
	1	1	0.05	40	Brilliant with burning on edges.
[(N-hydroxyethyldiethanolato-O,O′,N) (sorbitolato-O,O′,O″)]titanium (IV)	2	0.0	0.0	10	Bright with some smut.
	2	0.0	0.0	20	Bright with slight haze.
	2	0.0	0.0	30	Bright.
	4	0.0	0.0	20	Brilliant.
	4	0.0	0.0	30	Bright.
	4	0.0	0.0	40	Bright with slight haze.
	4	0.0	0.05	20–30	Brilliant.
	4	0.0	0.05	40	Semibright.
	4	1	20.0	20–60	Brilliant.

We claim:

1. The process for producing bright copper deposits which comprises electrodepositing copper from an aqueous alkaline solution containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, and from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines.

2. The process for producing bright copper deposits which comprises electrodepositing copper from an aqueous alkaline solution containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines, and from about ½ to about 20 millimols per liter of an alkali-soluble selenium compound.

3. The process for producing bright copper deposits which comprises electrodepositing copper from an aqueous alkaline solution containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, and from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines, from about ½ to about 20 millimols per liter of an alkali-soluble selenium compound, and from about 1/20 to about 20 grams per liter of a water-dispersible wetting agent.

4. The process for producing bright copper deposits which comprises electrodepositing copper from an aqueous alkaline solution containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines, and from about 1/20 to about 20 grams per liter of a polyoxy compound having the formula

$$R_2\text{—}[CH_2\underset{\displaystyle R_1}{\underset{|}{C}}H\text{—}O]_n\text{—}R_3$$

in which R_1 is a substituent selected from the group consisting of hydrogen and methyl, R_2 and R_3 are substituents selected from the group consisting of hydrogen, alkoxy, thioalkoxy, phenoxy, alkylphenoxy, thiophenoxy, alkylmercapto, and carboxamido, and n is an integer from 6 to 60.

5. The process for producing bright copper deposits which comprises electrodepositing copper from an aqueous alkaline solution containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, and from about ½ to about 25 millimols per liter of a titanium coordination compound selected from the group consisting of [(N-hydroxyethyldiethanolatoamine - O,O′,N) (sorbitolato - O,O′,O″)] titanium (IV), bis-[N-hydroxyethyldiethanolatoamine-O,O′,N]titanium (IV), and tris-[sorbitolato - O,O′,O″] titanium (IV).

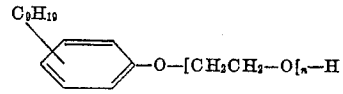
6. The process for producing bright copper deposits which comprises electrodepositing copper from an aqueous alkaline solution containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from about ½ to about 25 millimols per liter of a titanium coordination compound selected from the group consisting of [(N - hydroxyethyldiethanolatoamine - O,O′,N) (sorbitolato - O,O′,O″)] titanium (IV), bis - [N - hydroxyethyldiethanolatoamine-O,O′,N]titanium (IV), and tris - [sorbitolato - O,O′,O″] titanium (IV), from about ½ to about 20 millimols per liter of an alkali-soluble selenium compound, and from about 1/20 to about 20 grams per liter of a polyoxy compound having the formula

$$R_2\text{—}[CH_2\underset{\displaystyle R_1}{\underset{|}{C}}H\text{—}O]_n\text{—}R_3$$

in which R_1 is a substituent selected from the group consisting of hydrogen and methyl, R_2 and R_3 are sub-

stituents selected from the group consisting of hydrogen, alkoxy, thioalkoxy, phenoxy, alkylphenoxy, thiophenoxy, alkylmercapto, and carboxamido, and *n* is an integer from 6 to 60.

7. The process for producing bright copper deposits according to claim 6, in which the polyoxy compound has the formula

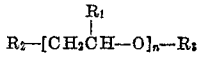


wherein *n* is an integer from 6 to 60.

8. An aqueous alkali-cyanide copper plating bath containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, and from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines.

9. An aqueous alkali-cyanide copper plating bath containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines, and from about 1/20 to about 20 grams per liter of a water-dispersible wetting agent.

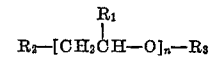
10. An aqueous alkali-cyanide copper plating bath containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from about ½ to about 25 millimols per liter of a titanium coordination compound having at least one ligand selected from the group consisting of polyols and alkanolamines, from about ½ to about 20 millimols per liter of an alkali-soluble selenium compound, and from about 1/20 to about 20 grams per liter of a polyoxy compound having the formula



in which R_1 is a substituent selected from the group consisting of hydrogen and methyl, R_2 and R_3 are substituents selected from the group consisting of hydrogen, alkoxy, thioalkoxy, phenoxy, alkylphenoxy, thiophenoxy, alkylmercapto, and carboxamido, and *n* is an integer from 6 to 60.

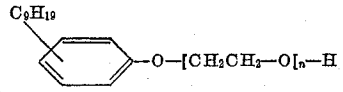
11. An aqueous alkali-cyanide copper plating bath containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, and from about ½ to about 25 millimols per liter of a titanium coordination compound selected from the group consisting of [(N - hydroxyethyldiethanolatoamine - O,O',N) (sorbitolato - O,O',O'')]titanium (IV), bis - [N-hydroxyethyldiethanolatoamine - O,O',N]titanium (IV), and tris-[sorbitolato - O,O',O'']titanium (IV).

12. An aqueous alkali-cyanide copper plating bath containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from about ½ to about 25 millimols per liter of a titanium coordination compound selected from the group consisting of [(N - hydroxyethyldiethanolatoamine - O,O',N) (sorbitolato - O,O',O'')]titanium (IV), bis - [N-hydroxyethyldiethanolatoamine - O,O',N]titanium (IV), and tris-[sorbitolato - O,O',O'']titanium (IV), and from about 1/20 to about 20 grams per liter of a polyoxy compound having the formula



in which R_1 is a substituent selected from the group consisting of hydrogen and methyl, R_2 and R_3 are substituents selected from the group consisting of hydrogen, alkoxy, thioalkoxy, phenoxy, alkylphenoxy, thiophenoxy, alkylmercapto, and carboxamido, and *n* is an integer from 6 to 60.

13. An aqueous alkali-cyanide copper plating bath containing from 20 to 75 grams per liter of copper, from 45 to 125 grams per liter of an alkali metal cyanide, from 1 to 3 millimols per liter of [(N - hydroxyethyldiethanolatoamine - O,O',N) (sorbitolato - O,O',O'')]titanium (IV), from about ½ to about 20 millimols per liter of sodium selenite, and from about ½ to about 20 grams per liter of a polyoxy compound having the formula



wherein *n* is an integer from 6 to 60.

References Cited in the file of this patent

UNITED STATES PATENTS

2,732,336 Ostrow ---------- Jan. 24, 1956

OTHER REFERENCES

Ser. No. 331,456, Weiner (A. P. C.), published July 13, 1943.

UNITED STATES PATENT OFFICE

Certificate of Correction

August 19, 1958

Patent No. 2,848,394

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 2, line 56, for "solenium" read —selenium—; column 9, line 10, right-hand portion of the equation, for "—O[$_n$—H" read ——O]$_n$—H—; column 10, line 38, right-hand portion of the equation, for "—O[$_n$—H" read ——O]$_n$—H—.

Signed and sealed this 25th day of November 1958.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.