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PROCESS FOR THE PRODUCTION OF METAL ELECTRODEPOSITS

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11 Claims. (Cl. 204—46)

This invention relates to a process for producing metal electrodeposits, and more particularly to additives for electroplating baths which are capable of eliminating the adverse effects of impurities in such baths upon the quality of the metal deposits produced by means of such baths.

It is well known in the electroplating art that inorganic impurities occurring in electroplating baths often have an adverse effect upon the metal deposits obtained therefrom, particularly if such baths contain brightening agents. Impurities which adversely affect the qualities of metal electrodeposits include those which cause the hardness of tap water as well as those contained in technically pure metal salts usually employed to make up the electroplating solution. The adverse effect of these impurities is particularly noticeable in electroplating processes for depositiing copper on metal objects, and in electroplating with sulfonic acid brightening agents.

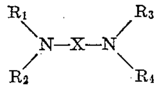
It is an object of the present invention to provide a method of modifying electroplating baths with additives which eliminate the adverse effects of inorganic impurities in such baths upon the metal deposit produced thereby.

Another object of this invention is to provide additives for modifying electroplating baths which will render inorganic impurities contained in such baths impotent as substances which reduce the qualities of electrodeposits produced from such baths.

Still another object of our invention is to provide additives for electroplating baths which will overcome the adverse effects of inorganic impurities contained in such baths on the brightness of the metal electrodeposited therefrom.

Other objects and advantages will become apparent as the description of our invention proceeds.

We have found and have described in our copending application Ser. No. 458,984, now abandoned, that the adverse effect of inorganic impurities in electroplating baths upon the qualities of electrodeposits produced from such baths can be eliminated by adding small amounts of amino compounds free from carboxyl groups to the electroplating baths. Compounds which fulfill this task in accordance with our prior application have the general structural formula



wherein R_1, R_2, R_3 and R_4 are hydrogen or hydrocarbon radicals, and X is a bivalent acyclic or cyclic hydrocarbon radical or a heterocyclic ring system which includes one or both of the nitrogen atoms. The hydrocarbon radicals above referred to may also include heteroatoms, such as oxygen, sulfur or nitrogen, as well as heteroatom groups derived therefrom. Furthermore, the above hydrocarbon radicals may also have substituents containing oxygen, sulfur or nitrogen atoms.

We have now found that sulfonic acid or sulfuric acid ester derivatives of such amino compounds, free from carboxyl groups, having the above formula, are improved additives; these derivatives may contain one or more sulfonic acid groups or sulfuric acid ester groups attached either on the X or R groups, and may be provided, if desired, in the form of their salts formed with inorganic or organic bases.

Examples of compounds of this type are the following:

N-ethyl-N-β-aminoethyl-aminoethane-sulfonic acid
N,N - diethyl-ethylenediamino-N',N'-bis-(ethanesulfonic acid)
1,3-diaminopropane-2-sulfonic acid
N,N,N',N' - tetra - n-butyl-1,3-diaminopropanol-2-monosulfuric acid ester
Piperazine-N,N'-bis-(2-hydroxypropane-sulfonic acid)
2,5-diaminobenzene-1-sulfonic acid
2,5-diaminobenzene-1,4-disulfonic acid

as well as other sulfonic acid or sulfuric acid ester derivatives of compounds of the described type as follows:

(1) N,N - diethyl - ethylenediamine-N'-propane-sulfonic acid
(2) N,N - diethyl - ethylenediamine-N',N'-bis-(propane-sulfonic acid)
(3) N,N' - diethyl - ethylenediamine-N,N'-bis-(propane-sulfonic acid)
(4) N,N,N'-triethyl-ethylenediamine-N'-propane-sulfonic acid
(5) N - ethyl - ethylenediamine-N,N'N'-bis-(propane-sulfonic acid)
(6) Ethylenediamine - N,N,N',N'-tetra-(propane-sulfonic acid)
(7) Ethylenediamine-N,N'-bis-(propane-sulfonic acid)
(8) N,N' - diethanol-ethylenediamine-N-propane-sulfonic acid
(9) N,N' - diethanol-ethylenediamine-N,N'-bis-(propane-sulfonic acid)
(10) N,N,N'-triethanol-ethylenediamine-N'-propane-sulfonic acid
(11) N - ethanol - ethylenediamine - N'-ethanol-2-sulfuric acid ester
(12) N,N,N'-triethanol-ethylenediamine-N'-ethanol-2-sulfuric acid ester
(13) 1,3 - propylenediamine - N,N' - bis-(butane-sulfonic acid)
(14) 1,3-propylenediamine-N-(butane-sulfonic acid)
(15) 1,4 - tetramethylenediamine - N,N,N',N'-tetra-(propane-sulfonic acid)
(16) 1,4 - tetramethylenediamine - N,N - bis - (isobutane-sulfonic acid)
(17) 1,6-hexamethylenediamine-N,N'-bis-(ethane-sulfonic acid)
(18) 1,6-hexamethylenediamine-N-propane-sulfonic acid
(19) 1,2-phenylenediamine-N-propane-sulfonic acid
(20) 1,4 - phenylenediamine - N,N' - bis-(butane-sulfonic acid)
(21) 1,4-naphthylenediamine-N,N'-bis-(propane-sulfonic acid)
(22) Diphenylamine-4-aminopropane-sulfonic acid
(23) Diphenylamine - 4,4' - bis - (aminopropane-sulfonic acid)
(24) Diphenylmethane - 4,4' - bis - (aminobutane-sulfonic acid)
(25) Diphenylene-4,4'-bis-(aminopropane-sulfonic acid)
(26) Pyridine-2-aminoethane-sulfonic acid
(27) Pyridine-4-aminodiethane-sulfonic acid
(28) 2-anilinopyridine-N-propane-sulfonic acid
(29) Quinoline-4-aminobutane-sulfonic acid

(30) Quinoline-4-aminodibutane-sulfonic acid
(31) 3-(3′-sulfopropylamino)-carbazole-9-N-propane-sulfonic acid
(32) 3,7-dimethyl-2,6-diamino-acridine-6-N-propane-sulfonic acid
(33) Piperazine-N-propane-sulfonic acid
(34) 2-methylpiperazine-N-butane-sulfonic acid
(35) 2,5-dimethylpiperazine-N,N′-bis-(propane-sulfonic acid)
(36) N-N′-propane-sulfonic acid
(37) Piperazine-N,N′-bis-(methanol-sulfuric acid ester)
(38) Piperazine-N,N′-bis-(phenyl-p-sulfonic acid)
(39) 2,5-diketopiperazine-N-propane-sulfonic acid
(40) N-ethyl-2,5-diketopiperazine-N′-butane-sulfonic acid
(41) Piperazine-N,N′-bis-(benzyl-p-sulfonic acid)
(42) 1,3-bis-(diethylamino)-propanol-2-sulfuric acid ester
(43) 1,3-bis-(dipropylamino)-propanol-2-sulfuric acid ester
(44) 1,3-bis-(diisopropylamino)-propanol-2-sulfuric acid ester
(45) 1,3-bis-(dimethylamino)-propanol-2-sulfuric acid ester
(46) 1-diethylamino-3-methyl-dodecyl-amino-propanol-2-sulfuric acid ester
(47) 1-diethylamino-3-dodecylamino-propanol-2-sulfuric acid ester
(48) 1-methylanilino-3-diethylamino-propanol-2-sulfuric acid ester
(49) 1-methylanilino-3-piperidino-propanol-2-sulfuric acid ester
(50) 1-methylanilino-3-morpholino-propanol-2-sulfuric acid ester
(51) 1-cyclohexylamino-3-diethylamino-propanol-2-sulfuric acid ester
(52) 1,3-bis-(cyclohexylamino)-propanol-2-sulfuric acid ester
(53) 1-dicyclohexyl-amino-3-diethylamino-propanol-2-sulfuric acid ester
(54) 1-dicyclohexyl-amino-3-cyclohexylamino-propanol-2-sulfuric acid ester
(55) 1,3-bis-(dicyclohexyl-amino)-propanol-2-sulfuric acid ester
(56) 1,3-bis-(methyl-ethyl-amino)-propanol-2-sulfuric acid ester
(57) 1,3-bis-(ethylamino)-propanol-2-sulfuric acid ester
(58) 1,3-bis-(methylamino)-propanol-2-sulfuric acid ester

These compounds are derivatives of the diamino compounds of our prior application Ser. No. 458,984.

When any of the above compounds or mixtures thereof, containing sulfonic acid, or sulfuric acid ester substituents, are added to electroplating baths containing brightening agents, electrodeposits produced thereby are bright and lustrous despite the fact that the bath contains impurities of the type described above, such as impurities which cause hardness, etc. Such bright deposits are obtained over the entire effective range of current densities. In addition, these additives have the further advantage that they increase the ductility of the electrodeposits. Furthermore, the above-mentioned additives are entrained with the metal electroplates to a substantially lesser degree than the corresponding compounds of the principal patent, which results in a much more economical consumption.

The amounts in which the additives in accordance with our invention can be added to produce the desired effect range from about 0.01 gm./liter of bath to about 15 gm./liter of bath, but the preferred amount is from 3 to 12 gm./liter of bath. The precise amounts required vary from one additive to the other and are also dependent upon the type of brightening agent employed and the amount and kind of inorganic impurities present in the bath. In general, objects can be electroplated in such baths at temperatures ranging from 20° C. to 60° C., and with current densities ranging from 0.5 to 15 amp./dm^2.

The use of the additives in accordance with our invention does not require any change in the composition of the electroplating baths commonly use, nor does it require any change in the conditions under which objects are usually electroplated, particularly with respect to the temperature of the plating bath and the current densities usually employed. In the form of amines the additives we use are soluble in the usual acid metal salt baths, and particularly in copper-plating baths containing the usual copper salts in an acid aqueous solution. The additives are not decomposed during the electroplating process.

The above-described additives for electroplating baths in accordance with our invention can be used in conjunction with any electroplating bath containing a brightening agent and in which the quality of the metal electrodeposits produced therefrom are adversely affected by impurities of the type described, such as, for example, in zinc-, chromium-, precious metal-, and particularly copperplating baths which contain brightening agents, and in particular sulfonic acid brightening agents.

Brightening agents usable for the process according to the above noted invention are listed in the following table:

(1) N,N-diethyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(2) N-ethyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(3) N-methyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(4) N,N-dimethyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(5) N-isopropyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(6) N,N-diisopropyl-dithiocarbamic acid-n-propylester-ω-potassium sulfonate
(7) N-butyl-dithiocarbamic acid-n-propylester-ω-potassium sulfonate
(8) N,N-dibutyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(9) N-octyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(10) N,N-dihydroxyethyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(11) N-hydroxyethyl-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(12) N,N-pentamethylene-dithiocarbamic acid-n-propylester-ω-sodium sulfonate
(13) N-piperazino-dithioformic acid-n-propylester-ω-sodium sulfonate
(14) 2-mercaptobenzthiazole-S-propan-ω-sodium sulfonate
(15) S-phenyl-trithiocarbonic acid-S-propane-ω-sodium sulfonate
(16) Isothiourea-S-propane-ω-sulfonic acid
(17) 5-phenyl-1,3,4-oxdiazolyl-2-mercaptopropane-ω-potassium sulfonate
(18) 1,3,5-triazine-2,4,6-tris-(mercapto-n-propane-ω-sulfonic acid)
(19) 1,3,5-triazine-2-mercapto-4,6-bis-(mercapto-n-propane-ω-sulfonic acid)
(20) 1,3,4-thiadiazole-2,5-bis-(mercapto-propane-ω-sulfonic acid)
(21) 1,3,4-triazole-2,5-bis-(mercapto-n-propane-ω-sulfonic acid)
(22) 1,3,4-oxadiazole-2,5-dis-(mercapto-n-propane-ω-sulfonic acid)
(23) N,N′-piperazino-bis-(dithioformic acid-n-propylester-ω-sulfonic acid)
(24) Dithiobiuret-S,S′-di-n-propane-ω-sulfonic acid

(25) N,N′-methylene-di-isothioureido-S-n-propane-ω-potassium sulfonate
(26) N,N′-ethylene-di-isothioureido-S-n-propane-ω-sodium sulfonate
(27) N,N′-hexamethylene-di-isothioureido-S-n-propane-ω-sodium sulfonate
(28) N,N′-phenylene-di-isothioureido-S-n-propane-ω-sodium sulfonate
(29) 2,2′-(α,β-ethylenedithio)-bis-[4,6-bis-(mercapto-n-propane-ω-sulfonic acid)-1,3,5-triazine]
(30) 2,2′-(α,β-ethylenedithio)-bis-[5-(mercapto-n-propyl-ω-sulfonic acid)-1,3,4-thiazole]

Instead of the "-n-propyl-" or "-n-propane" radical respectively the above named compounds may obtain likewise the following radicals:

(*a*) -methyl-
(*b*) -ethyl-
(*c*) -butyl-
(*d*) -2-hydroxypropyl-
(*e*) -2-chlorpropyl-
(*f*) -isopropyl-
(*g*) -benzyl-

The following examples will enable persons skilled in the art to understand our invention more completely. However, it will be understood that there is no intention on our part of limiting our invention to these examples.

Example I

In order to render impurities in the bath harmless, 2 gm./liter piperazine-N,N′-bis-(2-hydroxypropane-sulfonic acid) or its sodium salt are added to an acid copper-plating bath which contains 200 gm./liter technical-grade copper sulfate, 60 gm./liter concentrated sulfuric acid and, as a brightening agent, 1.2 gm./liter 1,3,5-triazine-2,4,6-tris-(mercapto-2-hydroxypropane-sulfonic acid) or its sodium salt. The copper electroplates produced in this bath on iron, iron alloys, etc. are full bright. When these objects are electroplated without the addition of piperazine-N,N′-bis(2-hydroxypropane-sulfonic acid) under otherwise identical conditions, less bright copper deposits are achieved.

Example II

When 1.5 gm./liter N,N,N′,N′-tetra-n-butyl-1,3-diaminopropanol-2-mono-sulfonic acid ester are added to an acid copper-plating bath containing 250 gm./liter technical-grade copper sulfate, 70 gm./liter concentrated sulfuric acid and 0.3 gm./liter N,N-diethyl-dithiocarbamic acid-ethylester-ω-sodium sulfonate, as brightening agent, electroplating of sheet iron preplated in a cyanide bath is provided with a full bright copper electroplate. The best copper electroplates are obtained when the electroplating step is carried out at 25° C. and within a current density range between 1 and 6 amp./dm.^{2}. When the sheet iron is electroplated without the addition of 1.5 gm./liter N,N,N′,N′-tetra-n-butyl-1,3-diaminopropanol-2-mono-sulfuric acid ester, a satisfactory brightening effect is achieved only within a current density range of 2 to 3 amp./dm.^{2}.

Example III

Particularly good brightening effects are achieved when a copper electroplating bath containing 180 gm./liter copper sulfate and 90 gm./liter concentrated sulfuric acid is modified with 0.3 gm./liter 1,3,5-triazine-2,4,6-tris-(mercapto-2-hydroxypropane-sulfonic acid) and 0.1 gm./liter N,N-diethyl-dithiocarbamic acid-ethylester-ω-sodium sulfonate, as brightening agents, and 1 gm./liter, 2,5-diamino-benzene-1,4-disulfonic acid. At temperatures between 20 and 45° C., objects may be electroplated at current densities up to 13 amp./dm.^{2}. Without the addition of 2,5-diaminobenzene-1,4-disulfonic acid the copper electroplates are much less bright.

Examples IV–XXVI

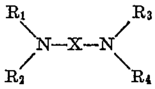
In the table some compositions for copper plating baths are listed. The copper baths contain 100–240 gm./liter $CuSO_4.5H_2O$, 20–120 gm./liter concentrated sulfuric acid and the following amounts of brightening agents according to the above noted list and the following amounts of sulfonic acid or sulfuric acid ester derivatives respectively of the diamino compounds free from carboxyl groups according to the above noted list:

Example No.	brightening agent	preferred concentration, gm./liter	diamino sulfonic acid or sulfuric acid ester	preferred concentration gm./liter
IV	27	0.5	9	4.0
V	19(*c*)	1.2	4	5.0
VI	9(*f*)	0.25	13	4.0
VII	8(*e*)	0.25	14	4.0
VIII	3(*g*)	0.75	11	4.0
IX	15	0.1	2	3.0
X	7(*c*)	0.25	25	2.0
XI	30	0.05	23	3.0
XII	23(*d*)	0.75	38	1.0
XIII	13(*a*)	0.5	18	8.0
XIV	29(*b*)	0.05	33	8.0
XV	21(*f*)	0.1	36	3.0
XVI	12(*b*)	0.25	47	0.5
XVII	14(*a*)	0.25	54	0.5
XVIII	16(*b*)	1.5	57	1.0
XIX	5(*e*)	0.2	51	2.0
XX	23	0.25	55	3.0
XXI	22(*b*)	0.1	49	0.5
XXII	20(*a*)	0.2	45	5.0
XXIII	18(*e*)	0.25	50	2.0
XXIV	26(*f*)	0.1	44	2.0
XXV	30(*d*)	0.1	46	0.5
XXVI	11(*a*)	1.5	31	0.3

While we have disclosed certain specific embodiments of our invention, it will be understood that we do not intend to be limited thereby and various changes and modifications may be made without departing from the spirit of the disclosure and the scope of the appended claims.

We claim:

1. In a process of producing bright metal electrodeposits said metal being selected from the group consisting of copper, zinc, chromium and precious metals, from electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of an organic amino compound free from carboxyl groups and having the general structural formula

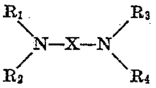


$$\begin{matrix} R_1 & & & & R_3 \\ & \diagdown & & \diagup & \\ & N & -X- & N & \\ & \diagup & & \diagdown & \\ R_2 & & & & R_4 \end{matrix}$$

wherein X is an organic radical selected from the group consisting of bivalent acyclic hydrocarbon radicals, bivalent cyclic hydrocarbon radicals and heterocyclic hydrocarbon radicals which include at least one of the nitrogen atoms, and R_1, R_2, R_3 and R_4 are radicals selected from the group consisting of hydrogen, substituted hydrocarbon radicals and unsubstituted hydrocarbon radicals, wherein at least one of the radicals selected from the group consisting of R_1, R_2, R_3, R_4 and X is substituted with a substituent selected from the group consisting of sulfonic acid and sulfuric acid ester groups, X being free of said substituent when said substituent is on one of said radicals selected from the group consisting of R_1, R_2, R_3 and R_4 whereby said impurities are prevented from interfering with the production of bright metal electrodeposits.

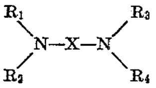
2. In a process of producing bright metal electrodeposits said metal being selected from the group consisting of copper, zinc, chromium and precious metals, from electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing

a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of an amino compound free from carboxyl groups having the general structural formula



wherein X is an organic radical selected from the group consisting of bivalent acyclic hydrocarbon radicals, bivalent cyclic hydrocarbon radicals, and heterocyclic hydrocarbon radicals which include at least one of the nitrogen atoms, and R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen, substituted hydrocarbon radicals and unsubstituted hydrocarbon radicals, wherein at least one of the radicals selected from the group consisting of R_1, R_2, R_3, R_4 and X is substituted with a sulfonic acid group, X being free of said substituent when said substituent is on one of said radicals selected from the group consisting of R_1, R_2, R_3 and R_4 whereby said impurities are prevented from interfering with the production of bright metal electrodeposits.

3. In a process of producing bright metal electrodeposits said metal being selected from the group consisting of copper, zinc, chromium and precious metals, from electroplating baths containing impurities found in hard water and in technical grade metal salts, and containing a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of an amino compound free from carboxyl groups having the general structural formula



wherein X is an organic radical selected from the group consisting of bivalent acyclic hydrocarbon radicals, bivalent cyclic hydrocarbon radicals, and heterocyclic hydrocarbon radicals which include at least one of the nitrogen atoms, and R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen, substituted hydrocarbon radicals and unsubstituted hydrocarbon radicals, wherein at least one of the radicals selected from the group consisting of R_1, R_2, R_3, R_4 and X is substituted with a sulfuric acid ester group, X being free of said substituent when said substituent is on one of said radicals selected from the group consisting of R_1, R_2, R_3 and R_4 whereby said impurities are prevented from interfering with the production of bright metal electrodeposits.

4. In a process of producing bright copper electrodeposits from electroplating baths containing impurities found in hard water and in technical grade copper sulfate, and containing a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of piperazine-N,N′-bis-(2-hydroxypropane-sulfonic acid) whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

5. In a process of producing bright copper electrodeposits from electroplating baths containing impurities found in hard water and in technical grade copper sulfate and containing 1,3-5-triazine-2,4,6-tris(mercapto-2-hydroxy-propane-sulfonic acid) as a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of piperazine-N,N′-bis(2-hydroxypropane-sulfonic acid), whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

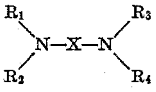
6. In a process of producing bright copper electrodeposits from electroplating baths containing impurities found in hard water and technical grade copper sulfate, and containing a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of N,N,N′N′-tetra-n-butyl-1,3-diaminopropanol-2-mono-sulfuric acid ester, whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

7. In a process of producing bright copper electrodeposits from electroplating baths containing impurities found in hard water and technical grade copper sulfate and containing N,N-diethyl-rithiocarbamic acid-ethylester-ω-sodium sulfonate as a brightening agent, the step which comprises adding 0.01 to 15 gm./liter of N,N,N′N′-tetra-n-butyl-1,3-diaminopropanol-2-monosulfuric acid ester to such electroplating baths, whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

8. In a process of producing bright copper electrodeposits from electroplating baths containing impurities found in hard water and technical grade copper sulfate and containing a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of 2,5-diaminobenzene-1,4-disulfonic acid, whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

9. In a process of producing bright copper electrodeposits from an electroplating bath containing impurities found in hard water and in technical grade copper sulfate and containing a mixture of 1,3,5-triazine-2,4,6-tris-(mercapto-2-hydroxypropane sulfonic acid and N,N-diethyl-dithiocarbamic acid-ethylester-ω-sodium sulfonate as brightening agents, the step which comprises adding to such electroplating bath 0.01 to 15 gm./liter of 2,5-diaminobenzene-1,4-disulfonic acid, whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

10. In an acid copper electroplating bath comprising technical grade copper salts and hard tap water, the improvement which comprises a component for rendering impurities in said bath harmless, comprising 0.01 to 15 gm./liter of an organic amino compound free from carboxyl groups having the general structural formula



wherein X is an organic radical selected from the group consisting of bivalent acyclic hydrocarbon radicals, bivalent cyclic hydrocarbon radicals and heterocyclic hydrocarbon radicals which include at least one of the nitrogen atoms, and R_1, R_2, R_3 and R_4 are radicals selected from the group consisting of hydrogen, substituted hydrocarbon radicals and unsubstituted hydrocarbon radicals, wherein at least one of the radicals selected from the group consisting of R_1, R_2, R_3, R_4 and X is substituted with a substituent selected from the group consisting of sulfonic and sulfuric acid ester groups, X being free of said substituent when said substituent is on one of said radicals selected from the group consisting of R_1, R_2, R_3 and R_4, whereby said impurities are prevented from interfering with the production of bright metal electrodeposits.

11. In a process of producing bright copper electrodeposits from electroplating baths containing impurities found in hard water and in technical grade copper sulfate, and containing a brightening agent, the step which comprises adding to such electroplating baths 0.01 to 15 gm./liter of N,N-diethyl-ethylenediamino-N′,N′-bis-(ethane-sulfonic acid) whereby said impurities are prevented from interfering with the production of bright copper electrodeposits.

References Cited in the file of this patent

UNITED STATES PATENTS

2,837,472 Gundel et al. ------------ June 3, 1958
2,849,351 Gundel et al. ---------- Aug. 26, 1958

FOREIGN PATENTS

1,118,019 France ----------------- Mar. 5, 1956

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,986,498 May 30, 1961

Wennemar Strauss 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 5, line 15, for "-n-propane" read -- -n-propane- --; column 8, line 7, for "rithiocarbamic" read -- dithiocarbamic --.

Signed and sealed this 21st day of November 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents