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BRIGHTENERS FOR ELECTROPLATING BATHS

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14 Claims. (Cl. 204—49)

This invention relates to an improvement in brighteners for electroplating baths, and more particularly to the use of organic sulfonic acid derivatives as brighteners for electroplating baths and various methods of making such brighteners.

Electroplating baths have heretofore been modified by the inclusion of organic sulfonic acids or organic sulfation products of various compounds. While the brighteners disclosed by the prior art have usually effected some improvement in the characteristics of the electrodeposits produced from baths modified therewith, these brighteners individually have not been sufficient to produce commercially desirable electrodeposits and had to be used with another and sometimes with even two or more supplemental brighteners to achieve the desired brightening effect.

It is an object of the present invention to provide electroplating compositions of improved character.

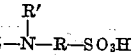
Another object of the present invention is to provide brightening additives for electroplating baths which may advantageously be used as sole brightening additives or with other additives to produce bright and lustrous electrodeposits.

Still another object of this invention is to provide electroplating baths which will produce bright and lustrous electrodeposits which, in many instances, may be used for their intended purpose without further polishing or buffing.

Yet another object of this invention is to provide various methods for producing the above brighteners.

Still further objects and advantages will become apparant as the description of the invention proceeds.

We have found that bright, highly lustrous and well-adhering electrodeposits can be obtained by modifying electroplating baths, containing the metal to be deposited primarily in the form of an acid solution of an inorganic salt of the metal, with organic sulfonic acids or their salts having the general structural formula



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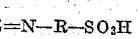
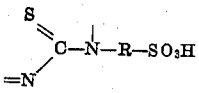


wherein Z is a radical comprising a carbon atom directly attached to two atoms at least one of which is a sulfur atom and the other is selected from the group consisting of nitrogen, sulfur and oxygen atoms, said carbon atom also directly attached to the nitrogen atom of the —N—RSO_3H group, R represents a bivalent aliphatic, cyclo-aliphatic or aromatic radical which may be unsubstituted or may carry other organic substituents, such as ethylene, propylene, alkyl propylene, hydroxy propylene, and pentylene or phenylene radicals, for example, and R′ is a hydrogen atom or a hydrocarbon radical. Radical R may also be interrupted by heteroatoms or heteroatom groups.

The sulfonic acid derivatives which are used as brighteners in electroplating baths according to the present invention fall into four basic groups:

(*a*) Compounds having the general structural formula



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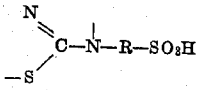
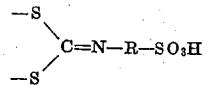


or their salts. Compounds of this type are, for example, the reaction products of 2 aminothiazoles with sultones, such as the product of a reaction between 2-amino-4-methylthiazole or 2-amino-6-methylbenzothiazole and propanesultone or butanesultone, and also thiourea-N-phenylsulfonic acids and their derivatives, such as thiourea-N-phenyl-4-sulfonic acid.

(*b*) Compounds having the structural formula



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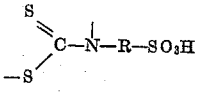
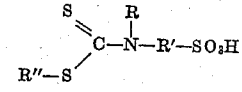
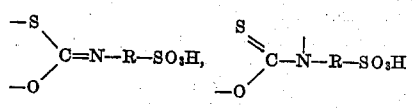


or their salts. Sulfonic acid derivatives of this type are, for example, the products of a reaction between 2-mercaptothiazole-S-alkylethers and sultones, such as the reaction product of 2-mercaptobenzothiazole-S-methylether and propanesultone, and also derivatives of dithiocarbamic acid-S-alkylesters which have an alkylsulfonic acid group attached to the nitrogen atom. Compounds of this group may be produced by first reacting a primary amine with a sultone to form the corresponding amino-sulfonic acids, thereafter reacting the amino-sulfonic acids with carbon disulfide in an alkaline medium to form dithiocarbamic acid salts, and finally alkylating the dithiocarbamic acid salts according to known methods, for example by reacting them with dimethylsulfate. In place of the sultones, halogenated alkanesulfonic acids may also be used. The dithiocarbamic acid derivatives obtained in this manner have the general structural formula



wherein R, R′ and R″ are hydrocarbon radicals of the character described.

(*c*) Compounds having the general structural formulas



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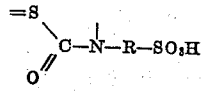
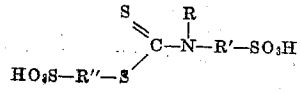


or their salts. Compounds of this type are, for example, the products of a reaction between 2-oxythiazoles and sultones.

(*d*) Compounds having the general structural formula



or their salts, wherein R is a hydrogen atom or an aliphatic, cycloaliphatic, or aromatic-aliphatic radical, R' and R'' are bivalent aliphatic, cycloaliphatic or aromatic radicals. The dithiocarbamic compounds of this group may readily be produced by first reacting salts of aminoalkane sulfonic acids which have at least one hydrogen atom attached to the nitrogen atom with carbon disulfide in the presence of equimolar amounts of a strong base, such as sodium hydroxide, whereby salts of dithiocarbamic acid-N-alkylsulfonic acids are formed, and thereafter reacting the dithiocarbamic acid-N-alkylsulfonic acid salt with a sulfonating agent, for example with an aliphatic, cycloaliphatic or aromatic sultone.

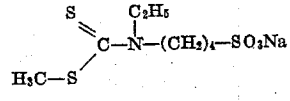
The four groups of sulfonic acid derivatives set forth above may be used in conjunction with all types of electroplating baths, such as in baths for electrodepositing copper, nickel, zinc, silver, cadmium, bronze or brass. They produce very bright, firmly adhering and ductile metal deposits. The brighteners can be used alone or together with already known brighteners, smoothing agents, antiporosity agents, wetting agents or salts which increase the conductivity of the electroplating bath.

The concentration of the brightening agents in accordance with the invention in the electroplating bath may range from 0.1 to 20 gm. per liter of bath and the optimum current densities may be from 0.5 to 12 amp./dm.^{2} at a bath temperature below 60° C. Since the brightening agents disclosed herein are, for all practical purposes, not consumed during the electroplating process, baths modified therewith remain operative for long periods of time.

The following examples will further illustrate the present invention and enable others skilled in the art to understand the invention more completely. It is understood, however, that we do not intend to limit the invention to the particular examples given below.

Example I

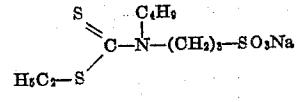
1 gm. dithiocarbamic acid-S-methylester-N-ethyl-N-butyl-ω-sodium sulfonate having the general structural formula



was added to each liter of an aqueous copper-plating bath containing 60 gm./liter sulfuric acid and 170 gm./liter crystalline copper sulfate. Thereafter, sheet iron objects which had previously been provided with a copper base-coat in a copper cyanide bath were electroplated in the above bath at room temperature and a current density range of 1 to 10 amp./dm.^{2} The objects, even those which were highly profiled, were provided with very bright and firmly adhering copper electrodeposits, which required no polishing or buffing subsequent to rinsing.

Example II

1 gm. dithiocarbamic acid-S-ethylester-N-butyl-N-propyl-ω-sodium sulfonate having the structural formula

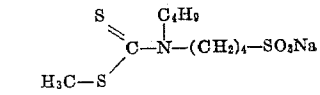


was added to each liter of the aqueous acid copper sulfate solution described in Example I. Sheet iron objects provided with a copper base-coat and electroplated in this bath, under the temperature and current density conditions described in the preceding example, were provided with very bright and well adhering copper deposits having a high ductility.

Example III

1 to 2 gm. of dithiocarbamic acid-S-methylester-N-

butyl-N-butyl-ω-sodium sulfonate having the structural formula



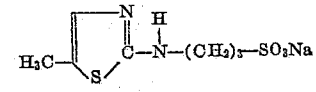
were added to each liter of an aqueous nickel electroplating solution containing 60 gm./liter nickel chloride, 220 gm./liter nickel sulfate and 35 gm./liter boric acid. Iron objects were then electroplated in the modified bath at room temperature and at current densities from 1 to 10 amp./dm.^{2} The objects were provided with firmly adhering, very bright nickel electrodeposits which required no polishing or buffing subsequent to rinsing.

Example IV

1 gm. dithiocarbamic acid-S-ethylester-N-butyl-N-propyl-ω-sodium sulfonate having the structural formula shown in Example II, was added to each liter of an aqueous zinc plating solution containing 200 gm./liter zinc sulfate and 1 gm./liter glacial acetic acid. Thereafter, sheet steel objects were electroplated in this modified bath at room temperature and a current density from 4 to 9 amp./dm.^{2} The objects were provided with a very bright zinc electroplate which required no buffing subsequent to rinsing. Without the addition of the brightener to the above zinc plating bath, sheet steel objects electroplated therein under substantially identical conditions of temperature and current density were provided with dull zinc electrodeposits which required considerable polishing to make them bright and lustrous.

Example V

3 gm. 2-amino-5-methylthiazole-N-propane-ω-sodium sulfonate having the structural formula



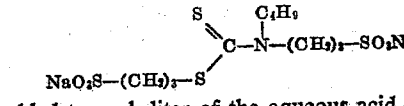
were added to each liter of the aqueous acid copper plating solution described in Example I. Thereafter, sheet steel objects which had previously been provided with a copper base-coating in an alkaline copper cyanide bath, were electroplated in the above modified bath at room temperature and a current density range of 2 to 8 amp./dm.^{2} The objects were provided with a very bright firmly adhering copper electrodeposit which required no polishing or buffing subsequent to rinsing.

Example VI

2 gm. of thiourea-N-phenyl-4-sodium sulfonate were added to each liter of the acid aqueous nickel-plating solution described in Example III. Iron objects electroplated in this modified bath at room temperature and a current density range of 1 to 10 amp./dm.^{2} were provided with very bright, firmly adhering nickel electrodeposits which required no buffing or polishing subsequent to rinsing.

Example VII

1 to 2 gm. of N-butyl-dithiocarbamic acid-N-S-bis-propane-ω-sodium sulfonate having the structural formula



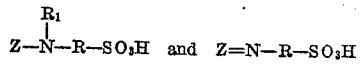
were added to each liter of the aqueous acid nickel electroplating solution described in Example III. Iron objects electroplated in this modified bath at room temperature and current densities between 1 and 10 amp./dm.^{2} were provided with very bright, firmly adhering, nonporous nickel electrodeposits.

While we have disclosed certain specific embodiments of our invention, it will be obvious to persons skilled in the art that various changes and modifications can be

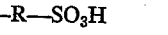
made without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an acid aqueous solution of an inorganic salt of the metal to be deposited and a compound selected from the group consisting of organic sulfonic acids having the structural formulas

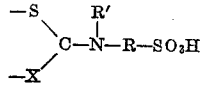


and their salts, wherein Z is a radical comprising a carbon atom directly attached to a sulfur atom, to an atom selected from the group consisting of sulfur, oxygen and nitrogen atoms and to the nitrogen atom of the



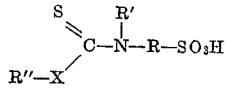
group, R is a bivalent organic radical selected from the group consisting of aliphatic and aromatic radicals, and R′ is selected from the group consisting of hydrogen and aliphatic radicals, said organic compound being dissolved in said bath in sufficient quantity to produce bright metal-plating deposits therefrom.

2. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound selected from the group consisting of organic sulfonic acids having the structural formula



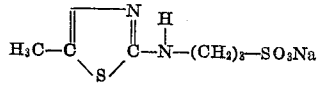
and their salts, wherein R is a bivalent aliphatic radical, R′ is an aliphatic radical and X is selected from the group consisting of sulfur, oxygen and nitrogen atoms.

3. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound selected from the group consisting of organic sulfonic acids having the general structural formula



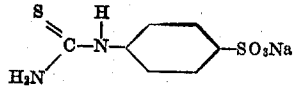
and their salts, wherein X is selected from the group consisting of oxygen, nitrogen and sulfur atoms, R is selected from the group consisting of bivalent aliphatic and aromatic radicals, R′ is selected from the group consisting of hydrogen and aliphatic radicals, and R″ is selected from the group consisting of hydrogen, alkyl and alkylsulfonic radicals.

4. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound having the structural formula

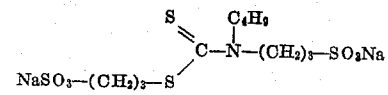


5. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and

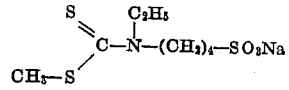
0.01 to 20 grams per liter of a compound having the structural formula



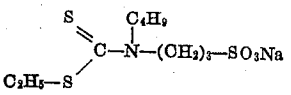
6. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound having the structural formula



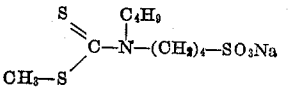
7. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound having the structural formula



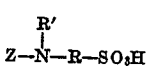
8. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound having the structural formula



9. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, comprising an aqueous acid solution of an inorganic salt of the metal to be electrodeposited and 0.01 to 20 grams per liter of a compound having the structural formula



10. The process of producing bright and lustrous electrodeposits of metals selected from the group consisting of copper, nickel and zinc, which comprises electrodepositing the metal from a bath containing said metal principally in the form of an acid aqueous solution of an inorganic salt of the metal in the presence of a brightener selected from the group consisting of organic sulfonic acid compounds having the general structural formula



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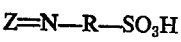
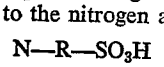


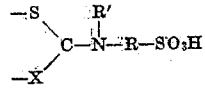
and their salts, wherein Z is a radical comprising a carbon atom directly attached to a sulfur atom, to an atom selected from the group consisting of sulfur, oxygen and nitrogen atoms, and to the nitrogen atom of the



group, R is a bivalent organic radical selected from the group consisting of aliphatic and aromatic radicals and R′ is selected from the group consisting of hydrogen and aliphatic radicals, said organic compound being dissolved in said bath in sufficient quantity to produce bright metal-plating deposits therefrom.

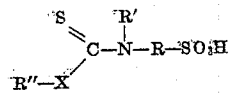
11. The process of producing bright and lustrous elec-

trodeposits of metals selected from the group consisting of copper, nickel and zinc, which comprises electrodepositing the metal from a bath containing said metal principally in the form of an acid aqueous solution of an inorganic salt of the metal in the presence of 0.01 to 20 grams per liter of a brightener selected from the group consisting of organic sulfonic acids having the structural formula



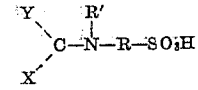
and their salts, wherein R is a bivalent aliphatic radical, R′ is an aliphatic radical and X is selected from the group consisting of sulfur, oxygen and nitrogen.

12. The process of producing bright and lustrous electrodeposits of metals selected from the group consisting of copper, nickel and zinc, which comprises electrodepositing the metal from a bath containing said metal principally in the form of an acid aqueous solution of an inorganic salt of the metal in the presence of 0.01 to 20 grams per liter of a brightener selected from the group consisting of sulfonic acids having the structural formula

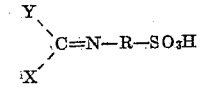


and their salts, wherein X is selected from the group consisting of oxygen, nitrogen and sulfur, R is selected from the group consisting of bivalent aliphatic and aromatic radicals, R′ is selected from the group consisting of hydrogen and aliphatic radicals, and R″ is selected from the group consisting of hydrogen, alkyl and alkylsulfonic radicals.

13. An electroplating bath for producing electrodeposits of metals selected from the group consisting of copper, nickel and zinc, said bath comprising an acid aqueous solution of an inorganic salt of the metal to be deposited and a compound selected from the group consisting of organic sulfonic acids having the structural formulas



and



and their salts, wherein Y is an atom selected from the group consisting of substituted and unsubstituted sulfur atoms, X is an atom selected from the group consisting of substituted and unsubstituted sulfur, oxygen and nitrogen atoms, R is a bivalent organic radical selected from the group consisting of aliphatic and aromatic radicals, and R′ is selected from the group consisting of hydrogen and aliphatic radicals, said organic compound being dissolved in said bath in sufficient quantity to produce bright metal-plating deposits therefrom.

14. The electroplating bath of claim 13, wherein the substituted X and Y atoms of the brightener compound are joined to form a heterocyclic compound.

References Cited in the file of this patent

UNITED STATES PATENTS

2,647,866	Brown	Aug. 4, 1953
2,663,684	Pierce	Dec. 22, 1953