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BRIGHTENERS FOR ELECTROPLATING BATHS

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This invention relates to brighteners for electroplating 15 baths, and more particularly to acyclic brightening compounds comprising at least two carbon atoms linked exclusively to heteroatoms one of which is a sulfur atom, said compounds being free from sulfonic groups.

We have found that very bright, firmly adhering, ductile 20 metal electrodeposits are 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 water-soluble acyclic organic compounds free from sulfonic groups which have at 25 least two carbon atoms in the molecule, said carbon atoms being linked exclusively to heteroatoms at least one of which is a sulfur atom. The atom groups formed by the carbon atoms and the heteroatoms, which may be identical or different, are further linked through one of said 30 heteroatoms to a lower hydrocarbon radical, preferably a bivalent lower alkyl radical, which may be further substituted and/or interrupted by heteroatoms.

The acyclic organic compounds used as brighteners for electroplating baths in accordance with the present 35 invention are known chemical compounds and can be produced very readily according to well known methods. These compounds can be represented by the following general structural formula:

$$\begin{array}{c} \mathbf{Q} - \mathbf{X} - \mathbf{C} - \mathbf{Z} - \mathbf{R} - \mathbf{Z}' - \mathbf{C} - \mathbf{X}' - \mathbf{Q}' \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array}$$

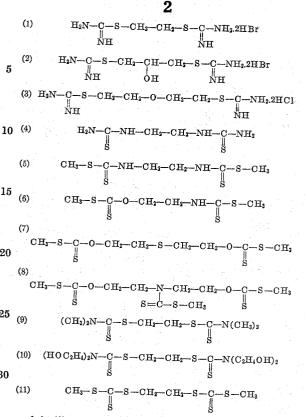
wherein R is a lower hydrocarbon radical, preferably a lower aliphatic radical which may carry substituent radicals other than sulfonic groups and/or may be interrupted by heteroatoms such as sulfur, oxygen and nitrogen, X, Y and Z are heteroatoms such as oxygen, sulfur and nitrogen or imino groups, at least one of them being a sulfur atom, X', Y' and Z' are also heteroatoms of the type represented by X, Y and Z or imino groups, at least one of them being a sulfur atom, and Q and Q' are hydrogen or lower aliphatic radicals free from sulfonic groups.

Thus, the brightening compounds according to the present invention are primarily bis- or poly-thiourea compounds, bis- or poly-isothiourea compounds, bis- or poly-thiocarbaminates, bis- or poly-dithiocarbaminates, bis- or poly-xanthogenates, bis- or poly-trithiocarbonates and the like. However, they also include compounds wherein the

or additional such groupings are not identical.

and

A few representative examples of the types of com- 70 pounds which we have found to be excellent brightening agents for electroplating baths are the following: 2,910,413 Patented Oct. 27, 1959



and the like.

35 The brighteners disclosed above are effective in all types of electroplating processes, for example for copper-plating, zinc-plating and silver-plating, or also for the production of bright cadmium, bronze and brass electrodeposits. They are especially effective in the 40 production of full-bright, firmly adhering, ductile metal electrodeposits from acidic electroplating baths.

While the brighteners according to the present invention produce the desired beneficial effects when used as the sole brightener in the electroplating bath, they may readily be employed in conjunction with other types of brightening compounds. Moreover, the novel brightening agents herein disclosed are fully compatible with other additives usually added to electroplating solutions, namely smoothing agents, anti-porosity agents, wetting agents or salts which increase the conductivity of the electroplating bath.

We have found that the brightening agents according to our invention are most advantageously used in conjunction with acid electroplating baths which also com-55 prise aliphatic or aromatic sulfonic acids or their salts which contain halogen atoms or atom groups related to halogen, such as cyano or thiocyano groups, as substituents. Specific examples of such sulfonic acid substitution products are the following:

60 Bromoethane sulfonic acid 2-cyanoethane-sulfonic acid 2-thiocyanoethane-sulfonic acid 3-bromopropane-sulfonic acid-1 3-iodopropane-sulfonic acid-1

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4-bromobenzyl-sulfonic acid 4-chloronaphthalene-sulfonic acid-1 4,4'-dibromodiphenyl-disulfonic acid-2,2'

and the like. Thus, by modifying an acid nickel elec-5 troplating bath, for example, with a brightening agent according to the present invention as well as with a sulfonic acid substitution product of the type above described, the characteristics of nickel electrodeposits produced therefrom are considerably improved over those 10 produced under similar conditions from electroplating baths modified with additives heretofore commonly used. In particular, such nickel electroplates are marked by their extraordinary smoothness, remarkable brightness, high ductility and complete freedom from porosity.

It is further advantageous to modify such electroplating baths in addition with polyvalent alcohols, such as glycerin, butanetriol, pentaerythrite, mannitol and the like, or with polymerization products of unsaturated carboxylic acids or their salts, such as the sodium salt of polyacrylic acid, for example. The addition of such compounds to electroplating baths modified in accordance with the present invention makes it possible to reduce the amount of brightening agent necessary to produce the desired brightening effect, and in some instances further to improve the characteristics of the metal electrodeposits.

The amounts in which the brightening agents according to our invention or mixtures thereof are added to the electroplating bath depend largely upon the composition of the bath in question, but they range generally from 0.01 gm. to 20 gm. per liter of electroplating bath. As a rule, the best results are obtained if the metal is deposited from the modified bath at a temperature between room temperature and about 70° C., and at current densities from 0.5 to 10 amp./dm.2.

The novel brighteners disclosed herein are, for all practical purposes, not consumed during the electroplating process and are chemically very stable compounds, so that electroplating baths modified therewith remain operative and effective for extremely long periods of time.

The following examples will further illustrate the present invention and enable others skilled in the art to understand our invention more completely. However, the recitation of these examples should not be construed as an intention on our part to limit our invention to the compounds and conditions mentioned in the examples.

Example I

1 gm. of ethylene-bis-(dimethylamino-dithiocarbaminate) having the structural formula

$$(CH_3)_2N - C - S - CH_2 - CH_2 - S - C - N(CH_3)_2$$

was added to each liter of an acid copper electroplating bath composed of water, 60 gm./liter sulfuric acid and 170 gm./liter crystalline copper sulfate. Sheet iron objects which had previously been provided with a copper base-coat in an alkaline copper cyanide bath, were then electroplated in the modified bath at room temperature and at current densities between 1 and 10 amp./dm.². They were provided with full-bright, firmly adhering copper deposits, even when highly profiled. The electrodeposits required no polishing, buffing or any other finishing treatment subsequent to rinsing.

Example II

1 gm. bromoethane-sodium sulfonate and 0.1 gm. ethylene-diisothiourea-hydrobromide having the structural formula

$$\begin{array}{c} \operatorname{H_{2}N-C-S-CH_{2}-CH_{2}-S-C-NH_{2}.2HBr} \\ \parallel \\ \operatorname{NH} \end{array} \\ \end{array}$$

were added to each liter of an acid nickel electroplating bath composed of water, 60 gm./liter nickel chloride, 220 gm./liter crystalline nickel sulfate and 35 gm./liter boric acid. Sheet iron objects electroplated in this modified 75 prises in addition a compound selected from the group

bath at a temperature of about 60° C. and a current density of 1 to 8 amp./dm.2 were provided with very bright, firmly adhering nickel-plates which required no finishing treatment of any kind subsequent to rinsing.

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Example III

0.2 gm. of 1,3-diisothiourea-propanol-2-hydrobromide having the structural formula

$$\begin{array}{c|c} H_2N-C-S-CH_2-CH-CH_2-S-C-NH_2.2HBr\\ \parallel & \parallel\\ NH & OH & NH \end{array}$$

8 gm. 3-bromopropane-sodium sulfonate and 5 gm. glycerin were added to each liter of an acid nickel electroplating bath composed of water, 60 gm./liter nickel chloride, 220 gm./liter crystalline nickel sulfate and 35 gm./liter boric acid. Sheet iron objects electroplated in 15 this modified bath at a temperature of about 60° C. and a current density between 1 and 8 amp./dm.2 were provided with exceptionally bright, firmly adhering nickel electroplates which required no finishing treatment of 20 any kind subsequent to rinsing.

Example IV

1 gm. of ethylene-bis-(thiourea) according to Formula 25 4 was used instead of the brightener in Example I. A full bright copper deposit was obtained.

Example V

1 gm. of ethylene-bis-(dithiomethylcarbaminate) according to Formula 5 was used instead of the first named brightener in Example II. A good nickel plating was ob-30 tained.

Example VI

1 gm. of ethylene-1-(methylxanthogenate)-2-(methylsulfthiocarbonate according to Formula 6 was substituted 35for the first named brightener in Example III. A bright

nickel deposit was formed.

While we have illustrated our invention with the aid of certain specific embodiments thereof, it will be apparent to persons skilled in the art that various changes and modifications may be made without departing from the spirit of the invention or the scope of the appended claims.

We claim:

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1. An electroplating bath for producing bright deposits of metals selected from the group consisting of copper, zinc, silver, nickel, cadmium, bronze and brass comprising an aqueous acid solution of an inorganic salt of the metal to be deposited and from about 0.01 to about 20 50 grams/liter of an acyclic organic compound having the

general structural formula

$$Q-X-C-Z-R-Z'-C-X'-Q'$$

wherein R is a lower aliphatic radical, Q and Q' are se-55 lected from the group consisting of hydrogen, lower alkyl and lower hydroxy-alkyl, X, Y and Z are selected from the group consisting of oxygen, sulfur, nitrogen and the imino radical, and X', Y' and Z' are selected from the group consisting of oxygen, sulfur, nitrogen and the imino 66 radical.

2. An electroplating bath as in claim 1, comprising in addition a compound selected from the group consisting of halogenated lower alkyl sulfonic acids, halogenated aryl sulfonic acids and salts of such sulfonic acids.

3. An electroplating bath as in claim 1, comprising in addition a compound selected from the group consisting of bromine-substituted lower alkyl and aryl sulfonic acids and salts of such sulfonic acids.

4. An electroplating bath as in claim 1, comprising in addition a compound selected from the group consisting of cyano- and thiocyano-substituted lower alkyl and aryl sulfonic acids and salts of such sulfonic acids.

5. An electroplating bath as in claim 1, which com-

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consisting of polyvalent alcohols, polymerization products of unsaturated carboxylic acids, and salts of such polymerization products.

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6. The electroplating bath of claim 1 wherein the aliphatic radical is substituted.

7. The electroplating bath of claim 1 wherein the aliphatic radical is interrupted by hetero atoms.

8. The process of producing bright and lustrous electrodeposits of metals selected from the group consisting of copper, zinc, silver, nickel, cadmium, bronze and brass, 10 which comprises electrodepositing said metal from a bath containing said metal principally in the form of an aqueous acid solution of an inorganic salt of said metal in the presence of from about 0.01 to about 20 grams/liter of a

$$\begin{array}{c} \mathbf{Q} - \mathbf{X} - \mathbf{C} - \mathbf{Z} - \mathbf{R} - \mathbf{Z}' - \mathbf{C} - \mathbf{X}' - \mathbf{Q}' \\ \downarrow & \downarrow , \\ \end{array}$$

wherein R is a lower aliphatic radical, Q and Q' are se- 20lected from the group consisting of hydrogen, lower alkyl and lower hydroxy-alkyl, X, Y and Z are selected from the group consisting of oxygen, sulfur, nitrogen and the imino radical, and X', Y' and Z' are selected from the group consisting of oxygen, sulfur, nitrogen and the imino 25 radical.

9. An electroplating process as in claim 8, comprising in addition a compound selected from the group consisting of halogenated lower alkyl sulfonic acids, halogenated aryl sulfonic acids and salts of such sulfonic acids.

10. An electroplating process as in claim 8, comprising in addition a compound selected from the group consisting of bromine-substituted lower alkyl and aryl sulfonic acids and salts of such sulfonic acids.

11. An electroplating process as in claim 8, comprising in addition a compound selected from the group consisting of cyano- and thiocyano-substituted lower alkyl and aryl sulfonic acids and salts of such sulfonic acids.

12. An electroplating process as in claim 8, which combrightener, said brightener being an organic acyclic com- 15 prises in addition a compound selected from the group consisting of polyvalent alcohols, polymerization products of unsaturated carboxylic acids, and salts of such polymerization products.

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