BRIGHTENERS FOR ELECTROPLATING BATHS

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This invention relates to brighteners for electroplating 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 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 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 heteroatoms to a lower hydrocarbox 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 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:

\[ \text{Q} - \text{X} - \text{C} - \text{Z} - \text{R} - \text{Z'} - \text{C} - \text{X'} - \text{Q'} \]

wherein R is a lower hydrocarbox 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-thiohioare compounds, bis- or poly-isothioare compounds, bis- or poly-thiocarbamates, bis- or poly-dithiocarbamates, bis- or poly-xanthogemates, bis- or poly-trithiocarbonates and the like. However, they also include compounds wherein the

\[ \text{X} - \text{C} - \text{Z} - \text{X'} \]

and

\[ \text{Z'} - \text{C} - \text{X'} - \text{Z} \]

or additional such groupings are not identical.

A few representative examples of the types of compounds which we have found to be excellent brightening agents for electroplating baths are the following:

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂N-C-S-CH₂-CH₃-CH₂-S-C-NH₂-H₂Br</td>
</tr>
<tr>
<td>2</td>
<td>H₂N-C-S-OH₂-CH₂-CH₂-S-C-NH₂-H₂Br</td>
</tr>
<tr>
<td>3</td>
<td>H₂N-C-S-CH₂-CH₂-O-CH₂-CH₂-S-C-NH₂-HCl</td>
</tr>
<tr>
<td>4</td>
<td>H₂N-C-NH₂-CH₂-CH₂-NH₂-CH₂-CH₂-S-C-NH₂</td>
</tr>
<tr>
<td>5</td>
<td>CH₄-S-C-NH₂-CH₂-CH₂-NH₂-S-CH₂</td>
</tr>
<tr>
<td>6</td>
<td>CH₄-S-C-O-CH₂-CH₂-NH₂-S-CH₂</td>
</tr>
<tr>
<td>7</td>
<td>CH₄-S-C-O-CH₂-CH₂-S-CH₂-CH₂-O-CH₂-CH₂-S-CH₂</td>
</tr>
<tr>
<td>8</td>
<td>CH₄-S-C-O-CH₂-CH₂-N-CH₂-CH₂-O-CH₂-CH₂-S-CH₂</td>
</tr>
<tr>
<td>9</td>
<td>(CH₂)₄-N-C-S-CH₂-CH₂-S-C-N(CH₃)₂</td>
</tr>
<tr>
<td>10</td>
<td>(HOCH₂)₄-N-C-S-CH₂-CH₂-S-C-N(CH₃)₂</td>
</tr>
<tr>
<td>11</td>
<td>CH₄-S-C-S-CH₂-CH₂-S-C-CH₂-CH₂-S-C-NH₂</td>
</tr>
</tbody>
</table>

and the like.

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 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 comprise aliphatic or aromatic sulfonic acids or their salts which contain halogen atoms or atom groups related to halogen, such as cyan or thiocyan groups, as substituents. Specific examples of such sulfonic acid substitution products are the following:

1. Bromoethane sulfonic acid
2. 2-cyanoethane-sulfonic acid
3. 2-thiocynoethane-sulfonic acid
4. 3-bromopropane-sulfonic acid-1
5. 3-iodopropane-sulfonic acid-1
6. 2,3-dichloropropene-sulfonic acid-1
7. 4-bromobutane-sulfonic acid-1
8. 3-chlorobenzene-sulfonic acid-1
9. 4-bromobenzene-sulfonic acid-1
10. 2,4,5-trichlorobenzene-sulfonic acid-1
11. 2-chlorophenol-sulfonic acid-4
12. 5-bromo-2-nitrobenzene-sulfonic acid-1
13. 4-iodotoluene-sulfonic acid-3
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.

**Example IV**

1 gm. of ethylene-bis-(thiourea) according to Formula 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 obtained.

**Example VI**

1 gm. of ethylene-1-(methylxanthogenate)-2-(methylsulfinicarbonate) according to Formula 6 was substituted for 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:

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 grams/liter of an acyclic organic compound having the general structural formula

$$\text{Q} \cdot \text{X} \cdot \text{Y}$$

wherein R is a lower aliphatic radical, Q and Q' are selected from the group consisting of hydrogen, lower alkyl and lower hydroxy-silyl, 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 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 thiocyanato-substituted lower alkyl and aryl sulfonic acids and salts of such sulfonic acids.

5. An electroplating bath as in claim 1, which comprises in addition a compound selected from the group

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**Chemical Formulas**

- 4-bromobenzyl-sulfonic acid
- 4-chloronaphthalene-sulfonic acid
- 4,4'-dibromodiphenyl-disulfonic acid
- 2,20 gin./liter crystalline nickel sulfate and 35 gm./liter boric acid.

**Example I**

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

$$\text{(CH}_3 \text{N} \cdot \text{O} \cdot \text{S} \cdot \text{CH}_3 \cdot \text{CH} \cdot \text{S} \cdot \text{CH}_3 \cdot \text{N} \cdot \text{CH}_3)$$

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

$$\text{HN} \cdot \text{O} \cdot \text{S} \cdot \text{CH} \cdot \text{CH} \cdot \text{S} \cdot \text{O} \cdot \text{N} \cdot \text{S} \cdot \text{Br}$$

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 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.

**Example III**

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

$$\text{NH} \cdot \text{O} \cdot \text{S} \cdot \text{CH} \cdot \text{CH} \cdot \text{O} \cdot \text{N} \cdot \text{S} \cdot \text{Br}$$

8 gm. 3-bromopropane-sodium sulfonate and 5 gm. glyc erin 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 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 electrodeposits which required no finishing treatment of any kind subsequent to rinsing.
consisting of polyvalent alcohols, polymerization products of unsaturated carboxylic acids, and salts of such polymerization products.

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 electroplating deposits of metals selected from the group consisting of copper, zinc, silver, nickel, cadmium, bronze and brass, 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 brightener, said brightener being an organic acyclic compound having the general structural formula

$$Q-X-O-Z-R-Z'-O-X'-OQ'$$

wherein R is a lower aliphatic radical, Q and Q' are selected 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 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 comprises 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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