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PRODUCTION OF METAL ELECTRODEPOSITS

Wolfgang Gündel, Dusseldorf-Oberkassel, and Wennemar Strauss and Hermann Haas, Dusseldorf-Holthausen, Germany, assignors to Dehydag, Deutsche Hydrierwerke G.m.b.H., Dusseldorf, Germany, a corporation of Germany

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10 Claims. (Cl. 204—44)

This invention relates to an improvement in the production of metal electrodeposits, and more particularly to electroplating baths modified with water-soluble organic brightening agents in order to enhance the brightness and luster of the electrodeposits produced therefrom.

Electroplating baths have heretofore been modified by the inclusion of organic sulfonic acids or organic sulfation products of various compounds. While the brightening agents disclosed by the prior art have usually effected some improvement in the characteristics of the electrodeposits produced from such modified baths, the additives individually have not been sufficient to produce commercially desirable deposits and had to be used with another and sometimes even with two or more supplemental addition agents in order to achieve the high quality metal electrodeposits demanded by industry today.

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

Another object of this invention is to provide an electroplating bath which will produce bright and lustrous electrodeposits that need no further polishing or buffing.

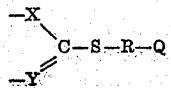
Still another object of the present invention is to provide additives for electroplating baths which may advantageously be used as sole brightening additives or with other types of additives to produce bright and lustrous metal electrodeposits.

Still further objects and advantages of our invention will become apparent as the description thereof proceeds.

We have found that bright, highly lustrous and well-adhering electroplates 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 organic compounds having the general structural formula

Z—S—R—Q

wherein Z is a radical comprising a carbon atom directly attached to two atoms selected from the group consisting of nitrogen, sulfur and oxygen atoms, said carbon atom also directly attached to the terminal sulfur atom of the —S—R—Q group, R represents a bivalent aliphatic radical, such as ethylene, propylene, alkyl propylene, hydroxy propylene or pentylene radicals, for example, which may be unsubstituted or may carry other organic substituents, and Q is a water-solubilizing group other than a sulfonic acid radical, or the salts of such compounds formed by neutralization with inorganic or organic bases. In other words, the brightening agents used in accordance with the present invention are water-soluble organic compounds or salts thereof which have the structural formulas



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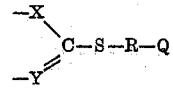

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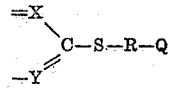
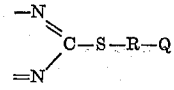


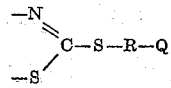
wherein X and Y are selected from the group consisting of nitrogen, sulfur and oxygen, and R and Q represent the radicals above defined.

Typical water-soluble compounds of this type are the following:

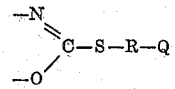
(1) Compounds derived from thiourea and, if the cation chain is closed, from 2-thioimidazoles or 2-benzimidazoles, having the structural formula



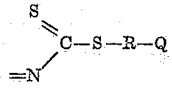
(2) Compounds derived from 2-mercapto-thiazoles or 2-mercaptobenzene-thiazoles and from thiocyanates, having the structural formula



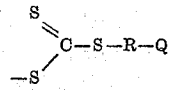
(3) Compounds derived from 2-thiobenzoxazoles and 2-thiocumazoles (2-thiobenzene-metaxazines), having the structural formula



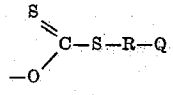
(4) Compounds derived from dithiocarbamic acids, having the structural formula



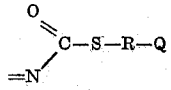
(5) Compounds derived from thioxanthic acid or trithiocarbonic acid, having the structural formula



(6) Compounds derived from xanthic acid, having the structural formula



(7) Compounds derived from carbabinothiol acids, having the structural formula



In all of the above compounds the free bonds may be connected to a hydrogen atom or to aliphatic, cycloaliphatic or aromatic hydrocarbon radicals. Such hydrocarbon radicals may also be interconnected among themselves or may carry substituents of further heteroatoms or heteroatom groups.

The water-solubilizing group represented by Q in the above structural formulas may, for example, be a sulfuric acid ester group, a phosphoric acid ester group, a phosphonic acid group (—$PO(OH)_2$), a phosphinic acid

group (—PO.R'.OH, wherein R' is hydrogen or a hydrocarbon radical), a primary, secondary or tertiary amino salt group formed by neutralization of the corresponding amino-compounds with inorganic or organic acids, or also a quaternary ammonium group or another water-solubilizing onium group.

Further suitable for use as brightening agents within the scope of the present invention are water-soluble compounds of the above type which contain one and preferably a plurality of hydroxyl groups, etheralcohol groups and polyetheralcohol groups, such as ethyleneoxide addition products and the like.

The following compounds are a few specific examples of the types of water-soluble brightening agents which are suitable for use in metal electroplating baths according to the present invention:

2-mercapto-benzothiazole-S-ethanol sodium sulfate
Thiobenzoxazole-S-ethanol sodium sulfate
2-mercapto-benzothiazole-S-ethanol sodium phosphates
2-mercapto-benzothiazole-S-ethane sodium phosphonate
2-thio-methoxazine-S-butane-ω-potassium phosphonate
The internal salt of isothiourea-S-propane-P-methyl-ω-phosphinic acid
N,N-diethyl-dithiocarbamic acid-n-butylester - ω - sodium phosphinate
N-phenyl-dithiocarbamic acid-propyl ester-P-ethyl-ω-ammonium phosphinate
Trithiocarbonic acid-bis-butyl ester-ω-potassium phosphinate
Isothiourea-S-ethane-polyglycolether with five glycolether radicals
Isothiourea-S-propanediol-2,3-hydrochloride
S-(2-aminoethyl)-2-mercaptobenzothiazole-hydrochloride
S-(2-dimethylaminoethyl)-2-mercaptobenzoxazole bisulfate and the like.

The above class of compounds can be used as brightening agents in conjunction with all types of metal electroplating processes, for example, in processes for electrodepositing nickel, copper, silver, zinc, bronze, brass and cadmium.

The brightening agents in accordance with the present invention may also be used in combination with other types of brightening agents, salts which increase the conductivity of the electroplating bath, surface-active agents or additives which tend to reduce the porosity of the electrodeposits. In some instances the brightening agents above-disclosed are more difficult to dissolve in the electroplating bath, depending upon their structure and the concentration of the bath; in those cases the addition of surface-active agents to the electroplating bath increases the solubility of the brightening agent.

The quantities in which the brightening agents are added to the electroplating bath to achieve the desired brightening effect range from about 0.01 to 20 gm. per liter of electroplating bath. In general, objects are electroplated in the modified baths above-described at temperatures below 60° C. and at current densities ranging from 0.5 to 12 amp./dm.^{2}. The range of current densities within which the brightening agents of the present invention will produce the optimum brightening effect is slightly different for each compound, but in most cases the range of optimum brightening effect is very wide. However, by using a mixture of brightening agents of the type disclosed herein, the current density range of optimum brightening effect for any given electroplating bath can be widened.

All types of metals may successfully be used for depositing electroplates thereon with the aid of plating baths modified in accordance with the present invention. Iron, steel, zinc and other non-precious metals or metal alloys may, as customary, first be provided with a preliminary copper deposit in an alkaline copper cyanide bath, but such metals may also be electroplated in acid electroplating baths modified in accordance with the present invention without providing them with the customary preliminary copper coating.

The electrodeposits produced from the modified electroplating baths set forth above are extremely bright and adhere well to the base. In most cases the brightness of such electrodeposits is so great that a subsequent polishing or buffing operation is not required, thereby obviating this particular manufacturing step.

The brightening agents disclosed herein have the further advantage that they are highly stable in acid solution and at higher temperatures, so that electroplating baths modified with these brighteners remain operative even after prolonged operation at relatively high temperatures.

The following examples will further illustrate the present invention and enable others skilled in the art to understand it more completely. It is understod, however, that the examples are given only for purposes of illustration with no intention of limiting the invention thereto.

Example I

0.5 to 1.0 gm. N,N-diethylamino-dithiocarbamic acid-S-propanediol-2,3 was added to each liter of an acid copper plating bath containing 60 gm./liter sulfuric acid and 170 gm./liter crystalline copper sulfate. Sheet steel which had been provided with a preliminary copper plate in an alkaline copper cyanide bath was then copper plated in the above acid plating bath at room temperature and a current density of 1 to 10 amp./dm.^{2}. Even on highly profiled sheet steel the copper electrodeposits formed thereby were very bright and adhered well to the steel base. They required no buffing or polishing after rinsing.

Example II

0.5–1 gm. of the isothiourea-S-propanediol-2,3-hydrochloride are used instead of the brightening agent in Example I. A valuable copper-plating is obtained.

Example III

0.75 gm. of the neutral sodium salt of the acid 1-ethylenethiourea-S-ethanol-phosphoric acid ester-2 was added to each liter of an acid copper-plating bath containing 60 gm./liter sulfuric acid and 220 gm. crystalline copper sulfate. Iron objects were then electroplated in this bath at about 20° C. and a current density of 1–10 amp./dm.^{2}. The copper deposits produced thereby were extremely bright and of uniform texture. After rinsing they required no buffing or polishing.

Example IV

0.75 gm. of the 2-mercapto-benzothiazole-S-ethanol sodium phosphate are used instead of the brightening agent in Example III. A valuable copper-plating is obtained.

Example V

1.5 gm. 2-mercapto-benzothiazole-S-butane-ω-sodium phosphinate were added to each liter of an acid copper electroplating bath containing 60 gm./liter sulfuric acid and 220 gm./liter crystalline copper sulfate. Iron objects electroplated in this solution at about 20° C. and a current density of 7.5 amp./dm.^{2} were provided with extremely bright copper plates which, after rinsing, required no further polishing or buffing.

Example VI

1.5 gm. of the internal salt of isothiourea-S-propane-P-methyl-ω-phosphinic acid are used instead of the brightening agent in Example V. A valuable copperplating is obtained.

Example VII

0.5 gm. of S-(2-aminoethyl)-2-mercapto-benzo-thiazole sulfate was added to each liter of an acid copper electroplating bath which contained 60 gm./liter sulfuric acid and 220 gm./liter crystalline copper sulfate. Iron objects electroplated therein at about 20° C. and a current density of 7.5 amp./dm.^{2} were provided with an extremely bright

copper plate which needed no buffing or polishing after rinsing.

Example VIII

0.5 gm. of the S-(2-dimethylaminoethyl)-2-mercaptobenzoxazole bisulfate are used instead of the brightening agent in Example VII. A valuable copperplating is obtained.

Example IX

0.1 to 0.3 gm. of the addition product of 4 mols ethyleneoxide and thiourea was added to an acid nickelplating bath containing 60 gm./liter nickel chloride, 220 gm./liter crystalline nickel sulfate and 35 gm./liter boric acid. Iron objects electroplated in this bath at room temperature and a current density between 1 and 10 amp./dm.^{2} were provided with a well-adhering, extremely bright nickel plate which required no further buffing or the like.

Example X

0.1 to 0.3 gm. of the addition product of 10 mols ethylene oxide and thiourea are used instead of the brightening agent in Example IX. A valuable copper-plating is obtained.

Example XI

1 gm. of 2-mercaptobenzothiazole-S-ethanol potassium sulfate was added to each liter of a zinc electroplating bath having the following composition:

50–70 gm./liter zinc cyanide
40–60 gm./liter sodium cyanide
10–20 gm./liter sodium hydroxide
0.5–2 gm./liter sodium sulfide

Iron objects electroplated in this bath at room temperature and a current density of 1 to 10 amp./dm.^{2} were provided with well-adhering, ductile, full-bright zinc plates, which required no buffing after rinsing.

Example XII

1 gm. of the thiobenzoxazole-S-ethanol sodium sulfate are used instead of the brightening agent in Example XI. A valuable zinc-plating is obtained.

Example XIII

0.5 to 1 gm. of dithiocarbamic acid-propane-ω-sodium phosphonate was added to each liter of a cadmium electroplating bath having the following composition:

40–80 gm./liter cadmium cyanide
30–70 gm./liter sodium cyanide
10–40 gm./liter sodium hydroxide

Sheet iron electroplated in this bath at room temperature and a current density of 2–10 amp./dm.^{2} was provided with a ductile, full-bright cadmium electroplate which needed no buffing after rinsing.

Example XIV

0.5 to 1 gm. of the 2-mercapto-benzthiazole-S-ethane sodium phosphonate are used instead of the brightening agent in Example XIII. A valuable cadmium-plating is obtained.

While we have given specific embodiments of our invention, we wish it to be understood that various changes and modifications may be made therein without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. An electroplating bath for producing deposits of metals selected from the group consisting of nickel, copper, zinc, silver, bronze, brass, and cadmium comprising an acid solution of an inorganic salt of the metal to be deposited and a compound having the general formula

Z—S—R—Q

wherein Z is an organic radical which includes a carbon atom bonded exclusively with three hetero atoms, one

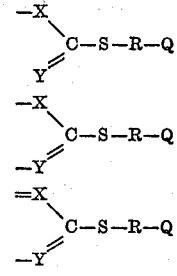
of which is the sulfur atom through which said organic radical Z is linked to the radical R—Q, the other two hetero atoms of said Z radical being selected from the group consisting of nitrogen, sulfur, and oxygen atoms, R is a bivalent aliphatic radical, and Q is a water solubilizing radical selected from the group consisting of sulfuric acid ester, phosphoric acid ester, phosphonic acid, phosphinic acid, polyether and polyalcohol radicals, said compound being added in a quantity sufficient to produce a bright metal deposit.

2. The process of producing bright and lustrous deposits of metals selected from the group consisting of nickel, copper, zinc, silver, bronze, brass, and cadmium which comprises electrodepositing said metal from a bath containing said metal principally in the form of an acid solution of an inorganic salt of the metal in the presence of a brightening agent

Z—S—R—Q

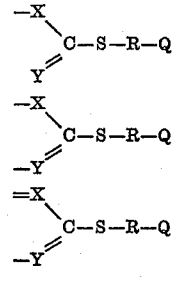
wherein Z is an organic radical which includes a carbon atom bonded exclusively with three hetero atoms, one of which is the sulfur atom through which said organic radical Z is linked to the radical R—Q, the other two hetero atoms of said Z radical being selected from the group consisting of nitrogen, sulfur and oxygen atoms, R is a bivalent aliphatic radical, and Q is a water solubilizing radical selected from the group consisting of sulfuric acid ester, phosphoric acid ester, phosphonic acid, phosphinic acid, polyether and polyalcohol radicals, said compound being added in a quantity sufficient to produce a bright metal deposit.

3. An electroplating bath for producing deposits of metals selected from the group consisting of nickel, copper, zinc, silver, bronze, brass and cadmium, comprising an acid solution of an inorganic salt of the metal to be deposited and a compound selected from the group consisting of compounds having the structural formulas



and their salts, wherein X and Y are atoms selected from the group consisting of nitrogen, oxygen and sulfur, R is a bivalent aliphatic radical and Q is a water-solubilizing radical selected from the group consisting of sulfuric acid ester, phosphoric acid ester, phosphonic acid, phosphinic acid, polyether and polyalcohol radicals said organic compound being dissolved in said bath in sufficient quantity to produce bright metal-plating deposits therefrom.

4. An electroplating bath for producing deposits of metals selected from the group consisting of nickel, copper, zinc, silver, bronze, brass and cadmium, comprising an acid solution of an inorganic salt of the metal to be deposited and about 0.01 to 20 grams per liter of a compound selected from the group consisting of compounds having the structural formulas

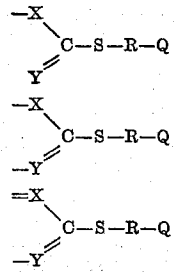


and their salts, wherein X and Y are atoms selected from the group consisting of nitrogen, oxygen and sulfur, R is a bivalent aliphatic radical and Q is a water-solubilizing radical selected from the group consisting of sulfuric acid ester, phosphoric acid ester, phosphonic acid, phosphinic acid, polyether and polyalcohol radicals.

5. An electroplating bath as in claim 3, said bivalent radical being substituted.

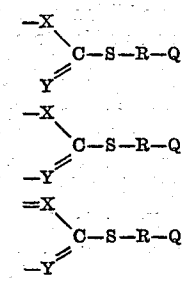
6. An electroplating bath as in claim 3, said bivalent radical being unsubstituted.

7. The process of producing bright and lustrous deposits of metals selected from the group consisting of nickel, copper, zinc, silver, bronze, brass and cadmium, which comprises electro-depositing said metal from a bath containing said metal in the form of an acid solution of an inorganic salt of the metal, in the presence of a brightening agent selected from the group consisting of compounds having the structural formulas



and their salts, wherein X and Y are atoms selected from the group consisting of nitrogen, oxygen and sulfur, R is a bivalent aliphatic radical and Q is a water-solubilizing radical selected from the group consisting of sulfuric acid ester, phosphoric acid ester, phosphonic acid, phosphinic acid, polyether and polyalcohol radicals said organic compound being dissolved in said bath in sufficient quantity to produce bright metal-plating deposits therefrom.

8. The process of producing bright and lustrous deposits of metals selected from the group consisting of nickel, copper, zinc, silver, bronze, brass and cadmium, which comprises electro-depositing said metal from a bath containing said metal in the form of an acid solution of an inorganic salt of the metal, in the presence of about 0.01 to 20 grams per liter of a brightening agent selected from the group consisting of compounds having the structural formulas



and their salts, wherein X and Y are atoms selected from the group consisting of nitrogen, oxygen and sulfur, R is a bivalent aliphatic radical, and Q is a water-solubilizing radical selected from the group consisting of sulfuric acid ester, phosphoric acid ester, phosphonic acid, phosphinic acid, polyether, and polyalcohol radicals.

9. A process as in claim 7, said bivalent aliphatic radical being substituted.

10. A process as in claim 7, said bivalent aliphatic radical being unsubstituted.

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