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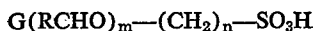
3,414,493

ELECTRODEPOSITION OF COPPER

Fred I. Nobel and Barnet D. Ostrow, Roslyn, N.Y. (both % Lea-Ronal Inc., 130-19 180th St., Jamaica, N.Y. 11434)

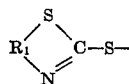
No Drawing. Filed Oct. 19, 1965, Ser. No. 498,084
8 Claims. (Cl. 204-52)

This invention relates to electroplating and more particularly to electrodepositing copper from an aqueous acidic copper plating bath in which there is dissolved a small amount of a brightening agent. According to this invention, the brightening agent is an organic sulfonic acid or its water soluble salts having the general structural formula:



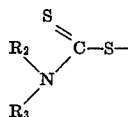
wherein R is H or an alkene radical having 1 to 3 carbon atoms, m and n are integers of which m is at least 1 and n is from 3 to 8, and G is a nitrogen-carbon-sulfur radical having the general structural formula:

(a)

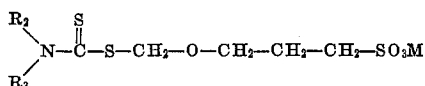


or

(b)



in which R_1 is an aromatic radical or its alkyl derivative, and R_2 and R_3 are alkyl radicals. R_1 and the combination of R_2 and R_3 may also be cyclic alkyl radicals linking to the single bonds of S and N in (a) for R_1 and the double bond of N in (b) for the combination of R_2 R_3 . A preferred brightener would have the following structural formula



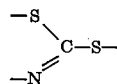
in which R_2 and R_3 are as defined above and M is H Na or K.

It is understood that in subsequent descriptions in the preparation of the brightener H, Na and K are interchangeable depending on the starting material.

Preferably, the brightening agents of this invention are prepared by initially reacting a nitrogen-carbon-sulfur organic compound with an alkyl aldehyde in an alkaline solution and subsequently adding a sulfone to the reaction mixture to produce the brightening agent of this invention.

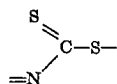
The nitrogen-carbon-sulfur organic compounds suitable for the present invention all contain an organic radical which comprises a carbon atom bonded exclusively to hetero atoms, nitrogen, and sulfur. In other words, the compounds contain the radical having the general structural formula:

(c)



or

(d)



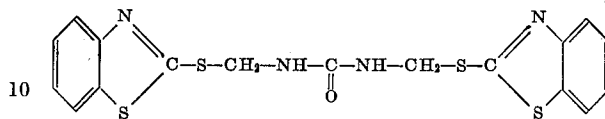
Linked to one of the S and the N in (c) may be an aromatic or a cyclic alkyl radical and to the N in (d)

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may be alkyl radicals or a cyclic alkyl radical. The second S is connected to a H, an alkyl or other nitrogen-sulfur radicals. Typical compounds of this type suitable for the present invention include:

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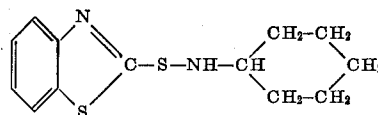
(I) 1,3-bis(2-benzothiazolylmercaptomethyl)urea



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(II) N-cyclohexyl-2-benzothiazolesulfenamide

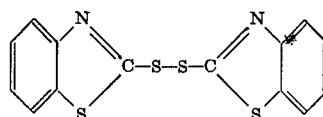
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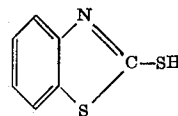
(III) 2,2'-dithiobis(benzothiazole)

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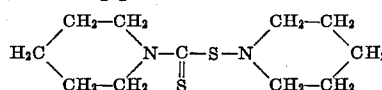
(IV) 2-mercaptobenzothiazole

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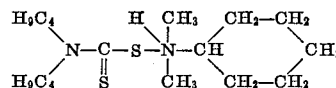
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(V) Piperidium-1-piperidinecarbodithioate



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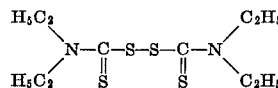
(VI) N,N-dimethylcycloamine salt of dibutylthiocarbamic acid



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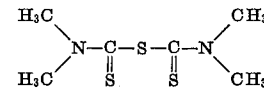
(VII) Bis(diethylthiocarbamyl) disulfide

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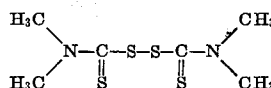
(VIII) Bis(Dimethylthiocarbamyl) sulfide

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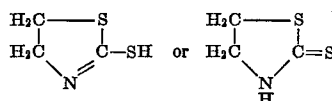
(IX) Bis(dimethylthiocarbamyl) disulfide

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(X) 2-thiazoleidine 2-thiol



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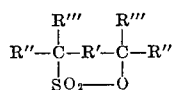
Among these compounds, we found Compounds IV, VII,

VIII, and IX to be eminently suitable and are the preferred starting materials.

The alkyl aldehyde used in the reaction is preferably a lower alkyl aldehyde containing not more than 3 carbon atoms. In reactions using the preferred nitrogen-carbon-sulfur organic compounds stated above, we found paraformaldehyde to be particularly suitable.

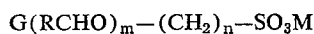
In the first stage of the reaction, the N-C-S organic compound is preferably dissolved in an alcoholic or an aqueous solution, or an alcohol-water mixture together with an equal molar amount of an alkali metal hydroxide, preferably sodium hydroxide, to form the N-C=S alkali metal salt in solution. Added to the reaction solution is one or more mols of aldehyde for each mol of N-C-S organic compound and the reaction mixture is refluxed for a period of time depending on the reactants used. Generally, one-half hour is sufficient to insure complete reaction. The resultant solution is used in the third stage of the reaction in which sultone is added therein. In the later stage, the reaction is also preferably carried out in the reflux temperature until completion.

The sultones used in the second stage have in general the structure:



wherein R'' and R''' are hydrogen atoms or alkyl radicals, and R' is an alkylene radical of up to 2 carbon atoms, preferably 1,1-alkylene. Sultones that are particularly suitable are those in which R' is methylene or R''-substituted methylene, and each R is hydrogen or alkyl of up to 4 carbon atoms. The total number of carbon atoms is preferably from 3 to 8. Typical sultones that are found to be suitable include: 1-propane sulfonic acid 3-hydroxysultone; 1-butane sulfonic acid 4-hydroxysultone; 1-butane sulfonic acid 3-hydroxysultone; 2-butane sulfonic acid 4-hydroxysultone; 2-pentane sulfonic acid 4-hydroxysultone; 1-pentane sulfonic acid 5-hydroxysultone; 2-methyl-2-pentane sulfonic acid 4-hydroxysultone; 4-heptane sulfonic acid 6-hydroxysultone; 1-heptane sulfonic acid 3-hydroxysultone; 1-heptane sulfonic acid 4-hydroxysultone; 6-methyl-1-heptane sulfonic acid 3-hydroxysultone; 3-methyl-4-heptane sulfonic acid 2-hydroxysultone.

We found the reaction product of the reaction described above to be particularly suitable as a brightening agent in an acid copper plating bath for electrodepositing copper. The process for producing bright and smooth copper deposits comprises electrodepositing copper from an aqueous acidic solution of at least one copper salt in which there is dissolved a water soluble brightener having the structural formula:

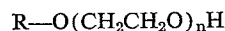


The symbols G, R, m, n, and M have the same meaning as defined previously.

Only a relatively small quantity of this organic sulfonic acid or its water soluble salt is required for the plating bath. We found concentrations as low as 0.005 gram per liter to be effective. There appears to be no sharp upper limit on the concentration of this organic sulfonic acid; however, there is generally no advantage in employing more than 1 gram per liter. In most plating baths, substantially the full benefit of the brightening agent is achieved with an amount in the range from 0.005 to about 0.05 gram per liter. Advantageously, the organic sulfonic acid or its water soluble salt of this invention is isolated from the reaction solution by precipitation or crystallization and subsequently is dissolved in water to form the additive solution to be added directly into the plating bath.

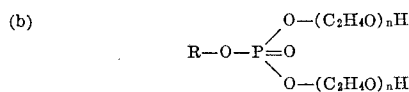
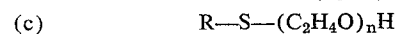
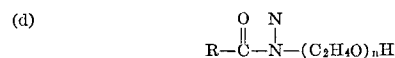
In the process of this invention, a full brightening effect is realized when the brightening agent of this invention is used in combination with an ethylene oxide

compound. Suitable ethylene oxide compounds have the general structural formula:

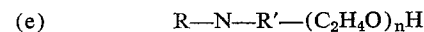


in which R is an aryl or alkyl containing 6 to 20 carbon atoms and n is an integer between 2 to 100. This type of compound is commonly used as a nonionic wetting agent which is produced by treating fatty alcohol or alkyl substituted phenols with excess ethylene oxides. The commercial available agents that we found to be eminently suitable are the type produced by reacting oleyl alcohol or stearyl alcohol with 6 or more mols of ethylene oxide, preferably 10 or more.

Other types of ethylene oxide compound under the general classification of amine, alkanol amine, amide and carbowax, and others containing sulfur and phosphorous heteroatoms, each of which contains a hydrophilic group and a large number of ethylene oxide groups, are also suitable. The ethylene oxide compounds have the following general formulas:



or



in which R is an alkyl or an aryl radical containing 6 to 20 carbon atoms and R' is a $(\text{CH}_2)_y$ group wherein y is an integer from 1 to 6 and n is an integer from 2 to 100.

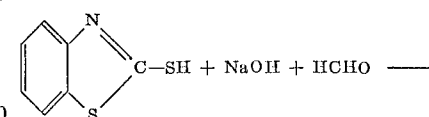
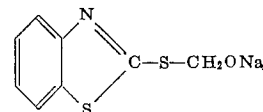
The amount required in the plating bath varies with the bath. In general, at least about 0.001 gram per liter of bath is used to secure the full brightness. An amount much more than 1 gram per liter appears to contribute no further beneficial result.

Most commercial leveling agents may also be incorporated into the plating bath without interfering with the brightening agent of this invention. However, we prefer to use the leveling agent disclosed in our copending patent application Ser. No. 469,323 filed on July 2, 1965. The leveling agents disclosed in that application are heterocyclic sulfur-nitrogen organic compounds, 2-thiazolidenethiones, 2-imidazolidinethiones and their reaction products with alkyl, aldehydes or dialdehydes.

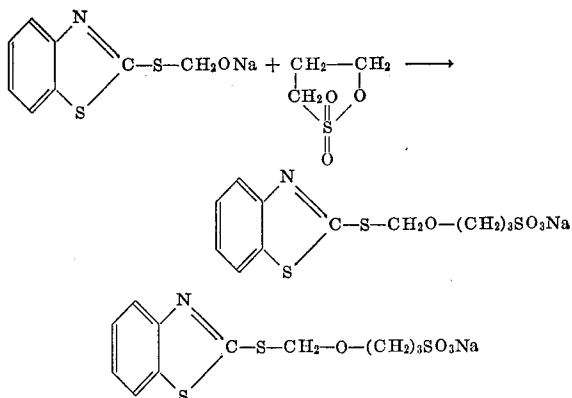
Further to describe this invention specific examples are used hereinbelow to illustrate the preparation of the specific brightening agents of this invention and their use in an acid copper plating bath for electrodepositing copper.

EXAMPLE I

Sufficient methyl alcohol is used to dissolve one mol of 2 mercaptobenzothiazole and one mol of sodium hydroxide. Into this alcoholic solution is added one mol of paraformaldehyde and the resultant reaction solution is refluxed for one-half hour. After the first stage reaction, 1 mol of propane sultone is added into the reaction mixture and is refluxed for an additional one-half hour. One series of reaction which can occur is illustrated by the following equations:



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recovered is a light yellow powder.

0.04 gm. per liter of this compound is added into an acid copper plating bath which has the following composition:

	G/L.
Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	240
Concentrated sulfuric acid	60

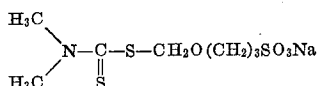
A brass sheet is plated at 1-5 amp/dm.² at 70° F. for 30 minutes. A lustrous to semilustrous coating is obtained over the current range.

EXAMPLE II

0.004 gm./liter of triethanolamine-ethylene oxide adduct having 30 mols of ethylene oxide is added to the bath described above. The resultant copper deposits are bright over the entire current density range and are apparently brighter than the copper deposits of Example I.

EXAMPLE III

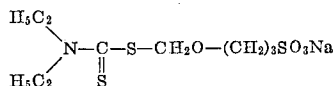
1 mol of bis(dimethylthiocarbamyl)disulfide and 2 mols of NaOH are added into a sufficient amount of methyl alcohol. To this solution is added 2 mols of formaldehyde and the resultant solution is refluxed for about one-half hour before the addition of propane sultone. After the sultone addition, the reaction is carried to completion. The resultant product has a structural formula:



0.03 gm./liter of this organic sulfonic acid salt and 0.004 gm./liter of triethanolamine-ethyleneoxide adduct having 30 mols of ethylene oxide are added into a standard acid copper plating bath as stated in Example I. A brass sheet is plated at 1-10 amp/dm.² at 70° F. for 30 minutes. Very bright copper deposits are observed over the entire current density.

EXAMPLE IV

Bis(diethylthiocarbamyl)disulfide instead of bis(dimethylthiocarbamyl)disulfide is used as the starting material to prepare an organic sulfonic acid salt having the structure:



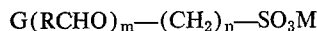
in substantially the same manner as described in the previous example. This product is used in electroplating similar to that described in Example III. Very bright copper deposits are obtained.

While the specific examples described above use one reaction product, it is understood that a mixture of brightening agents of this invention can be used. Particular satisfactory copper deposits can be obtained using 2 or more brightening agents of which one works better in the lower current density range and the other in the higher current density range.

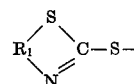
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We claim:

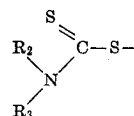
1. A process for producing bright and smooth copper deposits which comprises electrodepositing copper from an aqueous acidic solution of at least one copper salt in which there is dissolved a water soluble brightener having the structural formula:



wherein R is a hydrogen or an alkylene radical having 1 to 3 carbon atoms, m and n are integers of which m is at least 1 and n is from 3 to 8, M is H, Na or K, and G is a carbon-nitrogen-sulfur radical having the structural formula:

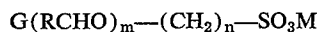


or

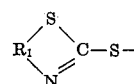


in which R₁ is an aromatic radical or its alkyl derivative, and R₂ and R₃ are alkyl radicals, in an amount sufficient to provide a brightening effect.

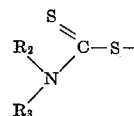
2. A process for producing bright and smooth copper deposits which comprises electrodepositing copper from an aqueous acidic solution of at least one copper salt in which there is dissolved more than about 0.005 g./liter of a brightener having the structural formula:



wherein R is a hydrogen or an alkylene radical having 1 to 3 carbon atoms, m and n are integers of which m is at least 1 and n is from 3 to 8, M is H, Na or K, and G is a carbon-nitrogen-sulfur radical having the structural formula:

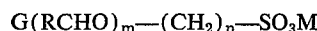


or

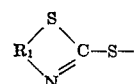


in which R₁ is an aromatic radical or its alkyl derivative, and R₂ and R₃ are alkyl radicals.

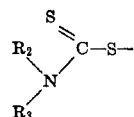
3. A process for producing bright and smooth copper deposits which comprises electrodepositing copper from an aqueous acidic solution of at least one copper salt in which there is dissolved (I) more than about 0.005 g./liter of a brightener having the structural formula:



wherein R is a hydrogen or an alkylene radical having 1 to 3 carbon atoms, m and n have integers of which m is at least 1 and n is from 3 to 8, M is H, Na or K, and G is a carbon-nitrogen-sulfur radical having the structural formula:



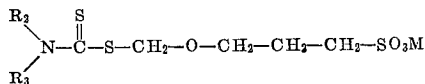
or



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in which R_1 is an aromatic radical or its alkyl derivative, and R_2 and R_3 are alkyl radicals, and (II) more than about 0.001 g./liter of a long chain ethylene oxide compound.

4. A process according to claim 3 wherein said brightener has the structural formula:

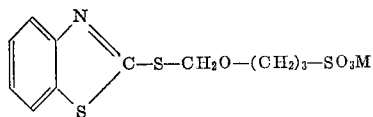


in which R_2 and R_3 are alkyl radicals having 1 to 3 carbon atoms, and M is H, Na or K.

5. A process according to claim 4 wherein R_2 and R_3 are methyl radicals.

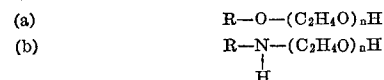
6. A process according to claim 4 wherein R_2 and R_3 are ethyl radicals.

7. A process according to claim 3 wherein said brightener has the structural formula:

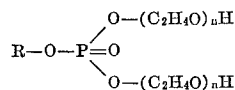
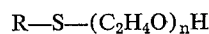
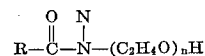


in which M is H, Na or K.

8. A process according to claim 3 wherein the said ethylene oxide compound is water soluble and has the general formula:



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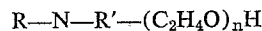
(c)

5 (d)

(e)

or

(f)



in which R is an alkyl or aryl radical containing 6 to 20 carbon atoms, R' is a $(CH_2)_y$ group wherein y is an integer from 1 to 6, and n is an integer from 2 to 100.

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