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Kessler et al.

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[54] **ELECTRODEPOSITION OF COPPER FROM ACIDIC BATHS**

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[52] **U.S. Cl.** .....**204/52 R**

[51] **Int. Cl.** **C23b 5/20**, C23b 5/46

[58] **Field of Search** .....204/52 R, 52 Y, 44, 106; 106/1; 117/130 E

[56] **References Cited**

UNITED STATES PATENTS

2,910,413	10/1959	Strauss et al.	204/44
3,101,305	8/1963	Roth et al.	204/52 R
3,203,878	8/1965	Willmund et al.	204/52 R
3,276,979	10/1966	Strauss et al.	204/52 R X
3,328,273	6/1967	Creutz et al.	204/52 R
3,359,297	12/1967	Gundel	204/52 R X
3,400,059	9/1968	Michael et al.	204/52 R
3,414,493	12/1968	Nobel et al.	204/52 R
3,502,551	3/1970	Todt et al.	204/52 R
3,542,655	11/1970	Kardos et al.	204/52 R

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[57] **ABSTRACT**

An acid copper plating bath which contains a copper metal salt and a minor amount of a sulfoniumalkanesulfonate or sulfoniumalkanecarboxylate as a brightening agent. Illustrative sulfonium compounds are N-cyclohexyl-2-benzothiazol sulfonium-1-propanesulfonate, bis (dimethylthiocarbamyl) sulfonium-1-propanesulfonate, and bis (dimethylthiocarbamyl) sulfonium-1-propanecarboxylate. Preferred amounts of the sulfonium compounds range from about 0.001 to 1.0 grams per liter. The use of such acid copper plating baths in the electrodeposition of copper metal is also disclosed.

13 Claims, No Drawings

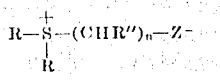
ELECTRODEPOSITION OF COPPER FROM ACIDIC BATHS

The present invention relates to the electroplating of copper from an aqueous acidic bath. More particularly the invention pertains to an acid copper plating bath containing a minor proportion of a novel brightening agent.

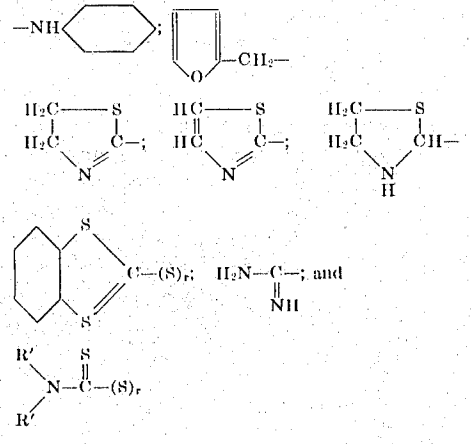
In the art of copper plating it has been customary to add various brightening agents to the acidic baths. Illustrative brightening agents are disclosed in U.S. Pat. Nos. 3,276,979; 3,288,690; 2,707,166; 2,707,167; 2,733,198; 2,830,014; and 2,910,413. Brightening agents such as the organic sulfonic acids and carboxylic acids or their salts offered considerable promise but suffer from certain serious disadvantages. For example, these brighteners have a limited low current density brightness range. On standing or after a period of electrolysis the decomposition products or sludge resulting from the use of these brighteners further reduced the low current density brightness range and furthermore required the use of auxiliary brighteners or purification procedures. Moreover, it was found that the degree of stability of the alkane mercapto sulfonates or carboxylates was markedly reduced or rendered ineffective in baths having high acid concentrations.

In accordance with the present invention it has now been found that the above described disadvantages can be avoided by utilizing organic sulfonium sulfonates or carboxylates as brightening agent additives in acidic aqueous baths for the electroplating of copper. The novel brightening agents of this invention are very stable in both standard and high acid concentration plating baths even after prolonged electrolysis or storage. In addition the low current density brightness range is not adversely affected as is the case with the previously described alkane mercapto sulfonates or carboxylates.

The novel sulfonium sulfonate or carboxylate brightening agents of this invention have the following formula:

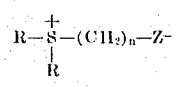


wherein each R radical, which may be the same or different, is selected from the group consisting of hydrogen; alkyl having from one to eight carbon atoms, for example; methyl or ethyl; aryl having from six to 12 carbon atoms, for example; phenyl or naphthyl;

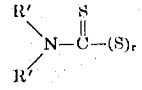


wherein each R′ radical may be the same or different and is a lower alkyl having from one to six carbon atoms; and *r* is 1 or zero; *n* is an integer from 1 to 6; R″ is selected from the group consisting of hydrogen and the methyl radical; and Z is an anion selected from the group consisting of SO_3^- and COO^-.

In the practice of this invention, the preferred brightening agents are those of the general formula



with each R being



wherein *r* is zero and each R′ is lower alkyl having from one to six carbon atoms; Z is SO_3^- and *n* is an integer from 1 to 6. Especially preferred is the brightening agent wherein each R′ is methyl; *n* is 3; Z is SO_3^-; and *r* is zero. However, it should be understood that other brightening agents of this invention also provide satisfactory results.

The sulfoniumalkanesulfonates encompassed by the above formulas are disclosed in U.S. Pat. No. 2,813,898 along with various methods for their preparation. Broadly the classes of sulfoniumalkanesulfonates include:

a. dialkylsulfoniumalkanesulfonates having from one to 18 carbon atoms in the alkyl radical,

b. diarlsulfoniumalkanesulfonates;

c. bis(alkaryl)sulfoniumalkanesulfonates;

d. bis(aralkyl)sulfoniumalkanesulfonates;

e. bis(alkarylalkyl)sulfoniumalkanesulfonates;

f. di(cycloalkyl)sulfoniumalkanesulfonates; and derivatives thereof, including nitrogen-containing derivatives.

Typical sulfoniumalkanesulfonates include for example:

N-cyclophenxyl-2-benzothiazol sulfonium-1-propanesulfonate;

Bis *benzothiazole-thio*-2-sulfonium-1-propanesulfonate;

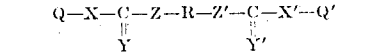
2-dimethylsulfonium-1-propanesulfonate;

Bis(dimethylthiocarbamyl)sulfonium-1-propanesulfonate;

2-(diphenyl)sulfonium-1-butanesulfonate;

Furfurylmethylsulfoniumpropanesulfonate; etc.

It should be understood that the use of other mono- and disulfonium sulfonates and carboxylates are also contemplated in the broad aspects of the present invention. For example, it would be possible to convert the sulfur-containing acyclic organic compounds disclosed in the Strauss et al. U.S. Pat. No. 2,910,413 to the corresponding sulfonates and carboxylates and to employ the resulting compounds as brighteners in the present invention. The general structural formula of the Strauss et al. acyclic organic compounds, which can be used as the raw material, is as follows:



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, at least one of them being sulfur; and X′, Y′, and Z′ are selected from the group consisting of oxygen, sulfur, nitrogen and the imino radical, at least one of them being sulfur. The conversion to the sulfonium derivative can be accomplished by use of the general procedures known to the art.

The sulfoniumalkanecarboxylates which can be effectively employed as brightening agents in the practice of the present invention are similar to the above described classes of sulfoniumalkanesulfonates except that a carboxyl radical is substituted for the sulfonate radical. Typical sulfoniumalkanecarboxylates include:

Bis(dimethylthiocarbamyl)sulfonium-1-propanecarboxylate;

Dibenzylsulfoniumpropanecarboxylate;

Methylbutylsulfoniumethanecarboxylate; etc.

Bis(dimethylthiocarbamyl)sulfonium-1-propanesulfonate can be prepared by the reaction of tetramethyl thiuram monosulfide and propane sultone in accordance with the procedure described by Gaertner in U.S. Pat. No. 2,813,898. Other sulfonium sulfonates can be prepared by the same general procedure utilizing the appropriate sulfides and sultones.

The corresponding bis(dimethylthiocarbamyl)sulfonium-1-propanecarboxylate can be prepared by the Gaertner procedure, except that propriolactone is substituted for the propane sultone.

Although the novel stable brightening agents of this invention may be employed by themselves to obtain very satisfactory brightening effects in the electroplating of copper, they may also be utilized in conjunction with known brightening agents or other additives to improve further the brightening and leveling. For example, the use of the brightening agents of this invention in conjunction with such prior art substances as the carbon-oxygen compounds disclosed in U.S. Pat. No. 3,288,690; polyethylene glycols and methoxy polyethyleneglycols, imparts excellent brightness and leveling qualities to the electroplated product. Furthermore, the qualities of the electroplated end product can be enhanced by the inclusion in the electroplating bath of such materials as amine dyes such as described in U.S. Pat. Nos. 2,707,166; and 2,882,209; or a triphenyl methane dye or such other leveling agents as disclosed in U.S. Pat. No. 2,733,198. Preferred other additives include polyethylene glycols and methoxy polyethylene glycols such as Carbowax 5000 having a molecular weight range of 2,000 to 6,000; aminothiazoles and aminothiazolines such as 2-thiazolidinethione; and dyes such as Methyl Violet, Crystal Violet, and Fuchsin. Mixtures of these other additives may also be employed. In general, these other additives are utilized in minor, conventional amounts.

To obtain the satisfactory results of this invention a minor but effective amount of the novel brightening agents of this invention are incorporated into the aqueous plating bath prior to the inception of the electrolytic plating operation. The amount of the novel brightening agent to be incorporated into the plating bath should be sufficient to obtain the brightening effect desired in each particular case as may be determined by the worker skilled in the art. It has been found in practice that satisfactory results are obtained when the novel brightening agents are present in the electrolyte plating bath in a concentration of from about 0.0001 to 1.5 grams per liter, and most preferably from 0.001 to 1.0 gram per liter.

Conventional acidic copper baths having the usual components and proportions can be employed in the practice of this invention.

The usual bath will have the following composition:

$CuSO_4(5H_2O)$ — 150–250 g./l.

Conc. sulfuric acid — 45–110 g./l.

The sulfuric acid may be substituted with sulfamic or fluoboric acids, while the copper may be salts of other acids such as sulfamic or fluoboric.

The invention will be further understood by reference to the following illustrative examples:

EXAMPLE 1

An aqueous acid copper plating bath was prepared having incorporated therein the following materials:

Material	Concentration
$CuSO_4(5H_2O)$	250 gm./liter
H_2SO_4	60 gm./liter
Cl^-	75 ppm
Bis(dimethylthiocarbamyl) sulfonium-1-propanesulfonate	0.01 gm./liter

The plating bath was operated at 70° F. in a Hull cell with vigorous air agitation at a current of 2.0 amps for 5 minutes. The copper deposit on the plated material was smooth and semi-lustrous over a current density range of from 2 to 75 amps/sq.ft. (ASF).

EXAMPLE 2

The procedure of Example 1 was followed except that the following material was also incorporated into the plating bath:

Material	Concentration
Carbowax 5000	0.4 gm./liter

The copper deposit on the plated material was bright and leveled over a current density range of from 1 to 100 ASF.

EXAMPLE 3

The procedure of Example 1 was followed except that the following materials were also incorporated into the plating bath:

Material	Concentration
Carbowax 5000	0.4 gm./liter
Methyl violet	0.015 gm./liter

The copper deposit on the plated material was very bright and leveled in the range of from 1 to 100 ASF, and showed increased brightness and leveling in the low current density range of from 1 to 10 ASF.

EXAMPLE 4

The procedure of Example 1 was followed except that the following materials were also incorporated into the plating bath:

Material	Concentration

Carbowax 5000	0.4 gm./liter
Methyl violet	0.015 gm./liter
2-Thiazolidienethione	0.001 gm./liter

A Hull cell panel which was preroughened with a 220 grit abrasive was electroplated in accordance with the procedure of Example 1 and provided a final plated product possessing optimum brightness and leveling properties.

EXAMPLE 5

The electroplating bath of Example 3 was set aside and allowed to remain standing for a period of 30 days. Thereafter, Hull cells were rerun in accordance with the procedure set forth in Example 1 yielding a plated final product which showed no substantial deterioration of the brightness or low current density dullness. In addition no brightener decomposition products formed in the plating tank.

EXAMPLE 6

An aqueous acid copper plating bath was prepared having incorporated therein the following materials:

Material	Concentration
$CuSO_4(5H_2O)$	250 gm./liter
H_2SO_4	60 gm./liter
Cl^-	35 ppm
Bis(dimethylthiocarbamyl) sulfonium-1-propanecarboxylate	3.2 gm./liter

The above bath was operated at room temperature in a Hull cell at 2.0 amperes for 5 minutes with mechanical agitation. The final plated product possessed a semi-bright to bright deposit over a current density range of from 20 to 100 ASF.

EXAMPLE 7

An aqueous copper plating bath was prepared having incorporated therein the following materials:

Material	Concentration
$CuCO_3$	105 gm./liter
HBF_4	sufficient to neutralize bath to pH 1.0
Cl^-	36 ppm
Bis(dimethylthiocarbamyl) sulfonium-1-propanesulfonate	0.60 gm./liter

A Hull cell panel was run at 2.0 amperes for 5 minutes with mechanical agitation at 70° F. yielding a bright lustrous deposit over a current density range of from 3 to 100 ASF.

It is well recognized that high acid-low copper plating bath formulations are particularly effective where better throwing power is required for proper copper plating. Heretofore, the high acid concentrations of the baths caused deterioration of the known organo-sulfur brightening agents which resulted in the baths being relatively short lived. This caused an increase in the stress of the copper deposit and led to dullness of the resultant copperplating, requiring frequent purification of the plating bath. By the practice of the instant invention, the prior art disadvantages experienced with these high acid-low copper plating baths have been obviated, in that these baths are stable over extended periods of time, breakdown of the brighteners into harmful by-products has been eliminated, and the copper deposits are bright with low stress properties. These advantages of the present invention are illustrated below:

EXAMPLE 8

A high acid-low copper aqueous electroplating bath was prepared having the following materials incorporated therein:

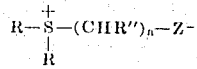
Materials	Concentration
$CuSO_4(5H_2O)$	75 gm./liter
H_2SO_4(1.84 sp. gr.)	184 gm./liter
Bis(dimethylthiocarbamyl) sulfonium-1-propanesulfonate	0.005 gm./liter
Carbowax 5000	0.16 gm./liter
Methyl Violet	0.006 gm./liter

A printed circuit board with hole dimensions of 0.06 inch in length and 0.06 inch in diameter was plated in the above bath at an average current density of 20 ASF, at 70° F., with 1 mil of copper which was very bright in appearance, and had a thickness ratio, surface to hole, of 1.1–1.0. The bath was then permitted to stand idle for a period of 30 days, whereupon the procedure set forth above was repeated. The same results were obtained without substantial loss of brightness, current density range or metal distribution ratio in the plated product.

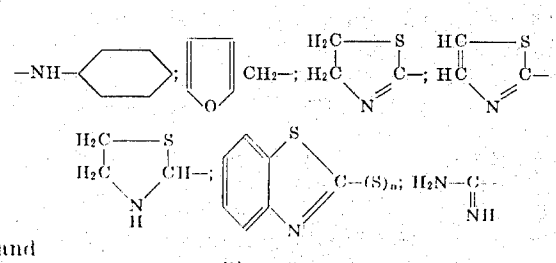
While particular embodiments of this invention are shown above, it will be understood that the invention is obviously subject to variations and modifications without departing from its broader aspects.

What is claimed is:

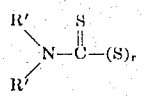
1. In an acid copper electroplating bath containing a salt of copper and a free acid as the essential constituents, the improvement which comprises the addition to said bath of an amount, sufficient to provide a bright electrodeposit, of a sulfonium compound having the structure



wherein R is a radical selected from the group consisting of hydrogen; alkyl having from one to eight carbon atoms; aryl having from six to 12 carbon atoms;



and



wherein R′ is a lower alkyl radical having from one to six carbon atoms, and *r* is 1 or zero; *n* is an integer from 1 to 6; R″ is selected from the group consisting of hydrogen and methyl; and Z is an anion selected from the group consisting of SO_3^- and COO^-.

2. In the acid copper plating bath of claim 1 wherein the sulfonium compound is added to said bath in an amount ranging from about 0.001 to 1.0 gram per liter.

3. In the acid copper plating bath of claim 1 wherein the sulfonium compound is N-cyclohexyl-2-benzothiazol sulfonium-1-propanesulfonate.

4. In the acid copper plating bath of claim 1 wherein the sulfonium compound is bis(dimethylthiocarbamyl) sulfonium-1-propanesulfonate.

5. In the acid copper plating bath of claim 1 wherein the sulfonium compound is bis(dimethylthiocarbamyl) sulfonium-1-propanecarboxylate.

6. In the acid copper plating bath of claim 1 wherein the sulfonium compound is bis(benzothiazole)sulfonium-1-propanesulfonate.

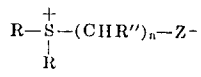
7. In the acid copper plating bath of claim 1 wherein the bath also contains a glycol selected from the group consisting of polyethylene glycol and methoxypolyethylene glycol in an amount sufficient to enhance the brightness of the electrodeposit.

8. In the acid copper plating bath of claim 7 wherein the bath also contains a triphenyl methane dye in an amount sufficient to enhance the brightness of the electrodeposit.

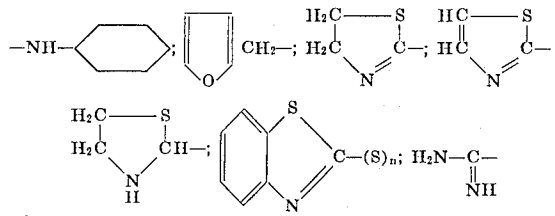
9. In the acid copper plating bath of claim 8 wherein the dye is Methyl Violet.

10. In the acid copper plating bath of claim 7 wherein the bath also contains 2-thiazolidienethione.

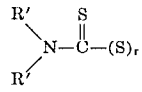
11. In a process of electrodepositing copper, the step which comprises electrolyzing an aqueous acid copper solution containing a copper metal salt and an amount, sufficient to provide a bright electrodeposit, of a sulfonium compound having the structure.



wherein R is a radical selected from the group consisting of hydrogen; alkyl having from one to eight carbon atoms; aryl having from six to 12 carbon atoms;



and



wherein R′ is a lower alkyl radical having from one to six carbon atoms, and *r* is 1 or zero; *n* is an integer from 1 to 6; R″ is selected from the group consisting of hydrogen and methyl; and Z is an anion selected from the group consisting of SO_3^- and COO^-.

12. In the process of claim 11 wherein the amount of the sulfonium compound ranges from about 0.001 to 1.0 gram per liter.

13. In the process of claim 11 wherein the sulfonium compound is bis(dimethylthiocarbamyl)sulfonium-1-propanesulfonate.

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