

1

3,798,138

ELECTRODEPOSITION OF COPPER

Barnet D. Ostrow and Fred I. Nobel, Roslyn, N.Y.
assignors to Lea-Ronal, Inc., Freeport, N.Y.

No Drawing. Continuation of application Ser. No. 790,854, Jan. 13, 1969, which is a continuation-in-part of application Ser. No. 469,323, July 2, 1965, both now abandoned. This application July 21, 1971, Ser. No. 164,893

Int. Cl. C23b 5/20, 5/46

U.S. Cl. 204—52 R

19 Claims

ABSTRACT OF THE DISCLOSURE

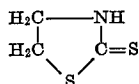
Copper is electrodeposited from an aqueous acid plating bath or solution containing at least one copper salt, a heterocyclic sulphur-nitrogen organic compound, such as water soluble derivatives of 2-thiazolidinethiones, 2-imidazolidinethiones or their reaction products with alkyl aldehydes or dialdehydes, and a water soluble brightener containing a carbon-sulphur group in which the carbon atom is attached to at least one other hetero-atom, such as sulphur or nitrogen.

This application is a continuation application of Ser. No. 790,854, filed Jan. 13, 1969, which in turn was a continuation-in-part of Ser. No. 469,323, filed July 2, 1965, and both now abandoned.

This invention relates to electroplating and more particularly to electrodepositing copper from an aqueous acidic copper plating bath. The invention is based on the discovery that heterocyclic sulfur-nitrogen organic compounds, 2-thiazolidinethiones, 2-imidazolidinethiones or their reaction products with alkyl aldehydes or dialdehydes, when incorporated in a copper electroplating bath particularly in conjunction with various other water soluble carbon-sulfur organic brighteners are remarkably effective for promoting the formation of bright electroplates which are much smoother than the basis metal plated in such a bath. This ability of an electroplating bath to improve on the smoothness of basis metal is known as "leveling ability" and can be used industrially to reduce or eliminate mechanical or electrochemical finishing of the basis metal.

Only a relatively small quantity of this heterocyclic sulfur-nitrogen organic compound is required for the plating bath for, in general, concentrations as low as 0.0001 grams per liter have been found to be effective. In many cases, however, about 0.0005 grams per liter should be employed to secure the full benefit of its presence in the bath. There appears to be no sharp upper limit on the concentration of these heterocyclic compounds, but there is generally no advantage in employing more than 1 gram per liter. In most plating baths, substantially the full benefit of the presence is achieved with an amount in the range from about 0.0005 to 0.05 gram per liter.

The heterocyclic sulfur-nitrogen compounds suitable for the present invention are (a) 2-thiazolidinethione and its lower alkyl derivatives, (b) 2-imidazolidinethione and its lower alkyl derivatives, and (c) the reaction products of (a) or (b) with an alkyl aldehyde or dialdehyde. 2-thiazolidinethione has the structural formula:

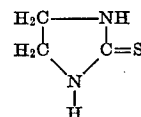


This compound has limited solubility in cold water, but it can be rendered more soluble preferably by dissolving it at first in concentrated sulfuric acid. An alcohol or a sodium hydroxide solution may also be used in a similar manner to make this compound more soluble. The hydro-

2

gen atoms in the heterocyclic ring of this compound can be substituted with lower alkyl radicals preferably alkyl groups containing less than 3 carbon atoms. The degree of substitution that can be made is limited by the solubility of the substituted product in the acid plating bath. Generally, increasing the number of alkyl groups or the carbon chain in the heterocyclic ring lowers the solubility of the substituted compound. The substituted compounds may also be made more soluble in the plating bath by first dissolving in a concentrated sulfuric acid, alcohol, or sodium hydroxide.

2-imidazolidinethione has the following structural formula:



This compound has higher solubility in water than 2-thiazolidinethione and, therefore, can be incorporated directly into the acidic plating bath. Advantageously, this compound may be first dissolved in water to form a standard solution and subsequently added to the plating bath. The hydrogen atoms in the heterocyclic ring of this compound also can be substituted by lower alkyl radicals. The number of alkyl radicals and the length of the carbon chain that can be introduced into the ring are governed by the solubility of the substituted product. The substituted compounds have lower solubility in the plating bath due to the presence of one or more alkyl radicals in their molecule. These compounds can be rendered more soluble in a similar manner as used for the 2-thiazolidinethiones. Preferably, concentrated sulfuric acid is used as a solvent in the solubilizing process. The resultant acidic solutions containing the dissolved heterocyclic sulfur-nitrogen compounds can be added to the plating bath directly.

The additives of type (c) are produced by reacting the heterocyclic sulfur-nitrogen compounds with an alkyl aldehyde or dialdehyde wherein the alkyl radical has 1 to 10 carbon atoms. Depending on the type and amount of the aldehyde used in the reaction, the products produced range from lightly colored liquid to a dark viscous resinous product. In general, the 2-imidazolidinethiones have a greater tendency to form a resinous product which is very soluble in concentrated sulfuric acid. The molar ratio of the two types of heterocyclic sulfur-nitrogen compounds to aldehyde used for the reaction may be varied from 1-1 to 1-10. Preferably, the molar ratio is maintained between about 1-1.5 and 1-2.0. Among the aldehydes that are suitable for the reaction, we find the dialdehydes, particularly glyoxal, to produce the more effective plating bath additives. Other aldehydes that are found to be eminently suitable include formaldehyde and adipaldehyde. The reactions between the aldehydes and the heterocyclic compounds of this invention are advantageously carried out in a temperature range preferably 150-210° F. At this temperature, the reactions proceed at a relatively rapid rate as indicated from the change of color of the reaction mixture.

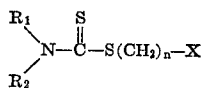
The preferred process of this invention for producing bright and smooth copper deposits comprises electrodepositing copper from an aqueous acidic solution of at least one copper salt in which there is dissolved (I) an organic compound selected from a group consisting of (a) water soluble derivatives of 2-thiazolidinethiones, (b) 2-imidazolidinethiones, and (c) water soluble reaction products of (a) or (b) with an alkyl aldehyde or dialdehyde, and (II) a water soluble brightener containing in

3

its molecule (a) a carbon-sulfur group in which the carbon atom is attached to at least one other hetero-atom selected from the group consisting of sulfur and nitrogen and (b) a water solubilizing group selected from carboxylic acid radical, sulfonic acid radical and their water soluble derivatives such as the alkali salts.

A number of Group II water soluble brighteners are available commercially and can be used satisfactorily when used conjointly with the Group I additives of this invention. Particularly satisfactory results have been obtained using the type of Group II compounds in which the carbon-sulfur group is bonded through its sulfur or nitrogen atoms to a RX radical in which R is a bivalent hydrocarbon radical having carbon atoms less than 11 and X is a carboxyl group, sulfonic acid group or its water soluble alkali salts. The type of a compound that is preferred from the present invention is characterized by which either the nitrogen or the sulfur can attach to the RX radical described above. The X group renders the compound hydrophilic.

Among these brighteners are the dithiocarbamic acid derivatives which have the general formula:



In the formula, R_1 and R_2 are hydrogen, aliphatic or aromatic groups, n is an integer from 1 to 10, and X has the same meaning as defined above. Also, included are the heterocyclic nitrogen compounds such as compounds of the pyridine, pyrimidine, triazine, tetrazine, pyrazole, imidazole, triazole, pyrrole, quinoline, and cinnoline series in which 1 or more hydrogen atoms linked to a carbon atom being adjacent to a nitrogen atom are substituted by the radical:



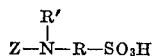
Suitable compounds under these two types of nitrogen-carbon-sulfur organic compounds are:

ethyl dithiocarbamoyl propionic acid
(N,N-diethyl dithiocarbamoyl) butyric acid pyrazine-3,6-dithioglycolic acid
3,6-dimercapto- β -hydroxy propyl pyrazine

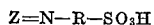
Other water soluble compounds that belong to this group which are suitable include propyl, butyl substituted dithiocarbamoyl propionic acid esters.

The amount of this type of brightener agent required is about 0.01 gram per liter or more and usually not more than 0.5 gram per liter is required to produce satisfactory bright deposits.

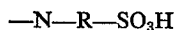
Another type of brightener that contains the carbon-sulfur group in its molecule suitable for the present invention is the organic sulfonic acids which have the general formula:



or



and their soluble salts. In the formula, Z is a radical comprising a carbon atom directly attached to a sulfur atom, to an atom selected from the group consisting of nitrogen, sulfur and oxygen atoms, and to the nitrogen atom of



group. In this group, R is a bivalent organic radical selected from the group consisting of aliphatic and aromatic radicals, and R' is selected from the group consisting of hydrogen and aliphatic radicals. Compounds of this type are:

dithiocarbamic acid - S - methylester - N - ethyl - N - butyl- ω -sodium sulfonate

4

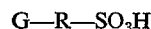
dithiocarbamic acid - S - methylester - N - butyl - N - propyl- ω -sodium sulfonate

dithiocarbamic acid-S-methylester - N - butyl - N - butyl- ω -sodium sulfonate

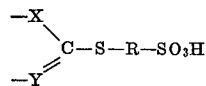
2-amino - 5 - methylthiazole - N - propane - ω - sodium sulfonate

N - butyl - dithiocarbamic acid - N - S - bispropane - ω -sodium sulfonate

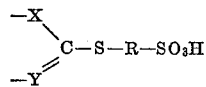
Still another type of brightener that contains the carbon-sulfur group in its molecule that are found suitable for the present invention is the organic sulfonic acids that have the general structural formula:



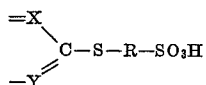
or its soluble alkali salts. In the formula, G is an organic radical which includes a carbon atom bonded exclusively with 3 hetero-atoms. One of the hetero-atoms is a sulfur atom. The R is a bivalent aliphatic radical such as ethyl- $R-SO_3H$. The other 2 hetero-atoms are selected from the group consisting of nitrogen, sulfur, and oxygen atoms. The R is a bivalent aliphatic radical such as ethylene, propylene, alkyl propylene, hydroxy propylene, pentylene radicals. The more detailed structure of this type of organic sulfonic acids can be represented by the following formulas:



or



or



and their salts, wherein X and Y are selected from the group consisting of nitrogen, sulfur and oxygen atoms.

Suitable compounds of this type are listed in Table 1:

TABLE 1

45	N,N-diethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
	N-ethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
	N-methyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
50	N,N-dimethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
	N-isopropyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
55	N,N-diisopropyl-dithiocarbamic acid-n-propylester- ω -potassium sulfonate
	N-butyl-dithiocarbamic acid-n-propylester- ω -potassium sulfonate
	N,N-dibutyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
60	N-octyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
	N,N-dihydroxyethyl-dithiocarbamic acid-n-propyl-ester- ω -sodium sulfonate
65	N-hydroxyethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
	N,N-pentamethylene-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
	N-piperazino-dithioformic acid-n-propylester- ω -sodium sulfonate
70	2-mercaptobenzothiazole-S-propane- ω -sodium sulfonate
	S-phenyl-trithiocarbamic acid-S-propane- ω -sodium sulfonate
	Isothiourea-S-butane- ω -sulfonic acid
75	5-phenyl-1,3,4-oxadiazolyl-2-mercapto-propane- ω -potassium sulfonate

5

Further examples of organic carbon-sulfur compounds that are suitable for the present invention are disclosed in the following U.S. Pats.: 2,830,014; 2,833,781; 2,837,472; 2,849,351; 2,849,352; 2,950,235; 3,000,800; 3,023,152; 3,030,283; 3,075,899; and 3,101,305.

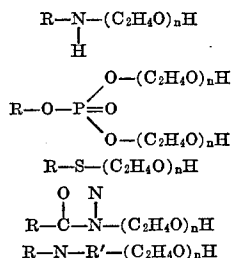
The amount of brightening agents which contain in their molecules the carbon-sulfur group is in the range between 0.01 to 20 grams per liter of electroplating bath when used conjointly with 2-thiazolidinethiones, 2-imidazolidinethiones or their reaction products with aldehyde.

In carrying out the process of this invention, preferably a small amount of surface active agent is added into the plating bath. The surface active agents that we find to be eminently suitable have the general formula:



in which R is an aryl or alkyl containing 6 to 20 carbon atoms and n can be an integer between 2 to 100. This type of compound is commonly used as a nonionic wetting agent. They are produced by treating fatty alcohol or alkyl substituted phenols with excess ethylene oxides. The alkyl carbon chain can range from 14 to 24 carbon atoms. The commercial available agents that we find suitable are the type produced by reacting oleyl alcohol or stearyl alcohol with 6 or more mols of ethylene oxide.

Amines, alkanol amines, amides, and carbowax types of surface active agents containing a hydrophilic group and a large number of ethylene oxide groups are also suitable. These agents have the following general formulas:



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

Further to illustrate the present invention, specific examples are described hereinbelow. The acid copper bath used in the examples has the following composition:

	G./l.
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	240
Conc. sulfuric acid	60

EXAMPLE 1

(a) A brass sheet is plated at 1–10 amp./dm² at 70° F. for 30 minutes in an acid copper bath containing 0.01 gram per liter of triethanolamine-ethylene oxide adduct having 30 mols of ethylene oxide radical and 0.05 gram per liter of N,N-dimethyl-dithiocarbamic acid- n propylester ω -sodium sulfonate. The resulting coating is bright but with only a slight degree of levelling.

(b) 0.0005 gram per liter of 2-thiazolidinethione is added to the bath described above. The resultant copper deposits are bright over the entire current density range and are appreciably smoother than the basis metal to which the particular deposit is plated. In comparison with Example 1(a), the levelling characteristic of the deposit is increased significantly.

EXAMPLE 2

0.005 gram per liter of 2-imidazolidinethione is added to the bath described in Example 1(a) similar levelling as shown in Example 1(b) is obtained and the deposits are bright over the entire current range.

EXAMPLE 3

0.12 mol of 2-thiazolidinethione is mixed with 0.18 mol of glyoxal and the mixture is heated to a temperature of

6

200° F. for about 2 hours. The color of the mixture darkens. The resultant product is dissolved in 50% sulfuric acid solution and is diluted with water for subsequent use. Sufficient amount of sulfuric acid solution to provide 0.0001 gram per liter of this reaction product is added in a bath described in Example 1(a). Similar levelling characteristic as shown in Examples 1(b) and 2 is observed.

EXAMPLE 4

0.1 mol of 2-imidazolidinethione is mixed with 0.25 mol of glyoxal and the mixture is heated to about 200° F. and allows the reaction product to form a resinous product. The resultant resin is dissolved in 50% sulfuric acid solution and is used subsequently in the plating bath described in Example 1(a). About 0.001 gram per liter of this reaction product is used. Same levelling characteristics as described in the previous examples is observed.

EXAMPLES 5–8

(a) A brass sheet is treated at 20° C. for 30 minutes in a bath similar to the one described in Example 1(a) with the exception that N,N-dimethyl-dithiocarbamic acid- n propylester ω -sodium sulfonate is replaced by pyrazine 3,6-dithioglycolic acid. The resulting coating is bright but little or no levelling or smoothing effect is observed.

(b) The electroplating is repeated under the same conditions with the addition to the bath (Example 5) of 0.0005 gram per liter of 2-thiazolidinethione, (Example 6) 0.0005 gram per liter of 2-imidazolidinethione, (Example 7) of 0.001 gram per liter of the reaction product described in Example 3, and (Example 8) of 0.001 gram per liter of the reaction product described in claim 4. The resulting electroplates from these examples are appreciably smoother than the basis metal to which the particular deposits were applied.

EXAMPLE 9

(a) 0.1 gram per liter of 2-amino-5-methylthiazole N-propane- ω -sodium sulfonate is added to the acid copper sulfate bath. A steel sheet provided with a preliminary copper coating in the presence of potassium cyanide is electroplated in the above bath in a current density of 6 amp./dm² at room temperature. The resultant coating is highly lustrous but shows little or no levelling effect.

(b) To the same bath 0.0005 gram per liter of 2-thiazolidinethione is added. The thiazolidinethione is dissolved in concentrated sulfuric acid before its addition to the bath. The electroplating is carried out in the same condition as (a) and the resultant electroplate shows significant levelling characteristics.

EXAMPLE 10

0.1 gram per liter of S-phenyl-trithiocarbamic acid- n propylester- ω -sodium sulfonate is placed in a bath similar to Example 9 replacing 2-amino-5-methylthiazole-N-propane- ω -sodium sulfonate. To this solution 0.0007 gram per liter of 2-imidazolidinethione is added. The resulting plates show substantial levelling and high luster.

EXAMPLE 11

Trithiocarbamic acid-bis-propylester- ω -sodium sulfonate is used in the bath as described in Example 9 replacing 2-amino-5-methylthiazole-N-propane- ω -sodium sulfonate in the bath. In addition 0.001 gram per liter of 2-imidazolidinethione is added therein. The resulting plate is appreciably smoother than the basis metal to which the electrodeposits are applied.

EXAMPLE 12

0.1 gram per liter of N,N-diethyl dithio-carbamoyl butyric acid is added to the copper plating bath containing 0.005 gram per liter of alkyl polyglycol wetting agent, 0.1 gram of hydrochloric acid and 0.0005 gram per liter of 2-thiazolidinethione. A brass sheet is electroplated with

a current density of 6 amp./dm.² at room temperature. Bright electrodeposit coatings with significant leveling are observed.

EXAMPLE 13

In a bath similar to Example 12 with the exception that 0.08 gram per liter of pyrazine-3, 6-dithioglycolic acid replaces the butyric acid of Example 12. The resulting coatings show similar levelling effect.

EXAMPLE 14

Instead of butyric acid of Example 12, the bath contains 0.1 gram per liter of dithiocarbamic acid-S-methylester-N-ethyl-N-butyl- ω -sodium sulfonate. The resulting plates show the same levelling effect as in the previous two examples.

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 (I) an effective amount of water soluble organic leveling compound selected from a group consisting of (a) water soluble 2-thiazolidinethione and its lower alkyl derivatives, (b) water soluble 2-imidazolidinethions and its lower alkyl derivatives, and (c) water soluble reaction products of (a) or (b) with from 1 to 10 moles of an alkyl aldehyde or dialdehyde per mole of (a) or (b), and (II) an effective amount of water soluble brightener containing in its molecule (a) an acrylic carbon-sulfur group in which the carbon atom is attached to at least one other hetero-atom selected from the group consisting of sulfur and nitrogen and (b) a water solubilizing group.

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 (I) more than about 0.0001 g./l. of a water soluble leveling compound selected from a group consisting of (a) water soluble 2-thiazolidinethione and its lower alkyl derivatives, (b) water soluble 2-imidazolidinethione and its lower alkyl derivatives, and (c) water soluble reaction products of (a) or (b) with from 1 to 10 moles of an alkyl aldehyde or dialdehyde per mole of (a) or (b), and (II) more than about 0.1 g./l. of a water soluble brightener containing in its molecule a water solubilizing group and an acyclic carbon-sulfur group in which the carbon atom is attached to at least one other hetero-atom selected from a group consisting of sulfur and nitrogen.

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 0.0001 g./l. of a water soluble organic leveling compound selected from a group consisting of (a) water soluble 2-thiazolidinethione and its lower alkyl derivatives, (b) water-soluble 2-imidazolidinethione and its lower alkyl derivatives, and (c) water soluble reaction products of (a) or (b) with from 1 to 10 moles of an alkyl aldehyde or dialdehyde per mole of (a) or (b), and (II) more than about 0.01 g./l. of a brightener containing in its molecule an acyclic carbon-sulfur group in which the carbon atom is attached to at least one other hetero-atom selected from the group consisting of sulfur and nitrogen, said carbon-sulfur group being bonded through its sulfur or nitrogen atom to a R—X radical in which R is a bivalent hydrocarbon radical having less than 11 carbon atoms and X is a sulfuric acid group, or a water soluble salt thereof.

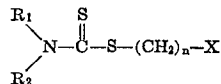
4. A process according to claim 3 wherein (c) is a water soluble reaction product of (a) or (b) with glyoxal.

5. 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 0.0001 g./l. of a water soluble organic leveling compound selected

from a group consisting of (a) water soluble 2-thiazolidinethione and its lower alkyl derivatives (b) water soluble 2-imidazolidinethione and its lower alkyl derivatives, and (c) water soluble reaction products of (a) or (b) with from 1 to 10 moles of an alkyl aldehyde or dialdehyde per mole of (a) or (b), and (II) more than about 0.01 g./l. of a brightener containing in its molecule an acyclic carbon-sulfur group in which the carbon atom is attached to at least one nitrogen atom, said carbon-sulfur group being bonded through its sulfur or nitrogen atom to a R—X radical in which R is a bivalent aliphatic radical having less than 11 carbon atoms and X is a sulfonic acid group, or a water soluble salt thereof.

6. A process according to claim 5 wherein (c) is a water soluble reaction product of (a) or (b) with glyoxal.

7. A process according to claim 5 wherein (II) is a dithiocarbamic acid derivative of the formula:



in which R₁ and R₂ are hydrogen, aliphatic or aromatic residues, n is an integer from 1 to 10 and X is a sulfonic group, or a water soluble salt thereof.

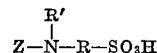
8. A process according to claim 5 wherein (II) is a heterocyclic nitrogen-containing compound with at least one carbon-linked hydrogen atom of said heterocyclic compound being substituted by the



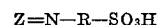
group, wherein X is a sulfonic acid group, or a water soluble salt thereof and n is an integer from 1 to 10.

9. A process according to claim 8 wherein (II) is pyrazine-3,6-dithioglycolic acid.

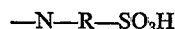
10. A process according to claim 5 wherein (II) is an organic sulfonic acid having the general structure formula



or



or its water soluble alkali salts, wherein Z is a radical comprising an acyclic carbon atom directly attached to a sulfur atom, to an atom selected from the group consisting of nitrogen, sulfur and oxygen atoms and to the nitrogen atom of the



group, R is a bivalent organic radical selected from the group consisting of aliphatic and aromatic radicals, and R' is selected from the group consisting of hydrogen and aliphatic radicals.

11. A process according to claim 5 wherein (II) is an organic sulfonic acid having the general structural formula



or its salt in which G is an organic radical which includes an acyclic carbon atom bonded exclusively with three heteroatoms, one of which is a sulfur atom through which said organic radical G is linked to the radical R—SO₃H, the other two heteroatoms being selected from the group consisting of nitrogen, sulfur and oxygen atoms, and R is a bivalent aliphatic radical.

12. A process according to claim 5 wherein the aqueous acidic solution contains a surface active agent.

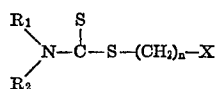
13. An electroplating bath for producing bright and smooth copper deposits which comprises an aqueous acidic solution of at least one copper salt in which there is dissolved (I) an effective amount of a water soluble organic leveling compound selected from a group consisting of (a) water soluble 2-thiazolidinethione and its lower alkyl derivatives, (b) water soluble 2-imidazolidinethione and its lower alkyl derivatives and, (c) water soluble reaction products of (a) or (b) with from 1 to 10 moles of an alkyl aldehyde or dialdehyde per mole of (a) or (b),

and (II) an effective amount of water soluble brightener containing in its molecule (a) an acyclic carbon-sulfur group in which the carbon atom is attached to at least one other hetero-atom selected from the group consisting of sulfur and nitrogen, and (b) a water solubilizing group.

14. An electroplating bath for producing bright and smooth copper deposits which comprises an aqueous acidic solution of at least one copper salt in which there is dissolved (I) more than about 0.0001 g./l. of a water soluble organic leveling 2-thiazolidinethione and its lower alkyl derivatives, (b) water soluble 2-imidazolidinethione and its lower alkyl derivatives, and (c) water soluble reaction products of (a) or (b) with from 1 to 10 moles of an alkyl aldehyde or dialdehyde per mole of (a) or (b), and (II) more than about 0.01 g./l. of a brightener containing in its molecule an acyclic carbon-sulfur group in which the carbon atom is attached to at least one nitrogen atom, said carbon-sulfur group being bonded through its sulfur or nitrogen atom to a R—X radical in which R is a bivalent aliphatic radical having less than 11 carbon atoms and X is a sulfonic acid group, or a water soluble salt thereof.

15. A bath according to claim 14 wherein (c) is a water soluble reaction product of (a) or (b) with glyoxal.

16. A bath according to claim 14 wherein (II) is a dithiocarbamic acid derivative of the formula



in which R₁ and R₂ are hydrogen, aliphatic or aromatic residues, n is an integer from 1 to 10 and X is a sulfonic acid group or a water soluble salt thereof.

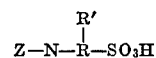
17. A bath according to claim 14 wherein (II) is a heterocyclic nitrogen-containing compound with at least one of its carbon-linked hydrogen atoms of said heterocyclic compound being substituted by the



group, X is a sulfonic acid group, or a water soluble salt thereof and n is an integer between 1 and 10.

18. A bath according to claim 14 wherein (II) is an

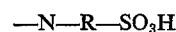
organic sulfonic acid or its water soluble alkali salt having the general structure formula



or

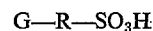


wherein Z is a radical comprising an acyclic carbon atom directly attached to a sulfur atom, to an atom selected from the group consisting of nitrogen, sulfur and oxygen atoms and to the nitrogen atom of the



group, R is a bivalent organic radical selected from the group consisting of aliphatic and aromatic radicals, and R' is selected from the group consisting of hydrogen and aliphatic radicals.

19. A bath according to claim 14 wherein (II) is an organic sulfonic acid having the general structural formula



or its salt in which G is an organic radical which includes an acyclic carbon atom bonded exclusively with three heteroatoms, one of which is a sulfur atom through which said organic radical G is linked to the radical R—SO₃H, the other two heteroatoms being selected from the group consisting of nitrogen, sulfur and oxygen atoms, and R is a bivalent aliphatic radical.

References Cited

UNITED STATES PATENTS

3,101,305	8/1963	Roth et al.	204—52 R
2,733,198	1/1956	Nobel et al.	204—52 R
2,830,014	4/1958	Gündel et al.	204—52 R X
2,837,472	6/1958	Gündel et al.	204—52 R X
2,849,351	8/1958	Gündel et al.	204—52 R X
2,853,443	9/1958	Harrover, Jr.	204—52 R
3,000,800	9/1961	Strauss et al.	204—52 R
3,023,152	2/1962	Strauss et al.	204—52 R
3,030,283	4/1962	Strauss et al.	204—52 R
3,075,899	1/1963	Strauss et al.	204—52 R
3,257,294	6/1966	Michael	204—52 R

GERALD L. KAPLAN, Primary Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,798,138

Dated March 19, 1974

Inventor(s) BARNET D. OSTROW, ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 69, "2-thiazolinethiones" should read
-- 2-thiazolidinethiones --

Column 3, lines 17-18, "characterized by which" should read
-- characterized by the nitrogen-carbon-sulfur group in the
molecule in which --

Column 4, line 18, "atoms. The R is a bivalent aliphatic radical
such as ethyl-" should read -- atom through which the organic
G is linked to the radical --

Column 5, line 68, "0.005" should read -- 0.0005 --.

Signed and sealed this 13th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents