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3,502,551

ACID ELECTROLYTE FOR THE DEPOSITION OF BRIGHT, LEVELLING COPPER COATINGS

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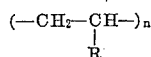
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6 Claims

ABSTRACT OF THE DISCLOSURE

Acid electrolyte copper baths have improved copper coatings by the inclusion in said baths of luster forming oxygen containing high molecular compounds, organic thio compounds and at least one compound having the generic formula:



wherein R is the amino group or its functional derivative, or a heterocyclic radical combined through a nitrogen atom, and possibly containing additional hetero atoms, and n is an integer ranging between about 5 and 1000.

This invention relates to an acid electrolyte for the deposition of bright leveling copper coatings. An object in particular is to improve electrolytic deposition from aqueous acid solutions of copper salts.

It has long been known that certain organic substances can be added in small quantities to acid, particularly the most widely used sulfuric acid—copper electrolytes, in order to obtain bright copper coatings instead of a crystalline-dull deposition. Thus, there has been proposed, for example, the use of organic thio compounds, such as thiourea, thiohydantoin, thiocarbamic acid esters, thiophosphoric acid esters and many derivatives of these compounds. However, these substances have many disadvantages, which have led to their being no longer used for modern bright copper baths. In addition, the ductility of the copper coating is greatly reduced and the uniformity of the film thickness distribution is reduced. Also in certain current density ranges, the deposit shows black streaks or is of the nature of a relief.

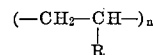
For the purpose named, there have further been proposed, in recent times, compounds which contain in the molecule not only one or more sulfur atoms of double negative charge but also one or more sulfonic acid groups or other water-solubilizing groups. These compounds are described in German Patents Nos. 1,037,801, 1,168,208, 1,196,464 and 1,201,152. If used alone, however, these compounds have no longer any luster effect in acid copper baths, or there is a limited duster effect only at high concentrations, at which the mechanical properties of the copper precipitates are so negatively influenced, however, that their practical use is no longer possible.

Only if these compounds, e.g. thioalkane sulfonic acids or thiophosphoric acid esters with water-solubilizing groups, are added to the copper electrolyte together with certain high-molecular substances does one obtain, as can be shown, bright copper precipitates. As high-molecular substances there enter into consideration for this, for example, fatty alcohol-ethylene oxide addition prod-

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ucts, nonyl-phenol-ethylene oxide addition products, polyethylene glycols and similar compounds. These combinations, too, however, do not meet the increased requirements of the practice, as their leveling effect is too small and polishing streaks or faults in the base material are still clearly visible after the copper-plating, so that additional mechanical treatment is necessary. But since, as is known, all additional polishing involves high costs, the practice increasingly demands leveling electrolytes with which the polishing costs can be reduced to a minimum.

It has now been found that the leveling effect of acid copper baths, containing as luster former oxygen-containing high-molecular compounds and organic thio compounds, can be substantially improved by adding to them one or more compounds of the general formula:



wherein R is the amino group or its functional derivatives or a heterocyclic radical combined through a nitrogen atom and possibly containing additional hetero atoms, and n is an integer between about 5 and 1000. More specifically, R is bound to said $(-CH_2-CH-)$ by a carbon-nitrogen bond and is the radical of a base selected from the group consisting of ammonia, dimethylamine, acetamide, thioethylurethane, carbamic acid, thiourea, succinimide, imidazole, N,N'-ethyleneurea, pyrrolidone-(2), morpholine, morpholinone-(3), benzimidazol, 5-alkyloxazolidone-(2), and caprolactam.

The additions to be used according to the invention are polyvinyl amine and its functional derivatives as well as N heterocyclic polyvinyl compounds. These are known per se and can be produced in a manner known in the art. Polyvinyl amine, for example, is formed by acid or alkaline saponification of cyclic N-vinyl imides, such as N-polyvinylphthalimide, as disclosed in U.S. Patent 2,484,423, or by saponification of poly-ethyl-N-vinyl carbamate, as disclosed in German Patent 865,901.

N-polyvinylacetamide is obtained, for example, by acylation of polyvinyl amine with acid chloride or acid anhydride by generally practiced methods disclosed in U.S. Patent 2,507,181.

N-polyvinyl carbamates (N-polyvinyl carbamide esters) are formed, for example, by polymerization of vinyl isocyanates with alcohols in the presence of azoisobutyric acid dinitrile, as disclosed in Belgian Patent 540,975.

N-polyvinyl pyrrolidone, as disclosed in German Patent 922,378; N-polyvinyl morpholinone-(3), as disclosed in British Patent 849,038; and N-polyvinyl-5-alkyl-oxazolidone-(2), as disclosed in U.S. Patent 2,946,773, can be prepared from the respective monomers, as by polymerization in solution in the presence of azoisobutyric acid dinitrile.

Naturally, these compounds are present in the copper bath as salts, for example as sulfates in the usual sulfuric acid electrolytes, but they may alternately be added in salt form, such as hydrochloride, methyl iodide, ethyl bromide, etc.

It is already known from German Patent 933,843 that polyvinyl amine or polyvinyl pyrrolidone are added to galvanic baths, namely in quantities between 0.02 and 1.0 g./liter. If used alone, however, as has been found, they do not achieve any luster effect or leveling in acid copper baths. The precipitate is merely fine-grained,

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smooth, and free from streaks. However, it thereby does not in the least fulfill the requirements that bright copper-plating must meet today. There is in this patent no reference to the surprising fact that these substances can drastically improve the leveling effect if they are added to copper electrolytes which contain oxygen-containing high-molecular compounds and organic thio compounds.

The quantities needed for a marked improvement of the copper deposition, in particular of the leveling effect are extremely small, ranging from between 0.0005 and 0.1 g./liter, generally 0.0005 to 0.03 g./liter, depending on which basic luster former the copper bath contains.

Generally, there is used as the electrolyte a sulfuric acid copper sulfate solution of the following composition

Copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	g./liter	15
Sulfuric acid H_2SO_4	125-260	
	20-85	

Instead of copper sulfates, other copper salts may be used at least in part. The sulfuric acid may be replaced in part or wholly by fluoroboric acid, phosphoric acid, or other acids. The electrolyte may be chloride free or, and this is advantageous for improvement of the luster, contain chlorides, e.g. alkali chlorides in quantities of 0.001 to 0.2 g./liter. As additional additives, other common lusters formers and/or wetting agents may be used.

Below are listed in Table 1, by way of example, substances which, according to the invention, are added to acid copper baths with oxygen-containing high-molecular compounds and organic thio compounds to obtain high-gloss copper precipitates with increased leveling effect.

TABLE 1

Substance:	Preferred concentration, g./liter	
(1) Polyvinyl amine	0.005-0.02	35
(2) N,N-dimethyl-polyvinyl amine --	0.005-0.03	
(3) N-polyvinyl acetamide	0.005-0.03	
(4) N-polyvinylthioethyl urethane --	0.0005-0.005	
(5) N-polyvinyl carbamate	0.001-0.02	40
(6) N-polyvinyl thiourea	0.0005-0.005	
(7) N-polyvinyl succinimide	0.005-0.02	
(8) N-polyvinylimidazole	0.01-0.03	
(9) N-polyvinyl-N,N'-ethylene urea -	0.02-0.07	
(10) N-polyvinyl pyrrolidone-(2) --	0.001-0.01	45
(11) N-polyvinyl morpholine	0.005-0.05	
(12) N-polyvinyl morpholinone-(3) -	0.001-0.02	
(13) N-polyvinyl benzimidazol	0.001-0.005	
(14) N-polyvinyl - 5 - alkyl - oxazol- idone-(2)	0.001-0.01	50
(15) N-polyvinyl caprolactam	0.0005-0.002	

Known copper electrolyte additions on the basis of oxygen-containing high-molecular compounds and organic thio compounds which contain preferably one or more water-solubilizing groups are listed in Tables 2 and 3 which, when used alone, do not develop a luster effect and when used jointly show an unsatisfactory leveling. The quantities which are added to the copper electrolyte are approximately within the following limits:

Oxygen-containing high-molecular compounds	0.01-10 g./liter, preferably 0.02-5 g./liter	60
Organic thio compounds with water-solubilizing groups	0.002-0.2 g./liter, preferably 0.005-0.1 g./liter	

TABLE 2

Substance:	Preferred concentration, g./liter	
(1) Polyvinyl alcohol	0.05-0.4	
(2) Carboxymethyl cellulose	0.05-0.1	
(3) Polyethylene glycol	0.05-0.5	70
(4) Polypropylene glycol	0.01-0.2	
(5) Stearic acid polyglycol ester	0.5-5.0	
(6) Oleic acid polyglycol ester	0.5-5.0	
(7) Steryl alcohol polyglycol ether	0.5-5.0	
(8) Nonylphenol polyglycol ether	0.5-2.0	75

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TABLE 3

Substance:	Preferred concentration, g./liter	
(1) Dithiophosphoric acid 0,0-diethyl-S (omega-sulfopropyl)-ester, sodium salt	0.005-0.1	
(2) Thiophosphoric acid 0-ethyl-bis-(omega-sulfopropyl)-ester, disodium salt	0.01-0.15	
(3) Thiophosphoric acid - tri - (omega-sulfopropyl) ester, trisodium salt ---	0.02-0.15	
(4) Sodium 3 - mercaptopropane - 1-sulfonate	0.005-0.08	
(5) N,N - diethyl - dithiocarbamic acid (omega - sulfopropyl) ester, sodium salt	0.01-0.1	
(6) Sodium 2-mercaptobenzothiazol-S-propane-sulfonate	0.02-0.1	
(7) Thioglycolic acid	0.001-0.003	

If the compounds of Tables 2 and 3 are used together with one or more substances of Table 1 in acid copper electrolytes, there is obtained a distinct and drastic improvement of the leveling effect. The mixture ratios of the individual components may vary within wide limits. It has proved to be favorable, if there is a ratio by weight of the substances listed by way of example in Tables 1, 2 and 3 of approximately 1:102 to approximately 1:200:20. As further additions, the electrolyte may contain other known luster formers, such as thiourea or its derivatives, dithiocarbamic acid esters, thiosemicarbazones, phenazine dyes, or alkaloids.

The following examples are illustrative of the invention, although not limited thereto.

EXAMPLE 1

To a copper bath of the composition:

	g./liter	
Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	200	
Concentrated sulfuric acid	55	
Sodium chloride	0.05	

there are added as luster formers

	g./liter	
Stearyl alcohol-polyglycol ether	2.0	
Sodium salt of dithiophosphoric acid, O,O-diethyl-S-(omega-sulfopropyl) ester	0.08	

At a temperature of 20-25° C., the electrolyte with a current density of an average of 4.0 a./sq. dm. and with cathode movement, bright copper precipitates are indeed obtained, but the leveling of the wrinkles of the base material is only 46% at a film thickness of 24 millimicrons. If additionally, 0.005 g./liter of N-polyvinyl pyrrolidone-(2) is charged in the bath, the leveling increases to 75% under the same operating conditions, an apparent increase of 63%.

EXAMPLE 2

To the electrolyte according to Example 1, there are added

	g./liter	
Polyethylene glycol	0.1	
Sodium 3-mercaptopropane-1-sulfonate	0.03	

Under the same operating conditions as in Example 1, the leveling effect at a film thickness of 24 millimicrons copper is about 50%. By an addition of 0.01 g./liter N-polyvinylamine, the leveling increases to 83%, so that the increment is 66%. An equally great improvement of the deposition is obtained if one adds to the copper bath, instead of the polyvinyl amine, 0.02 g./liter N-polyvinyl imidazole or 0.004 g./liter of an N-polyvinyl-5-alkyl-oxazolidone-(2).

Similarly, excellent effects can be attained with the

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joint use of the other substances listed in Table 1 with the compounds of Tables 2 and 3.

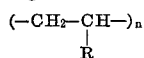
From the foregoing description and the illustrative examples of the invention, it will be noted that there is provided a novel combination of ingredients which substantially improve the leveling effects of acid copper baths.

Furthermore, while illustrative examples are given, it is to be noted that changes as to components and ingredients in the acid baths may be made without departing from the spirit and scope of the invention as claimed.

What is claimed is:

1. In an acid electrolyte for the deposition of bright copper containing as brighteners a member of a first group consisting of polyvinyl alcohol, carboxymethyl cellulose, polyethylene glycol, polypropylene glycol, stearic acid polyglycol ester, oleic acid polyglycol ester, stearyl alcohol polyglycol ether, and nonylphenol polyglycol ether, and a member of a second group consisting of the sodium salt of dithiophosphoric acid O,O-diethyl-S-(omega-sulfo-propyl)-ester, the disodium salt of thiophosphoric acid O-ethyl-bis-(omega-sulfo-propyl)-ester, the trisodium salt of thiophosphoric acid tri-(omega-sulfo-propyl)-ester, sodium 3-mercaptopropane-1-sulfonate, the sodium salt of N,N-diethyl-dithiocarbamic acid (omega-sulfo-propyl)-ester, sodium 2-mercaptobenzothiazol-5-propanesulfonate, and thioglycolic acid, the improvement which comprises:

(a) an additional brightener of the formula:



wherein n is an integer between 5 and 1000, and R is the radical of a base bound to said $(-\text{CH}_2-\text{CH}-)$ by a carbon-nitrogen bond, said base being selected from the group consisting of ammonia, dimethylamine, acetamide, thioethylurethane, carbamic acid, thiourea, succinimide, imidazole, N,N'-ethyleneurea, pyrrolidone-(2), morpho-

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line, morpholinone-(3), Benzimidazol, 5-alkyloxazolidone-(2), and caprolactam;

(b) said additional brightener being present in said electrolyte in an amount sufficient to produce a leveling effect on the deposited copper.

2. In an electrolyte as set forth in claim 1, the amount of said additional brightener being between 0.0005 and 0.1 gram per liter of said electrolyte.

3. In an electrolyte as set forth in claim 2, the amount of said additional brightener being not greater than 0.03 gram per liter.

4. in an electrolyte as set forth in claim 3, said member of said first group being present in said electrolyte in an amount of 0.02 to 5 grams per liter, and said member of said second group being present in said electrolyte in an amount of 0.005 to 0.1 gram per liter.

5. In an electrolyte as set forth in claim 2, said member of said first group being present in said electrolyte in an amount of 0.1 to 10 grams per liter, and said member of said second group being present in said electrolyte in an amount of 0.002 to 0.2 gram per liter.

6. A process for depositing bright copper coatings on an object wherein an object is made the cathode in the electrolyte set forth in claim 1.

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