United States Patent Office

3,101,305

Patented Aug. 20, 1963

3,101,305

ACID COPPER PLATING BATH

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No Drawing. Filed Mar. 12, 1958, Ser. No. 720,824
Claims priority, application Germany Mar. 16, 1957
6 Claims. (Cl. 204—52)

This invention relates to acid baths for producing brilliant copper levelling coatings.

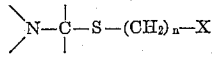
The state of the art of acid-bath copper plating is characterized by the use of two different forms of electrolyte:

(1) An electrolyte giving a high and uniform polish but without appreciable levelling or smoothing effect.
(2) An electrolyte with good levelling or smoothing properties, but not giving a brilliant or mirror finish or lacking a uniform brilliant effect over a wide range of current densities.

Neither of these types of bath, however, satisfies the technical requirements with regard to economizing in grinding and polishing costs.

The present invention relates to a class of substances which produce in acid copper-plating baths capable of imparting to articles treated therein a brilliant finish but no levelling or smoothing effect, a surprising smoothing or levelling action without affecting the originally obtained, uniform brilliant finish and without unfavorably influencing penetration in depth of the bath. The smoothing effect is so pronounced that grinding marks completely disappear after deposition of a copper coating of a thicknses of 26μ only. Such an effect is not attained in any of the known sulfuric acid bright copper-plating baths. They require a thickness of the copper coating of at least 42μ in order to completely cover and eliminate, i.e. to level the microscopic cracks obtained on grinding the surface to be copper plated.

According to the present invention an acid bath for the preparation of highly brilliant, smoothing or levelling copper coatings is provided which bath is characterized by the feature that it combines the use of basic brightening agents having in their molecule at least one group of the formula



wherein

X represents a member selected from the group consisting of the hydroxyl group, the carboxyl group, the sulfonic acid group, and a carboxylic acid ester group, while

n is an integer between 1 and 10,

and wherein such groups predominate, with the addition of specific thiourea derivatives as smoothing or levelling agents.

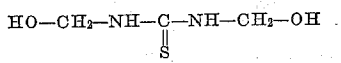
It has been observed that thiourea and certain derivatives of thiourea in acid, bright copper-plating baths, produce a moderate, levelling or smoothing effect.

The present invention consists in using primary condensation products of thiourea with aliphatic aldehydes, for instance, with formaldehyde. Such derivatives of thiourea have a considerably greater smoothing or levelling effect than the known thiourea compounds heretofore used for this purpose.

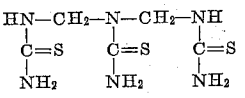
In the preparation of such primary thiourea condensation products, the temperature at which they are prepared, should not be too high since there is otherwise the danger that insoluble resins will be produced. The optimum temperature conditions for the preparation of the

thiourea condensation products are between about 110° C. and about 130° C. Depending on the exact temperature, reaction time, and catalysts employed, the following addition products can be obtained:

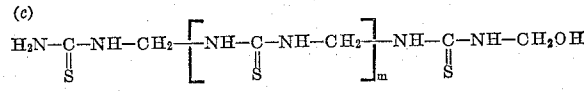
(a)



(b)



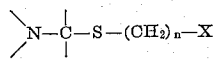
(c)



wherein m indicates an integral number.

However, the excellent levelling or smoothing properties of these thiourea derivatives are utilized only when employing said compounds in combination with particular, primary brightening agents which alone, i.e. by themselves, produce no levelling or smoothing effect.

Such primary brighteners may be any of the above mentioned compounds containing one or more groups of the formula

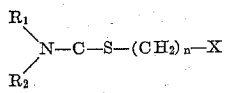


wherein

X indicates a member selected from the group consisting of the hydroxyl group, the carboxyl group, the sulfonic acid group, and a carboxylic acid ester group, while

n is an integer from 1 to 10.

Preferred brightening agents of this type are dithiocarbamic acid derivatives of the formula



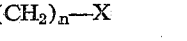
wherein

R_1 and R_2 indicate hydrogen, aliphatic, or aromatic residues,

n indicates an integer from 1 to 10, and

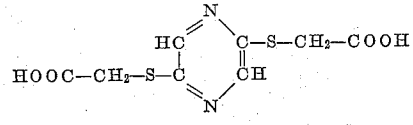
X indicates a member selected from the group consisting of the hydroxyl group, the carboxyl group, the sulfonic acid group, and a carboxylic acid ester group.

Especially suitable brighteners of this type are, furthermore, heterocyclic nitrogen compounds such as compounds of the pyridine, pyrimidine, triazine, tetrazine, pyrazole, imidazole, triazole, pyrrole, quinoline, cinnoline (5,6-benzopyridazine) series and the like in which one or more hydrogen atoms linked to carbon atoms are substituted by the radical



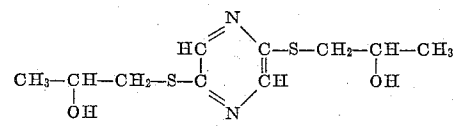
wherein X represents the hydroxyl group, the carboxyl group, or another water soluble group of a different anionic character. Such a group —S—$(CH_2)_n$—X need not necessarily occupy an end position in an aliphatic side chain. Compounds of the following formulas are especially suitable examples of this group of primary brighteners:

(a)



Pyrazine-3,6-dithioglycolic acid

(b)



3,6-dimercapto-β-hydroxy propyl pyrazine

The following comparative examples serve to illustrate the present invention and the effects achieved thereby without, however, being limited thereto.

Example 1

(*a*) A sheet of iron or steel is ground to a zero polish and is then copper plated in a bath of the following composition (in g. per liter):

210 g. of copper sulfate $CuSO_4.5H_2O$,
60 g. of concentrated sulfuric acid,
5 g. of an alkyl polyglycol known to the art as wetting agent,
0.3 g. of ethyl dithiocarbamoyl propionic acid ester, and
0.15 g. of hydrochloric acid,

at 4 amp./sq. dm. and 20° C. for 30 minutes. The resulting copper plated surface of the sheet is bright. The grinding marks, however, have not been eliminated.

(*b*) The plating is repeated under the same conditions with the above mentioned bath solution to which, however, 0.02 g. of the acid-soluble thiourea-formaldehyde condensation product are added. A copper deposit of about 26μ thickness and a high brilliancy is obtained. The grinding marks are almost completely levelled.

Example 2

(*a*) A brass sheet previously polished on a zero number grinding wheel is treated at 4 amp./sq. dm. and at 20° C. for 30 minutes in a bath containing per liter:

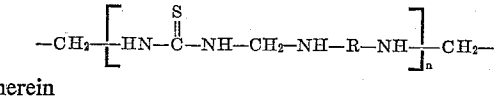
210 g. of copper sulfate $CuSO_4.5H_2O$,
60 g. of concentrated sulfuric acid,
5 g. of an alkyl polyglycol known to the art as wetting agent, and
0.4 g. of pyrazine-3,6-dithioglycolic acid.

The resulting coating is bright, but no levelling or smoothing effect is observed.

(*b*) Addition of 0.02 g. of the acid-soluble thiourea-formaldehyde condensation product to the above mentioned copper plating solution and exposing the polished brass sheet to said solution under the same reaction conditions produces a copper coating not only of the same brilliancy as produced with the bath given under (*a*) but also a perfectly smooth and levelled coating so that the grinding marks from a zero number wheel are no longer visible although the thickness of the deposited copper coating is only 26μ.

The smoothing and levelling effects achieved by such thiourea-formaldehyde condensation products are considerably improved by replacing said condensation products by products obtained by simultaneous condensation of thiourea, formaldehyde, and polyamino compounds containing at least two amino groups.

Such condensation products are characterized by containing not only thiourea moieties bridged by methylene moieties but also diamine moieties bridged by methylene moieties. Thereby, chain structures or two to three dimensionally cross-linked structures are obtained. The simplest condensation products of this type correspond approximately to the following formula



wherein

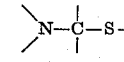
R represents a benzene, naphthalene, diphenyl, anthracene, phenanthrene, pyrene, triazine, or other heterocyclic, aliphatic, or cycloaliphatic residue and
n indicates an integral number.

To prepare these condensation products, the required amounts of thiourea, polyamine, and formaldehyde are condensed at a temperature of about 110–130° C. The molar ratio between the thiourea and the compound containing at least two amino groups, for instance, melamine, has an optimum value of 1:1, but other ratios may be employed, for instance, a ratio of 1:2. The aggressive action of the thiourea by such a cocondensation with a polyamine is considerably mitigated and its inhibitory effect is favorably adjusted for the purpose in view.

Instead of melamine, other substances containing at least two amino groups can be used as reaction component in such co-condensation reaction, such as diamino azobenzene, diamino diphenylamine, diamino diphenylurea, diamino stilbene, urea, o-dianisidine, o-toluidine, phenylene diamines, 2,4'-diamino diphenyl, parafuchsin, congo red, benzidine, guanidine, benzidine-2,2'-disulfonic acid, diamino stilbene disulfonic acid, 1,5-diamino naphthalene-3,7-disulfonic acid, naphthalene diamines, homologues and derivatives thereof, and the like polyamino compounds.

In co-condensation products, for instance, in the thiourea - formaldehyde - naphthalene diamine condensation products, the "activity" of the thiourea component is considerably reduced by the presence of less active groups. In addition, partial substitution of thiourea moieties by naphthalene diamine moieties produces condensation products of larger molecular size, which are particularly suitable for producing a uniform smoothing and/or levelling effect even at elevated temperatures.

The known fact that copper is inhibited with difficulty, especially at elevated temperature, can readily be compensated for by adding to the copper plating bath larger inhibitor molecules of a specific degree of condensation, while preserving its "active" characteritsics due to the presence of



groups. Copper baths composed in this manner furnish, even at 35–40° C., brilliant, excellently levelling copper coatings, while identical baths on a basis of thiourea-formaldehyde condensation products alone operate only at temperatures of 25° C. and lower.

The following examples serve to illustrate the use of thiourea-formaldehyde-polyamine condensation products as smoothing and levelling agents according to the present invention without, however, limiting the same thereto.

Example 3

A bath of the following composition in g. per liter is used for copper plating:

210 g. of copper sulfate $CuSO_4.4H_2O$,
60 g. of concentrated sulfuric acid,
5 g. of an alkyl polyglycol known to the art as wetting agent,
0.1 g. of γ-(N,N-diethyl dithio-carbamoyl) butyric acid,
0.1 g. of hydrochloric acid,
0.3 g. of an acid-soluble thiourea-formaldehyde-diamino diphenyl urea condensation product.

Copper plating is effected with a current density of 1–6 amp./sq. dm. at 15–35° C. Bright copper coatings of a thickness of 26μ of sufficient brilliancy and good levelling properties are obtained wherein the marks of a No. 0 grinding wheel are completely eliminated.

Example 4

A copper plating bath of the following composition in g. per liter is used:

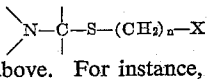
200 g. of copper sulfate $CuSO_4.5H_2O$,
90 g. of concentrated sulfuric acid,
8 g. of an alkyl polyglycol known to the art as wetting agent,
0.4 g. of pyrazine-3,6-dithioglycolic acid, and

0.04 g. of an acid-soluble thiourea-formaldehyde-diamino diphenylamine condensation product.

Copper plating is effected at current densities between 1–6 amp./sq. dm. and at a temperature range between 15° C. and 40° C. Brilliant, effectively levelling copper coatings are obtained thereby.

When replacing in the above mentioned bath the thiourea-formaldehyde-diamino diphenylamine condensation product by 0.02–0.04 g. of an acid-soluble thiourea-formaldehyde condensation product, the same brilliancy and leveling effect are obtained. However, the temperature must be kept at 25° C. or, preferably, lower when operating at a current density range between 2.5 amp./sq. dm. and 6.0 amp./sq. dm. At higher temperatures, such as between 25° C. and 40° C. the copper coatings are dull and no smoothing effect is observed.

It is understood that other brightening agents than those used in the preceding examples may be employed provided they contain the group



mentioned hereinabove. For instance, other esters of dithiocarbamoyl alkyl carboxylic acids than the ethyl dithiocarbamoyl propionic acid, such as propyl, butyl, and other alkyl, aryl, or aralkyl dithiocarbamoyl propionic acid esters, or ethyl dithiocarbamoyl acetic, butyric, valeric, capric and the like acids and their esters provided these compounds are soluble in the copper plating bath.

Other heterocyclic compounds with nitrogen as hetero atom in their nucleus than pyrazine-3,6-dithioglycolic acid, 3,6-dimercapto-β-hydroxy propyl pyrazine may also be used as brightening agents.

Such brightening agents are known to the art and their use in copper plating processes are known to the art.

The thiourea-formaldehyde condensation products used in Examples 1 and 2 as well as the thiourea-formaldehyde-polyamine condensation products used in examples 3 and 4 may be replaced by other condensation products wherein other aldehydes are employed than formaldehyde. The conditions of preparation of such condensation products must be such that the products are sufficiently soluble in the copper plating bath.

As stated hereinabove, addition of thiourea-aldehyde condensation products or thiourea-aldehyde-polyamine condensation products to copper plating baths has a number of advantages and more particularly permits to produce perfectly smooth and levelled copper surfaces in a thickness of about 26μ only. In addition thereto it was found that polishing of the precipitated thin copper coating is not required. As a result thereof it is possible to continuously subject suitable sheet material and the like articles to copper plating according to the present invention and immediately thereafter to nickel plate such copper plated sheets and the like articles without any intermediate treatment.

Furthermore, the copper plating baths according to the present invention permit operation with a current density of 6 amp./sq. dm. or even more while heretofore current densities of 4 amp./sq. dm. usually could not be exceeded.

The amounts of the thiourea-aldehyde condensation products or of thiourea-aldehyde-polyamine condensation products to be added to the copper plating bath may, of course, vary depending upon the composition of the bath and the composition of the smoothing and leveling agent. Amounts between about 0.001 g./l. and about 0.5 g./l. have proved satisfactory. The preferred amounts are between about 0.01 g./l. and about 0.04 g./l.

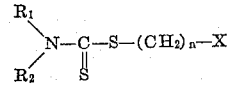
The brightening agents, i.e. the dithiocarbamic acid compounds and similar heterocyclic compounds are added as is known, in amounts between about 0.01 g./l. and about 0.5 g./l. although they are not limited to such amounts.

Of course, in place of alkyl polyglycols used as wetting agents, there may be employed other wetting agents compatible with the copper plating bath. Especially suitable are wetting agents based on ethylene oxide, i.e. polyglycol compounds and the like. Sulfonated wetting agents have proved of advantage due to their increased solubility in water. In general, non-ionogenic wetting agents, such as wetting agents with ether bridge bonds have proved to be useful additives.

Of course, many other changes and variations in the composition of the copper plating bath, in the brightening agents employed, in the thiourea-aldehyde condensation products and the thiourea-aldehyde-polyamine condensation products used as smoothing and levelling agents according to the present invention, the electro-precipitation conditions, such as current density, temperature, and duration, and the like may be made by those skilled in the art in accordance with the principles set forth herein and in the claims annexed hereto.

We claim:

1. An acid copper plating bath for producing smooth and levelled copper coatings of high brilliancy, said bath containing, as brightening agent, a basic brightening agent selected from the group consisting of dithiocarbamic acid compounds of the formula



wherein

R_1 and R_2 are members selected from the group consisting of hydrogen, aliphatic, and aromatic residues,

X is a member selected from the group consisting of the hydroxyl group, the carboxyl group, the sulfonic acid group, and the carboxylic acid ester group, and

n is an integer between 1 and 10,

and heterocyclic nitrogen-containing compounds, at least one of the carbon-linked hydrogen atoms of said heterocyclic compounds being substituted by the

$$—S—(CH_2)_n—X$$

group, X and n in said group representing the same members and numbers as indicated above, and between about 0.001 g./l. and about 0.5 g./l. of a levelling agent consisting of an acid-soluble condensation product of thiourea, an aliphatic aldehyde component consisting of formaldehyde, and a compound having at least two amino groups in its molecule.

2. An acid copper plating bath for producing smooth and levelled copper coatings of high brilliancy, said bath containing per liter

about 210 g. of copper sulfate $CuSO_4.5H_2O$,
about 60 g. of concentrated sulfuric acid,
about 5 g. of an alkyl polyglycol as wetting agent,
about 0.4 g. of pyrazine-3,6-dithioglycolic acid as brightening agent, and
about 0.02 g. of an acid-soluble thiourea-formaldehyde condensation product as smoothing and levelling agent.

3. An acid copper plating bath for producing smooth and levelled copper coatings of high brilliancy, said bath containing per liter

about 210 g. of copper sulfate $CuSO_4.5H_2O$,
about 60 g. of concentrated sulfuric acid,
about 5 g. of an alkyl polyglycol as wetting agent,
about 0.3 g. of ethyl dithiocarbamoyl propionic acid as brightening agent,
about 0.15 g. of hydrochloric acid, and
about 0.02 g. of an acid-soluble thiourea-formaldehyde condensation product as smoothing and levelling agent.

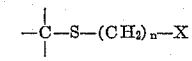
4. An acid copper plating bath for producing smooth and levelled copper coatings of high brilliancy, said bath containing per liter

about 210 g. of copper sulfate $CuSO_4.5H_2O$,
about 60 g. of concentrated sulfuric acid,
about 5 g. of an alkyl polyglycol as wetting agent,
about 0.1 g. of γ-(N,N-diethyl dithiocarbamoyl) butyric acid as brightening agent,
about 0.1 g. of hydrochloric acid, and
about 0.03 g. of an acid-soluble thiourea-formaldehyde-diamino diphenyl urea condensation product as smoothing and levelling agent.

5. An acid copper plating bath for producing smooth and levelled copper coatings of high brilliancy, said bath containing per liter

about 200 g. pf copper sulfate $CuSO_4.5H_2O$,
about 90 g. of concentrated sulfuric acid,
about 8 g. of an alkyl polyglycol as wetting agent,
about 0.4 g. of pyrazine-3,6-dithioglycolic acid as brightening agent, and
about 0.04 g. of an acid-soluble thiourea-formaldehyde-diamino diphenylamine condensation product as smoothing and levelling agent.

6. An acid copper plating bath for producing smooth and levelled copper coatings of high brilliancy, said bath containing, as brightening agent, a basic brightening agent having at least one group of the formula



in its molecule, X in said group indicating a member selected from the group consisting of the hydroxyl group, the carboxyl group, and a water soluble group of different anionic character, and *n* indicating a whole number between 1 and 10, and between about 0.001 g./l. and about 0.5 g./l. of a levelling agent consisting of an acid-soluble condensation product of thiourea and an aliphatic aldehyde component consisting of formaldehyde.

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