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3,778,357

ELECTROLYTE AND METHOD FOR ELECTRODEPOSITING COPPER

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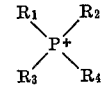
U.S. Cl. 204—52 R 5 Claims

ABSTRACT OF THE DISCLOSURE

The throwing and covering power of acid copper plating electrolytes at high average current densities, particularly in the presence of brighteners and levelling agents, is improved by small amounts of ions of the formula



wherein R_1 to R_4 may be lower alkyl, halo-, amino- or hydroxy derivatives thereof, benzyl, cyanobenzyl, carb-lower-alkoxy, carb-lower-alkoxy-lower-alkyl, naphthyl-lower - alkyl, trialkyl - phosphonium-alkyl-diphenylalkyl, phenyl, cycloalkyl having 5 to 8 carbon atoms, or lower alkenyl. Additionally, R_1 and R_2 jointly with the P may constitute phosphindolinium, and R_4 may also be

$$—(CH_2)_n—Y^-$$

wherein n is an integer between 1 and 4, and Y is SO_3, SO_4, PO_4, PO_3, or CO_2.

This invention relates to aqueous, acid copper plating electrolytes, and particularly to such electrolytes containing addition agents for improving the properties of the copper electrodeposit, and to the use of the electrolytes.

While the invention will be described hereinbelow with reference to acid copper sulfate electrolytes by way of example, it is not limited thereto but is equally applicable to acid copper plating electrolytes containing other sources of copper ions and hydrogen ions.

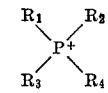
Aqueous electrolytes containing only copper sulfate and sulfuric acid as solutes yield visibly crystalline and dull cathodic copper deposits. It is known to add small amounts of certain organic addition agents to the basic electrolyte for obtaining bright copper deposits. The addition agents proposed heretofore are organic, sulfur-bearing compounds which, in addition to divalent sulfur, may contain phosphorus, sulfonic acid radicals, and polyether moieties.

The sulfur-bearing compounds have been found practically applicable only when employed in combination with an oxygen-bearing compound of high molecular weight. Such brightener compositions, however, are limited in their use to a narrow range of cathodic current densities, and particularly to a maximum cathode current density of approximately 85 amps./sq. ft. At higher current densities, enough hydrogen is co-deposited to make the deposit powdery, and thus useless.

The advantages of high cathode current density are obvious. The output of a copper plating installation is approximately proportional to the permissible cathode current density under otherwise constant conditions.

The primary object of this invention is the provision of an addition agent for acid copper plating electrolytes which permits bright and ductile copper electrodeposits to be produced at higher current densities than were permissible heretofore, more specifically, at cathode current densities greater than 100 amps./sq. ft.

The addition agents of the invention are sources of ions of phosphonium of the formula



wherein R_1, R_2, R_3, and R_4 may be identical or different. R_1, R_2, R_3 are members of the group consisting of alkyl haloalkyl, aminoalkyl, hydroxyalkyl, benzyl, cyanobenzyl, carbalkoxy, carbalkoxyalkyl, naphthylalkyl, and trialkyl-phosphonium-alkyl-diphenyl, in all these compounds the alkyl groups having one to four carbon atoms, also phenyl, cycloalkyl having 5 to 8 carbon atoms, and alkenyl having 2 to 4 carbon atoms, or R_1 and R_2 jointly with the P constitute phosphindolinium, while R_4 is a member of the afore-mentioned group or $—(CH_2)_n—Y^-$ wherein n is an integer between one and four, and Y is SO_3, SO_4, PO_4, PO_3, or CO_2.

When R_4 is a member of the aforementioned group, the addition agents are preferably hydroxides or salts of the phosphonium, and preferably sulfates, methylsulfates, chlorides, bromides, iodides, nitrates, or acetates. When R_4 is $—(CH_2)_n—Y^-$, the addition agent is a betaine, and Y is the radical of sulfuric, sulfurous, phosphoric, phosphorous acid or of the radical of a carboxyl group.

The addition agents of the invention are known in part. They can be prepared by known methods in an obvious manner, as far as they are novel, as by reacting suitable tertiary phosphines with organic halides or sulfonic acid esters.

Representative addition agents of the invention and their formulas are listed in Table I.

TABLE I

Tetrabutylphosphonium chloride

$$[(C_4H_9)_4P]Cl$$

Tetraethylphosphonium sulfate

$$[(C_2H_5)_4P]_2SO_4$$

Tributyl-benzylphosphonium chloride

$$[(C_4H_9)_3P—CH_2—C_6H_5]Cl$$

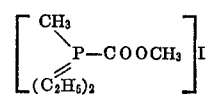
Tricyclohexyl-benzylphosphonium bromide

$$[(C_6H_{11})_3{\equiv}P—CH_2—C_6H_5]Br$$

Tris(hydroxymethyl)-butylphosphonium bromide

$$[(HOCH_2)_3P—C_4H_9]Br$$

Methyl-diethyl-carbomethoxyphosphonium iodide



Triethyl-β-chloroethylphosphonium chloride

$$[(C_2H_5)_3P—(CH_2)_2Cl]Cl$$

Triethyl-β-aminoethylphosphonium chloride

$$[(C_2H_5)_3P—(CH_2)_2NH_2]Cl$$

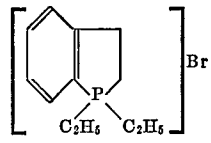
Triphenyl-propylsulfophosphonium betaine

$$(C_6H_5)_3{\equiv}P^{(+)}—(CH_2)_3SO_3^{(-)}$$

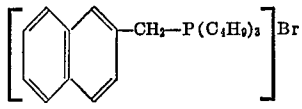
Trimethyl-acetophosphonium betaine

$$(CH_3)_3P^{(+)}.CH_2COO^{(-)}$$

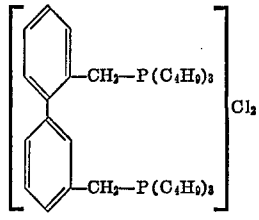
1,1-diethylphosphindolinium bromide



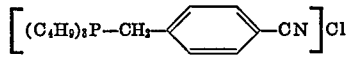
Tributyl-β-naphthylmethylphosphonium bromide



Bis-(2,2'-tributylphosphonionomethyl)-diphenyl dichloride



Tributyl-cyanobenzylphosphonium chloride



Tributyl-carbomethoxymethylphosphonium chloride

$$[(C_4H_9)_3P—CH_2COOCH_3]Cl$$

Tributyl-propylsulfophosphonium betaine

$$(C_4H_9)_3P^{(+)}.(CH_2)_3SO_3^{(-)}$$

Tetrabutylphosphonium methylsulfate

$$[(C_4H_9)_4P]CH_3O.SO_2$$

Tributyl-allylphosphonium chloride

$$[(C_4H_9)_3P.CH_2CH=CH_2]Cl$$

Among the compounds enumerated above, those having aromatic groups directly bound to the phosphorus atom are less effective than others.

The addition agents of the invention produce beneficial effects in copper plating electrolytes which may contain 100–280 g./liter copper sulfate pentahydrate and 20–100 g./liter sulfuric acid, but they are equally effective in electrolytes, otherwise known, in which the sulfate ions are replaced partly or entirely by fluoroborate ions, pyrophosphate ions, or those of other acids, At this time, the sulfate electrolytes are of greatest economic significance.

The electrolyte may be free from chloride ions, other than those introduced with an addition agent of the invention, or it may be mixed with alkali metal chlorides or hydrochloric acid in amounts of 0.001 to 0.5 g./liter for improved brightness and levelling effect.

Addition agents of the invention, used singly or jointly, in adequate amounts permit the average cathode current density to be increased substantially beyond 85 amps./sq. ft., and even to much more than 100 amps./sq. ft., without causing plating defects, more specifically, loosely adhering, powdery copper deposits in areas of highest current density. Simultaneously, throwing and covering power is greatly improved so that a satisfactory copper coating is obtained in areas of lowest actual current density which would not be covered in an electrolyte not containing the addition agent or agents of the invention. Electrolyte temperatures up to about 45° C. may safely be employed when using the addition agents.

Depending on the copper and hydrogen ion concentrations in the electrolyte, the configuration of the conductive object which is made the cathode in the electrolyte, and the desired effect, the concentration of addition agent in the electrolyte may be chosen between about 0.01 g./liter and 10.0 g./liter, useful results being obtained under

relatively rare, special conditions with amounts of electrolyte above or below these limits. Under many conditions normally encountered in common plating practice, concentrations between 0.2 g./liter and 2.0 g./liter produce consistently good results.

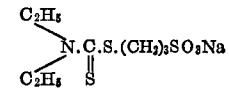
The addition agents of the invention, when used jointly with other known brighteners and/or wetting agents, permit copper electrodeposits of high brightness and free from haze to be produced at very high cathode current densities. The increase in the permissible current densities is particularly striking when the addition agents of the invention are mixed with copper plating electrolytes containing organic thio and seleno compounds. Such solutions may also contain levelling agents, known in themselves, such as nitrogen-bearing thio compounds, polymeric phenazonium compounds, and the like.

The thio or seleno compounds containing hydrophilic groups which make them water-soluble are employed jointly with addition agents of the invention in amounts of about 0.0005 to 0.2 g./liter, and preferably 0.01 to 0.1 g./liter, and the broad range of concentrations is the same for the nitrogen bearing thio compounds and phenazonium derivatives, although optimum concentrations are usually between 0.0005 and 0.02 g./liter.

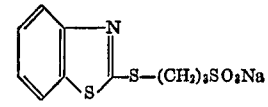
Suitable organic compounds containing divalent sulfur or selenium are listed in Table II.

TABLE II

Sodium ω-sulfopropyl-N,N-dithiocarbamate



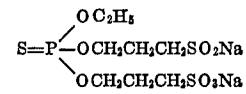
Sodium mercaptobenzthiazole-S-propylsulfonate



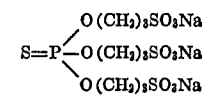
Sodium 3-mercaptopropane-1-sulfonate

$$HS\cdot(CH_2)_3SO_3Na$$

Bis(sodium O-ω-sulfopropyl)-O-ethyl thiophosphate



Tris(sodium O-ω-sulfopropyl) thiophosphate



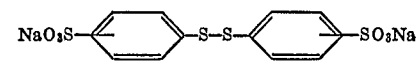
Sodium isothiocyanopropanesulfonate

$$S=C=N(CH_2)_3SO_3Na$$

Potassium thioglycolate

$$HS\cdot CH_2COOK$$

Disodium salt of bis(sulfophenyl) disulfide



Dipotassium salt of bis(sulfopropyl) diselenide

$$KO_3S\cdot(CH_2)_3Se—Se(CH_2)_3\cdot SO_3K$$

Nitrogen bearing organic thio compounds and polymeric phenazonium compounds that may be used jointly with the addition agents of the invention and the brighteners of Table II are listed in Table III.

TABLE III

Thiourea

$H_2N \cdot CS \cdot HN_2$

N-acetylthiourea

$CH_3CO \cdot NH \cdot CS \cdot NH_2$

N-trifluoroacetylthiourea

$CF_3CO \cdot NH \cdot CS \cdot NH_2$

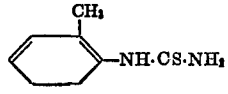
N-ethylthiourea

$C_2H_5NH \cdot CS \cdot NH_2$

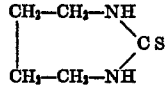
N-cyanoacetylthiourea

$NC—CH_2 \cdot CO \cdot NH \cdot CS \cdot NH_2$

o-Tolylthiourea



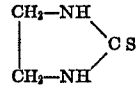
N,N'-butylenethiourea



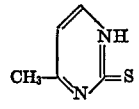
2-Thiazolidinethione

2-Thiazolethiole

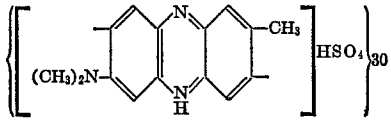
N,N'-ethylenethiourea



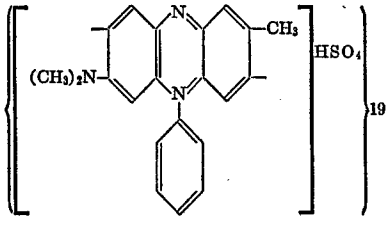
6-methyl-2-pyrimidinethiole



Poly(2-methyl-7-dimethylaminophenazonium sulfate)



Poly(2-methyl-7-dimethylamino - 5 - phenyl-phenazonium sulfate)



The following examples are further illustrative of this invention.

EXAMPLE 1

A copper plating electrolyte containing 200 g./liter copper sulfate pentahydrate and 55 g./liter concentrated sulfuric acid yielded dull copper deposits of unsatisfactory throwing power at all practical cathode current densities.

When 1 g. tributyl-carbomethoxymethylphosphonium chloride was added, a continuous copper deposit was obtained even in recessed areas of a workpiece in which the actual cathode current density was less than 1 amp./sq. ft.

EXAMPLE 2

Bright copper electrodeposits of good levelling properties were produced at cathode current densities of up to 150 amps./sq. ft. at 40° C. in an electrolyte of the following composition (per liter):

220 g. copper sulfate pentahydrate
60 g. concentrated sulfuric acid
40 mg. sodium chloride
1 g. tributyl-benzylphosphonium chloride
10 mg. sodium 3-mercaptopropane-1-sulfonate
6 mg. polymeric 2-methyl - 7 - dimethylamino-5-phenylphenazonium sulfate

EXAMPLE 3

Even better results than in Example 2 were obtained from an electrolyte containing, per liter:

220 g. copper sulfate pentahydrate
60 g. concentrated sulfuric acid
40 mg. sodium chloride
1 g. tetrabutylphosphonium chloride
20 mg. tris(sodium O-ω-sulfopropyl) thiophosphate
0.6 mg. N-ethylthiourea

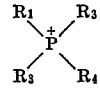
Good brightness over a wide range of actual current densities was obtained at an average cathode current density of 175 amps./sq. ft., and good levelling was observed. The electrolyte was operated at 40° C.

Analogous results were achieved with the addition agents of the invention listed in Table I, when they were substituted for those employed in Examples 1 to 3, and with their homologs and analogs within the limits of composition indicated above.

It should be understood, therefore, that the foregoing disclosure relates only to preferred embodiments, and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of the disclosure which do not constitute departures from the spirit and scope of the invention set forth in the appended claims.

What is claimed is:

1. An aqueous acidic electrolyte for the electrodeposition of copper comprising, as solutes, a source of copper ions, a source of hydrogen ions, and in an amount sufficient to provide better throwing and covering power, a source of ions of a phosphonium of the formula



wherein

R_1, R_2, and R_3 are members of the group consisting of alkyl, haloalkyl, aminoalkyl, hydroxyalkyl, benzyl, cyanobenzyl, carbalkoxy, carbalkoxyalkyl, naphthylalkyl, and trialkyl-phosphonium-alkyl-diphenylalkyl, the alkyl of said members having one to four carbon atoms, phenyl, cycloalkyl having 5 to 8 carbon atoms, and alkenyl having 2 to 4 carbon atoms, or

R_1 and R_2 jointly with said P constitute phosphindolinium, and

R_4 is a member of said group or $—(CH_2)_n—Y^-$, wherein n is an integer between one and four, and Y is SO_3, SO_4, PO_4, PO_3, or CO_2.

2. An electrolyte as set forth in claim 1, wherein the concentration of said source is 0.01 to 10 grams per liter.

3. An electrolyte as set forth in claim 2, wherein said concentration is 0.2 to 2.0 grams per liter.

4. An electrolyte as set forth in claim 2, wherein R_4 is a member of said group and said source is a hydroxide, sulfate, methylsulfate, chloride, bromide, iodide, nitrate, or acetate of said phosphonium.

5. A process of electrodepositing copper which comprises making a conductive object the cathode in an electrolyte defined in claim 1 at a cathode current density substantially greater than 100 amps. per square foot.

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GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

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