A bath for electrodepositing ductile, lustrous copper which comprises an aqueous acidic copper plating bath containing dissolved therein a brightening amount of the reaction product of polyethyleneimine and an alkylating agent which will alkylate the nitrogen of the polyethyleneimine to produce a quaternary nitrogen, wherein the reaction temperature for the imine and alkylating agent ranges from about room temperature to about 120°C and the reaction product is present in the bath in an amount from about 0.1 to 1,000 milligrams per liter.

12 Claims, No Drawings
ELECTRODEPOSITION OF COPPER FROM ACID BATHS

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of Ser. No. 11,024, filed Feb. 12, 1970, now abandoned.

This invention relates to the electrodeposition of copper from aqueous acidic plating baths, especially from copper sulfate and fluoroborate baths, and more particularly it relates to the use of certain organic compounds in the baths to give bright, highly ductile, low stress, good leveling copper deposits over a wider range of bath concentration and operating current densities.

Heretofore, numerous additives have been proposed for use in aqueous acidic plating baths for the electrodeposition of copper. For example, in U.S. Pat. Nos. 3,267,010 and 3,328,273, it is proposed to use bath-soluble polyether compounds, including those which are polymers of 1,3-dioxolane, in combination with various organic sulfide compounds, including organic sulfides which contain at least one sulfonic group and aliphatic polysulfide compounds. Although bright, ductile copper electrodeposits are produced from these baths containing these organic additives, in some instances the deposits formed have poor leveling characteristics and in low current density areas a dull plate may be produced. Accordingly, these patents further disclose the desirability of utilizing, in addition to the polyether and organic sulfide compounds a phenazine dye, such as diethyl or dimethyl Safranine Azo dimethyl aniline. With the addition of such dye materials full bright, leveled copper deposits are obtained.

See also French Patent 1,515,363 which describes the use of alkylated polyethyleneimine in copper plating solutions.

While these bright, ductile leveling copper plating baths are in large commercial use, nevertheless an important improvement would be the use of higher bath temperatures without causing excessive dulling of the plate. Even a 5°F increase in the optimum bath temperature for bright plate would allow a very significant increase in the current density used and thus in the speed of plating. With higher speed plating, shorter plating time can, of course, be used, thus allowing greater production with a given volume of plating solution.

It has now been found that the reaction product of polyethyleneimine with benzyl chloride or similar reactive organic halogen compounds are brightening additives in the acid copper plating baths, and can be employed instead of phenazine dyes with definite improvements. These improvements constitute the main objects of this invention, and are here listed:

1. An object of the present invention is to provide an improved process for the electrodeposition of copper from an aqueous acidic copper plating bath, by making possible the use of higher bath temperatures without causing excessive dulling of the plate.

2. Another object of the present invention is to provide an improved bright plating acid copper bath that provides smooth anode dissolution (less loose particles than normal).

3. A further object of the present invention is to provide an improved aqueous acidic bath for the electrodeposition of bright leveling, ductile, copper deposits over a wider bath temperature range without excessive dulling of low current density areas while still making possible brilliant plate at the highest current density ranges.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a bath for electrodepositing ductile, lustrous copper which comprises an aqueous acidic copper plating bath which contains a brightening amount of a material which is the reaction product of polyethyleneimine and an organic compound which will alkylate the nitrogen in the polyethyleneimine. By the use of such additives, particularly when used in conjunction with organic sulfide compounds and bath soluble polyether compounds, full bright, leveled copper deposits are obtained, along with better anode dissolution and improved adhesion of subsequently applied plates, over a wide range of operating temperatures, current densities and bath concentrations.

More specifically, in the practice of the present invention, the aqueous acidic copper plating baths contain the reaction product of the polyethyleneimine and the organic compound which will alkylate the nitrogen of the polyethyleneimine to produce a quaternary nitrogen in an amount which is desirably at least about 0.1 milligram per liter and preferably in an amount from about 0.1 to 1000 milligrams per liter. Various organic compounds which will alkylate the nitrogen of the polyethyleneimine to produce a quaternary nitrogen may be reacted with the polyethyleneimine to form the additive materials for use in the present acid copper plating baths. In this regard, it is to be noted that the alkylation may take place at the primary, secondary and/or tertiary nitrogen of the polyethyleneimine and that the number of nitrogen atoms of each type will vary, depending upon the amount of branching present in the polyethyleneimine.

When the alkylation agent reacts with the primary or secondary amine, it will be altered to the secondary and tertiary amine, respectively. This is accomplished by adding more alkylation agent as is desired. Where the alkylation takes place at the primary and/or secondary nitrogen, there will be a splitting off of the alkylation groups on the organic compound, e.g., halogen, sulfate, or the like. In the case of the tertiary nitrogen, however, a quaternization takes place, forming the quaternary salt.

It is preferred that as many nitrogen atoms as possible in the polyethyleneimine brightener should be quaternized, although as little as 5 percent of the nitrogen atoms being quaternary still gives desirable results, with 10% being more preferred and even more preferably 20 percent.

To effect this alkylation, both aliphatic and aromatic compounds, which may be either saturated or unsaturated may be used. Compounds which have proved to be of particular value are organic compounds which contain active halogens, such as the aralkyl halides, the alkyl, alkenyl and alkynyl halides, acid halides, acyl halides, and the like. Additionally, compounds such as the alkyl sulfates, alkyl sulfones, aldehydes, ketones, isocyanates, thioisocyanates, epoxides, acylamides, acids, anhydrides, ureas, cyanamides, guanidines, and the like, may also be used. It is to be appreciated that in some instances organic compounds may be used in which the reacting group is attached directly to an aromatic nucleus, rather than on an alkyl chain. Exem-
plary of such materials is 2,4-dinitrochlorobenzene, which will react with either the primary or secondary nitrogen of the polyethyleneimine and/or will quaternize with the tertiary nitrogen. Accordingly, in referring to the "alkylation" of the nitrogen in the polyethyleneimine, it is intended to include those cases in which the nitrogen is attached directly to an aryl or aromatic nucleus, as well as those in which it is attached to an aliphatic group. Specific compounds which have been found to give particularly good results are benzyl chloride, allyl bromide, dimethyl sulfate, and propylene sulfone. These compounds, however, are merely exemplary of the organic compounds which will alkylate the nitrogen of the polyethyleneimine. Preferably the alkylation agent is an aromatic halide.

In reacting the polyethyleneimine with the organic alkylation compound, to form the additive composition for the acid copper plating baths of the present invention, an excess of the organic alkylation compound, over the theoretical amount required to completely react with the polyethyleneimine, is preferred. While an excess of the alkylation agent is preferred, excellent results are also obtained with lesser degrees of alkylation. This reaction may be carried out by admixing the polyethyleneimine and the organic alkylation compound, either with or without a solvent. Illustrative of solvents which may be used is dioxane. The reaction temperature may vary from about room temperature to about 120°C, although where a solvent such as dioxane is used, reaction temperatures of from about 80° to 100°C are preferred. The resulting reaction product is then separated from any unreacted materials, using any convenient techniques. It is to be appreciated that although it is preferred to use an excess of the organic alkylation compound, so that substantially complete alkylation of the nitrogen in the polyethyleneimine is effected, this has not been found to be essential. In many instances, greatly improved plating results have been obtained when using a polyethyleneimine which is only partially or incompletely alkylated. The polyethyleneimine which is used in forming the plating bath additive may have a wide range of molecular weights. Typically, the molecular weight of the polyethyleneimine may be within the range of about 300 to several millions. In many instances, however, molecular weights within the range of about 300 to 1,000,000 are preferred.

In addition to the above described brightening agent, the aqueous acid copper plating baths of the present invention also desirably contain at least one bath-soluble polyether compound. Various polyether compounds which are soluble in the plating bath may be used. For example, in high sulfuric acid and low copper metal baths, non-ionic polyether wetting agents, such as polyglycols having carbon chains greater than 6 in length, may be useful. In general, however, the most preferred polyethers are those containing at least six ether oxygen atoms and being free from alkyl chains having more than six carbon atoms in a straight or branched chain. Of the various polyether compounds which may be used, excellent results have been obtained with the polypropylene propanols and glycols of average molecular weight of from about 360 to 1000, i.e., polyethers which contain a group \( \text{C}_2\text{H}_4\text{O}_x \) where \( y \) is an integer of from about 6 to 20. Excellent results have also been obtained with polyethers containing the group \( \text{C}_2\text{H}_4\text{O}_x \) where \( x \) is an integer of at least 6. Exemplary of the various preferred polyether compounds which may be used are those set forth in Table II appearing in columns 5 and 6 of U.S. Pat. No. 3,328,273. Desirably, the plating baths of the present invention contain these polyether compounds in amounts within the range of about 0.10 to 5 grams per liter, with the lower concentrations generally being used with the higher molecular weight polyethers.

In addition to the polyethyleneimine reaction product and the polyether compound, the aqueous acidic copper plating baths of the present invention also desirably contain an organic sulfide compound. Typical of the suitable organic sulfides which may be used are sulfonated organic sulfides, i.e., organic sulfide compounds carrying at least one sulfonic group. These organic sulfide sulfonic compounds may also contain various substituting groups, such as methyl, chloro, bromo, methoxy, ethoxy, carboxy and hydroxy, on the molecules, especially on the aromatic and heterocyclic sulfide sulfonic acids. The organic sulfide sulfonic acid may be used as the free acids, the alkali metal salts, organic amine salts, or the like. Exemplary of specific sulfonate organic sulfides which may be used are those set forth in Table I in columns 5 and 6 and columns 7 and 8 of U.S. Pat. No. 3,267,010. Other suitable organic sulfide compounds which may be used are mercaptans, thiocarboxamates, thiolcarboxamates, thioanethanes, and thioacetates which contain at least one sulfonic group. Additionally, organic polysulfide compounds may also be used. Such organic polysulfide compounds may have the formula \( \text{X}_n\text{R}_1\text{R}_2\text{SO}_4\text{H} \), wherein \( \text{R}_1 \), \( \text{R}_2 \), and \( \text{X} \) are the same or different alkylene group containing from about 1 to 6 carbon atoms, \( \text{X} \) is hydrogen or \( \text{SO}_4\text{H} \) and \( n \) is a number from about 2 to 5. These sulfide compounds are aliphatic polysulfides wherein at least two divalent sulfur atoms are vicinal and wherein the molecule has one or two terminal sulfonic acid groups. The alkylene portion of the molecule may be substituted with groups such as methyl, ethyl, chloro, bromo, ethoxy, hydroxy and the like. These compounds may be added as the free acids or as the alkali metal or amine salts. Exemplary of specific organic polysulfide compounds which may be used are set forth in Table I of column 2 of U.S. Pat. No. 3,328,273. Desirably, these organic sulfide compounds are present in the plating baths of the present invention in amounts within the range of about 0.0005 to 1.0 grams per liter.

The copper plating baths in which the above additives are used may be either acidic copper sulfate or acidic copper fluoroborate baths. As is known in the art, such acidic copper sulfate baths typically contain from about 180 to 250 grams per liter of copper sulfate and 30 to 80 grams per liter of sulfuric acid; while the acidic copper fluoroborate baths typically contain from about 200 to 600 grams per liter of copper fluoroborate and about 0 to 60 grams per liter of fluoroboric acid. Additionally, it is found that with the additives of the present invention, these acid copper plating baths may be operated under conditions of high acid and low metal content. Thus, even with plating baths which contain as little as about 7.5 grams per liter copper and as much as about 350 grams per liter sulfuric acid or 350 grams per liter of fluoroboric acid, excellent plating results are still obtained.

Desirably, these plating baths are operated at current densities within the range of about 10 to 100 amps per square foot, although, in many instances, current densi-
ties as low as about 0.5 amps per square foot may also be used. Typically, with low copper and high acid baths, current densities within the range of about 10 to 50 amps/ft² are used. Additionally, in high agitation baths, such as those used in plating rotogravure cylinders, current densities up to as high as about 400 amps/ft² may be used. The baths may be operated with air agitation, cathode-rod agitation, or solution agitation and cathode rod agitation, depending upon the particular bath and plating conditions which are used.

Typical bath temperatures are within the range of about 25° to 35° C, although both lower and higher temperatures, e.g., 50° C or more, may also be used. In this regard, it is to be noted that the plating baths of the present invention may also be used in copper electrowinning processes. In such processes, temperatures up to about 60°-70°C may be used.

Although it has been found to be desirable that chloride and/or bromide anions in the bath are below about 0.1 gram per liter, appreciably greater amounts of many inorganic cations, such as ferrous iron, nickel, cobalt, zinc, cadmium, and the like, may be present in the bath, e.g., amounts at least as high as about 25 grams per liter, without detrimental effect. It has further been found that not only do the acid copper plating baths of the present invention give excellent results when used under conditions of high acid and low copper metal content, but, additionally the baths have been found to be particularly well adapted for through-hole plating, and thus find appreciable utilization in the manufacture of printed circuit board.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, parts and percent are by weight and temperatures are in degrees centigrade.

**EXAMPLE 1**

An aqueous acidic copper electroplating bath was formulated containing the following components in the amounts indicated:

<table>
<thead>
<tr>
<th>Component</th>
<th>Ounces per gallon</th>
<th>Parts per million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper metal (from CuSO₄·5H₂O)</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>H₂SO₄ (100%)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>HCl (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S=S-(CH₃)₂=S-S-(CH₃)₂=S-OH</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

(Thioxanthate-S-propane sulfonic acid)

Polyethylene glycol (molecular weight about 600,000)

Reaction product of polyethyleneimine (molecular weight about 600) with benzyl chloride (in molar ratios). The imine reactant contained about 25% primary nitrogen; 50% secondary and 25% tertiary nitrogen.

The aqueous acidic copper plating baths of the preceding Examples 1 through 3 were operated using air agitation at an average current density of about 40 amps per square foot and a temperature of about 25° C. In each instance, full bright, leveled copper plates were obtained on the cathode and the anodes were evenly corroded on the surface.

The procedure of the preceding Examples 1–3 is repeated with the exception that in the preparation of the polyethyleneimine reaction product, propene sultone and dimethylsulfate are substituted for the benzyl chloride and the allyl bromide. In each instance, operation of the resulting plating bath produces full bright, leveled copper plate on the cathode and even surface corrosion of the anode.

**EXAMPLE 2**

An aqueous acidic copper electroplating bath was formulated containing the following components in the amounts indicated:

<table>
<thead>
<tr>
<th>Component</th>
<th>Ounces per gallon</th>
<th>Parts per million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper metal (from Cu(BF)₄·h₂O)</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>HBF₄·h₂O (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃S=S=S-S=CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycol (molecular weight 6000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction product of polyethyleneimine (molecular weight about 1200) with benzyl chloride (in molar ratios). The imine reactant contained about 25% primary nitrogen; 50% secondary and 25% tertiary nitrogen.</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>HCl (100%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE 3**

An aqueous acidic copper electroplating solution was formulated containing the following components in the amounts indicated:

<table>
<thead>
<tr>
<th>Component</th>
<th>Ounces per gallon</th>
<th>Parts per million</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ (100%)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>HCl (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S=S-(CH₃)₂=S-OH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Thioxanthate-S-propane sulfonic acid)

Polypropylene glycol (molecular weight 700)

Reaction product of polyethyleneimine (molecular weight about 1800) with allyl bromide (in molar ratios). The amine reactant contained about 25% primary nitrogen; 50% secondary and 25% tertiary nitrogen.

The aqueous acidic copper plating baths are prepared as in Examples 1–3 with the exception that the solutions contained 40 grams/liter copper (160 grams/liter CuSO₄·5H₂O) and 12 percent by volume H₂SO₄. These baths are used for copper electrowinning at current densities of 20 to 40 amps/ft² and temperatures of 55° to 65°C. In each instance a smooth, pure copper plate is obtained.
While there have been described various embodiments of the invention, the compositions and methods described are intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A bath for electrodeposition ductile, lustrous copper which comprises an aqueous acidic copper plating bath containing dissolved therein a brightening amount of the reaction product of polyethyleneimine and an alkylating agent which will alkylate the nitrogen on the polyethyleneimine to produce a quaternary nitrogen, said alkylating agent being selected from the group consisting of benzyl chloride, allyl bromide, propane sultone, and dimethyl sulfate, and wherein the reaction temperature for the imine and alkylation agent ranges from about room temperature to about 120°C and the reaction product is present in the bath in an amount ranging from about 0.1 to 1,000 milligrams per liter.

2. The bath as claimed in claim 1, wherein there is also present a bath soluble polyether compound and an organic sulfide compound selected from aliphatic polysulfides and organic sulfides carrying at least one sulfonic group.

3. The bath as claimed in claim 2, wherein the polyethyleneimine reaction product is present in an amount within the range of about 0.1 to 1,000 milligrams per liter, the polyether compound is present in an amount within the range of about 0.01 to 5 grams per liter and the organic sulfide compound is present in an amount within the range of about 0.0005 to 0.1 grams per liter.

4. The bath as claimed in claim 3, wherein the reaction product is formed by the reaction of polyethyleneimine and benzyl chloride, the polyether is polypropylene glycol and the organic sulfide is \( \text{HO}_3\text{S(CH}_2\text{)}\text{S-S(CH}_2\text{)}\text{SO}_3\text{H} \).

5. The bath of claim 1, wherein the alkylating agent is benzyl chloride.

6. The bath of claim 1, wherein the alkylating agent is allyl bromide.

7. A method for electrodepositing a ductile, lustrous copper which comprises the step of electrodepositing copper from an aqueous copper plating bath containing dissolved therein a brightening amount of the reaction product of polyethyleneimine and an alkylation agent which will alkylate the nitrogen, said alkylation agent being selected from the group consisting of benzyl chloride, allyl bromide, propane sultone, and dimethyl sulfate, and wherein the reaction temperature for the imine and alkylation agent ranges from about room temperature to about 120°C and the reaction product is present in the bath in an amount from about 0.1 to 1,000 milligrams per liter.

8. The method as claimed in claim 7, wherein the plating bath also contains a bath-soluble polyether compound and an organic sulfide compound selected from aliphatic polysulfides and organic sulfide compounds carrying at least one sulfonic group.

9. The method as claimed in claim 8, wherein the polyethyleneimine reaction product is present in the bath in an amount within the range of about 0.1 to 1,000 milligrams per liter, the polyether compound is present in the bath in an amount within the range of about 0.01 to 5 grams per liter and the organic sulfide compound is present in the bath in an amount within the range of about 0.0005 to 1.0 grams per liter.

10. The method as claimed in claim 9, wherein the reaction product is formed by the reaction of polyethyleneimine and benzyl chloride, the polyether compound is polypropylene glycol, and the organic sulfide compound is \( \text{HO}_3\text{S(CH}_2\text{)}\text{S-S(CH}_2\text{)}\text{SO}_3\text{H} \).

11. The method of claim 7, wherein the alkylation agent is benzyl chloride.

12. The method of claim 7, wherein the alkylation agent is allyl bromide.