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ELECTROPLATING COPPER

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This invention relates to new and useful electroplating compositions, and to a new and improved method for the electrodeposition of copper.

One of the objects of the invention is to prepare new and useful cyanide copper plating baths.

Another object of the invention is to prepare new and useful cyanide copper plating baths containing complex organic compounds which are soluble in alkaline solutions and which produce improved brightening effects.

An additional object of the invention is to provide a new and improved method for electrodepositing copper plates, in the form of a very fine grained, readily buffable deposit.

Other objects will appear hereinafter.

In accordance with the invention, new and useful cyanide copper plating baths are provided containing sulfided organic amines soluble in alkaline aqueous solutions.

The preferred mode of practicing the invention involves the use of sulfided triethanolamine which is preferably prepared by mixing a minor proportion of sulfur with triethanolamine, followed by agitation and successive heating and cooling of the reaction mixture over a period of several hours. The resultant product is a reddish-brown solution which can be diluted with equal volumes of water and employed directly as an addition agent to alkaline copper cyanide plating baths. With a quantity of the sulfided triethanolamine corresponding to from 5 mgs. to 10 mgs. of sulfur in the amine per gram of copper dissolved in the plating bath, excellent results have been obtained in electrodepositing copper at current densities within the range of 15-45 amperes per square foot. The copper deposits or plates thus produced are very fine grained, semibright and readily buffable.

Although it is preferable to employ as the addition agent, for the purpose of the invention, a condensation product of sulfur and triethanolamine, other addition agents which are suitable for the practice of the invention can also be prepared by sulfiding an amine in any one of several ways.

The final product should be soluble in water or any alkaline aqueous solutions; or it should be capable of being dissolved in such solutions by mixing therewith a mutual solvent for the sulfided amine and water, e. g., diethyleneglycolmonobutylether. As an illustration, toluidine may be reacted with sulfur to form an organic sulfide in which two molecules of toluidine are linked together by a sulfur atom. This intermediate product, which is insoluble in water, is then reacted with triethanolamine to form a

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product which can be dissolved in diethyleneglycolmonobutylether, and which, when so dissolved and agitated with water, will form an emulsion. This emulsion can then be employed as an addition agent for alkaline cyanide copper plating baths in the manner previously described with respect to the sulfided triethanolamine. However, since this product is more complex and more difficult to prepare, the sulfided triethanolamine is preferred for the practice of the invention.

The solubility of the amine employed as a starting material in preparing the sulfided amine can be increased by the presence of water-solubilizing groups, e. g., hydroxyl, carboxyl, and sulfonic groups. Thus, instead of using toluidine as a starting material, anthranilic acid may be employed. In a similar manner, other amino carboxylic acids of the benzene and naphthalene series may be employed in the practice of the invention.

The sulfiding of the amine may be accomplished with sulfur compounds instead of elemental sulfur, for example, P_2S_3 , P_2S_5 and KSH . It is also possible to introduce the sulfur into the organic amino compound by diazotizing the organic primary amine and treating the resultant diazonium compound with a solution of potassium sulfide or sodium sulfide, or with hydrogen sulfide (under pressure). Another method involves dissolving the amino compound in a solvent and treating it with ammonium thiocyanate and an oxidizing agent such as bromine.

In carrying out the invention, it has been found that good results are obtained with commercial triethanolamine which ordinarily contains about 85% triethanolamine, 10% diethanolamine and 5% monoethanolamine. Other examples of suitable primary, secondary and tertiary alkylolamines are aminoethylethanalamines, dimethylethanalamines, diethylethanalamines, mixed isopropanalamines, monoisopropanolamine, diisopropanolamine, triisopropanolamine, methyldiethanolamine, N-acetyl ethanolamine, phenylethanolamine, phenyldiethanolamine, cyclohexylethanolamine, trihexanolamine, benzylethanolamine, and octylethanolamine.

Since the reaction between the sulfur and the amino compound normally results in a condensation between one atom of sulfur and two mols of the amino compound, the resultant products may be defined as sulfided polyamines. Any of these reactions involving the use of an alkylolamine may also result in the condensation or polymerization of the alkylolamine. Where the final product still contains hydroxyl groups, as is the

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case with the water-soluble sulfided triethanolamines, this product may also be described generically as a sulfided alkylolpolyamine. In some cases, the polymerization or condensation of the alkylolamine, either alone or with other alkylolamines, will result in the partial elimination of water with the formation of alkoxy groups in the final product.

The invention will be further illustrated, but is not limited by the following examples, in which the quantities are stated in parts by weight unless otherwise indicated.

Example I

To 48 gallons of commercial triethanolamine, containing about 85% triethanolamine, 10% diethanolamine and 5% monoethanolamine, there was added 2 to 4.5 lbs. of sulfur. The addition of the sulfur to the triethanolamine was effected at relatively low temperatures, around 60° F., and the mixture was agitated and heated to 160° F., where the temperature was held for one-half hour. While continuing the agitation, the mixture was heated at 180° F., for one-half hour and then at 200° F. for one-half hour. The temperature was then dropped to 180° F., with agitation for 30 to 40 minutes, and thereafter raised to 200° F., with agitation for 20 to 25 minutes. The temperature was then dropped again to 180° F., with agitation for 30 to 40 minutes and again raised to 200° F. with agitation for 20 to 25 minutes. These operations were conducted in a jacketed vessel. The jacket of the vessel was then filled with cold water and the temperature allowed to drop to 140° F. with agitation. At this point, an equal volume of water was added.

In preparing sulfided amines in accordance with the invention, it will be understood that the proportions of the reactants may be varied somewhat. Where the reaction involves the use of an aromatic amine, as in Example III, the quantities of sulfur and amine can readily be calculated. On the other hand, where the reaction is between sulfur and triethanolamine, as in Example I, it has been determined that the maximum quantity of sulfur which reacts with the triethanolamine is approximately one part by weight per 100 parts by weight of triethanolamine. Additional quantities of sulfur apparently remain in the reaction mixture as free sulfur.

The resultant sulfided triethanolamine is then ready for use as an addition agent to electroplating baths.

Example II

This example illustrates the use of the sulfided triethanolamine of Example I, in an alkaline cyanide copper plating bath. A suitable bath may be prepared from the following ingredients:

Sodium cyanide	1/2 oz. to 1 3/4 oz.
Copper cyanide	2 oz. to 4 oz.
Sodium carbonate	2 3/4 oz. to 4 3/4 oz.
Water	In sufficient amount to make up a gallon of bath.

This bath is preferably employed as a plating bath at a temperature of 140-160° F. The sulfided triethanolamine, prepared as described in Example I, is then added to the bath, preferably in proportions with the range of 130-200 cc. of sulfided triethanolamine per gallon of bath. Since the sulfided triethanolamine, as prepared in Example I, has previously been diluted with an equal volume of water, only one-half of the

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addition agent is active material. Inasmuch as the copper plating bath contains about 15-30 gms. per liter of copper, it can be calculated that the preferred quantity of sulfided triethanolamine contains 5-10 mgs. of sulfur per gram of copper dissolved in the bath.

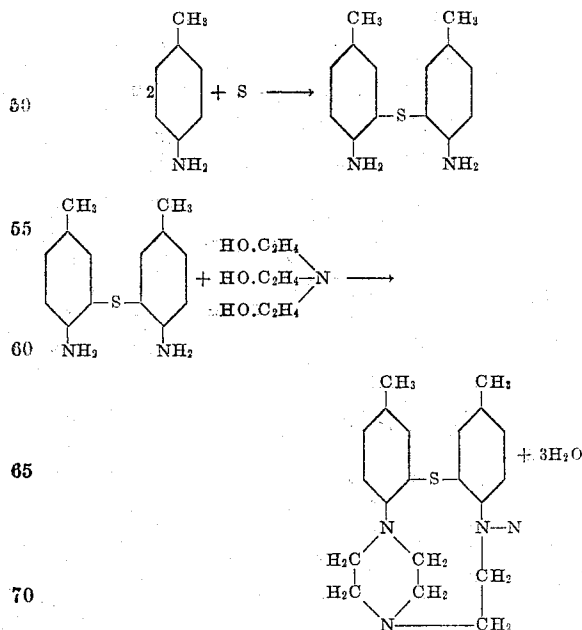
If the quantity of the addition agent is less than the preferred minimum, that is, less than the equivalent of 5 mgs. of sulfur per gram of copper dissolved in the bath, the full benefit of the addition agent is not obtained. It is, of course, possible to employ 3 or 4 times as much of the addition agent as the optimum or preferred range; but in that case the additional quantities do not result in additional benefits and merely add to the expense of the process.

The copper is preferably plated from the foregoing bath at current densities within the range from about 15 amperes per square foot to 45 amperes per square foot, and very fine grained, readily buffable copper deposits are obtained. For example, it is possible to plate 0.0002-0.0006 of an inch of copper on any suitable ferrous metal base material, and to thereafter plate over this copper deposit a bright nickel deposit, followed by a flash chromium deposit.

The invention can also be used in copper plating zinc die castings; for example, by buffing zinc die casts, plating .0001-.0002 of an inch of copper thereon in the manner herein described, and then forming a bright nickel deposit thereon, without buffing of the copper.

Example III

A composition was prepared by reacting together 2 mols of paratoluidine and 1 mol of sulfur with agitation at 180-200° C. for 4 to 5 hours. The reaction mixture was then cooled to 150° C. and 1 mol of triethanolamine was added. The temperature was held at 150-170° C. for 2 to 3 hours, and a water layer formed. The water layer was separated and the residual product was dissolved in diethyleneglycolmonobutylether and agitated with water to form an emulsion. The reactions involved may be written as follows:



The emulsified addition agent produced as above described can be employed as an addition agent for alkaline cyanide plating baths of the type

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described in Example II in substantially the same sulfur to copper ratio.

It will be recognized that if anthranilic acid or other primary amine carboxy or sulfonic acids are substituted for the toluidine in this example, the sulfided amines will have enhanced water solubility.

Instead of diethyleneglycolmonobutylether, other water-miscible and oil-miscible solvents may be used, such as isopropyl alcohol, diethyleneglycolmonomethylether, diethyleneglycolmonoethylether and ethyleneglycolmonobutylether.

As previously indicated, the invention is especially advantageous for use where it is desired to produce a copper deposit that is fine grained, relatively soft, and readily buffable. These deposits, produced in accordance with the practice of the invention, are semi-bright, and for certain purposes a bright nickel deposit can be applied thereover without buffing.

The invention is especially valuable therefore in copper-nickel-chromium plating. That is to say, in plating operations where a copper deposit is first applied to an article, followed by a nickel deposit or plating, and subsequently a chromium plating or deposit is applied over the nickel.

The invention is also very useful for plating zinc die casts with copper, in which case a bright nickel deposit can be applied over the copper plating without buffing. Many other applications of the invention will be apparent to those skilled in the art.

The invention is hereby claimed as follows:

1. A plating bath comprising an alkaline copper cyanide bath containing in solution a sulfided polyamine resulting from the condensation between one atom of sulfur and two mols of an amino compound.

2. A plating bath comprising an alkaline copper cyanide bath containing in solution a sulfided alkylolamine.

3. A plating bath comprising an alkaline copper cyanide bath containing in solution a sulfided alkylolpolyamine.

4. A plating bath comprising an alkaline copper cyanide bath containing in solution a sulfided triethanolamine.

5. A plating bath comprising an alkaline copper cyanide bath containing in solution a sulfided triethanolamine, the quantity of sulfided triethanolamine corresponding to at least 5 mgs. of sulfur per gram of copper, calculated on the basis of the sulfur in the amine and the copper dissolved in the bath.

6. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution a sulfided polyamine resulting from the condensation between one atom of sulfur and two mols of an amino compound.

7. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution a sulfided alkylolpolyamine.

8. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution a sulfided alkylolpolyamine.

9. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution a sulfided triethanolamine.

10. In the electrodeposition of copper, the step which comprises electrodepositing copper from

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an alkaline copper cyanide bath containing in solution a sulfided triethanolamine, the quantity of sulfided triethanolamine corresponding to at least 5 mgs. of sulfur per gram of copper, calculated on the basis of the sulfur in the amine and the copper dissolved in the bath.

11. A copper plating bath comprising an alkaline copper cyanide bath, containing in solution the reaction product of triethanolamine and a sulfiding compound.

12. A copper plating bath comprising an alkaline copper cyanide bath, containing in solution the reaction product of triethanolamine and sulfur.

13. A copper plating bath comprising an alkaline copper cyanide bath, containing in solution the reaction product of triethanolamine and a sulfiding compound, said reaction product being characterized by the condensation of one atom of sulfur and two mols of triethanolamine.

14. A copper plating bath comprising an alkaline copper cyanide bath, containing in solution the reaction product of triethanolamine and sulfur, the maximum quantity of sulfur which reacts being approximately one part by weight per 100 parts by weight of triethanolamine.

15. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution the reaction product of triethanolamine and a sulfiding compound.

16. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution the reaction product of triethanolamine and sulfur.

17. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution the reaction product of triethanolamine and a sulfiding compound, said reaction product being characterized by the condensation of one atom of sulfur and two mols of triethanolamine.

18. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution the reaction product of triethanolamine and sulfur, the maximum quantity of sulfur which reacts being approximately one part by weight per 100 parts by weight of triethanolamine.

19. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution the reaction product of triethanolamine and a sulfiding compound, the quantity of reaction product corresponding to at least 5 mgs. of sulfur per gram of copper, calculated on the basis of the sulfur in the product and the copper dissolved in the bath.

20. In the electrodeposition of copper, the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing $\frac{1}{2}$ to $1\frac{1}{4}$ ounces of sodium cyanide, 2 to 4 ounces of copper carbonate, sufficient water to make up a gallon of bath, and in solution a quantity of the reaction product of triethanolamine and sulfur corresponding to at least 5 mgs. of sulfur per gram of copper, calculated on the basis of the sulfur in the product and the copper dissolved in the bath.

21. A copper plating bath comprising an aqueous alkaline copper cyanide bath containing $\frac{1}{2}$ to $1\frac{1}{4}$ ounces of sodium cyanide, 2 to 4

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ounces of copper cyanide, $2\frac{3}{4}$ to $4\frac{3}{4}$ ounces of sodium carbonate, sufficient water to make up a gallon of bath, and in solution a quantity of the reaction product of triethanolamine and sulfur corresponding to at least 5 mgs. of sulfur per gram of copper, calculated on the basis of the sulfur in the product and the copper dissolved in the bath.

22. A plating bath comprising an alkaline copper cyanide bath containing in solution a bath soluble reaction product of an amine and a sulfiding compound.

23. In the electrodeposition of copper the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in solution a bath soluble reaction product of an amine and a sulfiding compound.

24. A plating bath comprising an alkaline copper cyanide bath containing in solution a bath soluble reaction product resulting from the reaction of two mols of paratoluidine with one mol of sulfur and the subsequent reaction of the resultant product with one mol of triethanolamine.

25. In the electrodeposition of copper the step which comprises electrodepositing copper from an alkaline copper cyanide bath containing in

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solution a bath soluble reaction product resulting from the reaction of two mols of paratoluidine with one mol of sulfur and the subsequent reaction of the resultant product with one mol of triethanolamine.

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