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ACID COPPER ELECTROPLATING BATHS

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19 Claims. (Cl. 204—52)

This invention relates to full bright copper electroplating methods and baths. It more particularly relates to acid copper electroplating baths and to additives therefore which make it possible to obtain full bright copper deposits in extremely low current density ranges, as well as in normal current density ranges.

It is known in the art that acid copper electroplating baths which contain brightening agents often produce semi-dull or dull electrodeposits within low and extremely low current density ranges of about 0.01 to 0.5 ampere per square decimeter. This disadvantage may also occur in full bright copper electroplating baths. In this connection it has been observed that the occurrence of dull zones in these current density ranges may be of a permanent as well as temporary type; in other words, dull zones occur for no apparent reason, disappear again without external influence or remain despite all attempts to correct the situation. Obviously, this condition represents a substantial uncertainty in the operation of such full bright copper electroplating baths. This disadvantage has a particularly disturbing effect when copper plating highly profiled object which are subjected during the copper plating to current density ranges of 0.01 to 0.5 ampere per square decimeter, despite the application of high net current densities of six to 8 amperes per square decimeter, for example.

It is an object of our invention to provide an electroplating method and bath for producing full bright copper deposits in a broader current density range including extremely low current density ranges.

Another object is to provide additives for a full bright copper electroplating bath whereby hazy deposits are eliminated in low current density ranges and full bright deposits are obtained throughout the entire current density range.

A further object of our invention is to provide additives for a full bright copper electroplating bath which eliminate haze in low current density ranges and which are compatible with the full brightening agent used in the bath and with other auxiliary additives.

Yet another object is to provide an electroplating method and bath for obtaining full bright copper deposits over the entire area of an object having a highly profiled surface.

These and other objects of our invention will become apparent as the description thereof proceeds.

We have now found that the above described shortcomings of the prior art can be overcome and the above objects attained by performing the copper electroplating procedure in an acid bath in the presence of basic dyestuffs which contain an ethylenechromophore, that is one or more >C=C< groups, in addition to nitrogen.

Dyestuffs of this type are, for example, diarylmethane dyestuffs and triarylmethane dyestuffs, and other polymethene dyestuffs, quinoline dyestuffs and thiazol dyestuffs, containing basic groups. Members of the group of dyestuffs which are derived from diarylmethane particularly include those compounds which, for example, under ring formation with the two phenyl radicals, also contain other auxochromic groups in the molecule and are derived from acridines, pyronines and thiopyronines.

Examples of basic triarylmethane dyestuffs are the following: para-amino triphenyl carbenium chloride, Dobner's violet, malachite green, parafuchsine, newfuchsine and paraphenylamino triphenyl carbenium chloride. Among the cyanine dyestuffs the following are suitable: quinoline blue, 3,3' diethyloxacyanine iodide, pinacyanol and the indolenines. An example of a thiazol dyestuff is thioflavin.

The basic dyestuffs themselves usually possess a certain brightening effect, but they may be used with particular advantage in those copper electroplating baths which already contain brightening agents, that is N-mono- or di- substituted dithiocarbamic acid alkylester-ω-sulfonic acids or their water soluble salts, such as the sodium salt of N,N-diethyl dithio carbamic acid n-propylester-ω-sulfonic acid, as well as water soluble salts of 1,3,5-triazine-2,4,6-tris mercaptoalkane sulfonic acids, dithiocarbamic acid-S-methylester - N-ethyl - butyl - ω-sulfonic acid, thioamides or isothioamides which contain a sulfonic acid group attached to a hydrocarbon radical which is, in turn, attached to the nitrogen atom of the thioamide or isothioamide groups. Such brightening agents are disclosed in United States Patent Numbers 2,849,351 and 2,849,352.

The baths may, in addition, contain substances that serve to render harmless bath impurities which may be introduced into the baths by the use of technical grade copper salts or tap water; examples of such substances are amino compounds free from carboxyl groups, such as N,N,N',N'-tetraethyl - 1,3 - diamonopropanol-2,N,N-dimethyl-4-bromoaniline, 3-diethylamino - 1-chloropropanol-2, as disclosed in Ser. No. 735,360, now U.S. Patent 3,030,283, and United States Patent Number 2,842,488 as well as other halogen salts of quarternary ammonium compounds which are formed from the last-mentioned substance or similar halogen-substituted amino alcohols by internal rearrangement.

The concurrent use of wetting agents and also of leveling agents is often advantageous. Suitable wetting agents are polyethylene oxide addition products with high molecular, organic compounds, such as alcohols, mercaptans, amines, carboxylic acids or carboxylic acid amides, whereas suitable leveling agents are thiourea derivatives the nitrogen atoms of which are substituted by oxygen-containing groups, such as ether, hydroxyl or carboxyl groups, which are attached to the molecule through alkyl or aryl radicals as disclosed in Ser. No. 728,033, now U.S. Patent 3,000,800.

If required, for the prevention of anode sludge, organic sulfonic acids or their water-soluble salts which contain at least one azido group in the molecule, such as the sodium salt of ω-azido-propane sulfonic acid, may concurrently be used as disclosed in copending, commonly assigned application Ser. No. 778,075, now U.S. Patent No. 2,950,235.

The basic dyestuffs are added to the acid copper electroplating baths in the amount of 0.001 to 1 gram per liter, preferably 5 to 200 milligrams per liter. The baths may be operated at a temperature up to 55° C. Use of the basic dyestuffs in acid copper plating baths makes possible the production of full bright deposits within a current density range as low as 0.01 amp./decimeter and up to 8 amp./decimeter.

The following specific examples are given to illustrate the invention and to enable persons skilled in the art to better understand and practice the invention and are not intended to be limitative.

Example I

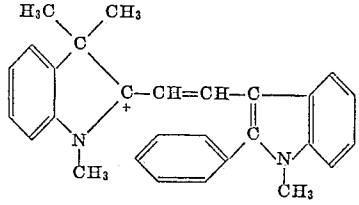
Highly profiled objects were copper plated in an acid copper bath which contained, in addition to 220 grams

per liter copper sulfate and 60 grams per liter sulfuric acid, 0.1 gram per liter N,N-diethyl-dithiocarbamic acid-ethylester-ω-sodium sulfonate, 0.4 gram per liter N,N, N',N'-tetra-n-butyl-1,3-diaminopropanol-2 and 2 grams per liter of the reaction product of dodecylalcohol and 8 mols ethylene oxide, at a net current density of 6 amperes per square decimeter at room temperature. The copper electroplates were full bright in a current density range of 1 to 8 amperes per square decimeter, whereas in a current density range of 0.25 to one ampere per square decimeter hazy and dull copper deposits occurred. However, when the bath was modified additionally with 8 milligrams per liter thioflavin, a satisfactory brightening effect was achieved under the same current density conditions even in the range of 0.5 to 1 ampere per decimeter square.

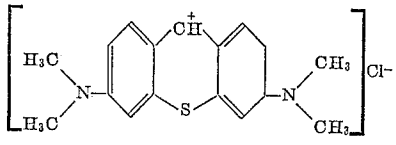
Similar effects were also obtained when 20 to 30 milligrams per liter p-dimethylamino-triphenyl-carbeniumchloride or 15–20 milligrams per liter 3,3'-diethylthiocyanine iodide were used in place of thioflavin.

Example II

A copper electroplating bath consisting of 220 grams per liter copper sulfate, 60 grams per liter sulfuric acid, 0.05 gram per liter 1,3,5-triazine-2,4,6-trimercapto-ω-sodium sulfonate, 0.6 g./l. N,N'dicyclohexyl-1,3-diaminopropanol-2, 1 g./l. ω-azidopropane-sodium sulfonate and 2 g./l. of the reaction product of dodecylalcohol and 8 mols ethylene oxide, produced full bright metal electroplates when highly profiled objects were electroplated in this bath at a current density range of 0.25 to 8 amperes per decimeter square. After a bath load of about 300 ampere hours per liter, the current density range within which full bright copper electroplates were still noted receded to a range of 1.5 to 8 amperes per square decimeter. The original brightening effects in the range of 0.25 to 8 amperes per square decimeter could not be restored despite attempts to correct the deficiency with the above brightening agents and treatment of the bath with hydrogen peroxide. However, after the bath was modified with 40 milligrams per liter of the chloride of an indolenin dyestuff of the formula,



the bath produced full bright electrodeposits not only within the original bright current density range of 0.25 to 8 amperes per square decimeter, but even in the range of 0.1 to 8 amp./dm.^{2}. In place of the above dyestuff, 20 to 30 mg./l. of a thiopyronin dyestuff of the formula



was also used with equivalent results.

While we have set forth certain specific embodiments and preferred modes of practice of our invention, it will be understood that the invention is not limited thereto and that various changes and modifications may be made in the invention without departing from the spirit of the disclosure and the scope of the appended claims.

We claim:

1. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt and from about 0.001 to 1 g./liter of bath of thioflavin.

2. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt and from about 0.005 to 0.2 g./liter of bath of thioflavin.

3. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, a brightening agent, and from about 0.001 to 1 g./liter of bath of thioflavin.

4. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, a brightening agent, a leveling agent, and from about 0.001 to 1 g./liter of bath of thioflavin.

5. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, from about 0.5 to 5 g./liter of bath of organic sulfonic acids and their water soluble salts, which comprise at least one azido group in the molecule, and from about 0.001 to 1 g./liter of bath of thioflavin.

6. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, from about 0.02 to 4 g./liter of bath of organic compounds which comprise at least one carbon atom which is attached exclusively to heteroatoms, the carbon atom being linked through an atom selected from the group consisting of sulfur and nitrogen atoms, to a hydrocarbon radical which carries a sulfonic acid substituent group as brightening agents, and from about 0.001 to 1 g./liter of bath of thioflavin.

7. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, from about 0.002 to 4 g./liter of bath of thioamides and isothioamides which have a hydrocarbon radical attached to the nitrogen atom of the thioamide or isothioamide group, said hydrocarbon radical carrying a sulfonic acid group substituent as brightening agents, and from about 0.001 to 1 g./liter of bath of thioflavin.

8. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, from about 0.1 to 20 g./liter of bath of amino compounds free from carboxyl groups which render bath impurities harmless, and from about 0.001 to 1 g./liter of bath of thioflavin.

9. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, from about 0.001 to 0.1 g./liter of bath of thiourea derivatives in which at least one nitrogen atom is substituted by a radical selected from the group consisting of an alkyl and aryl radical which, in turn, carry groups selected from the groups consisting of ether, hydroxyl and carboxyl groups, as leveling agents, and from about 0.001 to 1 g./liter of bath of thioflavin.

10. An acid copper plating bath for producing bright copper electrodeposits in lower current density ranges which comprises an aqueous acid solution containing an inorganic copper salt, a brightening agent, from about 0.001 to 0.1 g./liter of bath of thiourea derivatives in which at least one nitrogen atom is substituted by a radical selected from the group consisting of an alkyl and aryl radical which, in turn, carry groups selected from the groups consisting of ether, hydroxyl and carboxyl groups, as a leveling agent, from about 0.1 to 20 g./liter of bath of amino compounds free from carboxyl groups which render bath impurities harmless, from about 0.5 to 5 g./liter of bath of organic sulfonic acids, and their water soluble salts, which comprise at least one azido

group in the molecule, and from about 0.001 to 1 g./liter of bath of thioflavin.

11. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, and thioflavin in sufficient amount to eliminate hazy deposits in lower current density ranges and obtain bright deposits over the entire surface of said object.

12. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, a brightening agent, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

13. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, a brightening agent, a leveling agent, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

14. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, from about 0.5 to 5 g./liter of bath of organic sulfonic acids and their water soluble salts, which comprise at least one azido group in the molecule, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

15. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, from about 0.02 to 4 g./liter of bath of organic compounds which comprise at least one carbon atom which is attached exclusively to heteroatoms, the carbon atom being linked through an atom selected from the group consisting of sulfur and nitrogen atoms, to a hydrocarbon radical which carries a sulfonic acid substituent group as brightening agents, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

16. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, from about 0.002 to 4 g./liter of bath of thioamides and isothioamides which have a hydrocarbon radical attached to the nitrogen atom of the thioamide or isothioamide group, said hydrocarbon radical carrying a sulfonic acid group substituent as brightening agents, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

17. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, from about 0.1 to 20 g./liter of bath of amino compounds free from carboxyl groups which render bath impurities harmless, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

18. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, from about 0.001 to 0.1 g./liter of bath of thiourea derivatives in which at least one nitrogen atom is substituted by a radical selected from the group consisting of an alkyl and aryl radical which, in turn, carry ether, hydroxyl and carboxyl groups, as leveling agents, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

19. A process for producing bright copper electrodeposits on highly profiled objects which comprises electroplating said objects in a bath comprising an aqueous acid solution containing an inorganic copper salt, a brightening agent, from about 0.001 to 0.1 g./liter of bath of thiourea derivatives in which at least one nitrogen atom is substituted by a radical selected from the group consisting of an alkyl and aryl radical which, in turn, carry ether, hydroxyl and carboxyl groups, as a leveling agent, from about 0.1 to 20 g./liter of bath of amino compounds free from carboxyl groups which render bath impurities harmless, from about 0.5 to 5 g./liter of bath of organic sulfonic acids, and their water soluble salts, which comprise at least one azido group in the molecule, and from about 0.001 to 1 g./liter of bath of thioflavin, whereby hazy deposits are eliminated in lower current density ranges and bright deposits are obtained over the entire surface of said object.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,081,240 March 12, 1963

Wennemar Strauss et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 15, for "0.5" read -- 0.05 --.

Signed and sealed this 8th day of October 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWIN L. REYNOLDS
Acting Commissioner of Patents