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2,805,194

BRIGHT COPPER PLATING

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12 Claims. (Cl. 204—52)

This invention relates to electro-deposition of copper from aqueous acidic electrolyte solutions. The invention deals more particularly with bright copper plating, and wherein use is made of secondary addition agents which give a wider range of bright metal plating and a higher allowable current density without incurring detrimental effects such as burning and treeing of the deposit.

It has been found, when copper plating with acid baths, that when certain selected secondary addition agents are added in small amounts to a bright or semi-bright acid copper plating bath containing a primary brightener such as thiourea or thiourea derivative, e. g., acetylthiourea or thiosemicarbazide and the like, as described in U. S. Patents Nos. 2,391,289; 2,602,774; and 2,696,467, the range of proportionate constituents which may be used to produce bright, smooth metal deposits is widened or increased without encountering the difficulties such as hereinbefore mentioned.

Accordingly, it is an object of this invention to provide a bright copper acid plating bath and method of electroplating copper from such acid baths which is operable using a relatively wider range of concentration, current densities and voltage than has been possible heretofore.

Another object of the invention is to produce a bright copper deposit by electrolysis from an acid plating bath, wherein the plating operation can be carried out satisfactorily utilizing varied concentrations of constituents in the bath and current densities without noticeable deterioration of the bath or impairment of the coating.

It is another object of the invention to provide a bright copper deposit by electrolysis and improved electrolyte bath which does not require frequent renewal of electrolyte.

Another object of the invention is to provide a bright copper plating electrolyte using an acid bath, and wherein addition agents are added in conjunction with conventional bright copper producing agents to increase the efficiency of the plating bath and range of concentration in which the electrolyte is operative for plating bright copper deposits.

Another object of the invention is to provide a new and improved bath and process for electro-deposition of

copper deposits having a high degree of luster and brightness and at the same time provide a bath having a relatively high throwing power.

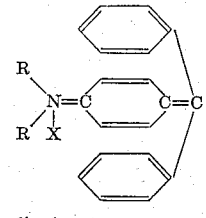
The present invention broadly concerns the discovery that the addition of certain selected addition agents in small amounts to a bright copper plating bath permits the use of higher current densities and the production of smoother and improved deposits while at the same time permitting a wider variety of objects to be plated.

The new addition agents, which are conveniently referred to as secondary addition agents, are effective with or without the presence of such substances as molasses, lignin, dextrin, caramel, etc., and are particularly useful as addition agents for plating baths that have been in operation for a period of several days, or weeks, or longer. Introduction of these secondary addition agents into acid copper plating baths, as hereinafter described, produces beneficial grain refinement of the metal deposit, even when used alone, and more especially when employed in conjunction with primary brightening agents as aforementioned.

The novel compounds found useful as secondary addition agents are organic dyes, and such as selected from one or more of the compounds hereinafter described, the same being used either singly or in combination, and wherein the total amount of the dyes added to the copper plating bath does not exceed a certain concentration. The compounds effective contain at least one amino group. Dyes useful are Malachite Green, Malachite Green G (Brilliant Green), Crystal Violet, Gentian Violet (methylrosaniline chloride), also referred to as Methyl Violet, and Crystal Violet, Methyl Green (heptamethyl-p-rosaniline chloride), and Ethyl Violet.

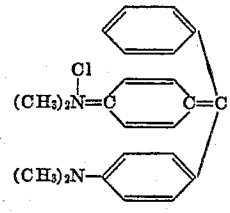
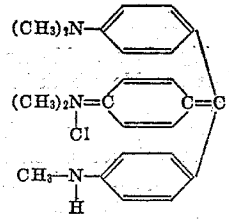
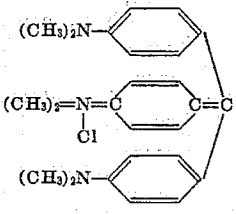
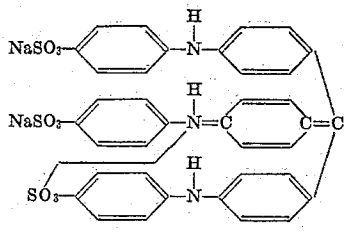
The following are typical groups of the secondary addition agents which have been found effective, however, it is to be understood that these groups are typical and that the invention is not to be specifically restricted to these dyes or compounds alone. The compounds found particularly useful are as follows:

GROUP I

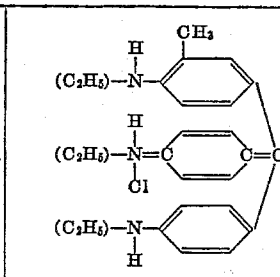


wherein R is a radical selected from the group of hydrogen, methyl, ethyl or phenyl radicals, and X is an anion such as halide, sulfate, or nitrate, or a variety of other anions which are compatible in the plating bath. The presence of other substituents on the rings does not materially effect the beneficial results obtained. These compounds are triphenylmethane dyes.

Typical examples of this group are:

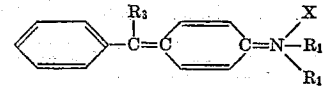
		Conc., grams/liter	Optimum, grams/liter
1	 Malachite Green	.002-.05	.004-.01
2	 Crystal Violet	.002-.05	.004-.01
3	 Gentian Violet	.002-.05	.004-.01
4	 Methyl Blue	.002-.05	.004-.01

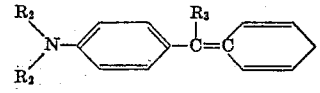
nitrogen in a valence of 5 is almost always ionized when in solution, the fifth linkage being polar in character.

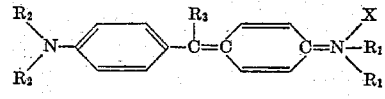
		Conc., grams/liter	Optimum, grams/liter
5	 Hofmann's Violet	.002-.05	.004-.01

Other compounds which have been found to be particularly useful as secondary agents are as follows:

GROUP II

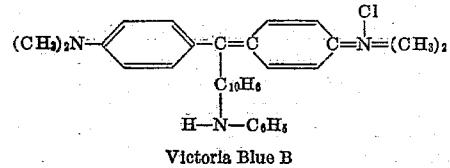
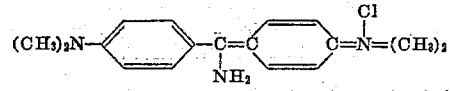
1. 

2. 

3. 

wherein Formulae 1, 2, 3 and 4 R_1 and R_2 are radicals selected from hydrogen, methyl, ethyl, or phenyl, X is an anion, and R_3 may be any radical compatible in the solution, such as phenyl, naphthol, amino, alkyl, hydrogen, etc. These compounds are known as diphenylmethane dyes. The compounds which have at least one amino group in the formula have been found to work best and are preferred.

Typical examples of this group are:

		Conc., grams/liter	Optimum, grams/liter
1	 Victoria Blue B	.002-.05	.004-.01
2	 Auramine	.002-.05	.005-.01

While this example at first glance may not seem to satisfy the claim for an anion X on one of the nitrogen atoms, it is assumed that a change takes place in solution and the central nitrogen atom becomes ionized, since

To further illustrate specific examples of electrolyte baths found useful for copper plating in accordance with this invention, the following are typical and illustrative, and in which the described quantities of the constituents are present per liter of aqueous solution.

Example 1

	Gr./l.
Copper sulfate	240
Sulfuric acid	60
Acetylthiourea	0.015
Auramine	0.01
Dextrin	0.05

Utilizing the electroplating bath at a temperature of 90° F. with agitation, as by blowing air through the bath and utilizing current density of 125 amp. per square foot, and voltage of 5 volts, a bright copper plate is deposited.

Example 2

	Gr./l.
Copper sulfate	240
Sulfuric acid	60
Thiourea	0.015
Lignin sulfonic acid	0.15
Malachite Green	0.005

The electrolyte in this instance was utilized under like temperature and agitation conditions as in Example 1, to produce a bright, smooth copper deposit.

Example 3

	Gr./l.
Copper sulfate	240
Sulfuric acid	60
Thiourea	0.015
Dextrin	0.05
Gentian Violet	0.005

Example 4

Same as in Example 3, except that thiosemicarbazide is used in lieu of thiourea.

Example 5

Same as in Example 3, except that acetyl thiourea is used in lieu of thiourea.

Example 6

Same as in Example 3, except that Malachite Green is used instead of Gentian Violet.

Example 7

Same as in Example 3, except that Methyl Blue is used instead of Gentian Violet.

Example 8

Same as in Example 3, except that Hofmann's Violet is used instead of Gentian Violet.

It is also found beneficial to employ a bath containing the chloride anion, preferably being maintained within a range of about 0.001 to 0.020 gram per liter of electrolyte. The presence of substantially lower or higher amounts of the chloride anion in the plating bath, however, does not produce the beneficial plating results, the copper deposit being less bright and not as smooth and even grain textured as where the amount of anion is held strictly within the range aforementioned.

It is also advantageous, though optional, to add an agent which acts as a carrier for the primary brightener. Dextrin, molasses and caramel are excellent for this purpose. Further, in some instances it is also desirable to add a wetting agent, e. g., sodium lauryl sulfate and sodium octyl or cetyl sulfate.

The articles to be plated are advantageously subjected to a preliminary treatment prior to the coating proper. For this purpose they are cleaned with an alkaline cleaner, dipped into acid in order to remove any rust, neutralized and then rinsed in water. It is also preferable to first apply a thin copper coating from a cyanide bath. Such a bath may contain from 3 to 5 ounces of copper metal per gallon, 1½ to 3 ounces of free sodium cyanide and from 2 to 8 ounces of sodium carbonate. Plating with this bath for from 3 to 4 minutes is sufficient. After this flash plating the article is washed to remove the cyanide.

It is further advantageous to agitate the electrolyte during electrolysis. This may be carried out either by moving the cathode or by stirring the electrolyte, the latter being preferred. In particular has it been found satisfactory to effect stirring by blowing air through the bath. If stirring is carried out this way, however, it is advisable to restrict the quantity of the wetting agent to a minimum or omit it entirely, because otherwise excessive foaming takes place which impairs the operation.

The utilization of the secondary addition agent permits bright copper plating using bath temperatures and current densities of wider range than has been permitted heretofore, the same may be varied considerably, satisfactory deposits may be obtained at bath temperatures of between about 60° F.–140° F. When operating with large commercial production operation, it may be preferred to maintain the electrolyte bath at or near room temperature, for example between about 85 and 95° F. Electric current densities may be varied over a range between about 5–250 amps. per square foot of cathode area. Higher current densities require increased agitation of the solution. The agitation may be accomplished by bubbling air through the electrolyte solution as aforementioned, or by rapid movement of the cathode or by circulating the electrolyte.

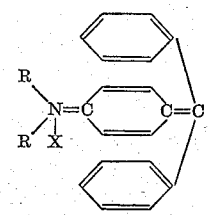
The baths described produce plating deposits of copper or chiefly of copper, which are bright and smooth. Employing the secondary addition agents in conjunction with the usual primary added agents produces bright deposits even if the conditions are not so accurately maintained as was heretofore required where only primary addition agents are used. The plating deposits are characterized by extreme fineness of metal structure and the production of a brilliant, smooth copper plating which does not require buffing.

The bright copper plated articles produced according to this process may be readily electroplated with other metal such as bright nickel, chromium or the like, as desired, to form a final bright plate which requires little or no buffing. This is particularly advantageous inasmuch as buffing removes a portion of the plate and endangers the cutting through of a thin plate. This, of course, is entirely eliminated by utilizing the present invention.

While certain embodiments of the electrolyte bath have been set forth as specific embodiments of my invention it is not intended thereby to limit the invention to the specific examples and details given in view of the fact that the invention is susceptible to various changes and modifications, particularly as to the concentration and current densities for producing a bright metal deposit. Such modifications and changes are intended to come within the spirit and scope of this invention, and which are more particularly set forth in the appended claims.

What is claimed is:

1. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing deposits, said brightener compound comprising a triphenylmethane dye having the general structural formula:



wherein R is a radical selected from the group consisting

of hydrogen, methyl, ethyl and phenyl radicals and X is an anion compatible in the plating bath.

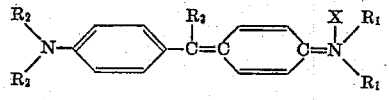
2. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing deposits, said brightener compound being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl Blue, Hofmann's Violet, Victoria Blue, Auramine, Methyl Violet, Methyl Green, Ethyl Violet, Brilliant Green, and mixtures thereof.

3. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing deposits, said brightener compound being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl blue, Hofmann's Violet, Victoria Blue, and Auramine, and mixtures thereof, said brightener being present in the bath in an amount of between about 0.002 and 0.05 gm./l. of electrolyte solution.

4. An aqueous copper sulfate-sulfuric acid bath for electro-deposition of copper which contains a grain refining addition agent, said grain refining agent comprising a dye selected from the group consisting of diphenylmethane and triphenylmethane dyes containing at least one amino group in its molecule structure being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl Blue, Hofmann's Violet, Victoria Blue, Auramine, Methyl Violet, Methyl Green, Ethyl Violet, Brilliant Green, and mixtures thereof, and, said dye being present in an amount of about 0.002 to 0.05 gram per liter of said bath.

5. An aqueous copper sulfate-sulfuric acid bath for electro-deposition of copper which contains a grain refining addition agent, said grain refining agent comprising a dye selected from the group consisting of diphenylmethane and triphenylmethane dyes containing at least one amino group in its molecule structure being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl Blue, Hofmann's Violet, Victoria Blue, Auramine, Methyl Violet, Methyl Green, Ethyl Violet, Brilliant Green, and mixtures thereof, and, said dye being present in a minor proportion.

6. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing deposits, said brightener compound comprising a diphenylmethane dye having the general structural formula:



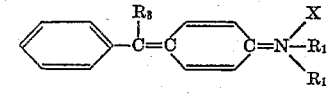
wherein R_1 and R_2 are radicals selected from the group consisting of hydrogen, methyl, ethyl, and phenyl radicals and X is an anion compatible in the plating bath, and R_3 is a radical selected from the group consisting of phenyl, naphthol, amino, alkyl, and hydrogen.

7. An aqueous copper sulfate-sulfuric acid bath for electro-deposition of copper which contains a grain refining addition agent, said grain refining agent comprising a dye selected from the group consisting of diphenylmethane and triphenylmethane dyes containing at least one amino group in its molecule structure being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl Blue, Hoffmann's Violet, Victoria Blue, Auramine, Methyl Violet, Methyl Green, Ethyl Violet, Brilliant Green, and mixtures thereof, and said dye being present in the amount of about 0.002 to 0.05 gram per liter of said bath.

8. An aqueous copper sulfate-sulfuric acid bath for electro-deposition of copper which contains a grain refining addition agent, said grain refining agent comprising diphenylmethane dye containing an amino group in its molecular structure in the amount of about 0.002 to 0.05 gram per liter of said bath, said acid bath containing chloride anion within a range of about 0.001 to 0.02 gram per liter of the bath, said dye being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl Blue, Hoffmann's Violet, Victoria Blue, Auramine, Methyl Violet, Methyl Green, Ethyl Violet, Brilliant Green, and mixtures thereof.

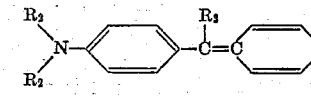
9. An aqueous copper sulfate-sulfuric acid bath for electro-deposition of copper which contains a grain refining addition agent, said grain refining agent comprising triphenylmethane dye containing at least one amino group in its molecular structure in the amount of about 0.002 to 0.05 gram per liter of said bath, said acid bath containing chloride anion within a range of about 0.001 to 0.02 gram per liter of the bath, said dye being selected from the group consisting of Malachite Green, Crystal Violet, Gentian Violet, Methyl Blue, Hoffmann's Violet, Victoria Blue, Auramine, Methyl Violet, Methyl Green, Ethyl Violet, Brilliant Green, and mixtures thereof.

10. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing deposits, said brightener compound having the general structural formula:



wherein R_1 is a radical selected from the group consisting of hydrogen, methyl, ethyl, and phenyl radicals, and X is an anion compatible in the plating bath, and R_3 is a radical selected from the group consisting of phenyl, naphthol, amino, alkyl, and hydrogen.

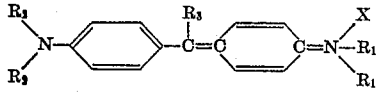
11. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing deposits, said brightener compound having the general structural formula:



wherein R_2 is a radical selected from the group consisting of hydrogen, methyl, ethyl, and phenyl radicals, and R_3 is a radical selected from the group consisting of phenyl, naphthol, amino, alkyl, and hydrogen.

12. In a method of electro-depositing copper from an aqueous copper sulfate-sulfuric acid bath, the step which comprises electrolyzing said aqueous acid copper bath containing a minor proportion of a brightener compound which widens the range of solution concentration and electric current densities wherein plating can be conducted without encountering burning and forming treeing

deposits, said brightener compound having the general structural formula:



wherein R_1 and R_2 are radicals selected from the group consisting of hydrogen, methyl, ethyl, and phenyl radicals and X is an anion compatible in the plating bath, and R_3 is a radical selected from the group consisting of phenyl, naphthol, amino, alkyl, and hydrogen.

References Cited in the file of this patent

UNITED STATES PATENTS

2,238,861	Lind et al.	Apr. 15, 1941
2,707,167	Hoover	Apr. 26, 1955