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2,738,318

ELECTRODEPOSITION OF COPPER FROM AN ACID BATH

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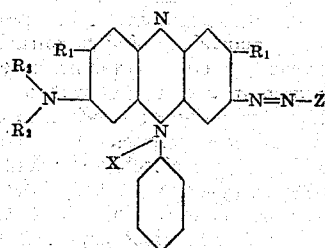
The present invention relates to the electrodeposition of copper from an aqueous acidic bath, and more particularly concerns the utilization of selected addition agents to aqueous acidic baths for the purposes herein-after stated.

One of the primary objects of this invention is the production of electrodeposits of copper having a high degree of luster and brightness as obtained directly from the electroplating bath, and without buffing or polishing operations.

Another object is the production of electrodeposits of copper having good leveling properties, that is, deposits capable of almost completely leveling polishing lines characteristically obtained in commercial practice.

In accordance with the present invention, it has been found that the luster, brightness and brilliancy of electrodeposits of copper may be materially improved by the conjoint use of organic compounds represented by Formula A and typified by the examples of Table 1, together with certain sulfur compounds selected from the group consisting of thiourea and certain acyl thioureas as set forth more fully hereinafter in Table 2. Broadly, the organic compounds which are useful for the purposes of this invention may be represented by Formula A.

FORMULA A



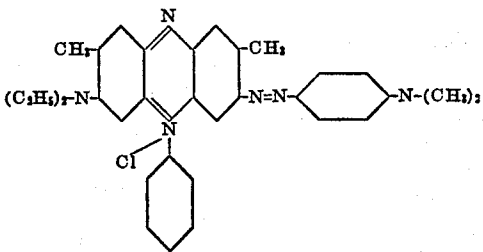
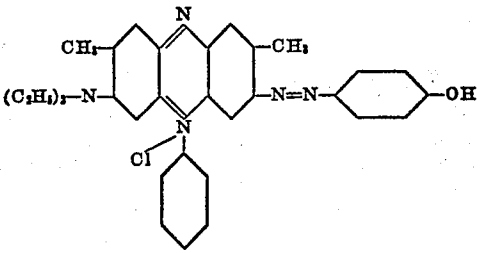
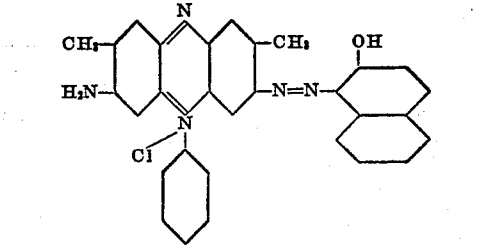
wherein R₁ and R₂ are radicals selected from the group consisting of hydrogen, methyl and ethyl radicals, and X is an anion selected from the group consisting of chloride, bromide, iodide, fluoride, sulfate, bisulfate and nitrate, and Z is an aromatic radical selected from the group consisting of phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and alkoxy substituent groups. The anion X is relatively unimportant and in addition to the anions above given may be any one of a wide variety of other anions including organic anions, such as formate, acetate, propionate, etc. It will be appre-

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ciated that the compounds represented by the above formula when present in an acid copper bath are highly ionized substances and the anion X is in ionic admixture with the other anions of the bath such as the sulfate anion, the nitrate anion, etc.

Thiourea and acetyl thiourea, as well as the compounds represented by Formula A have been used separately previously. The use of thiourea is disclosed in U. S. Patent 2,489,538 and the compounds represented by Formula A are disclosed and claimed in copending application, Serial No. 290,091, now Patent 2,707,166. Thiourea when used alone suffers from a number of disadvantages including embrittlement of the plate at even low concentrations, relatively narrow range of current densities within which brightness is obtained, requirement of low temperature of operation, etc. The compounds represented by Formula A when used alone are incapable of producing a lustrous, bright, deposit. For example, the use of the dye designated briefly as diethyl-safranin-azo-dimethyl-aniline, alone in an acidic copper sulfate bath at its optimum concentration produces a fine-grained plate over a wide range of current density, but the luster and brightness are not of the highest order. Electrodeposits produced from copper sulfate baths containing thiourea are dull on all areas in which the current density was low or medium or similarly are dull when produced from baths operating at temperatures above about 75° F. It has now been surprisingly discovered that the use of both of the above-identified agents in combination gives better electrodeposits, as evaluated both by appearance and leveling properties, and by a decrease in the criticality of conditions of operation of the bath, than the use of either of them alone.

In actual practice when these two compounds are used together, a brighter plate over a much wider current density range is obtained and polishing lines are almost completely leveled by a deposit having a thickness of approximately .6 mil. to 1 mil. Furthermore the concentration of the thioureas is less critical, and bath temperatures of 85° F. to 95° F. can be used to produce a truly brilliant deposit which does not require any buffing or polishing whatsoever to prepare the deposit for direct bright chromium plating. The electrodeposits obtained in accordance with this invention have been carefully compared with plate produced from baths containing thiourea and other addition agents such as molasses, dextrin and certain wetting agents, and the effect obtained by the addition agents of this invention far exceeds the enhanced results obtained with the molasses, dextrin or wetting agent combinations. Copper deposits are obtained having the high degree of brilliance necessary for the production of bright chromium plate directly over the copper. Somewhat better results are obtained, however, by depositing a bright nickel plate directly upon the copper plate in its unbuffed and unpolished condition, and thereafter plating chromium over the bright nickel deposit. Even very thin bright nickel deposits having thicknesses in the range of approximately .1 mil to .2 mil plated directly on top of the unbuffed copper, usually having a thickness of .6 mil to .7 mil, have a luster similar to that which is obtained from thick deposits of bright nickel, for example 1 mil to 1.5 mils, plated directly on steel or other metallic surfaces having a comparable initial surface condition. Illustrative examples of addition agents represented by the above given Formula A which may be utilized in accordance with this invention and in the ranges of proportions indicated, are given in Table 1.

	Conc., grams/liter	Optimum Conc., grams/liter
1. 	.0015-.05	.015
Diethyl safranin azo dimethyl aniline—Janus Green B		
2. 	.0015-.05	.015
Diethyl safranin azo phenol—Janus Black		
3. 	.0015-.05	.015
Safranin azo naphthol—Janus Blue		
4. Janus Gray (Color Index 137, Society of Dyers & Colourists, by F. M. Rowe, 1924).	.0015-.05	.015
5. Dimethyl safranin azo dimethyl aniline.....	.0015-.05	.015

Mixtures of the dyes shown in Table 1 may also be employed with beneficial effects. Where mixtures are employed, however, the total concentration of the mixed dye in the aqueous acidic bath preferably approximates the concentration of any component indicated in Table 1. For general purposes concentrations of the dyes of Table 1 falling within the range of .005 to .04 gram/liter represent preferred quantities.

Sulfur compounds which may be used in combination with a compound represented by Formula A or mixtures thereof, in the general ranges of proportions indicated, are set forth in Table 2.

Mixtures of the sulfur compounds of Table 2 may be used in combination with one or a mixture of the compounds of Table 1, and when such mixtures are used, the total quantity of the mixture should fall within the range of about .001 to .05 gram/liter.

Instead of the compounds represented by Formula A, it is possible to use safranines in conjunction with the thioureas to obtain enhanced brightening of the copper deposit. However, the degree of brightness and leveling action is not as high as that obtained with the use of the compounds represented by Formula A in conjunction with the thioureas of Table 2. Mixtures of the safranines with the compounds represented by Formula A when used in conjunction with the thioureas, also give copper deposits having high brightness. Examples of safranines which have been found to increase the brightness of the

copper deposit when used in combination with the thioureas of Table 2 or in admixture with any of the compounds represented by Formula A and the thioureas of Table 2 include phenosafranin, tolosafranin, fuchsia, amethyst violet, mauveine, diethyl safranin, and dimethyl safranin. When a safranin or a mixture of safranines is used in conjunction with a compound of Table 2, the concentration of a safranin or a mixture of safranines may vary between about .002 gram/liter to .03 gram/liter and preferably is maintained in the range of .003 gram/liter to .01 gram/liter. In admixture with the compounds of Formula A and the compounds of Table 2, safranines are preferably used in minor quantities, for example, .003 gram/liter safranin in admixture with .012 gram/liter Janus Green B and .003 gram/liter N-propionyl thiourea.

Somewhat superior operating bath life is obtained from the use of N-trifluoroacetyl thiourea and N-propionyl thiourea at concentrations ranging between .006 and .015 gram/liter, and for this reason these materials represent preferred compounds. Outstanding results have been obtained with the combination of Janus Green B in concentrations of .006 to .015 gram/liter and N-trifluoroacetyl thiourea and N-propionyl thiourea in concentrations of .006 to .015 gram/liter. It is preferable to maintain a concentration of chloride, or its equivalent in bromide or iodide, of about .003 to about .020 gram/liter in the solution. It is to be understood that

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Table 2

		Conc., grams/liter	Preferred Conc., grams/liter
1.	$\begin{array}{c} \text{H}_2\text{N} \\ \\ \text{C}=\text{S} \\ \\ \text{H}_2\text{N} \end{array}$ Thiourea	.001-.05	.002-.015
2.	$\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{CH}_3\text{C}-\text{N} \\ \\ \text{C}=\text{S} \\ \\ \text{H}_2\text{N} \end{array}$ N-acetyl thiourea	.001-.05	.002-.015
3.	$\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{CH}_3\text{CH}_2\text{C}-\text{N} \\ \\ \text{C}=\text{S} \\ \\ \text{H}_2\text{N} \end{array}$ N-propionyl thiourea	.001-.05	.002-.015
4.	$\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{CF}_3\text{C}-\text{N} \\ \\ \text{C}=\text{S} \\ \\ \text{H}_2\text{N} \end{array}$ N-trifluoroacetyl thiourea	.001-.05	.002-.015
5.	$\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{C}_2\text{F}_5\text{C}-\text{N} \\ \\ \text{C}=\text{S} \\ \\ \text{H}_2\text{N} \end{array}$ N-pentafluoropropionyl thiourea	.001-.05	.002-.015
6.	$\begin{array}{c} \text{HC}=\text{CH} \quad \text{O} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{HC} \quad \text{O} \quad \text{C}=\text{N} \\ \quad \quad \quad \quad \\ \quad \quad \text{O} \quad \quad \text{C}=\text{S} \\ \quad \quad \quad \quad \\ \quad \quad \quad \quad \text{H}_2\text{N} \end{array}$ N-furfuryl thiourea	.001-.05	.002-.015
7.	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{N} \\ \\ \text{C}=\text{S} \\ \\ \text{CH}_3-\text{N} \\ \\ \text{H} \end{array}$ Dimethyl thiourea	.001-.05	.002-.015
8.	$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \\ \text{NC}-\text{C}-\text{C}-\text{N} \\ \quad \quad \\ \text{H} \quad \quad \text{C}=\text{S} \\ \quad \quad \\ \quad \quad \text{H}_2\text{N} \end{array}$ Cyanoacetyl thiourea	.001-.05	.002-.015

when X is either fluoride, sulfate, bisulfate or nitrate, that chloride, bromide or iodide ions in an amount equivalent to about .003-.020 gram/liter of chloride is preferably present in addition. As initially made up, a solution containing a compound in which X is a halide other than fluoride, contains at least the preferred minimum halide concentration; but it is usually preferable to replenish the halide during use in order to maintain the minimum concentration of about .003 gram/liter.

The composition of the acidic copper bath may vary over rather wide limits, although for the best grain refinement, rate of brightening and for the widest bright plating range, the following composition, designated Formula B, is recommended for use:

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FORMULA B

	Conc., grams/liter	Preferred Conc., grams/liter
5		
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	150-250	170-200
H_2SO_4	10-30	15

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Other well-known acidic copper plating baths may be used satisfactorily. Other copper salts such as copper sulfamate, copper fluoborate, copper methyl sulfonate and copper ethyl sulfonate may be used as a substitute for or an adjunct to the copper sulfate of the above formula. The use of these substitute copper salts enables somewhat higher speed plating than is possible from the copper sulfate bath. For best results when using any of these substitute copper salts, somewhat smaller concentrations are preferred, for example, 50-150 grams/liter.

The preferred conditions of operation of baths containing proportions of addition agents indicated in Table 1 include controlled temperatures, bath agitation and cathode current densities. For example, the bath temperatures may be from about 17° C. to 40° C. (approximately 70° F. to 105° F.). The warmer temperatures above 40° C. tend to decrease the brightness of the plate, but temperatures up to 50° C. may be used satisfactorily. Cathode agitation and preferably uniform air agitation is desirable. Cathode current densities of 10-100 amps./sq. ft. (approximately 1-10 amps./sq. dm.) may be satisfactorily employed with the particular current density depending primarily upon the degree of agitation of the cathode film and the shape of the article to be plated. For general purposes, and average cathode current density of 30-50 amps./sq. ft. may be used.

As a substitute for the sulfuric acid of Formula B, nitric acid or phosphoric acid may be used in approximately equivalent proportions. Additionally, Formula B may include other ions for the purpose of increasing the conductivity of the solution such as sodium, potassium or ammonium ions. These ions are usually present in only minor concentrations. Furthermore, the copper sulfate of Formula B may be replaced by copper nitrate in approximately equivalent proportions, and when acidified with small amounts of phosphoric acid, nitric acid or sulfuric acid, the beneficial effect of reducing the grain size and increasing the luster of the deposit by additions of small concentrations of compounds of the type shown in Table 1 is also evident. The degree, however, of grain size, reduction and increase in luster is somewhat less extensive than is produced from the use of acidic baths made up primarily of copper sulfate. In general, the copper sulfate or copper nitrate concentration in the bath may satisfactorily vary from as low as about 100 grams/liter up to saturation. Concentrations of acid above the equivalent in acidity of about 80-100 grams/liter of sulfuric acid decrease the brightening effect of the addition agents represented by Formula A and are therefore to be avoided.

Small concentrations of wetting agents may be advantageously present in the baths of this invention. For example, the surface active compounds, sodium decyl sulfate and the sodium salt of sulfated monoethylene glycol ether of decyl alcohol when present in small concentrations of about 0.1 to .06 gram/liter are effective in decreasing pitting and striation formation in the deposit due to the presence of harmful organic compounds or excessive concentrations of brighteners. These wetting agents normally cause excessive frothing with air agitation, but in the presence of the addition agents of Table 1, the frothing is minimized.

The following typical plating baths are given by way of example to illustrate the invention in greater detail:

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EXAMPLE I

CuSO ₄ ·5H ₂ O	grams/liter	200
H ₂ SO ₄	do	15
Janus Green B	do	.015
Thiourea	do	.010
Temperature	° F	70-95
Cathode current density	amps./sq. ft.	30-40
Air agitation.		

EXAMPLE II

CuSO ₄ ·5H ₂ O	grams/liter	200
H ₂ SO ₄	do	15
Janus Green B	do	.010
N-trifluoroacetyl thiourea	do	.006
Sodium N-decyl sulfate	do	.01-.03
Temperature	° F	70-95
Cathode current density	amps./sq. ft.	30-40
Air agitation.		

EXAMPLE III

CuSO ₄ ·5H ₂ O	grams/liter	200
NH ₄ NO ₃	do	20-30
H ₂ SO ₄	do	15
Janus Green B	do	.015
N-propionyl thiourea	do	.001
Temperature	° F	70-95
Cathode current density	amps./sq. ft.	30-50
Air agitation.		

EXAMPLE IV

Cu(NO ₃)	grams/liter	200
HNO ₃	do	10
Janus Black	do	.010
N-furfuroyl thiourea	do	.015
Sodium salt of sulfated monoethylene glycol ether of decyl alcohol	grams/liter	.01-.03
Temperature	° F	70-95
Cathode current density	amps./sq. ft.	30-50
Air agitation.		

EXAMPLE V

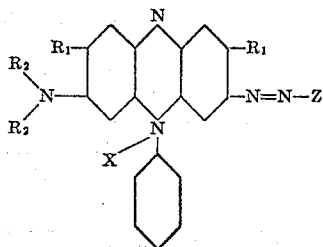
CuSO ₄ ·5H ₂ O	grams/liter	200
H ₂ SO ₄	do	15
Janus Green B	do	.006-.015
N-pentafluoropropionyl thiourea	do	.02
Sodium salt of sulfated monoethylene glycol ether of decyl alcohol	grams/liter	.01-.03
Temperature	° F	70-95
Cathode current density	amps./sq. ft.	30-40
Air agitation.		

EXAMPLE VI

CuSO ₄ ·5H ₂ O	grams/liter	200
H ₂ SO ₄	do	15
Janus Green B	do	.05
Dimethyl thiourea	do	.03
Temperature	° F	70-95
Cathode current density	amps./sq. ft.	30-40
Air agitation.		

What is claimed is:

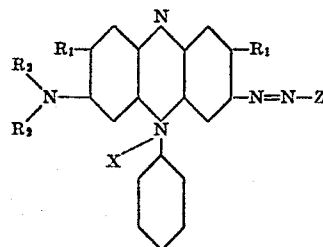
1. A bath for the electrodeposition of copper comprising an aqueous acidic solution of copper salts, a safranin, minor proportions of at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea, cyanoacetyl thiourea, and a compound having the structure:



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wherein R₁ and R₂ are radicals selected from the group consisting of hydrogen, methyl and ethyl radicals, X is an anion selected from the group consisting of chloride, bromide, iodide, fluoride, sulfate, bisulfate and nitrate, and Z is an aromatic radical selected from the group consisting of phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and alkoxy substituent groups.

2. A bath for the electrodeposition of copper comprising an aqueous acidic solution of copper salts, from .001 to .05 gram/liter of at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoro acetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea, cyanoacetyl thiourea and .0015 to .05 gram/liter of a compound having the structure:



wherein R₁ and R₂ are radicals selected from the group consisting of hydrogen, methyl and ethyl radicals, X is an anion selected from the group consisting of chloride, bromide, iodide, fluoride, sulfate, bisulfate and nitrate; and Z is an aromatic radical selected from the group consisting of phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and alkoxy substituent groups.

3. A bath for the electrodeposition of copper comprising an aqueous acidic solution of copper salts and minor proportions of at least one compound selected from the group consisting of Janus Green, Janus Blue, Janus Black, Janus Gray and dimethyl safranin azo dimethyl aniline and at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoro acetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea.

4. A bath for the electrodeposition of copper comprising an aqueous acidic solution of copper salts and .0015-.05 gram/liter of at least one compound selected from the group consisting of Janus Green, Janus Blue, Janus Black, Janus Gray and dimethyl safranin azo dimethyl aniline, and .001-.05 gram/liter of at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoro acetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea.

5. A bath for the electrodeposition of bright copper consisting essentially of copper sulfate, sulfuric acid, .0015-.05 gram/liter of Janus Green B, and .001-.05 gram/liter of N-trifluoro acetyl thiourea.

6. A bath for the electrodeposition of bright copper consisting essentially of copper sulfate, sulfuric acid, .0015-.05 gram/liter of Janus Green B and .001-.05 gram/liter of thiourea.

7. A bath for the electrodeposition of bright copper consisting essentially of copper sulfate, sulfuric acid, .0015-.05 gram/liter of Janus Green B and .001-.05 gram/liter of N-acetyl thiourea.

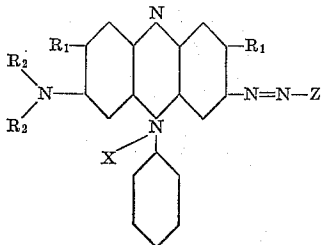
8. A bath for the electrodeposition of bright copper consisting essentially of copper sulfate, sulfuric acid, .0015-.05 gram/liter of Janus Green B and .001-.05 gram/liter of N-propionyl thiourea.

9. A bath for the electrodeposition of bright copper consisting essentially of copper sulfate, sulfuric acid,

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.0015-.05 gram/liter of Janus Green B and .001-.05 gram/liter of N-furfuroyl thiourea.

10. In a process of electrodepositing copper, the step which comprises electrolyzing an aqueous acidic solution of copper salts, said aqueous solution also containing a safranin and minor proportions of at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea, cyanoacetyl thiourea and a compound having the structure:

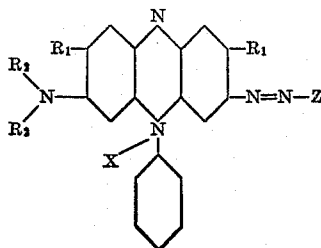


wherein R₁ and R₂ are radicals selected from the group consisting of hydrogen, methyl and ethyl radicals, X is an anion selected from the group consisting of chloride, bromide, iodide, fluoride, sulfate, bisulfate and nitrate, and Z is an aromatic radical selected from the group consisting of phenyl, naphthyl and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and alkoxy substituent groups.

11. In a process of electrodepositing copper, the step which comprises electrolyzing an aqueous acidic solution of copper salts, said aqueous solution also containing minor proportions of at least one compound selected from the group consisting of Janus Green B, Janus Black, Janus Gray, Janus Blue, dimethyl safranin azo dimethyl aniline and at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea.

12. In a process of electrodepositing copper, the step which comprises electrolyzing an aqueous acidic solution of copper salts, said aqueous solution also containing .0015-.05 gram/liter of a compound selected from the group consisting of Janus Green, Janus Blue, Janus Black, Janus Gray and dimethyl safranin azo dimethyl aniline, and .001-.05 gram/liter of a compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea.

13. In a process of electrodepositing copper, the step which comprises electrolyzing an aqueous acidic solution of copper salts, a halide selected from the group consisting of chloride, bromide and iodide in an amount equivalent to about .003 gram/liter to about .020 gram/liter of chloride, and minor proportions of a compound having the structure:

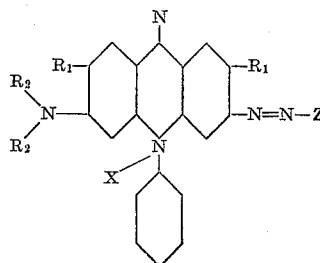


wherein R₁ and R₂ are radicals selected from the group

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consisting of hydrogen, methyl and ethyl radicals, X is an anion selected from the group consisting of chloride, bromide, iodide, fluoride, sulfate, bisulfate and nitrate, and Z is an aromatic radical selected from the group consisting of phenyl, naphthyl and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and alkoxy substituent groups, and at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea.

14. A bath for the electrodeposition of copper comprising an aqueous acidic solution of copper salts, a halide selected from the group consisting of chloride, bromide and iodide in an amount equivalent to about .003 gram/liter to about .020 gram/liter of chloride, and minor proportions of a compound having the structure:



wherein R₁ and R₂ are radicals selected from the group consisting of hydrogen, methyl and ethyl radicals, X is an anion selected from the group consisting of chloride, bromide, iodide, fluoride, sulfate, bisulfate and nitrate; and Z is an aromatic radical selected from the group consisting of phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and alkoxy substituent groups, and at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea.

15. A bath for the electrodeposition of copper comprising an aqueous acidic solution of copper salts and .0015-.05 gram/liter of at least one compound selected from the group consisting of Janus Green, Janus Blue, Janus Black, Janus Gray and dimethyl safranin azo dimethyl aniline, .001-.05 gram/liter of at least one compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea and a small amount of a wetting agent.

16. In a process of electrodepositing copper, the step which comprises electrolyzing an aqueous acidic solution of copper salts, said aqueous solution also containing .0015 to .05 gram/liter of a compound selected from the group consisting of Janus Green, Janus Blue, Janus Black, Janus Gray and dimethyl safranin azo dimethyl aniline, .001 to .05 gram/liter of a compound selected from the group consisting of thiourea, N-acetyl thiourea, N-propionyl thiourea, N-trifluoroacetyl thiourea, N-pentafluoropropionyl thiourea, N-furfuroyl thiourea, dimethyl thiourea and cyanoacetyl thiourea and a small amount of a wetting agent.

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