United States Patent

[11] 3,615,735

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[54] ELECTROLESS COPPER PLATING

18 Claims, 4 Drawing Figs.

[52] **U.S. Cl.** **106/1,**
117/47, 117/130, 117/160
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[50] **Field of Search** 106/1;
117/130, 130 E, 47 R, 32 S, 213, 160

[56] **References Cited**

UNITED STATES PATENTS

3,093,509	6/1963	Wein	117/35 X
3,134,690	5/1964	Eriksson	117/47 X
3,329,512	7/1967	Shipley et al.	106/1
3,436,233	4/1969	Jackson	106/1
3,475,186	10/1969	Dutkewych	106/1

FOREIGN PATENTS

401,083	1/1965	Japan	106/1

Primary Examiner—Lorenzo B. Hayes
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ABSTRACT: An electroless copper-plating solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde or a formaldehyde precursor preferably paraformaldehyde and a complexing agent for copper; said solution characterized by the addition of a member selected from the group consisting of a formaldehyde addition agent, a solution soluble salt of a Group VIII metal of the Periodic Chart of the elements, preferably a combination thereof and most preferably, the two in combination with an organic silicon compound. The copper plate deposited from the preferred solution is alloyed with the Group VIII metal cation and is distinguishable from prior art electroless copper deposits by substantially improved bending or tensile properties and a smoother, more highly reflecting surface appearance. The electroless copper-plating solution is capable of providing a rapid rate of copper deposition dependent upon the selection of the complexing agent and the stability of its chelate with copper without sacrifice in tensile or bending properties of the copper deposit.

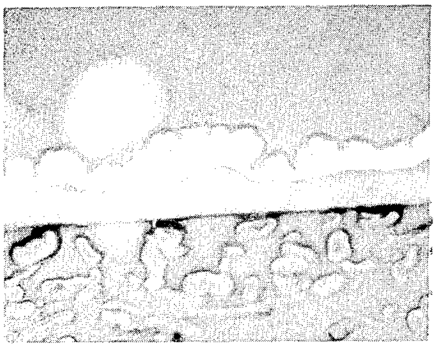


Fig. 1

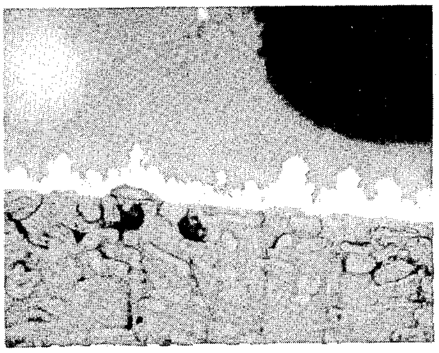


Fig. 2

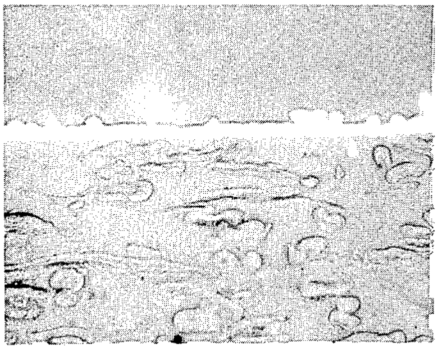


Fig. 3

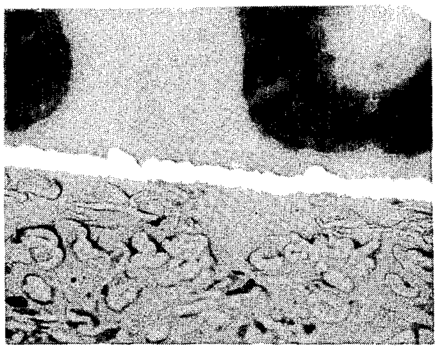


Fig. 4

ELECTROLESS COPPER PLATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a metal-depositing composition and more particularly, to an electroless copper-plating solution capable of providing an electroless copper deposit of improved appearance and bending or tensile properties.

2. Description of the Prior Art

Electroless copper deposition refers to the chemical plating of copper over clean catalytically active surfaces by chemical reduction in the absence of an external electric current. Such processes and compositions useful therefor are known and are in substantial commercial use. They are disclosed in a number of prior art patents, for example, U.S. Pat. Nos. 2,938,805; 3,011,920; 3,310,430; and 3,383,224.

Known electroless copper deposition solutions generally comprise four ingredients dissolved in water. They are (1) a source of cupric ions, usually a copper salt, such as copper sulfate (2) a reducing agent such as formaldehyde, or preferably, a formaldehyde precursor such as paraformaldehyde, (3) hydroxide, generally an alkali metal hydroxide and usually sodium hydroxide, sufficient to provide the required alkaline solution in which said compositions are effective, and (4) a complexing agent for copper sufficient to prevent its precipitation in alkaline solution. A large number of suitable complexing agents are known and described in the above cited patents, and also in U.S. Pat. Nos. 2,874,072; 3,075,856; 3,119,709; 3,075,855 and 3,329,512 all incorporated herein by reference. Known electroless plating solutions of the above type usually provide a plate which, if mechanically dense and strong, is somewhat brittle such that it can withstand only limited bending or thermal stress without fracture. This is not a substantial disadvantage where the electroless plate is of the order of millionths of an inch in thickness and is overplated with ductile electrolytic copper. However, where the entire desired thickness, typically 1 to 3 mils in an electrical application, is provided by electroless plating, limited ductility is a serious limitation.

One means of improving the bending or tensile characteristics of an electroless copper plate is described in U.S. Pat. No. 3,257,215 which discloses the addition of a cyanide or sulfur compound to a copper plating solution. An additional means is described in U.S. Pat. No. 3,310,430 which discloses the addition to a copper plating solution of a water-soluble compound of cyanide, vanadium, molybdenum, niobium, tungsten, rhenium, arsenic, antimony, bismuth, rare earth of the actinium series and rare earths of the lanthanum series. Certain members of the above groups, especially the vanadium compounds, provide significantly improved bending characteristics. The reason for this is not fully understood but it is stated in the patent that the agents poison the catalytic surface so as to promote formation and release of hydrogen gas at the catalytic surface, thereby inhibiting the inclusion of hydrogen in the deposit as it forms. It has been found that where a complexing agent or a bath formulation is used permitting rapid deposition of copper with rapid evolution of hydrogen gas at the surface, the improved ductility or bending characteristics frequently sacrificed or lost.

An alternative means for improving the tensile properties of an electroless copper deposit while simultaneously improving brightness and other appearance properties is described in U.S. Pat. No. 3,475,186 incorporated herein by reference. Improved properties are obtained by the addition of an organic silicon compound to an electroless copper solution where silicon is believed to be the active agent. A major advantage of this system is that the rate of copper deposition does not substantially affect tensile or bending properties. The manner in which silicon compound improves tensile properties is not fully understood but is believed to be due, at least in part, to a surface effect resulting in deposition of a smoother deposit having fewer structural defects as will be explained in greater detail below.

STATEMENT OF THE INVENTION

The subject invention is an improvement over that described in the above-noted patents and provides an electroless copper solution capable of depositing an electroless copper plate of improved bending or tensile properties. The copper solution is characterized by the addition of a member selected from the group consisting of a formaldehyde addition agent, a Group VIII metal salt of the Periodic Chart of the elements, preferably mixtures thereof, and most preferably, mixtures thereof with a solution-soluble organic silicon compound. The addition of either a formaldehyde addition agent or a Group VIII metal salt provides some improvement in tensile properties. Combination of the two provides an additive improvement in tensile properties. Combination of the two with a silicon compound provides a synergism that results in a substantial improvement in tensile properties. In addition to the above-noted improvement in tensile properties, electroless copper deposits from the solutions of this invention provide the advantages of excellent laydown properties, excellent solderability and improved smoothness, brightness, and overall appearance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A typical electroless copper solution in accordance with the invention will have additives having the following concentration ranges:

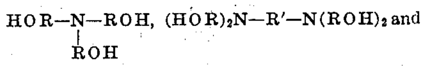
		Preferred
Copper salt	0.002 moles to saturation.	0.02 to 0.12 moles.
Formaldehyde	0.05 to 3.5 moles	0.1 to 1 moles.
Complexing agent	Minimum necessary to maintain copper in solution.	About 1 to 3 times the moles of cupric ion.
Free hydroxide	Sufficient to provide pH 10 or greater.	0.1 to 0.8 moles.
Silicon compound	Greater than 1 p.p.m.	5 to 250 p.p.m.
Formaldehyde addition agent.	Up to that amount that retards deposition.	0.1 to 1 times the moles of formaldehyde.
Group VIII metal salt	5 to 2,500 p.p.m	30 to 1,000 p.p.m.
Water	To 1 liter of solution	To 1 liter of solution.

It should be understood that the above concentration ranges are preferred, but not critical. Variations in the ranges are possible without departing from the scope of the invention. In most cases, additives may be added in an amount up to that amount that poisons the solution.

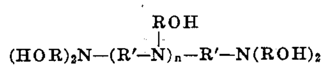
In the above formulations, any water-soluble copper salt heretofore used for preparing electroless copper deposition solutions may be used. For example, the halides, nitrate, acetate, sulfate and other organic and inorganic acid salts of copper are generally suitable as is known in the art. Copper sulfate is preferred.

Suitable complexing agents for the copper ions are well known in the art and include Rochelle salts, the sodium salts (mono-, di-, tri-, and tetrasodium salts) of ethylene diaminetetraacetic acid, nitrilotriacetic acid and its alkali metal salts, triethanolamine, modified ethylene diaminetetraacetic acids such as N-hydroxyethylenediaminetriacetate, hydroxyalkyl substituted dialkylene triamines such as pentahydroxypropyl diethylenetriamine, sodium salicylate, and sodium tartrate. Other complexing agents for copper ions are disclosed in U.S. Pat. Nos. 2,996,408; 3,075,855; 3,075,856; and 2,938,805.

The preferred class of complexing agents are those described in U.S. Pat. No. 3,329,512 noted above. They include hydroxyalkyl-substituted tertiary amines corresponding to one of the following structures:



$$\mathrm{HOR{-}}\underset{\underset{\mathrm{ROH}}{|}}{\mathrm{N}}\mathrm{{-}ROH},\quad \mathrm{(HOR)_2N{-}R'{-}N(ROH)_2}\text{ and}$$



$$\mathrm{(HOR)_2N{-}(R'{-}}\overset{\overset{\mathrm{ROH}}{|}}{\mathrm{N}}\mathrm{)_n{-}R'{-}N(ROH)_2}$$

where R is an alkyl group having from two to four carbon atoms, R′ is a lower alkylene radical and *n* is a positive integer. Examples of these complexing agents include tetrahydroxypropyl ethylene diamine, pentahydroxypropyl diethylene triamine, trihydroxypropylamine (tripropanolamine), trihydroxypropyl hydroxyethyl ethylene diamine, etc. As disclosed in said patent, the aforesaid amines are preferably used in small amounts in combination with other complexing agents and with certain polymers dispersed in solution such as cellulose ethers, hydroxyethyl starch, polyvinyl alcohol, polyvinylpyrrolidone, peptones, gelatin, polyamides and polyacrylamides.

The rate of copper deposition is, to some extent, dependent upon the selection of the complexing agent. Complexing agents such as pentahydroxypropyl diethylene triamine provide a fast rate of copper deposition, usually in excess of 1.0 mil per hour. Though the copper solutions of this invention provide copper deposits from solutions containing any of the known complexing agents for copper ions, they are particularly well adapted for copper solutions having complexing agents that provide a rapid rate of copper deposition.

The silicon additive is one that is soluble in the copper solutions and comprises the organic silicon compounds disclosed in the above-noted copending U.S. Pat. No. 3,475,186. It should be noted that many silicon compounds are not fully soluble in aqueous alkaline solutions and many are considered insoluble. However, the silicon, for purposes of the present invention, is required in solution in parts per million and silicon compounds termed insoluble in aqueous solution usually are soluble to the extent of a few parts per million and suitable for purposes of the present invention. For these silicon compounds considered insoluble in water, it is desirable to dissolve the compound in a solvent, such as alcohol, and add the solution to the electroless copper solution with agitation to form a dispersion or an emulsion. An excess of the silicon compound will be required to provide the necessary concentration of silicon compound in solution.

Exemplary of the silicon compounds within the scope of the invention are the silanes, such as silane itself, disilane, tetramethylsilane, trimethylethylsilane, tetraethylsilane, tetraphenylsilane, dimethyldichlorosilane, etc., and low to intermediate molecular weight polysiloxanes, such as silicone fluids, gums, and resins substituted with methyl-, ethyl-, vinyl-, phenyl-, chloro-, bromo-, methoxy-, hydroxy-, etc. Other suitable organic silicon compounds are disclosed in the above-noted U.S. Pat. No. 3,475,186.

The polysiloxanes are the least soluble silicon compounds in basic copper solutions, but are preferred because they provide the greatest increase in ductility and also enhance appearance by yielding a finer grained, more highly reflecting copper deposit. Of the polysiloxanes, the silicon fluids are most preferred. The solid polysiloxanes are preferably dissolved in a solvent such as alcohol and added to the copper solution.

The formaldehyde addition agent for purposes of this invention is one that may be added to solution in amounts sufficient to undergo reaction with formaldehyde to form a relatively unstable formaldehyde adduct without poisoning the solution. Reactions of this nature and formaldehyde addition agents are well known in the art and described in various publications, such as "Formaldehyde" by J. Frederick Walker, Reinhold Publishing Company, Third Edition 1964, pgs. 219–221, included herein by reference. Preferred formaldehyde addition agents are sulfites, bisulfites and phosphites of a metal cation that does not codeposit with copper and preferably, an alkali metal cation. Preferred formaldehyde addition agents are sodium sulfite, potassium bisulfite, and sodium phosphite.

The formaldehyde addition agent and formaldehyde or preferably, paraformaldehyde are reacted with each other to form the adduct prior to addition to the remaining components of the copper solution.

The Group VIII metal salts are preferably water-soluble inorganic salts of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum; salts of iron, nickel, and platinum being most preferred and salts of palladium being least preferred due to solution stability problems caused by palladium. Suitable salts include phosphates, nitrates, halides and acetates of the above metals. Iron, nickel and platinum to a greater extent and the remaining Group VIII metals to a lesser extent codeposit with copper to form a copper alloy. The Group VIII metal codeposits in a smaller proportion relative to copper present in the original electroless solution.

A wetting agent may be added to solution in accordance with art-recognized procedure.

The baths may be used at widely varying temperatures, e.g., at least room temperature and preferably up to about 140°F. As temperature is increased, it is customary to find an increase in the rate of plating. Temperature is not highly critical, and within the usual operating range, excellent, bright deposits of electroless copper having excellent tensile properties are obtained. Preferably, the bath is used without agitation.

In using the electroless copper solutions to plate metal, the surface to be plated should be catalytically active and free of grease and contaminating material. Where a nonmetallic surface is to be plated, the surface area to receive the deposit must first be sensitized to render it catalytically active as by the well-known treatment with an acidic aqueous solution of stannous chloride followed by treatment with a dilute aqueous acidic solution of palladium chloride. Alternatively, extremely good sensitization of nonmetallic surfaces is achieved by contact with an acidic colloidal formulation formed by the admixture of stannous chloride and a precious metal chloride, preferably palladium chloride, the stannous chloride being present in stoichiometric excess based upon the amount of precious metal chloride.

The invention will be better understood by reference to the following examples where all parts were plated using the following procedure:

a. Cut a phenolic substrate to a size of 2 inches by 2 inches.
b. Scrub part clean using an abrasive cleaner.
c. Rinse in cold water.
d. Immerse in a solution of a wetting agent identified as Shipley Conditioner 1159 at room temperature for 1 to 3 minutes.
e. Rinse in cold water.
f. Immerse in a colloidal stannic acid-palladium catalyst (identified as Cuposit Catalyst 6F) maintained at room temperature for 1 to 5 minutes.
g. Rinse in cold water.
h. Immerse in cuposit Accelerator 19 or a mild perchloric acid solution maintained at room temperature for 3 to 10 minutes.
i. Rinse in cold water.
j. Immerse in electroless copper solution maintained at between 110°and 130°F. for a period sufficient to provide a deposit of desired thickness not to exceed 3 hours.
k. Dry parts and examine deposit for appearance and ductility. Ductility is determined by peeling a copper deposit from the substrate and bending it through 180°in one direction, creasing at the fold, then returning it to its original position with pressing along the crease to flatten it. This cycle constitutes one bend. The procedure is repeated until the sample breaks at the crease. A sample unable to withstand at least one-half bend is considered brittle.

EXAMPLES 1–20

$CuSO_4 \cdot H_2O$	8.0 g.
Paraformaldehyde	7.5 g.
NaOH (25% solution by wt.)	50.0 ml.
Tetrahydroxypropylethylene diamine	12.0 g.
Triisopropanolamine	2.0 g.
Water	to 1 liter of solution

The above formulation, with various additives, is used to deposit electroless copper. Additive composition and deposit properties are set forth in the following table.

Ex. No.	Additives	Additive concentration	Deposit appearance	Deposit thickness in.×10^{-3}	Ductility (bends)
1	Control		Poor	0.50	Brittle.
2	$NiSO_4$	300 p.p.m	do	0.37	Do.
3	$Fe_2(SO_4)_3$	300 p.p.m	do	0.25	Do.
4	H_2PtCl_6	150 p.p.m	do	0.10	Do.
5	OsO_4	100 p.p.m	Fair	0.14	Do.
6	$CoSO_4$	300 p.p.m	Poor	0.36	Do.
7	Na_2SO_3	8 g./l	do	0.46	Do.
8	$NaHSO_3$	20 g./l	do	0.43	Do.
9	$Na_2HPO_3.5H_2O$	20 g./l	Fair	0.45	Do.
10	F-1-3514 [1]	200 p.p.m	do	0.34	½.
11	Methylvinylsilane	250 p.p.m	do	0.87	½.
12	SF-1138 [2]	200 p.p.m	do	0.46	½.
13	F-1-3514 [1] $NaHSO_3$	200 p.p.m 20 g./l	do	0.41	1.
14	Methylvinylsilane $NaHSO_3$	250 p.p.m 20 g./l	do	0.42	1.
15	F-1-3514 [1] H_2PtCl_6	200 p.p.m 150 p.p.m	Unstable	0.38	1.
16	Methylvinylsilane H_2PtCl_6	250 p.p.m 150 p.p.m	Good	0.22	½.
17	F-1-3514 [1] H_2PtCl_6 $NaHSO_3$	200 p.p.m 150 p.p.m 20 g./l	do	0.18	3.
18	Methylvinylsilane H_2PtCl_6 $NaHSO_3$	250 p.p.m 150 p.p.m 20 g./l	do	0.39	5.
19	SF-1138 [2] OsO_4 $NaHSO_3$	200 p.p.m 100 p.p.m 20 g./l	do	0.41	2.
20	SF-1138 [2] $NiSO_4$ $Na_2HPO_3.5H_2O$	200 p.p.m 300 p.p.m 20 g./l	do	0.35	3.

(1) F-1-3514 A silicone fluid believed to be a dimethylpolysiloxane-ethylene glycol copolymer available from the General Electric Co.

(2) SF-1138 A silicone fluid believed to be a dimethylpolysiloxane-polyalkylene oxide copolymer available from the General Electric Company.

In the above examples, a deposit was considered poor if it was dark in color and powdery in appearance. A fair deposit was one lighter in color though powdery in appearance. A good deposit was one having a fine-grained metallic copper appearance.

The improvements in tensile properties using the preferred electroless copper solutions of the present invention are readily apparent by reference to the above examples. Examples 2 to 6 illustrate copper containing only a Group VIII metal salt. Examples 7 to 9 illustrate copper solutions containing only a formaldehyde addition agent. No recordable improvement in properties is apparent using either of these additives in the above copper solution. Examples 10 to 12 illustrate the use of a silicon compound and show some improvement in both appearance and tensile properties. The combination of a silicon compound with either a Group VIII metal salt or a formaldehyde addition agent (examples 13 to 16) provides a somewhat greater improvement. Combination of the silicon compound with both a formaldehyde addition agent and a Group VIII metal salt (examples 17 to 20) provides substantial improvement in tensile properties as evidenced by the ductility in all cases in excess of two bends and in some cases, as high as five bends.

EXAMPLES 21-28

$CuSO_4 \cdot 5H_2O$	8.0 g.
Paraformaldehyde	7.5 g.
NaOH (25% solution by weight)	50.0 ml.
pentahydroxypropyldiethylenetriamine	20.0 g.
	to 1 liter of solution

The above formulation, with various additives, is used to deposit electroless copper. Additive composition and deposit properties are set forth in the following table:

Ex. No.	Additives	Additive concentration	Deposit appearance	Deposit thickness in.×10^{-3}	Ductility (bends)
21	Control		Poor	0.30	Brittle.
22	SF-1138 [2]	200 p.p.m.	Good	0.34	½.
23	$NiSO_4$	300 p.p.m.	Poor	0.46	½.
24	$NaHSO_3$	20g./l	Fair	0.43	½.
25	SF-1138 [2] $NiSO_4$	200 p.p.m. 300 p.p.m.	do	0.15	½.
26	SF-1138 [2] $NaHSO_3$	200 p.p.m. 20 g./l	Good	0.30	½.
27	$NiSO_4$ $NaHSO_3$	300 p.p.m. 20 g./l	Fair	0.41	½.
28	SF-1138 [2] $NaHSO_3$ $NiSO_4$	200 p.p.m. 20 g./l 300 p.p.m.	Good	.025	3.

Example 28, using an electroless copper composition containing a silicon compound, a formaldehyde addition agent and a Group VIII metal salt provides a copper deposit having a significant improvement in tensile properties. Formulations having one additive only show some improvement.

EXAMPLE 29

a) $CuSO_4 \cdot 5H_2O$	8.0 g.
b) Paraformaldehyde	7.5 g.
c) NaOH (25% solution by weight)	50.0 ml.
d) trihydroxypropylhydroxyethyl ethylene diamine	20.0 g.
e) SF-1138(2)	200 p.p.m.
f) $NiSO_4$	300 p.p.m.
g) $NaHSO_3$	20 g.
h) Water	to 1 liter of solution

Electroless copper deposited from the above solution was bright and withstood three and one-half bends. Copper deposited from a control solution free of additives e, f, and g had a poor appearance and was brittle.

EXAMPLE 30

a) $CuSO_4 \cdot 5H_2O$	8.0 g.
b) Paraformaldehyde	7.5 g.
c) NaOH (25% solution by weight)	50.0 ml.
d) Tetrahydroxypropylethylene diamine	15.0 g.
e) SF-1138(2)	200 p.p.m.
f) $NiSO_4$	300 p.p.m.
g) $NaHSO_3$	20 g.
h) Water	to 1 liter of solution

Copper deposited from the above solution was bright in color and capable of withstanding in excess of five bends. Copper deposited from a solution free of additives e, f, and g was found to be brittle.

EXAMPLES 31-38

$CuSO_4 \cdot 5H_2O$	8.0 g.
Paraformaldehyde	7.5 g.
NaOH (25% solution by weight)	50.0 ml.
Ethylenediaminetetraacetic acid	25.0 g.
Tetrahydroxypropylethylene diamine	6.0 g.
Water	to 1 liter of solution

The above formulation, with various additives was used to deposit electroless copper. Additive composition and deposit properties are set forth in the following table:

Ex. No.	Additives	Additive concentration	Deposit appearance	Deposit thickness in.×10⁻³	Ductility (bends)
31	Control		Poor	0.35	Brittle.
32	SF-1138[2]	200 p.p.m.	Fair	0.15	1½.
33	$NiSO_4$	300 p.p.m.	Poor	0.32	1.
34	$NaHSO_3$	20 g./l.	do	0.33	1.
35	SF-1138[2] $NiSO_4$	200 p.p.m. 300 p.p.m.	Fair	0.18	3.
36	SF-1138[2]	200 p.p.m.	do	0.24	1.
37	$NiSO_4$ $NaHSO_3$	300 p.p.m. 20 g./l.	Poor	0.27	Brittle.
38	SF-1138[2] $NiSO_4$ $NaHSO_3$	100 p.p.m. 100 p.p.m. 20 g./l.	Fair	0.19	4½.

Each additive, alone or in combinations of two, increased ductility substantially. However, the combination of the three additives (example 38) provided a substantially greater increase in ductility.

EXAMPLE 39

a) $CuSO_4 \cdot 5H_2O$	8.0 g.
b) Paraformaldehyde	7.5 g.
c) NaOH (25% solution by weight)	50.0 ml.
d) Sodium/potassium tartrate	25.0 g.
e) pentahydroxypropyl-diethylene triamine	6.0 g.
f) SF-1138(2)	200 p.p.m.
g) $NiSO_4$	300 p.p.m.
h) $NaHSO_3$	20 g./l.
i) Water	to 1 liter of solution

Copper deposited from the above solution was bright and withstood in excess of five bends. Copper deposited from the same solution free of additives f, g, and h was found to be brittle.

EXAMPLES 40–47

$CuSO_4 \cdot 5H_2O$	8.0 g.
Paraformaldehyde	7.5 g.
NaOH (25% solution by weight)	50.0 ml.
Sodium/potassium tartrate	40.0 g.
Water	to 1 liter of solution

The above formulation, containing various additives, was used to deposit electroless copper. Additive composition and deposit properties are set forth in the following table:

Ex. No.	Additive	Additive Concentration	Deposit Appearance	Deposit thickness in. × 10⁻³	Ductility (Bends)
40	Control		Fair	0.06	½
41	F-1-3514[1]	200 p.p.m.	do	0.10	5
42	$NiSO_4$	300 p.p.m.	do	0.09	3
43	$NaHSO_3$	20 g./l.	do	0.09	1
44	F-1-3514[1] $NiSO_4$	200 p.p.m. 300 p.p.m.	Good	0.13	3
45	F-1-3514[1] $NaHSO_3$	200 p.p.m. 20 g./l.	do	0.09	5
46	$NiSO_4$ $NaHSO_3$	300 p.p.m. 20 g./l.	do	0.34	1½
47	F-1-3514[2] $NiSO_4$ $NaHSO_3$	200 p.p.m. 300 p.p.m. 20 g./l.	do	0.24	5

In the particular copper solution used, the addition of any additive alone was effective. However, use of the silicon compound in combination with the nickel sulfate and the sodium hypophosphite produced a substantial improvement in ductility. In example 47, there was no indication of fracture of the copper deposit following the fifth bend.

EXAMPLES 48–54

$CuSO_4 \cdot 5H_2O$	8.0 g.
Paraformaldehyde	7.5 g.
NaOH (25% solution by weight)	50.0 ml.
Tetrahydroxypropyl-ethylene diamine	12.0 g.
Triisopropanolamine	2.0 g.
Water	to 1 liter of solution

The above formulation containing various additives was used to deposit electroless copper. Additive compositions and deposit properties are set forth in the following table:

Ex. No.	Additive	Additive concentration	Deposit appearance	Ductility (bends)
48	Control		Poor	Brittle.
49	F-68[3]	350 p.p.m.	Fair	½.
50	F-68[3] SF-1138[2]	350 p.p.m. 200 p.p.m.	Good	½.
51	F-68[3] SF-1138 $NaHSO_3$ $NiSO_4$	350 p.p.m. 200 p.p.m. 20 g./l. 300 p.p.m.	do	5.
52	F-68[3] SF-1138[2] $NaHSO_3$ H_2PtCl_6	350 p.p.m. 200 p.p.m. 20 g./l. 150 p.p.m.	do	5.
53	F-68[3] SF-1138[2] $NaHSO_3$ $CoSO_4$	350 p.p.m. 200 p.p.m. 20 g./l. 300 p.p.m.	do	4.
54	F-68[3] SF-1138[2] $NaHSO_3$ $Fe_2(SO_4)_3$	350 p.p.m. 200 p.p.m. 20 g./l. 300 p.p.m.	do	3.

(3) F–68. A wetting agent

EXAMPLE 55

$CuSO_4 \cdot 5H_2O$	8.0 g.
Formaldehyde	7.5 g.
NaOH (25% solution by weight)	50.0 ml.
Tetrahydroxypropyl-ethylene diamine	12.0 g.
Triisopropanolamine	2.0 g.
SF-1138(2)	200 p.p.m.
$NiSO_4$	300 p.p.m.
H_2PtCl_6	150 p.p.m.
$NaHSO_4$	20 g./l.
Water	to 1 liter of solution

The electroless copper deposited from the above formulation was capable of withstanding in excess of five bends.

Deposits from representative examples were analyzed for the codeposition of the Group VIII metal cation with results as set forth in the following table:

Ex. No.	Cu Conc. (%)	Ni Conc. (%)	Pt. Conc. (%)
17	97.85	—	1.83
47	98.65	0.170	—
51	99.35	0.056	—
55	97.07	0.036	2.48

From the above table, it can be seen that the Group VIII metal codeposits with copper to form an alloy.

Though not wishing to be bound by theory, it is believed that one of the major causes of improved tensile and bending properties is increased smoothness of deposit. Increased smoothness is shown by reference to the following examples:

	56	57	58	59
$CuSO_4 \cdot 5H_2O$ (g.)	8.0	8.0	8.0	8.0
Paraformaldehyde (g.)	7.5	7.5	7.5	7.5
NaOH (25% solution)	50.0	50.0	50.0	50.0
Tetrahydroxypropyl-ethylene diamine				

(g.)	12.0	12.0	12.0	12.0
Triipropanolamine (g.)	2.0	2.0		2.0
Water		to 1 liter of solution		
SF-1138 (p.p.m.)	—	200	200	200
$NaHSO_3$ (g.)	—	—	20	20
H_2PtCl_6 (p.p.m.)	—	—	150	—
$FeSO_4$ (p.p.m.)	—		—	300

Electroless copper was deposited from the above formulations. Samples having the deposited copper were cut in cross section and photomicrographs taken thereat. The results are represented in the drawings where FIG. 1 shows a cross section of the copper deposited from the formulation of example 56; FIG. 2 shows a cross section of the copper deposited from the formulation of example 57; FIG. 3 shows a cross section of the copper deposited from the formulation of example 58; and FIG. 4 shows the cross section of the copper deposited from the formulation of example 59. FIGS. 3 and 4 show substantially smoother deposits than those of FIGS. 1 and 2. The rough deposit in FIGS. 1 and 2 are believed to be more readily fractured by bending due to the troughs in the deposit which act as the weakest point of the deposit.

Copper solutions of this invention find utility for all purposes for which electroless copper solutions have heretofore been used including both decorative and industrial applications. They are especially useful for the formation of printed circuit boards where the deposits act as ductile conductors and as ductile connectors plated onto the walls of through-holes. The formation of a printed circuit board having conductive through-holes is illustrated in the following example.

EXAMPLE 60

a. Sandblast one side of a phenolic substrate leaving the second surface smooth.
b. Drill through-holes at desired locations.
c. Silk screen a reverse image of a printed circuit pattern onto the roughened surface of the phenolic substrate using an epoxy resin.
d. Immerse in a colloidal palladium sensitizing solution maintained at room temperature for a period of 5 minutes.
e. Immerse in a stripping solution comprising 10 grams of copper chloride, 100 grams of 37 percent hydrochloric acid and water to 1 liter maintained at room temperature for 6 minutes.
f. Deposit electroless copper of example 18 with copper deposition taking place on the walls of the through-holes and on the roughened surfaces in the image pattern. No copper deposition takes place on the epoxy resist or on the smooth sides of the plastic laminate.

It should be understood that various changes may be made in the embodiments described above without departing from the spirit and scope of the invention as defined by the following claims.

1. In an aqueous electroless copper-plating solution comprising a source of cupric ions, hydroxyl radicals, a source of formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of at least two members selected from the group consisting of a formaldehyde addition agent in an amount of from at least 0.1 moles times the moles of formaldehyde to that amount that restricts copper deposition, a solution soluble salt of a Group VIII metal of the Periodic Chart of the elements in an amount of from 5 to 2,5000 parts per million parts of solution and an organic silicon compound in solution in an amount of from 1 part silicon per million parts of solution to that amount that restricts deposition of copper from solution.

2. In an electroless copper-plating solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of a combination of (a) an organic silicon compound selected from the group of silanes and polysiloxanes in an amount of from 5 to 250 parts of silicon in solution per million parts of solution, (b) a formaldehyde addition agent selected from the group of alkali metal sulfites, bisulfites and phosphites in an amount of from 0.1 to 1 times the moles of formaldehyde in solution and (c) a solution-soluble salt of a member selected from the group of iron, nickel and platinum salts in an amount of from 5 to 2,500 parts per million parts of solution, said solution soluble salt having an anionic portion noninterfering with the plating solution.

3. The copper-plating solution of claim 2, having as additives an organic silicon compound and a formaldehyde addition agent.

4. The copper-plating solution of claim 2, having as additives an organic silicon compound and a solution soluble salt of a Group VIII metal of the Periodic Chart of the elements.

5. The copper-plating solution of claim 2, having as additives an organic silicon compound, a formaldehyde addition agent and a solution soluble salt of a Group VIII metal of the Periodic Chart of the elements.

6. The copper-plating solution of claim 5 having the following formation:

copper salt	0.02 to 0.12 moles
formaldehyde	0.1 to 1 moles
complexing agent	1 to 3 times the moles of cupric ion
free hydroxide	0.1 to 0.8 moles
silicon compound	5 to 250 ppm
formaldehyde addition agent	0.1 to 1 times the moles of formaldehyde
Group VIII metal salt	30 to 1000 ppm
water	to 1 liter of solution

7. The copper solution of claim 5 where the organic silicon compound is selected from the group consisting of silanes and polysiloxanes.

8. The copper solution of claim 7, where the organic silicon compound is a polysiloxane.

9. The copper solution of claim 7, where the silicon compound is added to the copper solution by dissolution in a solvent and addition of the solution to the copper solution.

10. The copper solution of claim 5, where at least a portion of the complexing agent is mixture of complexing agents with one member of the mixture comprising a hydroxyalkyl substituted teritary amine.

11. The copper solution of claim 10 where the complexing agent is in combination with a member selected from the group of cellulose ethers, hydroxyalkyl starch, polyvinyl alcohol, polyvinyl pyrrolidone, peptones, gelatin, polyamider and polyacrylamides.

12. In an aqueous electroless copper-plating solution comprising a source of cupric ions, hydroxyl radicals formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of a small but effective amount of an organic silicon compound in an amount of from 1 part silicon in solution per million parts of solution to that amount that restricts deposition of copper from solution and at least one member selected from the group consisting of a formaldehyde addition agent selected from the group consisting of alkali metal sulfites, bisulfites and phosphites in an amount of from 0.1 moles times the moles of formaldehyde to that amount that restricts copper deposition and a solution soluble salt of a Group VIII metal selected from the group of iron, nickel and platinum in an amount from 5 to 2,500 parts per million parts of solution.

13. The copper-plating solution of claim 12, having as additive the organic silicon compound and a combination of the formaldehyde addition agent and the Group VIII metal salt.

14. The copper solution of claim 13 having the following formulation:

copper salt	0.02 to 0.12 moles
formaldehyde	0.1 to 1 moles
complexing agent	1 to 3 times the moles of cupric ion
free hydroxide	0.1 to 0.8 moles
silicon compound	5 to 250 ppm
formaldehyde addition agent	0.1 to 1 times the moles of formaldehyde
Group VIII metal salt	30 to 1000 ppm
water	to 1 liter of solution

15. The copper solution of claim **14**, where the Group VIII metal salt is selected from the group consisting of $NiSO_4$, $Fe_2(SO_4)B3$ and H_2PtCl_6.

16. The copper solution of claim **14**, where the formaldehyde addition agent is selected from the group consisting of Na_2SO_3, $NaHSO_3$ and Na_2 $HPO_3 \cdot 5H_20$.

17. The copper solution of claim **14** where the organic silicon compound is a dimethylpolysiloxane-polyalkylene oxide copolymer.

18. In an electroless copper-plating solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of a combination of at least two members of the group consisting of an organic silicon compound, a formaldehyde addition agent and a Group VIII metal salt of the Periodic Chart of the elements, said organic silicon compound and said Group VIII metal salt being present in the solution in minor amount sufficient to improve ductility of a copper deposit and said formaldehyde addition agent being present in an amount of from 0.1 moles per mole of formaldehyde to that amount that restricts deposition.