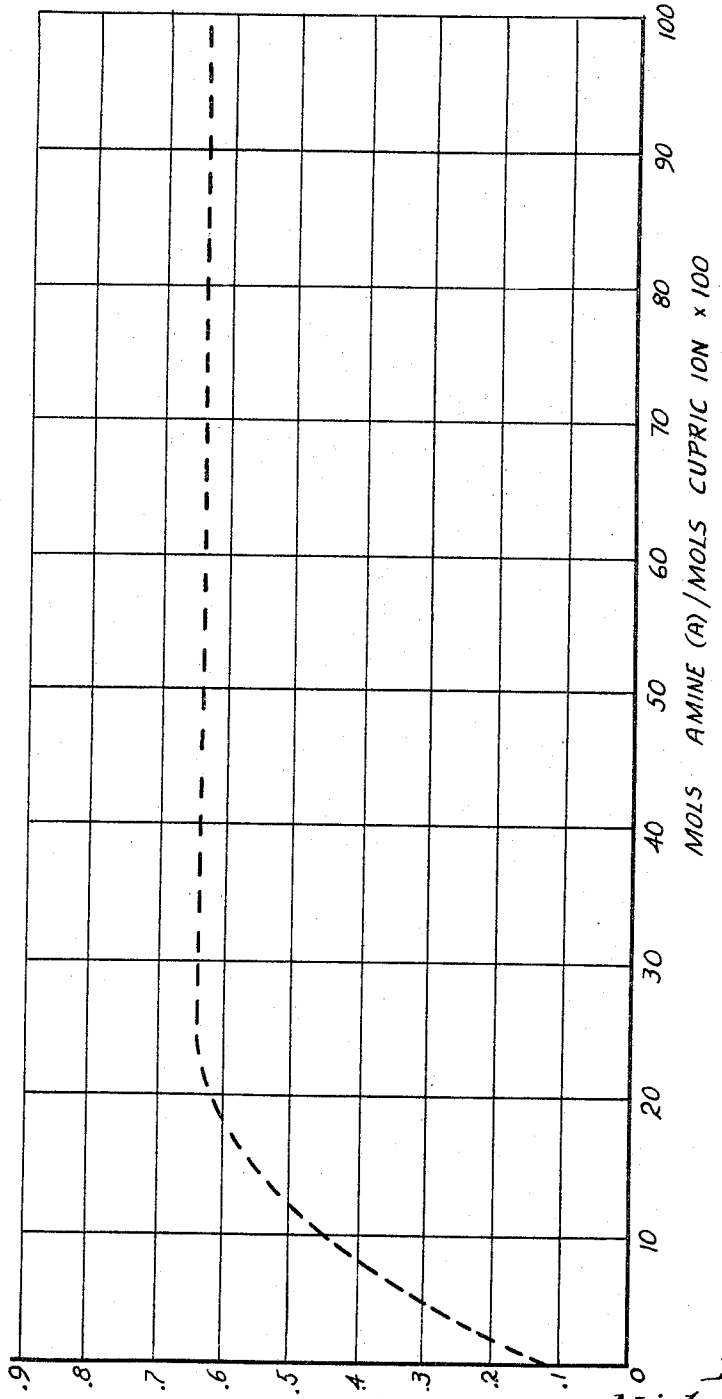
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CHEMICAL DEPOSITION OF COPPER AND SOLUTIONS THEREFOR

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CHEMICAL DEPOSITION OF COPPER AND SOLUTIONS THEREFOR

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This invention relates to electroless copper deposition and more particularly to the provision of improved methods of providing such deposits and improved copper deposition solutions therefor. Electroless copper deposition refers to the chemical deposition on a receptive surface of an adherent copper coating in the absence of an external electric source. Such deposition is useful, for example, in the manufacture of printed electric circuits, as linings for wave-guide cavities, as an initial conductive coating in electroforming, and for decoration. This application is a continuation-in-part of application Ser. No. 207,434, filed July 3, 1962, now abandoned.

A number of electroless copper deposition processes and solutions have been heretofore known and are partially summarized, for example, in United States Patent No. 2,938,805. Such solutions comprise an aqueous solution of cupric ions, formaldehyde, hydroxide, and a complexing agent to render the cupric ions soluble in alkaline solution. Deposition occurs by the reduction of cupric ion to copper by the formaldehyde, initiated by the presence of a suitable catalytic surface, for example various metal surfaces or catalyzed plastic as disclosed in the above-mentioned patent or as further disclosed in United States Patent No. 3,011,920.

Prior electroless copper processes and solutions have had a number of limitations. The quality or rate of deposit, or both, have been less than is sometimes desirable. Known solutions having a relatively high initial plating rate have generally given inferior quality and the rate declines sharply, and sometimes ceases altogether, typically within one or two to about 15 minutes after deposition commences. Consequently, it has been the usual practice to employ the slower, more stable depositing solutions to provide an initial plate of a few millionths to about 100 millionths of an inch in thickness, this chemical deposit being built up to the desired thickness by overplating with electrolytic copper. Most often copper plating thicknesses of 1 to 3 mils or more are desired and the subsequent electroplating necessitates a substantial investment in electroplating equipment and additional steps. The only known solution and process of electroless copper deposition heretofore capable of producing thicknesses of a mil or more of quality copper have been quite slow, requiring more than 24 hours of deposition at room temperature to plate 1 mil.

It is the principal object of the present invention to provide improved methods of depositing electroless copper on catalytic surfaces and improved deposition solutions therefor. An important further object is to provide solutions and processes capable of depositing metallic copper to a thickness of at least 1 mil at the rate of at least 0.25 mil per hour and preferably higher at any suitable operating temperature. "Metallic copper" as herein employed refers to electroless plating which has generally the appearance and properties of metallic copper, in distinction to dark, rough or poorly adherent coatings of unacceptable quality.

A still further object of the present invention is to provide processes and solutions therefor which not only provide relatively thick electroless copper platings but which provide means for controlling the ductility and brightness or reflectivity thereof. Ductility as herein employed refers to the degree of brittleness of the resulting plate which can be qualitatively ascertained by microscopic inspection, the more smooth coatings being generally more ductile, and which can be more specifically determined for comparison by measuring the temperature at which cracks appear in an electroless copper plate over a plastic substrate. This is believed to be influenced and at least partially determined by the nature of the grain structure of the deposited copper, generally laminar crystals being more ductile than vertically columnar crystals which will crack or shatter at lower temperatures due to the stresses introduced by the differential rates of expansion. Ductile plates are also generally softer than brittle plates.

According to the present invention, it has been discovered that the inclusion of certain polymers dispersible in alkaline solutions of the above type, namely, those containing formaldehyde and a complexed cupric ion in basic hydroxide solution, provides solutions and processes with substantial benefits. More particularly, the polymers act as brighteners which improve the quality of the deposit, provide finer grain structure in the deposit, provide greater quality for extended deposition, sometimes provide deposits with improved bond strength to copper, provide baths with improved stability, and permit greater variation in relative concentrations of other ingredients. Solutions according to the present invention will deposit bright adherent coatings for at least several hours. Furthermore, the polymers help to regulate the rate of deposit in the manner to be more fully explained hereinafter.

It has been further discovered that inclusion of hydroxyalkyl substituted amines as at least one complexing agent for the cupric ions in solutions containing the polymers is especially beneficial in enhancing the rate and extent of deposit, often providing a synergistic effect. Most of these amines are known complexing agents for cupric ions, but, without the polymer, usually provide deposits of very limited or sub-standard quality, especially under extended deposition. While some of them provide, without polymer, a relatively high initial rate of deposit, the rate and quality rapidly falls. In the absence of the polymers, such amines are incapable of providing heavy copper deposits of as much as 1 mil or more of acceptable copper. In the presence of the polymers, however, both the quality and high initial rate can be maintained for periods measured in hours to provide total copper thicknesses on the substrate of at least one mil and generally of at least several mils, thereby providing thick practical coatings of quality copper in feasibly short periods. Electroplating can therefore be eliminated where desired. Furthermore, while the polymers with complexing agents other than those herein disclosed usually retard the rate of deposit, with the amines, they often further enhance the initial as well as the sustainable rate of deposit.

In electroless copper compositions of the type described above, the complexing agent complexes cupric ions generally on a mole for mole basis although it is usually preferred to employ an excess of complexing agent. If desired, the above amines may be used as the sole complexing agent but the rate and quality aspects are obtained, as illustrated hereinafter, by small quantities in admixture with other complexing agents. The amines are preferred in amounts, in mol ratio to cupric ions, of at least .08 to 1 and more preferably of at least 0.3 to 1.

The polymers useful herein must be dispersible in the above alkaline solution, preferably as a colloidal solution, in the quantities required. Useful polymers include cellulose ethers hereinafter described, hydroxyethyl starch, polyvinyl alcohol, polyvinylpyrrolidone and copolymers thereof, peptones, gelatine, polyamides, and polyacryl-

amides and copolymers thereof. Molecular weight of the polymers does not appear to be critical, some of the above materials having been used in liquid form and others in the form of polymers with very high molecular weight. Research indicates that surfactant properties, ability to increase viscosity of water solutions, and the presence of a secondary or tertiary nitrogen atom, or the presence of hydroxyl groups, are important features.

The amount of the addition of such polymer to the electroless plating solution is not critical, from a few parts per million (e.g., .002 gram per liter) up to several thousand parts per million (e.g. about 3.0 grams per liter) are useable, the smaller quantities providing some benefit and the larger quantities being useful although undesirably increasing solution viscosity. Preferred amounts are from about 10 parts per million (.01 g./l.) to about 600 parts per million (0.6 g./l.) while the most preferred portions are from about 20 parts per million to about 100 parts per million.

The above polymers are believed to improve solution performance solely through physical action, principally as a dispersing agent for the hydrogen gas generated at the substrate surface and by surfactant action at the substrate surface to prevent formation of momentarily stagnant boundary layers which may become starved in one or more reactant thereby promoting formation and deposition of the undesirable cuprous oxide. They also may possess a limited complex formation capacity which may affect the mechanism whereby cupric ion is released from its complex and reduced to the metal at the substrate surface.

The substituted amine complexing agents, useful in combination with said polymers are hydroxyalkyl substituted tertiary amines soluble in said bath and include substituted monoamines, substituted lower alkylene diamines, or substituted poly-lower alkylene polyamines in which the amine nitrogen atoms are substituted with hydroxy alkyl groups having from two to four carbon atoms, inclusive. These amines have the following structures:

$$HOR—N(ROH)—ROH, \quad (HOR)_2N—R'—N(ROH)_2$$

or

$$(HOR)_2—N(ROH)—(R'—N)_n—R'—N(ROH)_2$$

wherein R is an alkyl group having from two to four carbon atoms, inclusive, and in which a majority are preferred as propyl radicals, R' is a lower alkylene divalent radical, and *n* is a positive integer. The size of the integer *n* is not important since the structure is essentially repeating and does not decrease solubility within broad limits with increasing molecular weight. Such materials are currently available as ethylene diamines and low polymers thereof such as diethylene triamine. R' does not take part in the reaction and is unimportant provided it is not adversely reactive in the bath and providing it does not render the substituted amine insoluble. While it is preferred that all N substituents be —ROH, a minor proportion of the substituents may be —RCOOH or inert radicals such as alkyl or alkoxy radicals, if desired.

The above amines substituted with hydroxybutyl groups have limited solubility in the bath, but, when used in such small quantities in admixture with other such amines, for example, hydroxypropyl or hydroxyethyl amines, they have a marked and beneficial effect in producing far softer and more ductile platings. They are especially useful in controlling the hardness and ductility of the resulting coatings. Similar control can be obtained by mixing the above resins or by selecting amines as hereinafter illustrated.

Exemplary solutions according to the present invention are given in the following examples of Table I:

TABLE I

Ingredient	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
$CuSO_4 \cdot 5H_2O$, mols/l.	.04	.04	.04	.04	.04
HCHO, mols/l.	.24	.32	.16	.24	.24
Rochelle Salts, mols/l.	.12	.12	.12	.12	.12
NaOH, mols/l.	.24	.16	.32	.24	.24
Hydroxyethyl Cellulose, g./l.	.30	.30	.30	.30	.15
Optional:					
N,N,N'N' tetrakis (2 hydroxypropyl) ethylenediamine, g./l.	.20	.20	.20	.20	
Sodium Carbonate, mols/l.	.025	.025	.025	--------	--------

All of the above concentrations are in mols per aqueous liter excepting the diamine and cellulose which are given in grams per liter. The hydroxide in the concentrations stated are for free hydroxide not combined with acid or cupric salts present so as to be free to enter into the reduction reaction. Thus the concentrations exclude amounts of hydroxide used to neutralize acids and acid salts, for example twice the molar equivalent of acidic copper salts. Examples 1–4 are for preferred use at room temperature while Example 5 is for preferred use at elevated temperature, for example at 90° F. In the above solutions, copper sulfate is a source of cupric ion, the Rochelle salts are complexing agents for the cupric ions in basic solutions, the hydroxide provides the desired pH and the formaldehyde is the reducing agent. Other suitable copper salts, complexing agents therefore, and alkali can be employed as is well known and illustrated in the following examples. For example, .045 mol per liter of the tetrahydrated, tetra sodium salts of ethylenediamine tetraacetic acid may be substituted for the Rochelle salts in the above examples. The formaldehyde can be the dissolution product of paraformaldehyde if desired, the formaldehyde concentration being calculated on the assumption that all the paraformaldehyde is reconverted to formaldehyde on dissolution. Other known ingredients such as sodium acetate or sodium carbonate can be employed if desired. The total amount of complexing agent is not critical provided sufficient is used to prevent precipitation under the alkaline conditions employed, generally at least 1 mol, and is preferably from 2 to 5 mols total complexing agent per mol of cupric ion employed. At least 2 and preferably 4 or more mols each of formaldehyde and free hydroxide are employed per mol of cupric ions, the concentration of each being preferably held below about 0.6 molar.

The hydroxyethyl cellulose used in the above examples is understood to have a degree of substitution approximating 2 and is a lower viscosity grade, giving 75–150 cps. (Brookfield) in 5% aqueous solution at 25° C. Higher viscosity materials are available, are useful herein, and are, in some instances, preferred. Materials having a degree of substitution approximating 1 have also been successfully employed.

In the cellulose ethers illustrated in the above examples, hydroxyethyl cellulose is preferred. Other hydroxy lower alkyl and alkyl cellulose ethers can be used. While they can be substituted for the cellulose in the above examples, the examples are considered optimum for the preferred hydroxyethyl material and some adjustment of concentrations may be necessary for optimum results with a different material. And, while hydroxyethyl cellulose containing hydroxyethyl radicals as the sole ether radical is preferred, additional ether radicals may also be present, for example carboxymethyl, hydroxyethyl cellulose and ethyl, hydroxyethyl cellulose.

Additional polymers and amine complexing agents are illustrated in the following Examples 6–44 which also illustrate the variation in plating rate obtained. While the plating rates are given for plating at room temperature (70–75° F.) and in 10^{-6} inches in 10 minutes, it should be appreciated that higher temperatures, for example 100–120° F., or higher, increases the rate of deposition,

in many instances, severalfold. Temperatures as high as 150° F. can also sometimes be employed. And while some of the plating rates for compositions omitting the polymers herein disclosed indicate a high initial plating rate, it should be understood that the plating rate thereof and the quality of the copper deposited decline sharply after a few minutes of deposition and may cease altogether, or provide a copper plating of unacceptable quality. Plating rates for examples containing the polymers remain substantially constant for periods up to several hourfs. Amounts are given in grams per aqueous liter unless otherwise indicated, excepting that polymer amounts are stated in parts per million by weight.

In the following examples, the polymers and amine complexing agents have the following identifications:

POLYMERS

(1) HEC—hydroxyethyl cellulose, e.g., "METHOCEL," "NATROSOL" or "CELLOSIZE," of Dow Chemical Corp., Hercules Powder Co., or Union Carbide Corp., respectively, specifically Cellosize 100 M and Natrosol 250 MR.
(2) "CERON CN"—hydroxyethyl starch of Hercules Powder Co.
(3) PVP—polyvinyl pyrrolidone, e.g., LUVISCOL (K–30) of the BASF Chemicals Co., or "ALBIGEN A" of General Aniline and Film Corp.
(4) PVP/VA—copolymers of vinyl pyrrolidone/vinyl acetate, available from General Aniline and Film Corp. in mol ratios 30/70 to 70/30; specifically employed in the examples given: 50/50.
(5) "Bacto-peptone"—a peptone obtained from DiFCO of Denver, Colo.
(6) Gelatin—a granular grade sold by Matheson, Coleman & Bell as a culture medium.
(7) "CYANAMER–P–250"—polyacrylamide from the American Cyanamid Corp.
(8) "CYANAMER–P–26"—a polyacrylamide copolymer from the American Cyanamid Corp.
(9) "RETEN 205 MH"—modified polyacrylamide from Hercules Powder Co.
(10) "RETEN 210"—same as No. 9.
(11) "RETEN 763"—same as No. 9.
(12) "CMHEC 43L"—carboxymethyl hydroxyethyl cellulose from Hercules Powder Co.
(13) "VERSAMIDE 140"—a polyamide from General Mills.
(14) PVA—polyvinyl alcohol, ELVANOL 50–42 of Du Pont.

AMINE COMPLEXING AGENTS

(A) Tetrahydroxypropyl ethylene diamine
(B) Pentahydroxypropyl diethylene triamine
(C) Trihydroxypropyl amine (tripropanolamine)
(D) Trihydroxypropyl hydroxyethyl ethylene diamine
(E) Dihydroxypropyl dihydroxyethyl ethylene diamine
(F) Trihydroxyethylamine
(G) Tetrahydroxybutyl ethylene diamine (triethanolamine)
(H) Diethanol glycine

OTHER INGREDIENTS

(1) ROCH—Rochelle salts
(2) EDTA—tetra-sodium ethylene diamine tetra-acetic acid, di-hydrate

In each of Examples 6–39 below, the basic formulation, in addition to the complexing agents (listed as "chelate") and polymers, specified, includes the following in grams per aqueous liter:

BASE FORMULA

$CuSO_4 \cdot 5H_2O$	16.7
HCHO	11.1
NaOH	13.0

TABLE II

Additional Ingredients	Example							
	6	7	8	9	10	11	12	13
Chelate:								
ROCH	40	40	40			40		
(A)			4	22	22	4	22	22
Polymer:								
(1) p.p.m.		50			50	50		
(2) p.p.m.							50	
(3) p.p.m.								20
Rate	35	20	75	75	120	120	115	115

TABLE III

Additional Ingredients	Example							
	14	15	16	17	18	19	20	21
Chelate: (A)	22	22	22	22	22	22	22	22
Polymer:								
(4) p.p.m.	25							
(14) p.p.m.		50						
(5) p.p.m.			50					
(6) p.p.m.				50				
(7) p.p.m.					50			
(8) p.p.m.						50		
(9) p.p.m.							50	
(10) p.p.m.								50
Rate	100	95	95	120	90	100	120	95

TABLE IV

Additional Ingredients	Example							
	22	23	24	25	26	27	28	29
Chelate:								
(A)	22	22						
(C)			22	22				
(D)					22	22		
(E)							22	
(F)								22
Polymer:								
(11) p.p.m.	50							
(12) p.p.m.		50						
(1) p.p.m.				20		20	20	20
Rate	95	95	25	150	40	100	105	85

TABLE V

Additional Ingredients	Example					
	30	31	32	33	34	35
Chelate:						
(G)						
(H)		22				
EDTA			33	33	33	33
(A)	22			3	3	3
Polymer:						
(1) p.p.m.		20				
(10) p.p.m.				50		
(2) p.p.m.					50	
(12) p.p.m.						50
(13) p.p.m.	40					
Rate	73	80	65	80	75	70

TABLE VI

Additional Ingredients	Example			
	36	37	38	39
Chelate:				
(B)	22	22	22	22
(G)				0.6
Polymer:				
(9) p.p.m.		40	20	20
(11) p.p.m.			20	20
Rate	75	100	85	50

Examples 38 and 39 above illustrate the effects of using hydroxybutyl and mixed polymers to control ductility and brightness of deposit. Example 38 is the brightest copper while Example 39 is the most ductile; a copper plate thereof on a flat ABS plastic substrate withstanding 230° F. without cracking, a temperature at which the plastic exhibited heat distortion. Example 38 withstood about 180° F. Gelatin added to either of Examples 38 or 39 provides even softer deposits of bright copper. Selection of amine also affects softness and ductility, amine (B) deposits being generally softer than amine (A) deposits.

A particularly fast, quality copper plating in excess of 1 mil per hour at 75° F. is given in Example 40 below.

Example 40

$CuSO_4 \cdot 5H_2O$	20
HCHO	13
NaOH	15.5
Chelate:	
(D)	16
(B)	8
Polymer, p.p.m.:	
Cellosize 100 M	100
Rate	170

Further examples illustrating the large quantities of cupric ion which can be used with the present invention are given in Table VII below.

TABLE VII

Ingredient	Example		
	41	42	43
$CuSO_4 \cdot 5H_2O$	32	43	65
HCHO	24	30	45
NaOH	30	37	45
Polymer (9), p.p.m.	50	50	50
Chelate:			
(A)	25	25	25
(B)	11	22	45
(D)	6	12	24
Rate	120	120	130

In each of Examples 41 to 43, omission of the polymer produces a plate of markedly inferior quality and lesser rate and total obtainable thickness.

Finally, to illustrate that even relatively small amounts of amine substantially affect rate, the figure attached hereto is a plot of the rate versus the Amine (A) content, expressed as mol ratio of (A) to cupric ion, times 100 (100 Amine/Cu^{++}), in the following formulation of Example 44.

Example 44

$CuSO_4 \cdot 5H_2O$	16.7
HCHO	11.0
NaOH	13.0
ROCH	40.0
Polymer (1), p.p.m.	20
Water to make 1 liter.	
Amine (A)	As specified

As illustrated above, cupric ion concentration is not critical and can be increased by means of the present invention. Initial amounts between about 0.04 to 0.08 mol per liter are preferred. As little as 0.01 is usable at elevated temperature while, as shown in Example 43, amounts of 0.25 mol per liter and higher can be employed although of little effect on rate.

The examples also illustrate that, while the amines are useful alone, they can be used in admixture with other chelates. Additional known examples of such secondary chelates include salicylic acid, glycerine, gluconic acid, glycolic acid and the solution soluble alkali metal salts thereof. They are referred to as "secondary" even when present in predominate amount because the effect and performance is primarily determined by the amine.

Where desired, chemical or other stabilization can be employed, for example, aeration as disclosed in United States Patent No. 2,938,805.

It should be understood that the foregoing description is for the purpose of illustration and that the invention includes all modifications within the scope of the appended claims.

We claim:

1. For electroless plating of copper, a basic aqueous bath containing a source of cupric ions, a complexing agent for said ions to render them soluble in alkaline solution, hydroxyl radicals, and formaldehyde, said bath being characterized by additionally containing in dispersed, colloidally soluble form and as a non-reactive polymer additive, a cellulose ether selected from the group consisting of lower alkyl cellulose and hydroxy-lower alkyl cellulose; hydroxy-lower alkyl starch, polyvinyl pyrrolidone, polyvinyl alcohol, gelatin, a peptone, a polyamide which is the condensation product of a dimeric fatty acid with a polyamine, polyacrylamide, or mixtures thereof, said polymer being present in an amount sufficient to improve the quality and performance of said bath.

2. A bath according to claim 1 wherein said polymer is present in an amount between about 0.002 and 3 grams per liter.

3. A bath according to claim 1 wherein said bath is further characterized in that at least a portion of said complexing agent for said cupric ions is a hydroxyalkyl substituted tertiary amine soluble in said bath and selected from the group consisting of a trialkanolamine, a lower alkylene diamine, or a poly-lower alkylene polyamine, the amine nitrogen atoms being substituted with hydroxyl alkyl groups having from two to four carbon atoms, inclusive.

4. A bath according to claim 3 wherein said tertiary amine complexing agent is present in the mol ratio of amine to cupric ion of at least about 0.08 to 1.

5. A bath according to claim 3 wherein said tertiary amine complexing agent is present in the mol ratio of amine to cupric ion of at least about 0.3 to 1.

6. A bath according to claim 3 wherein said additives are present in amounts sufficient to provide on a substrate a total deposit of at least 1 mil metallic copper at a rate of at least 0.25 mil per hour.

7. A bath according to claim 3 wherein a majority of said hydroxy lower alkyl groups are hydroxy propyl radicals.

8. A bath according to claim 3 wherein at least a portion of said hydroxy lower alkyl groups are hydroxy butyl radicals, said hydroxy butyl radicals being present in an amount sufficient to provide ductile metallic copper.

9. A bath according to claim 1 wherein said polymer is hydroxy-lower alkyl starch, polyvinyl pyrrolidone, polyvinyl alcohol, gelatin, a peptone, polyamide, polyacrylamide, or mixtures thereof.

10. A bath according to claim 3 wherein said polymer is polyacrylamide.

11. For electroless plating of copper, a basic aqueous bath containing a source of cupric ions, a complexing agent for said ions to render them soluble in alkaline solution, hydroxyl radicals, and formaldehyde, said bath additionally containing a cellulose ether selected from the group consisting of lower alkyl cellulose and hydroxy-lower alkyl cellulose.

12. For electroless plating of copper, a basic aqueous bath containing a source of cupric ions, a complexing agent for said ions to render them soluble in alkaline solution, hydroxyl radicals and formaldehydes, said bath additionally containing a cellulose ether selected from the group consisting of lower alkyl cellulose and hydroxy-lower alkyl cellulose, and N, N, N′, N′ tetrakis (2-hydroxylpropyl) ethylenediamine.

13. A bath according to claim 11 wherein said cellulose ether comprises hydroxyethyl cellulose.

14. An electroless chemical plating process for plating copper on objects having a catalytic surface comprising the steps of providing a basic aqueous solution of a source of cupric ions, a complexing agent for said ions to render them soluble in alkaline solution, formaldehyde and a cellulose ether selected from the group consisting of lower alkyl cellulose and hydroxy-lower alkyl cellulose; contacting a surface of said object with said solution; and plating copper on said surface by the reductive reaction of said solution at the catalytic surface.

15. An electroless process according to claim 14 wherein said aqueous solution additionally contains N, N, N', N', tetrakis (2-hydroxypropyl) ethylenediamine.

16. An electroless process according to claim 14 wherein said cellulose ether comprises hydroxyethyl cellulose.

17. An electroless chemical plating process for plating copper on objects having a catalytic surface comprising the steps of providing a basic aqueous solution according to claim 1, contacting a surface of said object with said solution, and plating copper on said surface by the reductive reaction of said solution at the catalytic surface.

18. An electroless chemical plating process for plating copper on objects having a catalytic surface comprising the steps of providing a basic aqueous solution according to claim 3, contacting a surface of said object with said solution, and plating copper on said surface by the reductive reaction of said solution at the catalytic surface.

19. An electroless chemical plating process for plating copper on objects having a catalytic surface comprising the steps of providing a basic aqueous solution according to claim 4, contacting a surface of said object with said solution, and plating copper on said surface by the reductive reaction of said solution at the catalytic surface.

20. An electroless chemical plating process for plating copper on objects having a catalytic surface comprising the steps of providing a basic aqueous solution according to claim 9, contacting a surface of said object with said solution, and plating copper on said surface by the reductive reaction of said solution at the catalytic surface.

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