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3,257,215

ELECTROLESS COPPER PLATING

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This application is a continuation-in-part of copending application U.S. Serial Number 26,401, now U.S. Patent No. 3,095,309.

The present invention relates to autocatalytic plating of copper, and more particularly to improved autocatalytic copper plating baths and processes.

According to the referred to co-pending application, addition of cyanide compounds to certain autocatalytic copper plating baths results in greater stability of the bath, and improved brightness and ductility of the copper deposit produced from such baths. As further described in the co-pending application, the cyanide compounds serve as complexers for the cuprous ions of the baths.

An object of the present invention is to further improve the stability of autocatalytic copper baths of the type described in our co-pending application.

Another object of this invention is to avoid autosensitization of non-catalytic areas of non-metallic surfaces heretofore caused by protracted immersion of such surfaces in autocatalytic copper baths.

These and other objects may be achieved by utilizing as the cuprous complexing agent in the autocatalytic copper baths to be described, in combination, a cyanide compound and a sulfur compound.

As the cyanide component of the cuprous complexing agent may be mentioned alkali cyanides, such as sodium and potassium cyanide, and nitriles, such as chloroacetonitrile, aliphatic nitriles, e.g., glycolnitrile and lactonitrile, and dinitriles, e.g., succinonitrile, iminodiacetonitrile, and 3,3'-iminodipropionitrile.

The sulfur component should be capable of forming a stable but dissociable chelate with cuprous ion.

Among the organic sulfur compounds may be mentioned the following: aliphatic sulfur-nitrogen compounds, such as thiocarbamates, e.g., thiourea; 5-membered heterocyclics containing S-N in the 5-membered ring, such as thiazoles and iso-thiazoles, e.g., 2-mercapto benzol thiazole and the like; dithiols, e.g., 1,2-ethanedithiol and the like; 6-membered heterocyclics containing S-N in the ring, such as thiazines, e.g., 1,2-benzisothiazine, benzothiazine, and the like; thioamino acids, such as methionine, cystine, cyteine, and the like; thio derivatives of alkyl glycols, such as 2,2'-thiodiethanol, dithiodiglycol, and thioglycollic acid; and the like. Among the inorganic sulfur compounds may be mentioned: alkali metal sulfides, e.g., sodium sulfide, potassium sulfide, sodium polysulfide, potassium polysulfide; alkali metal thiocyanates such as sodium and potassium thiocyanates; and alkali metal dithionates, such as sodium and potassium dithionate.

Compounds which contain both sulfur and cyanide are known and may be used as the cuprous complexing agent. Typical of such compounds are 3,3'-thiodipropionitrile and homologs thereof.

The foregoing sulfur compounds are merely typical of sulfur compounds which are capable of stabilizing autocatalytic copper baths as taught herein.

The amount of sulfur compound required is a small effective amount and will vary, depending upon the particular compound used, from a trace to about 300 parts per million (p.p.m.) or more. For most sulfur compounds, 1 p.p.m. will be the upper limit and about 0.001

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p.p.m. the lower limit. A good working limit for most sulfur compounds is between about 0.01 and 0.2 p.p.m.

The amount of the cyanide compound to be added to the bath is between about 0.00001 to 0.06 mole per liter, preferably between about 0.00005 to 0.01 mole per liter.

It should be emphasized however that the amount of sulfur compound will vary with the nature and activity of the compound. The upper limit of the sulfur compound is an amount which will stop the bath, i.e., render it non-autocatalytic. The lower limit is that amount which will be effective in producing the results described herein.

The copper deposits produced by autocatalytic baths containing the cyanide and sulfur components of the type described are bright and ductile. Additionally, the baths are more stable than the baths of the co-pending application containing cyanide alone, and are also more sensitive in distinguishing between catalytic and non-catalytic areas of a non-metallic substratum.

The electroless plating baths of the present invention are alkaline aqueous solutions comprising water soluble copper salts, such as cupric sulfate, chloride, nitrate, and acetate; a complexing agent for cupric ion; and an active reducing agent, such as formaldehyde, in addition to the complexing agent for cuprous ions already described.

Rochelle salts, the sodium salts (mono-, di-, tri-, and tetrasodium) salts of ethylenediaminetetraacetic acid nitrilotriacetic acid and its alkali salts, gluconic acid, gluconates, and triethanolamine are preferred as cupric ion complexing agents, but commercially available gluconolactone and modified ethylenediamineacetates are also useful, and in certain instances give even better results than the pure sodium ethylenediaminetetraacetates. One such material is N-hydroxyethylethylenediaminetriacetate. Other materials suitable for use as cupric complexing agents are disclosed in U.S. Patents Nos. 2,996,408, 3,075,856, 3,075,855, and 2,938,805.

The quantities of the various ingredients in the bath are subject to wide variation within certain ranges which may be defined as follows:

Copper salt	0.002 to 0.60 moles.
Formaldehyde	0.03 to 1.3 moles.
Cupric ion complexing agent	0.7 to 2.5 times the moles of copper.
Cyanide compound	0.00001 to 0.06 moles.
Sulfur compound	Less than 300 p.p.m.
Alkali metal hydroxide	Sufficient to give a pH of 10.0 to 14.0.
Water	Sufficient to make 1 liter.

The sodium salts are preferred over the corresponding more costly potassium and other alkali metal salts in the baths of this invention.

Cupric sulfate is the preferred copper salt but other soluble copper salts may be used, such as the nitrate, chloride, and acetate, as has already been indicated.

More preferably, the plating baths of the present invention are compounded within more narrow limits than set forth immediately above, and the preferred embodiments comprise:

A soluble cupric salt, preferably cupric sulfate	0.002 to 0.2 mole
Alkali metal hydroxide, preferably sodium hydroxide, to give	pH. 10 to 13.
Formaldehyde	0.06 to 0.50 mole.
Cupric ion complexing agent	0.001 to 0.60 mole (and usually at least about 10% molar excess based on the amount of cupric salt employed.)

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Cyanide compound	0.00005 to 0.01 mole.
Sulfur compound	0.001 p.p.m. to 1 p.p.m.
Water	sufficient to make 1 liter.

In considering these general formulae, and the specific working formulae which are set forth below, it should be understood that as the baths are used up in plating, the cupric salt, and the formaldehyde reducing agent may be replenished from time to time, and also that it may be advisable to monitor the pH, and the cyanide and sulfur content of the bath, and to adjust them to their optimum value as the bath is used.

For best results, surfactants in an amount of less than about 5 grams per liter are added to the baths disclosed herein. Typical of suitable surfactants are organic phosphate esters, and oxyethylated sodium salts. Such surfactants may be obtained under the trade names Gafac RE-610 and Triton QS-15, respectively.

The baths are ordinarily used at temperatures between 25° and 70° C., although they may be used at lower temperatures or at even higher temperatures. As the temperature is increased, it is usual to find that the rate of plating is increased, and that the ductility of the deposit is increased to a slight extent, but the temperature is not highly critical and, within the usual operating range, excellent bright, ductile deposits are produced. The efficiency of the copper recovery from the baths often exceeds 90 percent.

Typical examples of electroless copper deposition baths prepared following the teachings described herein are as follows:

Example 1

Copper sulfate	grams	14
Sodium hydroxide	grams	20
Formaldehyde (37%)	ml.	40
Thioglycolic acid (70% solution)	ml.	.001
Sodium cyanide	mg.	10
Surfactant	gram	1
Water		(1) 40

¹ To make 1 liter.

Example 2

Copper sulfate	grams	5
Trisodium N-hydroxyethylethylenediaminetriacetate (41% solution)	ml.	15
Sodium cyanide	mg.	10
Ammonium thiocyanate	mg.	3.2
Formaldehyde (37%)	ml.	6
Wetting agent	gram	1
Sodium hydroxide	do.	2
Water		(1)
Temperature	° C.	45
Temperature	° C.	30

¹ To make 1 liter.

Example 3

Copper sulfate	grams	10
Tetrasodium ethylenediaminetetraacetate	do.	20
Succinonitrile	mg.	20
Thiourea	mg./l.	.02
Formaldehyde (37%)	ml.	6
Wetting agent	gram	1
Sodium hydroxide	do.	3
Water		(1)
Temperature	° C.	60

¹ To make 1 liter.

Example 4

Copper sulfate	grams	5
Trisodium N-hydroxyethylethylenediaminetriacetate (41% solution)	ml.	15
Sodium hydroxide	grams	2
Formaldehyde (37%)	ml.	6
Thiodiethanol	ml.	.000015

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Sodium cyanide	mg.	10
Surfactant	gram	1
Water		(1)
Temperature	° C.	45

¹ To make 1 liter.

Example 5

Copper sulfate	grams	5
Trisodium N-hydroxyethylethylenediaminetriacetate (41% solution)	ml.	15
Chloroacetonitrile	grams	2
2-mercapto benzol thiazole	mg.	0.007-0.1
Formaldehyde (37%)	ml.	6
Wetting agent	gram	1
Sodium hydroxide	do.	2
Water		(1)
Temperature	° C.	45

¹ To make 1 liter.

Example 6

Copper sulfate	grams	10
Tetrasodium ethylenediaminetetraacetate	do.	20
Lactonitrile	mg.	30
2-mercapto benzol thiazole	mg.	0.1
Formaldehyde (37%)	mg.	6
Wetting agent	gram	1
Sodium hydroxide	do.	3
Water		(1)
Temperature	° C.	56

¹ To make 1 liter.

Example 7

Copper sulfate	grams	5
Trisodium nitrilotriacetic acid (40% solution)	ml.	23
Glyconitrile	mg.	12
2-mercapto benzol thiazole	mg.	0.07 to 0.1
Formaldehyde (37%)	ml.	10
Sodium hydroxide	grams	2.1
Wetting agent	do.	2.5
Water		(1)
Temperature	° C.	20

¹ To make 1 liter.

Example 8

Copper sulfate	grams	5
Trisodium N-hydroxyethylethylenediaminetriacetate (41% solution)	ml.	15
Sodium cyanide	mg.	10
Potassium polysulfide	mg./l.	.01
Formaldehyde (37%)	ml.	6
Wetting agent	gram	1
Sodium hydroxide	do.	2
Water		(1)
Temperature	° C.	45

¹ To make 1 liter.

The surfactants in Examples 1 to 8 may be either of those mentioned hereinabove.

In using the autocatalytic or electroless copper solutions, the surface to be plated must be free of grease and other contaminating material.

Where a non-metallic surface is to be plated, the surface areas to receive the deposit should first be treated, as in conventional processes, with conventional sensitizing and seeding solutions, such as stannous chloride (SnCl₂), followed by treatment with a dilute solution of palladium chloride (PdCl₂).

Alternatively, extremely good sensitization is achieved by using a bath containing a mixture of stannous chloride and precious metal chloride, such as palladium chloride, the stannous chloride being present in stoichiometric excess, based on the amount of precious metal chloride.

Other ways of sensitizing non-metallic surfaces for reception of an electroless copper deposit from the baths

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described herein are disclosed in co-pending application Serial No. 785,703, filed January 8, 1959, by Frederick W. Schneble, Jr. and Rudolph J. Zeblicky, now abandoned but referred to in U.S. Patent No. 3,226,256 granted December 28, 1965.

Where metal surface, such as stainless steel, is to be treated, it should be degreased, and then treated with acid, such as hydrochloric or phosphoric acid, to free the surface of oxides.

Following pre-treatment and/or sensitization, the surface to be plated is immersed in the autocatalytic copper baths, and permitted to remain in the bath until a copper deposit of the desired thickness has been built up.

In the past, difficulty has been experienced in plating from autocatalytic copper baths on restricted areas of non-metallic surfaces. With non-metallic substrates, there is a tendency for non-sensitized areas of the substrate, following prolonged immersion in autocatalytic copper baths, to become sensitized and to receive scattered spot deposits of copper. As will be readily appreciated, deposition of copper in areas of the substratum where copper is not desired would raise havoc with control techniques in the preparation, for example, of printed circuits.

Additionally, with autocatalytic copper baths, difficulty has been experienced in the past with deposition of copper on non-metallic walls of containers housing the bath following prolonged exposure of the container walls to the bath. This leads to inefficiency of the bath, and also causes difficulty with the control of the plating operation, since one of the methods of controlling autocatalytic copper baths is by calculating the amount of copper actually deposited on substrates. When the copper is deposited on the container walls of the bath, such calculations have little meaning.

The baths of the present invention are remarkable in the sense that they will deposit copper on non-metallic surfaces only in those areas which have been sensitized to provide catalytically active sites, as described for example hereinabove. These baths have a remarkable capacity for distinguishing non-metallic areas which have not been so sensitized from those which have, and for depositing copper only on the latter areas. Even though a non-pretreated, non-metallic surface, including the housing walls of the baths, may be exposed to the baths of this invention for prolonged periods of time, random spot deposition on such areas does not occur.

The reason why non-pretreated, non-metallic surface areas when exposed to autocatalytic copper baths become sufficiently active to promote a random deposit of copper in spots is not readily understood. Without wishing to be limited to this explanation, one theory to explain this phenomenon is that a non-activated plastic surface contains small pores or pit holes. Upon prolonged exposure to the bath, hydrogen gas gradually accumulates in the pores and pit holes, and the accumulated hydrogen eventually acts as a catalytic site for the autocatalytic copper bath. As a result, copper deposits in the areas of the pits or pore holes, thereby causing the problems with the plating operation as described hereinabove.

The addition of cyanide and sulfur to autocatalytic copper baths as described herein apparently renders the bath so stable that hydrogen either does not accumulate in the pits or pores of the non-sensitized plastic or non-metallic surface areas, or, alternatively, if the hydrogen does accumulate in such areas, it by itself is not sufficient to promote reduction of the baths in those areas so as to produce unwanted and deleterious spot deposits of copper.

As will be readily understood, this property of the baths of the present invention is unique and has wide commercial importance.

If desired, admixtures of the cyanide compound and sulfur compound in suitable proportions, may be sepa-

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ately prepared, and then added to baths of the type described. It will be understood that such admixtures, which constitute new and useful compositions of matter, form a part of the present invention.

The invention in its broader aspects is not limited to the specific steps, processes and compositions shown and described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. A bath for the electroless plating of copper which comprises: water; a water soluble copper salt, from 0.002 to 0.60 mole per liter; a complexing agent for cupric ion, from 0.7 to 2.5 times the moles of the copper salt; an alkali metal hydroxide, enough to give a pH of from 10.0 to 14.0; formaldehyde, from 0.03 to 1.3 moles per liter; a cyanide compound capable of complexing cuprous ion, from 0.00001 to 0.06 mole per liter; and from a trace to about 300 parts per million of a sulfur compound capable of stabilizing the bath, the amount of said sulfur compound being insufficient to prevent autocatalytic deposition of copper from the bath.

2. A bath for the electroless plating of copper according to claim 1, in which the pH is adjusted to about 12.0.

3. The bath of claim 1 wherein the cyanide compound is a member selected from the group consisting of inorganic cyanides and organic nitriles.

4. The bath of claim 1 wherein the sulfur compound is a member selected from the group consisting of thio derivatives of alkyl glycols; aliphatic S-N compounds; 5-membered heterocyclics containing S-N in the 5-membered ring; dithiols; 6-membered heterocyclics containing S-N in the ring; thioamino acids, alkali sulfides; alkali polysulfide; alkali thiocyanate; alkali dithionates; and mixtures of the foregoing.

5. A bath for the electroless plating of copper which consists essentially of: water; a water soluble copper salt, 0.002 to 0.2 mole per liter; alkali metal hydroxide, enough to give a pH of about 10 to 13; a complexing agent for cupric ion, 0.001 to 0.50 mole per liter, formaldehyde, 0.06 to 0.50 mole per liter; a cyanide compound capable of complexing cuprous ion, 0.00005 to 0.01 mole per liter; from about 0.001 to 1 part per million of a sulfur compound capable of stabilizing the bath, the amount of said sulfur compound being insufficient to prevent autocatalytic deposition of copper from the bath.

6. The bath of claim 3 wherein the pH is adjusted to about 12.0.

7. The process of claim 1 wherein the cyanide and sulfur are supplied by the same compound.

8. The process of claim 1 wherein the cyanide and sulfur are supplied by different compounds.

9. A process of electroless copper plating which comprises immersing a receptive surface to be plated in an alkaline, autocatalytic copper bath comprising water; a water soluble copper salt, from 0.002 to 0.60 mole per liter; a complexing agent for cupric ion, from 0.7 to 2.5 times the moles of the copper salt; an alkali metal hydroxide, enough to give a pH of from 10.0 to 14.0; formaldehyde, from 0.03 to 1.3 moles per liter; a cyanide compound capable of complexing cuprous ion, from 0.00001 to 0.06 mole per liter; and from a trace to about 300 parts per million of a sulfur compound capable of stabilizing the bath, the amount of said sulfur compound being insufficient to prevent autocatalytic deposition of copper from the bath.

10. In a process for plating copper on non-metallic surfaces, only selected portions of which have been catalyzed for the reception of electroless copper, by immersing the surface in an autocatalytic alkaline aqueous solution comprising, in proportions capable of effecting electroless deposition of copper a water soluble copper salt; a complexing agent for cupric ion; and a reducing agent for cupric ion; the improvement for preventing autosensitiza-

tion of the non-catalyzed areas of the surface upon prolonged immersion in the solution which comprises maintaining in the bath a cyanide compound and a sulfur compound, said cyanide and sulfur compounds being present in small effective amounts which are insufficient to prevent electroless deposition of copper from the bath.

11. In a process for plating copper on insulating surfaces which have been catalyzed for the reception of electroless copper by immersing the surface in a solution comprising, in proportions capable of effecting electroless copper deposition: a soluble copper salt; a complexing agent for cupric ion; and a reducing agent for cupric ion; the improvement for reducing the tendency towards autosensitization of non-catalyzed areas of insulating surfaces upon contact with the solution which comprises maintaining cyanide and sulfur in said solution, said cyanide and sulfur being present in solution in amounts which are insufficient to prevent deposition of electroless copper from the bath.

12. In a process of electroless copper plating which includes immersing a receptive surface to be plated in a solution comprising a soluble copper salt; a complexing agent for cupric ion and a reducing agent for cupric ion in proportions capable of effecting electroless copper deposi-

tion, the improvement for deducing the tendency of non-catalyzed surface areas in contact with the solution to become sensitized to the reception of electroless copper deposition which comprises, maintaining in the bath a small effective amount of cyanide within the range 0.00001 to 0.06 mole per liter but insufficient to prevent deposition of copper from the bath, and a small effective amount of sulfur within the range from a trace to about 300 parts per million, but insufficient to prevent deposition of copper from the bath.

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