United States Patent Office 3,728,137
Patented Apr. 17, 1973



3,728,137

# ELECTROLESS COPPER PLATING

Charles R. Shipley, Jr., Lucia H. Shipley, and Michael Gulla, Newton, and Oleh B. Dutkewych, Medfield, Mass., assignors to Shipley Company, Inc., Newton, Mass.

No Drawing. Continuation-in-part of application Ser. No. 752,250, Aug. 13, 1968. This application Aug. 23, 1971, Ser. No. 174,157

Int. Cl. C23c 3/02

U.S. Cl. 106—1 7 Claims

## ABSTRACT OF THE DISCLOSURE

An electroless copper plating solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde or a formaldehyde precursor such as paraformaldehyde and a complexing agent for copper; said solution characterized by the addition of a formaldehyde addition agent. The formaldehyde addition agent provides for the slow release of formaldehyde into solution and contributes to improved tensile properties of a copper deposit.

## CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of co-pending U.S. patent application Ser. No. 752,250 filed Aug. 13, 1968 now U.S. Pat. No. 3,615,735.

## 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 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 sulphate, (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 aforesaid cited patents, and also in U.S. Pat. Nos. 2,874,072; 3,075,856; 3,119,-709; 3,075,855 and 3,239,512, all incorporated herein by reference.

Known electroless copper plating solutions of the above type usually provide a plate which, if mechanically dense and strong is brittle such that it can withstand only limited bending or thermal stresses 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 one to three 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. 3,213,430 discloses the addition to the copper plating solution of a water soluble compound of cyanide, vanadium, molybdenum, niobium, tungsten, rhenium, arsenic, antimony, bismuth, rare earths of the actinium series and rare earth of the lanthanum series. Certain members of the above groups, especially the vanadium compounds provide improved bending characteristics. The reason for this is not fully understood, but it is stated in the patent that the agents act on the catalytic surface so as to prevent formation and release of the hydrogen gas, 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 are frequently sacrificed or lost.



## STATEMENT OF THE INVENTION

The subject invention is an alternative method for improving the ductility of electroless copper. The copper solution of the invention is characterized by the addition of a formaldehyde addition agent to the solution which is believed to be responsible for forming an unstable addition product with formaldehyde. Because of the formation of the addition product with formaldehyde, it is theorized that formaldehyde is slowly released into solution thereby reducing the evolution of hydrogen gas at the surface of the part being plated which results in a copper deposit having improved bending or tensile properties.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Any water soluble copper salt heretofore used for preparing electroless copper deposition solutions may be used for the solutions of this invention. For example, the halides, nitrate, acetate, sulphate and other organic and inorganic acid salts of copper are generally suitable as is known in the art. Copper sulphate is preferred.

Suitable complexing agents for the copper ions are also well known in the art and include Rochelle salts, the sodium salts of ethylenediamine tetraacetic acid, nitrilotriacetic acid and its alkali metal salts, triethanolamine, modified ethylenediamine tetraacetic acids such as N-hydroxyethylenediamine triacetate, hydroxyalkyl substituted dialkaline triamines such as pentahydroxypropyldiethylenetriamine, and the like. A preferred class of complexing agents are those described in U.S. Pat. No. 3,329,512 and include hydroxyalkyl substituted tertiary amines such as tetrahydroxypropyl ethylene diamine, pentahydroxypropyl diethylene triamine, trihydroxypropyl amine (tripropanolamine), trihydroxypropylhydroxyethyl ethylene diamine and the like.

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 mil per hour. Though the copper solutions of this invention provide copper deposits from solution 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 and which themselves, provide more ductile deposits.

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 de-

scribed in various publications, such as "Formaldehyde" by J. Fredrick Walker, Reinhold Publishing Company, third edition, 1964, pp. 219 to 221, included herein by reference. Preferred formaldehyde addition agents are sulfites, bisulfites and phosphites of a metal cation non-interfering with the copper solution and preferably an alkali metal cation. The most preferred formaldehyde additon agents are sodium sulfite, sodium or potassium bisulfite and sodium phosphite.

The formaldehyde addition agent and formaldehyde or preferably paraformaldeye, are reacted with each other to form the adduct prior to addition to the remaining components of the copper solution. The amount of formaldehyde addition agent used is typically in molar excess of the amount of formaldehyde but may be used in equimolar amounts, though lesser amounts may be used if desired, it being understood that small amounts provide some benefit and larger amounts provide greater benefit. In this respect, the formaldehyde addition agent may be present in an amount of 1 mole per hundred moles of formaldehyde to that amount that restricts deposition, but preferably varies from about 1 to 3 moles per mole of formaldehyde.

The plating baths of this invention 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 critical, and within the usual operating ranges, electroless copper deposits having improved tensile properties are obtained. Preferably, the bath is used without agitation.

In using the electroless copper solution to plate metal, the surface to be plated should be catalytically active and free of grease and contaminating materials. Where a non-metallic 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 non-metallic surfaces is achieved by contact with an acidic formulation formed by the admixtures of stannous chloride and a precious metal chloride, preferably palladium chloride, the stannous chloride being present in molar excess of the 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" by 2".

(b) Scrub part clean using an abrasive cleaner.

(c) Rinse with 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 stannic acid-palladuim 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 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 three hours.

(k) Dry parts and examine deposits 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 ½ bend is considered brittle and a sample able to withstand ½ bend or more is defined herein as ductile.

EXAMPLE 1

| | | |
|---|---|---|
| Cupric sulphate pentahydroxide | gm. | 8 |
| Paraformaldehyde | gm. | 7.5 |
| Sodium hydroxide (25% by wt. solution) | ml. | 50 |
| Pentahydroxypropyl diethylenetriamine | gm. | 20 |
| Sodium bisulfite | gm. | 20 |

Water to 1 liter.

In the above example, the sodium bisulfite and paraformaldehyde are mixed in water and added as a 20% by weight solution. The above formulation yields a copper deposit of 0.43 mils in thickness able to withstand ½ bend. Omission of the sodium bisulfite results in a brittle deposit unable to withstand even ½ bend. Substitution of sodium phosphite for sodium bisulphite yields substantially similar results.

EXAMPLE 2

| | | |
|---|---|---|
| Cupric sulphate pentahydroxide | gm. | 8 |
| Paraformaldehyde | gm. | 7.5 |
| Sodium hydroxide (25% by wt. solution) | ml. | 50 |
| Ethylenediaminetetraacetic acid | gm. | 25 |
| Tetrahydroxypropylethylene diamine | gm. | 6 |
| Sodium bisulfite | gm. | 20 |

Water to 1 liter.

The addition product of sodium bisulphite and paraformaldehyde is formed as in Example 1. A deposit having a thickness of 0.33 mil is able to withstand 1 bend whereas a control sample without the sodium bisulfite is brittle. Substitution of sodium sulfite for sodium bisulfite yields substantially the same results.

EXAMPLE 3

| | | |
|---|---|---|
| Cupric sulphate pentahydrate | gm. | 8 |
| Paraformaldehyde | gm. | 7.5 |
| Sodium hydroxide (25% by wt. solution) | ml. | 50 |
| Sodium/potassium tartrate | gm. | 40 |
| Sodium bisulfite | gm. | 20 |

Water to 1 liter.

The sodium bisulfite and paraformaldehyde are added as in Example 1. A deposit having a thickness of 0.09 mil is capable of withstanding 1 bend. A slightly thinner deposit of a control sample free of sodium bisulfite withstands ½ bend.

Copper solutions of this invention find utility for all purposes for which electroless copper solutions have heretofore been used including 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 4

(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 one-step palladium sensitizing solution maintained at room temperature for a period of five minutes.

(e) Immerse in a stripping solution of 10 grams of copper chloride, 100 grams of 37% hydrochloric acid and water to 1 liter maintained at room temperature for 6 minutes.

(f) Deposit electroless copper of Example 1 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 side of the plastic laminate.

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

We claim:

1. In an aqueous electroless copper plating solution capable of depositing ductile copper and comprising a source of cupric ions, hydroxyl radicals, a source of formaldehyde and sufficient complexing agent to render said cupric ion soluble in alkaline solution, the improvement comprising a formaldehyde addition agent in said solution in an amount of at least 0.01 mole per mole of formaldehyde to that amount that restricts deposition of copper from solution.

2. The copper plating solution of claim 1 where the formaldehyde addition agent and formaldehyde or its precursor are mixed together and reacted to form an adduct prior to addition to the copper plating solution.

3. The copper plating solution of claim 2 where the formaldehyde addition agent is selected from the group of salts of sulphites, bisulphites and phosphites, said salts having a cation non-interfering with the plating solution.

4. The copper plating solution of claim 3 where the formaldehyde addition agent is present in an amount of from 0.1 to 3 moles per mole of formaldehyde in solution.



5. The copper plating solution of claim 3 where the formaldehyde addition agent is present in an amount of 1 to 3 moles per mole of formaldehyde in solution.

6. The copper plating solution of claim 3 where the formaldehyde addition agent is sodium bisulfite.

7. The copper plating solution of claim 3 where the complexing agent is a mixture of complexing agents with one member of the mixture comprising a hydroxyalkyl substituted tertiary amine.

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LORENZO B. HAYES, Primary Examiner

U.S. Cl. X.R.

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