3,095,309
Patented June 25, 1963

3,095,309

ELECTROLESS COPPER PLATING

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No Drawing. Filed May 3, 1960, Ser. No. 26,401
12 Claims. (Cl. 106—1)

The present invention relates to a new and improved process for the electroless plating of copper, and to a novel and improved electroless copper plating bath.

The present invention has for its object the provision of a novel and improved process for the electroless plating or deposition of a ductile, bright layer of copper on various surfaces such as insulating members, metal, ceramic and other supporting surfaces. A further object of the invention is the provision of a novel and improved electroless plating bath which is simple to use, operates with certainty and which is economical in use. The invention provides an improved electroless copper depositing bath and process which produces a copper deposit of better color than has heretofore been realized, and which may exhibit substantially the same ductility as good electrodeposited copper.

The invention consists in the novel steps, processes, compositions and improvements herein shown and described.

Heretofore, a wide variety of electroless copper plating baths and processes have been proposed and put into extensive commercial operation for the deposition of thin layers of copper upon insulating surfaces, ceramics, plastics and other materials, but in general none of these have been useful to any substantial degree in the electroless deposition of copper on metal surfaces, such as nickel, steel and stainless steel. Furthermore, in all instances within our knowledge, the deposits produced by electroless copper depositing baths have produced copper deposits which are brittle, break under vibration and bending, and otherwise exhibit poor ductility, although many of them are commercially useful within recognized limits. Furthermore, the deposits produced by most prior electroless copper depositing baths do not produce copper deposits which are bright, but they usually exhibit a dull surface, of poor color, often yielding a "smutty" layer of copper. Additionally, the baths of the prior processes are often subject to instability and as impurities accumulate in the bath, the bath finally reaches a condition in which it spontaneously decomposes, throwing down the copper as a useless sludge or precipitate. On the contrary, the baths of the present invention may be used until substantially exhausted, and may be replenished from time to time so that the remaining useful ingredients in the bath are more efficiently used, thereby reducing the over-all cost of the operation.

In general, the electroless plating baths of the present invention consist essentially of a soluble copper salt, such as copper sulfate, cupric chloride, cupric nitrate, copper gluconate and cupric acetate; a complexing agent for the copper ions, such as Rochelle salts, ethylenediaminetetraacetic acid and its sodium salt, triethanolamine, sugar (sucrose, dextrose, lactose, levulose or maltose), mannitol, sorbitol, or gluconic acid; sodium or potassium hydroxide; an active reducing agent such as formaldehyde; and a small amount of a complexing agent for the cuprous ions, such as a soluble cyanide, such as sodium or potassium cyanide.

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

Copper sulfate from 0.5 g. to saturated solution 0.002 to .15 mol or more.
Alkali metal hydroxide to give pH 10.5 to 14, preferably pH 13.5.
Formalin (40%) 5 ml. to 100 ml., 0.06 to 1.3 mol.
Complexing agent 0.5 to 2.5 times moles of copper.
A soluble inorganic cyanide 0.001 g. to 3.0 g., 0.00002 M. to 0.06 mol.
Water, sufficient to make 1 liter.

The ratio of the cupric salt to the complexing agent is such that there are from 0.5 to 2.5 as many moles of complexing agent as of cupric salt; e.g. 5 grams of $CuSO_4—5H_2O$ requires from 2.5 to 8.5 grams of Rochelle salts. The amount of formaldehyde may be 0.4 to 3.4 moles per liter.

Sodium hydroxide and sodium cyanide are preferred over the corresponding more costly potassium and other alkali metal salts and the thiocyanates, which are of greater molecular weight.

Rochelle salts, the sodium salts (mono-, di-, tri- and tetra-sodium salts) of ethylenediaminetetraacetic acid, gluconic acid, gluconates, and triethanolamine are preferred as complexing agents, but commercially available glucono-γ-lactone and modified-ethylenediaminetetraacetates are also useful, and in certain instances give even better results than the pure sodium ethylenediaminetetraacetate. One such material is Glyco Products "Tetrine M."

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

More preferably, the plating baths of the present invention are compounded within narrower limits than set forth immediately above, and they consist essentially of:

A soluble cupric salt, preferably cupric sulfate	0.002 to 0.04 mole.
Alkali metal hydroxide, preferably Sodium hydroxide to give	pH 13.5.
Formaldehyde	0.25 to 0.50 mole.
Complexing agent, from	0.0014 to 0.10 mole and usually approximating the molal concentration of the cupric salt employed.
A soluble inorganic cyanide, preferably sodium cyanide	0.001 to 0.02 mole.

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 cyanide content of the bath, and to adjust it to its optimum value as the bath is used.

The baths are ordinarily used at slightly elevated temperatures, such as from 35° to 65° C. although many of them may be used at lower temperatures, and others may be used 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 deposits are produced which exhibit greatly improved properties over those obtained with conventional baths and processes.

With electroless copper plating baths according to the present invention, the efficiency of the copper recovery by electroless deposition from the bath often exceeds 90%, which is much greater than has heretofore been observed in working with conventional baths. The cuprous complexing agent in the bath serves to prevent or minimize the formation of cuprous oxide in the bath and also appears to inhibit the formation of resultant hydrogen in the electroless deposited metal.

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 ($SnCl_2$), followed by treatment with a dilute solution of palladium chloride ($PdCl_2$). 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 any oxide. If the electroless deposit is to be made on a plastic or ceramic base which is impregnated with cuprous oxide (Cu_20), the cleaned base is immersed in the electroless plating bath and allowed to remain until the deposit is sufficiently thick.

It will be understood that the foregoing general description and the following detailed description as well are exemplary and explanatory of the invention but are not restrictive thereof.

Example 1

A bath which is especially suited for the copper plating at about 65° C. of an epoxy or polyethylene terephthalate (Mylar) resin base sheet which is to form a printed circuit, and which has been treated with stannous chloride and palladium chloride in selected areas corresponding to the circuitry to be produced, is immersed in a bath consisting of:

Cupric sulfate ($CuSO_4$—$5H_2O$)	7.5 grams.
Sodium salt of E.D.T.A.	15.0 g.
Sodium hydroxide	20.0 g.
Sodium cyanide	0.1 to 1.0 g., 0.5 g. preferably.
Formaldehyde (40%)	40.0 ml.

Water enough to make 1000 ml.

Example 2

A bath for similar use, but which gives even better ductility of the deposited copper, when used at a temperature of about 25° to 40° C., is as follows:

Cupric sulfate ($CuSO_4$—$5H_2O$)	1.0 g. 0.004 M.
Rochelle salts	2.7 g. 0.01 M.
Sodium hydroxide, pH 13.5	About 20.0 g.
Sodium cyanide	0.05 g. 0.001 M.
Formaldehyde, 40%	35.0 ml. 0.5 M.

Water enough to make 1000 ml.

Example 3

For use in the electroless plating of copper on a sheet of stainless steel which has been degreased and acid dipped, and which will deposit a bright ductile layer of copper about 0.001" thick in a period of 24 hours at an operating temperature of about 50° C., the following bath is preferred:

Cupric sulfate	g.	7.5
Ethylenediamine tetraceticacidtetrasodium salt	g.	15.0
Sodium hydroxide	g.	20.0
Sodium cyanide	g.	0.4
Formaldehyde 40%	ml.	20.0

Water enough to make 1000 ml.

Other baths suitable for the electroless deposition of bright, ductile layers of copper on sensitized and seeded plastic sheets or parts are, as follows:

Example 4

Cupric sulfate ($CuSO_4$—$5H_2O$)	g.	7.5
Triethanolamine	g.	5.0
Sodium hydroxide	g.	20.0
Sodium cyanide	g.	0.5
Formaldehyde, 40%	ml.	40.0

Water enough to make 1000 ml.

In place of the 5.0 g. of triethanolamine, the following may be substituted, in whole or in part for the triethanolamine, without a major change in the results, although some differences in ductility and brightness, as well as in the rapidity of deposition, or of the optimum operating temperature will be noted in use:

	G.
Sucrose	5
Lactose	6
Dextrose	6
Levulose	6
Maltose	12
Mannitol	6
Sorbitol	6

In the various formulae, the complexing agents may be used as mixtures and additional amounts of the complexing agent may be added, but such excess additions beyond 2.5 times the molal concentration of the copper content of the bath do not result in any improvement and are merely wasteful under ordinary circumstances.

Example 5

Another bath which operates somewhat more rapidly at 40° C. than those specified above for the electroless plating of copper on insulating bases of plastic materials, such as phenolformaldehyde resins, polyester resins, nylon, polystyrene and epoxy resins, and has a greater life, but does not produce as ductile a deposit of copper as is produced by the bath of Example 1, is as follows:

Cupric nitrate ($Cu(NO_3)_2$—$3H_2O$)	g.	14.0
Gluconic acid, 50%	ml.	10
Sodium hydroxide	g.	20
Formaldehyde, 40%	ml.	30
Sodium cyanide	g.	0.005 to 0.05

Water sufficient to make 1000 ml.

Example 6

A bath having still higher concentration of ingredients is, as follows:

Cupric chloride ($CuCl_2$—$2H_2O$)	g.	35
Rochelle salts	g.	85 to 100
Sodium hydroxide	g.	60
Formaldehyde, 40%	ml.	35
Sodium cyanide	g.	0.01 to 0.1

The following are further examples of other baths which are comprised within the scope of the present invention, and which are especially useful for the deposition of bright, ductile metallic layers of copper on suitably prepared sheets or moldings of plastic materials, such as the melamine or phenol-formaldehyde sheet-stock used in the making of printed circuits.

Example No.	7	8	9	10	11	12	13	14	15
$CuSO_4$—$5H_2O$ grams	0.5	0.5	0.5	0.5	10	10	10	100	100
Tetrasodium E.D.T.A. [1] do	1.0	1.0	1.0	1.5	25	20	30	200	200
NaOH to give pH	13	14	13.5	------	12.5	------	13.5	13.0	13
KOH to give pH	------	------	------	12.0	------	13.5	------	------	------
Formaldehyde 40% milliliters	5	10	10	5	10	40	50	50	500
Sodium cyanide grams	0.002	------	0.006	0.01	------	1.5	------	------	3.0
Potassium cyanide do	------	0.003	------	------	0.02	------	0.5	3.0	------
Water enough to make one liter.									

[1] Sodium salt of ethylenediaminetetraacetic acid.

Baths which give an excellent deposit but which are always easily controlled throughout their entire life because of the low copper concentration and the necessity of replenishing the copper content of the bath, may be prepared according to the following formulae:

	Example 16	Example 17
Cuprous cyanide..................grams..	0.9	0.5
Sodium hydroxide..................do....	20	20
"Tetrine M"..................milliliters..	5	5
Formalin 40%..................do....	40	40

These baths are preferably operated at a temperature of from 40 to 50° C. and the copper content may be replenished to a limited extent by additions of cuprous chloride.

In the process according to the present invention, and as applied to the electroless deposition of copper on an insulating base such as sheet nylon, polystyrene, melamine resin, cast epoxy resin, the surface of the sheet is first wetted with a detergent, such as a 1% water solution of Triton X-100 (Rohm & Haas Co.) or is roughened slightly by rubbing with an abrasive. The surface is then thoroughly cleaned with an alkaline cleaner, such as a hot solution of trisodium phosphate in water, rinsed with water and is sensitized with a solution containing about 70 grams of stannous chloride ($SnCl_2$—$2H_2O$) and 40 ml. of 37% hydrochloric acid per liter for a period of about 10 minutes. The surfaces are again thoroughly rinsed with water, and may be further treated with a solution of from 0.5 to 25 ml. per liter of hydrochloric acid (37%). The surface is then "seeded" by treating the surface with a solution of 0.10 gram of palladium chloride ($PdCl_2$), 1 ml. of 37% hydrochloric acid and 1 ml. of Triton X-100 per liter, for two or more minutes. Thereafter, the surface is again thoroughly rinsed with water and is then ready for immersion in the electroless depositing bath, such as the bath of Example 1, or Example 2.

A similar sensitizing and seeding treatment may be used as a preliminary treatment in connection with the use of any of the other examples given above, although when a metal surface is to be plated it is seldom necessary to do more than treat the metal surface, as by a solvent or a hot solution of an alkaline cleanser (e.g. trisodium phosphate), to insure that it is grease-free and with an acid, such as hydrochloric acid if the surface has any oxide coating thereon.

The present invention is not limited to the use of the foregoing specific sensitizing and seeder solutions, and in many instances it is only necessary to roughen the surface of the insulating base material, or to thoroughly clean the metal surface. Likewise, the process and baths may be used for the electroless deposition of copper on a base material which comprises a thermoplastic or thermosetting resin, such as an epoxy resin which contains from 30% to 50% of cuprous oxide, and which have been subjected to light abrasion in those areas where the copper is to be selectively deposited.

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 is:

1. A bath for the electroless plating of copper consisting essentially of: water, and a water-soluble copper salt, from 0.002 to 0.15 mole per liter; a copper complexing agent, from 0.5 to 2.5 times the moles of the copper salt; an alkali metal hydroxide, to give a pH of from 10.5 to 14; formaldehyde, from 0.06 to 3.4 moles per liter; and a soluble inorganic cyanide, from 0.00002 to 0.06 mole per liter.

2. A bath for the electroless plating of copper according to claim 1 in which the copper salt is present in a quantity from 0.002 to 0.04 mole per liter, the complexing agent from 0.0014 to 0.10 mole per liter, and the cyanide is present in a quantity from 0.001 to 0.02 mole per liter.

3. A bath according to claim 1 in which the copper salt is copper sulfate, the complexing agent is a sodium salt of ethylenediamine tetraacetic acid, and the hydroxide and cyanide are their sodium compounds.

4. A bath for the electroless plating of copper consisting essentially of: water, and a water-soluble copper salt, from 0.002 to 0.15 mole per liter; a complexing agent for cupric ion, from 0.5 to 2.5 times the moles of the copper salt; an alkali metal hydroxide, to give a pH of from 10.5 to 14; formaldehyde, from 0.06 to 3.4 moles per liter; and, as a complexing agent for cuprous ion a water soluble cyanide salt.

5. A process of electroless copper plating which comprises immersing the receptive surface to be plated in a bath consisting essentially of: water, and a water-soluble copper salt, from 0.002 to 0.15 mole per liter; a copper complexing agent, from 1 to 2.5 times the moles of the copper salt; an alkali metal hydroxide, to give a pH of from 10.5 to 14; formaldehyde, from 0.06 to 3.4 moles per liter; and a soluble inorganic cyanide from 0.00002 to 0.06 mole per liter.

6. A process as claimed in claim 5 in which the copper salt is present in a quantity from 0.002 to 0.04 mole per liter, the complexing agent from 0.0014 to 0.10 mole per liter, and the cyanide is present in a quantity from 0.001 to 0.02 mole per liter.

7. A process as claimed in claim 5 in which the copper salt is copper sulfate, the complexing agent is a sodium salt of ethylenediamine tetraacetic acid, and the hydroxide and cyanide are their sodium compounds.

8. A process of electroless copper plating which comprises immersing the receptive surface to be plated in a bath consisting essentially of water, and a water-soluble copper salt, from 0.002 to 0.15 mole per liter; a cupric ion complexing agent, from 1 to 2.5 times the moles of the copper salt; an alkali metal hydroxide, to give a pH of from 10.5 to 14; formaldehyde, from 0.06 to 3.4 moles per liter; and, as a complexing agent for cuprous ion a water soluble cyanide salt.

9. In a process of electroless copper plating which includes immersing a receptive surface to be placed in an alkaline aqueous bath having a pH of between about 10.5 and 14 and comprising water, a water soluble copper salt, a complexing agent for cupric ion, and formaldehyde, the improvement which comprises maintaining in the bath a water soluble cyanide salt in the amount of between about 0.00002 and 0.06 mole per liter.

10. The process of claim 9 wherein the water soluble cyanide is an alkali metal cyanide.

11. In an alkaline electroless copper plating bath having a pH of between about 10.5 and 14 and comprising water, a water soluble copper salt, a complexing agent for cupric ion, and formaldehyde, the improvement which comprises a water soluble cyanide salt which is present in the bath in an amount of between about 0.00002 and 0.06 mole per liter.

12. The copper plating bath of claim 11 wherein the water soluble cyanide is an alkali metal cyanide.

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