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METHOD AND BATH FOR CHEMICALLY PLATING COPPER

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ABSTRACT OF THE DISCLOSURE

A process and bath for chemically plating copper on a non-electric-conducting substrate in which a higher alkylmercaptan stabilizing agent is used. The stabilizing agent has the structure



in which n is an integer ranging from 7 to 15. The use of the stabilizing agent provides a plating bath having a greatly improved work life and also allows for the preparation of plated objects having a highly lustrous plating which is strongly adherent to other layers applied thereto in subsequent electrical plating operations.

The present invention relates to a method for chemically plating copper and the bath used therefor.

In plating various metal platings on such non-electric-conductive materials as synthetic resins, glass, porcelains, wood, etc., a method has been adopted by those in the art in which, generally, the materials are first chemically plated with copper, then the resultant copper layer is thickened by electrical copper plating, and then on this surface, arbitrary metals are plated.

This chemical copper plating method has been long known as a method for plating non-electric-conductive materials. The well-known copper plating bath consists of an alkaline aqueous solution containing water-soluble copper salts, complexing agents for forming complex compounds of cupric ion, and formaldehyde as a reducing agent for precipitating metallic copper by reducing the above-mentioned complex compounds. In order to make the above-mentioned reducing reaction with formaldehyde proceed, a catalyst of some type is required and the surface to be plated is preliminarily subjected to an activating or sensitizing treatment. When the thus treated material is then immersed in the bath, metallic copper deposits on the material by the reducing action of the formaldehyde, and thereafter, this deposited metallic copper provides the catalysing action itself which is needed to permit the plating operation to proceed to completion.

However, various difficulties are encountered in plating by this method. The first difficulty lies in the fact that the decomposition velocity of the solution is very high, the solution decomposing only in a few hours, rendering it impossible to conduct further plating operations therein, and, furthermore, the high reducing reaction velocity can not be controlled. The second difficulty lies in the fact that with the lapse of time, the surface of copper depositing on the material being plated becomes roughened, and the surface cannot be maintained in a lustrous condition, with the result that in the subsequent electric plating process, a lustrous plated surface is difficult to obtain, and moreover, the coherency of the plating to subsequently applied layers becomes inadequate. The third difficulty lies in the fact that cuprous oxide is produced as a by-product during the process and mixes into the plated copper surface, embrittling the surface being plated.

Accordingly, an object of this invention is to provide

a new, improved chemical copper plating method using a bath which permits appropriate control of the reduction reaction velocity, and accordingly, is a bath having an improved ability to endure long continuous use thereof.

Another object of this invention is to provide a chemical copper plating method and the bath used therefor whereby the plated layer obtained is always fine in texture and lustrous, thus allowing one to obtain upon subsequent electrical plating a plated surface having good coherency and luster.

A further object of this invention is to provide a chemical copper plating method and the bath used therefor whereby the copper ion in the bath may be consumed quite economically, by depositing only metallic copper on the material being plated, and by avoiding the production of cuprous oxide as a by-product.

The above objects and other objects of this invention which will become apparent in view of the following descriptions may be accomplished by the use of a chemical copper plating bath which is an alkaline aqueous solution containing water-soluble copper salt, complexing agent for cupric ion and formaldehyde, to which is added a small amount of higher alkylmercaptan represented by the general formula,



wherein, n designates an integer ranging from 7 to 15.

Among the higher alkylmercaptans of the general formula given above which are made use of in accordance with the present invention, desirable ones are dodecylmercaptan, octylmercaptan and stearylmercaptan.

That is to say, the present invention is based on the discovery that by the addition of a small amount of higher alkylmercaptan represented by the above-mentioned general formula, the reduction reaction velocity can be well controlled, thus improving upon the stability of the plating bath, and it is thereby made possible to use the plating bath continuously for periods of time that are 20 to 40 times longer in comparison to the work life of plating baths used in conventional practice, which latter baths usually become inoperable after only a few hours use. The present invention is also based on the discovery that more than about 90% of the copper ion existing in the bath may be consumed without loss, and moreover, the plated layer thereby obtained is always fine in texture and highly lustrous, and has good coherency with respect to contact with the layer subsequently produced by the electrical plating, giving a lustrous finished plated surface.

The desirable proportion of each component in the chemical plating bath of the present invention is as follows:

Compounding material:	Proportion (mol./l.)
Water-soluble copper salt -----	0.02-0.35
Complexing agent for cupric ion -----	0.04-1.75
Formaldehyde -----	0.5-1.5
Higher alkylmercaptan -----	0.0001-0.001

in addition to the above-listed materials, alkali metal hydroxides and salts such as sodium hydroxide and sodium carbonate, etc., are required to be employed to make the pH of the bath alkaline.

The alkali metal hydroxides and salts should be used in such amounts as to thereby make it possible to adjust the pH of the bath to 10.5-14, desirably 11-12, when the above-listed compounding materials are diluted with water to make a one liter solution. It is to be noted further that whereas the copper salt, complexing agent and formaldehyde, being water-soluble, may be dissolved in water, the higher alkylmercaptans, being oily materials and insoluble in water, are desirably first emulsified in water, using a suitable non-ionic surface active agent as, for example, polyoxyethylene, higher alkyl ether, etc., and this emul-

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sion is then added to the bath and dispersed therein. The especially desirable amounts of the higher alkylmercaptan which are to be used are 0.0003 to 0.0007 mol per liter. In the above-mentioned compounding ratio, the complexing agent is always required to be used in amounts which correspond to 2 to 5 times, in mols, the amount of the copper salt employed.

As the water-soluble copper salt, copper sulfate, cupric chloride, cupric nitrate, cupric acetate and cupric gluconate, may be used, with the especially desirable one being copper sulfate. As the complexing agent, there can be made use of various materials, which are themselves water-soluble and capable of forming complex compounds with cupric ion in an alkaline aqueous solution having a pH in the range of from 10.5 to 14, and representative materials thereof are Rochelle salts, sodium citrate, sodium gluconate, ethylenediamine tetraacetic acid, triethanolamine, etc. For the formaldehyde, 30-40% formalin is gesnerally employed, and in addition to it, paraformaldehyde and trioxane may also be used. In whatever form the formaldehyde is used, the amount thereof used should be so chosen that the concentration of the formaldehyde in the bath falls within the above-mentioned range.

The non-electric-conductive materials to be plated include various thermoplastic or thermosetting synthetic resins, for example, polyamide, polystyrene, acrylic resins, epoxy resins and phenol resins, etc., and glass, porcelains as well as wood, etc.

In plating the above-mentioned materials, using the plating bath of this invention, the surface to be plated is first subjected to the well-known pretreatment for activation or sensitization by forming on such surface a film formed of various metals which provide the catalytic action for the reduction reaction of this invention. The metals used in this regard include palladium, gold, platinum, silver, rhodium, copper, cobalt, and nickel, etc. Thus the surface of the material to be plated is first uniformly roughened by liquid honing or barrel tumbling. The liquid honing is carried out, for example, by playing onto the surface of the material to be plated water containing the honing agent, and in barrel tumbling a method is employed by which the surface of the material to be plated is abraded and roughened by the use of a grinding material. Then, the thus treated surface is washed with water desirably containing a neutral detergent. Subsequently, this washed surface is subjected to a chemical etching treatment. For this treatment, various methods may be employed, and representatively, a method is employed in which the surface to be plated is treated with a solution having dissolved therein 50-250 g. chromic acid and 500-1000 ml. of concentrated sulfuric acid per 1 liter of water. Then, after the treated surface is rinsed, this washed surface is treated, so as to be sensitized with a solution having dissolved therein 5-150 g. of stannous chloride and 40-100 ml. of concentrated hydrochloric acid per 1 liter of water. Further the surface to be plated which has been subjected to the above-mentioned treatment is, after rising, treated with a solution having dissolved therein 0.045-1.8 g. of palladium chloride per liter of water to form a film of palladium on the surface, thus sensitizing or activating it, followed by rinsing. It is to be noted further that paladium chloride may be substituted by chloroauric acid (HAuCl_4), for example, or other metal salts which will provide the desired catalytic action.

The above-mentioned pre-treatment illustrates but one example thereof; in addition to it various other methods may be employed including those disclosed in Metal Finishing, June, 70 (1962), whereby the metal catalyst film may be formed on the surface of the nonelectric conductive material being plated.

The chemical copper plating method of this invention is carried out by immersing the material to be plated which has been subjected to the above-mentioned activation treatment in the plating bath of this invention. The bath temperature used is 14-40° C., desirably 20-35° C.

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This plating process is finished usually in 3-10 minutes, and a plated product having a fine textured and lustrous surface is obtained. In this method, the bath has a useful continuous work life of about two weeks during which a succession of objects may be plated therein.

In the following, are given embodiments of the present invention. These examples are included to help understand this invention, and the applicable scope of this invention is not thereby restricted. Modes of application embodying the present invention that do not depart from the spirit of this invention, will be apparent to those skilled in the art from the above explanations and examples which follow:

Example 1

The surface to be plated of a 100 x 100 x 2 mm. polyvinylchloride specimen, was roughened by jetting water thereonto which contained one-tenth by weight of 400 mesh emery powder under air pressure of 3-5 kg./cm.², followed by rinsing, and thereafter, was immersed for one minute in a solution having dissolved therein 100 g. of chromic acid and 500 ml. of 98% sulfuric acid per 500 ml. of water, and then washed in running water. Then the specimen was immersed for one minute in a solution having dissolved therein 50 g. of stannous chloride, 100 ml. of 35% hydrochloric acid, and 0.5 g. of wetting agent per liter of water, washed in running water, and thereafter, immersed for one minute in a solution having dissolved therein 0.1 g. of palladium chloride per liter of water, whereby the pretreatment was finished.

This pretreated polyvinylchloride specimen was immersed to be plated, in a plating solution held at 30° C. and of the following composition:

Copper sulfate	-----g--	30
Rochelle salts	-----g--	100
Sodium hydroxide	-----g--	20
37% formalin	-----ml--	50
Dodecylmercaptan	----- (0.0005 mol) ml--	0.1
Water required to make a 1 liter solution.		

After five minutes of this latter treatment, a plated product having a lustrous, fine textured plated layer of 0.5 μ in thickness was obtained.

This plating bath was quite stable; after two weeks of continuous use, a small deposit of metallic copper on the inner surface of the vessel was observed.

It is to be noted further that dodecylmercaptan was added in the form of an emulsion prepared by emulsifying 7 ml. of it in 100 ml. of water with 3 ml. of polyoxyethylene oleylether.

Example 2

An acryl resin specimen of 100 x 100 x 2 mm. in dimension was pretreated just as in Example 1, was then immersed in a plating bath held at 20° C. and of the following composition:

Copper sulfate	-----g--	30
Rochelle salts	-----g--	100
Sodium hydroxide	-----g--	10
37% formalin	-----ml--	50
Octylmercaptan	----- (0.0007 mol) ml--	0.1
Water required to make a 1 liter solution.		

After five minutes of this latter treatment, a plated product having a lustrous, fine textured plated surface of 0.5 μ in thickness was obtained.

This plating bath was quite stable; after 10 days of continuous successive use, almost no metallic copper was deposited on the inner surface of the vessel.

It is to be noted further that octylmercaptan was added after being emulsified just as the dodecylmercaptan was emulsified as in Example 1.

Example 3

A glass specimen of 100 x 100 x 2 mm. in dimension was immersed in a solution having dissolved therein 35 g. of hydrogen fluoride and 20 g. of ammonium fluoride

per liter of water to roughen its surface, by etching, which was not the surface roughening treatment described in Example 1, and thereafter it was subjected to the same pretreatment as in Example 1. Then, this treated specimen was immersed for 5 minutes in a copper plating bath held at 35° C. and of the following composition:

Copper sulfate -----g--	30
Rochelle salts -----g--	100
37% formalin -----ml--	50
Sodium hydroxide -----g--	10
Sodium carbonate -----g--	20
Stearylmercaptan -----(0.00035 mol) ml.	0.1

Water required to make a 1 liter solution.

As in Example 1, a 0.5 μ thick plated layer having fine texture and luster was formed, and this plating bath was quite stable; it withstood 10 days of continuous use, and left almost no deposit of metallic copper on the inner surface of the vessel.

It is to be noted also that the stearylmercaptan was added after being emulsified as was the dodecylmercaptan in Example 1.

What we claim is:

1. An aqueous chemical copper plating bath solution consisting of, for each liter thereof,
0.02 to 0.35 mol of water soluble copper salt,
0.05 to 1.5 mols of formaldehyde,
0.04 to 1.75 mols of cupric ion complexing agent, the mols of said complexing agent used being 2 to 5 times the mols of said water soluble copper salt used,
0.0001 to 0.001 mol of higher alkylmercaptan having the structure



in which n represents an integer ranging from 7 to 15,

such quantities of alkaline compound as are needed to provide said solution with a pH in the range of from 10.5 to 14, and such quantities of water as are needed to make a one liter solution.

2. An aqueous chemical copper plating bath solution as in claim 1 in which said higher alkylmercaptan is selected from the group of compounds consisting of dodecylmercaptan, octylmercaptan and stearylmercaptan.

3. An aqueous chemical copper plating bath solution as in claim 2 in which said higher alkylmercaptan is dodecylmercaptan.

4. An aqueous chemical copper plating bath solution in claim 2 in which said higher alkylmercaptan is octylmercaptan.

5. An aqueous chemical copper plating bath solution as in claim 2 in which said higher alkylmercaptan is stearylmercaptan.

6. An aqueous chemical copper plating bath solution as in claim 1 in which 0.0003 to 0.0007 mol of said higher alkylmercaptan are used in each liter of said solution.

7. An aqueous chemical copper plating bath solution

as in claim 1 in which such quantities of said alkaline compound are used as are needed to provide said solution with a pH in the range of from 11 to 12.

8. An aqueous chemical copper plating bath solution as in claim 1 in which said water soluble copper salt is selected from the group of compounds consisting of copper sulfate, cupric chloride, cupric nitrate, cupric acetate and cupric gluconate.

9. An aqueous chemical copper plating bath solution as in claim 8 in which said water soluble copper salt is copper sulfate.

10. An aqueous chemical copper plating bath solution as in claim 1 in which said cupric ion complexing agent is selected from the group of compounds consisting of Rochelle salts, sodium citrate, sodium gluconate, ethylene diamine tetraacetic acid and triethanolamine.

11. An aqueous chemical copper plating bath solution as in claim 10 in which said cupric ion complexing agent is Rochelle salts.

12. An aqueous chemical copper plating bath solution as in claim 1 in which said alkaline compound is selected from the group of compounds consisting of alkali metal hydroxides and salts.

13. An aqueous chemical copper plating bath solution as in claim 12 in which

said water soluble copper salt is copper sulfate, said cupric ion complexing agent is Rochelle salts, and said higher alkylmercaptan is dodecylmercaptan.

14. An aqueous chemical copper plating bath solution as in claim 12 in which

said water soluble copper salt is copper sulfate, said cupric ion complexing agent is Rochelle salts, and said higher alkylmercaptan is octylmercaptan.

15. An aqueous chemical copper plating bath solution as in claim 12 in which

said water soluble copper salt is copper sulfate, said cupric ion complexing agent is Rochelle salts, and said higher alkylmercaptan is stearylmercaptan.

16. A chemical copper plating process which comprises immersing, in the aqueous chemical copper plating bath solution of claim 1 maintained at 15 to 40° C., the surface of a non-electric-conductive material, said surface having been previously provided with a film of metal selected from the group of metals consisting of palladium, gold, platinum, silver, rhodium, copper, cobalt and nickel,

for a period of time sufficient to allow for the plating of copper in the desired thickness on said surface.

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