

1

2

METHOD AND BATH FOR CHEMICALLY PLATING COPPER

3,377,174
Eiichi Torigai, 32 Mitsui, Yao-shi, Osaka-fu, Japan; Giichi Okuno, 2-48 Yokobori, Higashi-ku, Osaka-shi, Japan; and Hiroshi Mackawa, 365 Uenoshiba-cho, 8-cho, Sakai-shi, Osaka-fu, Japan

No Drawing. Filed Aug. 21, 1964, Ser. No. 391,278

Claims priority, application Japan, Oct. 24, 1963, 38/57,004

13 Claims. (Cl. 106-1)

ABSTRACT OF THE DISCLOSURE

A process and bath for chemically plating copper on a non-electric-conducting substrate in which chelating agents such as 2,2'-biquinoline, 2,9-dimethylphenanthroline and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline are used in the bath. The chelating agent forms a tetrahedral chelated compound selectively with cuprous ion which thereby allows for a control of the cuprous ion content of the bath in the vicinity of the substrate being plated, which in turn leads to a control of the velocity of a reduction reaction between formaldehyde and certain cupric ion complex compounds which latter reaction provides the copper used in the plating process.

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

In executing various metal platings on such non-electric-conductive materials as synthetic resins, glass, porcelains, wood, etc., a method is used in which generally, the non-electric conductive 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 which is used 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 catalyser of a sort is required and the surface to be plated is preliminarily subjected to an activating or sensitizing treatment. When the above-mentioned treated material to be plated is immersed in the bath, metallic copper deposits on the material to be plated by the reducing action of the formaldehyde, and thereafter, this deposited metallic copper provides the catalysing action by itself, whereby the plating is carried on 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, resulting in the impossibility of plating, and moreover, this high reducing reaction velocity can not be controlled. The second difficulty lies in the fact that with the lapse of time, the surface of the copper depositing on the material to be 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 coatings becomes inadequate. The third difficulty lies in the fact that cuprous oxide is formed as a by-product, which mixes into the plated copper surface, embrittling the surface to be 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 improved in its ability to endure long continuous use.

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, thereby 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 only depositing metallic copper on the material to be plated, and by avoiding the production of by-product cuprous oxide.

These objects and other objects of this invention which will become apparent in view of the following descriptions may be achieved with a chemical copper plating bath which is an alkaline aqueous solution containing water-soluble copper salt, cupric ion complexing agent and formaldehyde, to which is added a small amount of a chelating reagent which forms a tetrahedral chelated compound selectively with cuprous ion.

The present invention is based on the discovery that by the addition of the above-mentioned specified chelating reagent to the chemical copper plating bath, the cuprous ion concentration in the vicinity of the surface of the material to be plated can be controlled, and as result, the reduction reaction velocity can be readily controlled, 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 more than 20 to 40 times longer than the periods of time in which the conventional treating baths have been used and wherein the conventional bath usually becomes unusable only in a few hours; as well as 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.

Among various reagents which form chelated compounds with copper ion, those exhibiting such an effect are limited, for the purposes of the present invention, to the chelating reagents capable of forming a tetrahedral chelated compound selectively with cuprous ion only. Other reagents, for example, dithiocarbamic acids, dithizone and its derivatives, form stable chelated compounds with cupric ion rather than with cuprous ion, and are therefore unable to control the cuprous ion concentration. With them, the object of this invention cannot be achieved.

Representative chelating agents which may be used as illustrations of the chelating agents which may be used in the present invention include reagents capable of forming chelated compounds with cuprous ion by interposing a nitrogen atom; e.g., pyridyl derivatives such as 2,2'-biquinoline, etc., and phenanthroline derivatives such as 2,9 - dimethylphenanthroline, 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline, etc.

The desirable amount of each component in the chemical plating bath solution of this invention is as follows:

Compounding material:	Proportion (mols/l.)
Water-soluble copper salt	0.02-0.35
Cupric ion complexing agent	0.04-1.75
Formaldehyde	0.5-1.5
Chelating reagent	0.00001-0.001

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 bath alkaline.

The alkali metal hydroxides and salts should be used in such amounts as to make it possible to adjust the pH of the bath to 10.5-14, and to desirably 11.0-13.0, when the above-listed compounding materials are diluted with water to make a 1 liter solution. The desirable amount of reagent used to form the chelated compound selectively with cuprous ion in this invention is 0.00003-0.0001 mols./liter. In the above-mentioned compounding ratio, the complexing agent is always required to be used in amounts corresponding to 2-5 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, the especially desirable one being copper sulfate. As the complexing agent, there can be made use of various materials, which are also 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 of such complexing agents are Rochelle salts, sodium citrate, sodium gluconate, ethylenediamine tetra-acetic acid, triethanolamine, etc. be mentioned. For the formaldehyde, 30-40% formalin is generally employed, and besides it, paraformaldehyde and trioxane may be used. In whatever form it may be used, the amount thereof used should be so chosen that the concentration of formaldehyde in the bath falls within the above-mentioned range.

As the material to be plated, non-electric-conductive materials, such as 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., are made use of.

In plating these non-electric-conductive materials, using the plating bath of this invention, the surface of the material to be plated is subjected to the well-known pre-treatment for activation or sensitization so as to first form on such surfaces films of various metals which exhibit the catalytic action required for the reduction reaction of this invention, such metals including 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 surface treated as above-mentioned 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 liter of water. Then, after the treated surface is rinsed, this washed surface is treated, to be sensitized, with a solution having dissolved therein 5-150 g. of stannous chloride and 40-100 ml. of concentrated hydrochloric acid per liter of water. Further the surface to be plated which has been subjected to the above-mentioned treatment is, after rinsing, treated with a solution having dissolved therein 0.045-1.8 g. of palladium chloride per liter of water to form a palladium film on the surface, followed by sensitizing or activating the palladium film, followed by rinsing. It is to be noted further that palladium chloride may be substituted by chloroauric acid (HAuCl_4), for example, or other metal salts that will provide the desired catalytic action.

The above-mentioned pre-treatment illustrates only one example of such procedures; beside it, by various other methods such as shown in Metal Finishing, June, 70 (1962), the metal catalyst film may be formed on the surface of the non-electric-conductive material to be plated.

The chemical copper plating method of this invention is executed by immersing the material to be plated which has been subjected to the above-mentioned activation treatment in the plating bath of this invention. At this time, the bath temperature used is 15-40° C., desirably 20-35° C. This plating process is finished usually in 3-10 minutes, and a plated product having fine textured and lustrous surface is obtained. In this method, the bath has a useful life of about two weeks of continuous plating operations during which a succession of objects may be plated therein.

In the following example there 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 on the basis of the above explanations and examples which follow:

EXAMPLE 1

The plating surface a polyvinylchloride specimen of 100 x 100 x 2 mm. in dimension was roughened by jetting water onto such surface which contained one tenth by weight of 400 mesh emery powder under an air pressure of 3-5 kg./cm.², followed by rinsing, and thereafter, was immersed for 5 minutes in a solution having dissolved therein 50 g. of chromic acid and 250 ml. of 98% sulfuric acid per 500 ml. of water, then washed with running water. Subsequently, the above-treated specimen was dipped for 3 minutes in a solution dissolving therein 50 g. of stannous chloride and 100 ml. of 35% hydrochloric acid per liter of water, and was then rinsed.

The vinylchloride resin specimen subjected to this pre-treatment was plated by immersing it in a plating bath of the following composition held at 30° C.:

Copper sulfate	-----g--	50
Rochelle salts	-----g--	150
Sodium hydroxide	-----g--	30
Sodium carbonate	-----g--	20
37% formalin	-----ml--	100
2,2'-biquinoline (0.000028 mol)	-----g--	0.01
Water required to make 1 liter solution.		

Five minutes thereafter, a plated product of 0.5 μ in thickness with lustrous, fine textured plated surface was obtained. This plating bath was quite stable, and it was only after two weeks use that small deposits of metallic copper were observed on the inner surface of the vessel.

EXAMPLE 2

A 100 x 100 x 2 mm. plate specimen of "Kralastic" (acrylonitril-butadiene-styrene copolymer resin produced by Sumitomo Kagaku Kogyo Kabushiki Kaisha, Osaka, Japan) which has been subjected to a pretreatment as in Example 1 was dipped in a chemical plating bath of the following composition:

Copper sulfate	-----g--	50
Rochelle salts	-----g--	150
37% formalin	-----ml--	100
Sodium hydroxide	-----g--	30
Sodium carbonate	-----g--	25
2,9-dimethylphenanthroline (0.000087 mol)	-----g--	0.02
Water required to make 1 liter solution.		

Five minutes thereafter, a plated product of 0.5 μ in thickness with lustrous, fine textured plated surface was obtained. This plating bath was also quite stable; 10 days

5

continuous use thereof did not result in any observable metallic copper deposits.

What we claim is:

1. An aqueous chemical copper plating bath solution consisting of, for each liter thereof,

	Mols
Water-soluble copper salt -----	0.02 to 0.35
Formaldehyde -----	0.5 to 1.5
Cupric ion complexing agent -----	0.04 to 1.75

the mols of said complexing agent used being 2 to 5 times the mols of said water soluble copper salt used,

0.00001 to 0.001 mol of a chelating agent selected from the group of compounds consisting of 2,2'-biquinoline, 2,9-dimethyl-phenanthroline and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline,

such quantities of alkaline compound as are needed to provide said solution with a pH in the range 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 chelating agent is 2,2'-biquinoline.

3. An aqueous chemical copper plating bath solution as in claim 1 in which said chelating agent is 2,9-dimethyl phenanthroline.

4. An aqueous chemical copper plating bath solution as in claim 1 in which 0.00003 to 0.0001 mol of said chelating agent are used in each liter of said solution.

5. An aqueous chemical copper plating bath solution as in claim 1 in which such quantities of alkaline compound are used as are needed to provide said solution with a pH in the range of from 11 to 12.

6. 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 the alkali metal hydroxides and carbonates.

7. 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.

6

8. An aqueous chemical copper plating bath solution as in claim 7 in which said water-soluble copper salt is copper sulfate.

9. 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.

10. An aqueous chemical copper plating bath solution as in claim 9 in which said cupric ion complexing agent is Rochelle salts.

11. An aqueous chemical copper plating bath solution as in claim 6 in which

said water-soluble copper salt is copper sulfate, said cupric ion complexing agent is Rochelle salts, and said chelating agent is 2,2'-biquinoline.

12. An aqueous chemical copper plating bath solution as in claim 6 in which

said water-soluble copper salt is copper sulfate, said cupric ion complexing agent is Rochelle salts, and said chelating agent is 2,9-dimethylphenanthroline.

13. 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 a 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.

References Cited

UNITED STATES PATENTS

3,095,309	6/1963	Zeblisky et al.	106—1
3,259,559	7/1966	Schneble et al.	106—1 X

JAMES A. SEIDLECK, *Primary Examiner*.

ALEXANDER H. BRODMERKEL, *Examiner*.

L. HAYES, *Assistant Examiner*.