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3,415,666

ELECTROLESS COPPER PLATING BATH

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No Drawing. Filed June 16, 1966, Ser. No. 557,893

Claims priority, application Japan, June 19, 1965,

40/36,245

2 Claims. (Cl. 106—1)

The present invention relates to an electroless copper plating bath. Heretofore, an electroless plating process has been used in order to impart electroconductivity to a surface of an insulating material, e.g. a material made of wood, paper or plastics. Electroless copper plating is to use copper mirror reaction. The electroless copper plating is practiced by dipping an electrically insulated material in a plating bath to reduce and deposit copper on the surface of the material. The plating bath is made by adding a reductive aqueous solution containing alkalis to an aqueous solution of Formalin, hydrazine, hydroxylamines, hydroquinone of acid metal salts such as sodium hypophosphite. The Formalin is most familiar as the base of the plating bath because it is the cheapest. However, the Formalin base plating bath has fault that reduction of Formalin proceeds, once prepared and even before and after plating, to deposit copper in the bath and copper ion substantially disappears only after 2 or 3 hours, with the result that the plating bath does not work at all. Hereinafter, the time required from which copper begins to deposit in the electroless plating bath is referred to as holding time.

From a practical point of view, as above-mentioned the holding time is so short that a great trouble is caused in the operation, and that the characteristic of copper film produced is not so good.

An object of the invention is to provide an improved plating bath. Another object of the present invention is to provide an electroless copper plating bath of good stability and having extended holding time. The other object is to provide an electroless copper plating bath which can deposit a copper film enabling to electroplate a pretreated body to be plated in a short time (1–2 minutes). Further object is to provide an electroless copper plating bath in which a compact and lustrous electroless copper film is deposited on a body to be plated.

According to the present invention, an aqueous solution of acid salt of copper mentioned above and a reducing aqueous solution are mixed or small amounts of sodium thiosulfate and lower alcohol are added to the reducing aqueous solution, thereby effectively depositing copper on the pretreated body to be plated in a short period of time. The deposition of copper, however, ceases in the bath for a prolonged period of time when the plating of body to be plated is not carried out therewith. Accordingly, the holding time of the bath is remarkably extended before plating, thereby providing a good working efficiency and depositing on the body to be plated the copper film having excellent characteristic features. Thus, the present invention is advantageous from the industrial point of view.

Thus, the present invention is to provide an electroless copper plating bath prepared by adding 0.000001–0.100000 part by weight of sodium thiosulfate and 0.00080–2.400000 parts by weight of lower alcohol to 100 parts by weight of an electroless copper plating solution consisting of 35–70 parts by weight of copper sulfate, 20–200 parts by weight of Formalin, 17–340 parts by weight of Rochelle salt, 5–100 parts by weight of sodium hydroxide, 8–160 parts by weight of sodium carbonate and 1,000 parts by volume of water. It is, however, preferable to add sodium thiosulfate and lower alcohol to

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add to a mixture when prepared by mixing an aqueous solution of acid metal salt containing copper sulfate and Formalin and a reducing aqueous solution containing sodium hydroxide, Rochelle salt and sodium carbonate, are previously added to the reducing aqueous solution.

Suitable lower alcohol to be used in the present invention includes such as methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol and the like. In the electroless copper plating bath according to the present invention, when the amount of sodium thiosulfate added thereto is less than 0.00001 part by weight based on 100 parts by weight of an electroless copper plating solution, the velocity of reaction of the electroless copper plating solution becomes so fast and the holding time of said bath is so shortened that an effect and advantage cannot be obtained as desired similarly to the conventional electroless copper plating bath. Furthermore, when more than 0.100000 part by weight of sodium thiosulfate is added thereto, the deposition of copper does not take place at all on the surface of body to be plated and the function as the electroless copper plating solution is lost.

Furthermore, in the electroless copper plating bath of this invention, when the amount of lower alcohol added thereto is less than 0.000080 part by weight the copper deposited on the surface of body to be plated has no luster at all and when it is more than 2.400000 parts by weight, sodium thiosulfate does not completely dissolve, and consequently the holding time of the electroless copper plating solution cannot be extended. The holding time of the electroless copper plating bath according to this invention has more than about forty times that of the conventional electroless copper plating solution. Accordingly, in a process for the industrial scale operation the conventional bath type method can be altered to an automatic continuous method, thereby accomplishing a drastic curtailment of production cost. When the electroless copper plating bath is used, furthermore, the film of copper deposited on the surface of body to be plated had good luster and subsequent process such as electro plating of copper, nickel, chrome or the like can be smoothly carried out with ease, thereby obtaining good luster on a deposited metal. Still more, one of the great advantages of the process of this invention is that buffing which is extremely hazardous for a body having low thermal resistance is not required at all.

The present invention will be further explained fully by referring to the following examples.

EXAMPLE 1

First, an aqueous solution of acid metal salt and a reducing aqueous solution were prepared respectively according to the formulations set forth hereinbelow.

A. Aqueous solution of acid metal salt:

Copper sulfate	g--	18
Formalin	g--	100
Water	cc--	500

B. Reducing aqueous solution:

Rochelle salt	g--	85
Sodium hydroxide	g--	25
Sodium carbonate	g--	40
Water	cc--	500

Next, the electroless copper plating bath was prepared by mixing the above-mentioned two solutions with each other and adding as additives 0.019 g. of sodium thiosulfate and 3.2 g. of ethyl alcohol thereto with mixing.

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EXAMPLE 2

By the same manner as in Example 1, an electroless copper plating bath was prepared according to the following formulations.

A. Aqueous solution of acid metal salt:

Copper sulfate -----g--	10
Formalin -----g--	57
Water -----cc--	500

B. Reducing aqueous solution:

Rochelle salt -----g--	49
Sodium hydroxide -----g--	12
Sodium carbonate -----g--	23
Water -----cc--	500

C. Additive:

Sodium thiosulfate -----g--	0.0095
Methyl alcohol -----g--	1.8

EXAMPLE 3

An electroless copper plating bath was prepared according to the following formulations by the same manner as in Example 1.

A. Aqueous solution of acid metal salt:

Copper sulfate -----g--	5
Formalin -----g--	29
Water -----cc--	500

B. Reducing aqueous solution:

Rochelle salt -----g--	25
Sodium hydroxide -----g--	6
Sodium carbonate -----g--	11
Water -----cc--	500

C. Additive:

Sodium thiosulfate -----g--	0.0048
Butyl alcohol -----g--	2.4

Comparative Example 1

For comparison, an electroless copper plating solution was prepared by an aqueous solution of acid metal salt and a reducing aqueous solution previously prepared respectively by the following formulations.

A. Aqueous solution of acid metal salt:

Copper sulfate -----g--	18
Formalin -----g--	100
Water -----cc--	500

B. Reducing aqueous solution:

Rochelle salt -----g--	85
Sodium hydroxide -----g--	25
Sodium carbonate -----g--	40
Water -----cc--	500

The electroless copper plating baths and the electroless copper solution illustrated respectively in the above-mentioned Examples 1-3 and Comparative Example 1 were allowed to stand, as they are. The holding times thereof were measured with the result as denoted in the following table. The holding time was determined by the visual observation at the moment when the foam of hydrogen gas just begins to generate.

TABLE

Example No:	Holding time (hr.)
1 -----	80
2 -----	110
3 -----	100
Comparative Example 1 -----	2

As is clear from the above results, the holding time of the electroless copper plating bath distinctively extends over for a long space of time, compared with that of the conventional electroless copper plating solution.

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Next, the samples of ABS resin (acrylonitrile-butadiene-styrene copolymer) subjected to pretreatment, i.e. (1) surface roughing, (2) degrease-washing with water, (3) surface cleaning, (4) washing with water, (5) sensitization, (6) washing with water, (7) activation and (8) washing with water, were respectively immersed in the electroless copper plating baths of Examples 1-3 and the electroless copper plating solution of Comparative Example 1, so that the time required for depositing a copper film of 0.3μ in thickness capable of enabling subsequent electro plating, can be measured. As a result, in each case of Examples 1-3 it took one minute 30 seconds and in case of Comparative Example 1, 12 minutes. Furthermore, the luster of copper film attained in Examples 1-3 using the electroless copper plating bath of this invention was precise and good, compared with that attained in Comparative Example 1 using the conventional electroless copper plating solution.

EXAMPLE 4

An electroless copper plating bath was prepared according to the following formulations.

A. Aqueous solution of acid metal salt:

Copper sulfate -----g--	17.5
Formalin -----g--	100
Water -----cc--	500

B. Reducing aqueous solution:

Rochelle salt -----g--	42
Sodium hydroxide -----g--	22.5
Sodium carbonate -----g--	10
Water -----cc--	500

C. Additive:

Sodium thiosulfate -----g--	0.005
Propyl alcohol -----g--	3

The resultant electroless copper plating bath was allowed to stand for measuring its holding time. As a result, the holding time was 110 hours. Furthermore, the sample of ABS resin pretreated by the same manner as in the aforementioned example was immersed in said bath to measure the depositing time for obtaining a copper film of 0.3μ in thickness. As a result, it was 1 minute 30 seconds.

EXAMPLE 5

An electroless copper plating bath was prepared according to the following formulations in the same manner as in Example 1.

A. Aqueous solution of acid metal salt:

Copper sulfate -----g--	15
Formalin -----g--	100
Water -----cc--	500

B. Reducing aqueous solution:

Rochelle salt -----g--	42
Sodium hydroxide -----g--	22.5
Sodium carbonate -----g--	10
Water -----cc--	500

C. Additive:

Sodium thiosulfate -----g--	0.001
Isopropyl alcohol -----g--	1

The resultant electroless copper plating bath was allowed to stand for measuring its holding time. As a result, it was 90 hours. Furthermore, the sample of ABS resin pretreated by the same manner as in the aforementioned example was immersed in said bath to measure the depositing time for obtaining a copper film of 0.3μ in thickness. As a result, it was 1 minute 30 seconds.

As above, besides that the holding time of the electroless plating bath of the present invention extends over a long space of time, as compared with the conventional electroless solution, its velocity of the deposition of copper on a body to be plated is fast, its copper film has a precise luster and its working efficiency is improved. Thus, the present invention is to make a distinctive contribution to the industries concerned.

What is claimed is:

1. An electroless copper plating bath comprising 0.000001–1.00000 part by weight of sodium thiosulfate, 0.000080–2.400000 parts by weight of lower alcohol, in 100 parts by weight of an electroless copper plating solution consisting of 3.5–70 parts by weight of copper sulfate, 20–200 parts by weight of Formalin, 17–340 parts by weight of Rochelle salt, 5–100 parts by weight of sodium hydroxide, 8–160 parts by weight of sodium carbonate and 1000 parts by volume of water.

2. An electroless copper plating bath of claim 1, wherein lower alcohol is one kind or more selected from the group consisting of methyl alcohol, ethyl alcohol,

propyl alcohol, isopropyl alcohol, butyl alcohol and isobutyl alcohol.

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U.S. Cl. X.R.

117—47, 71, 130, 160