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(54) ELECTROLESS COPPER PLATING BATH

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London EC2V 8AH, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to aqueous electroless copper plating baths and to products obtained by means of such baths.

Electroless copper plating baths usually contain formaldehyde, or a compound which yields formaldehyde, as a reducing agent, cupric ions and one or more compounds which form a complex with cupric ions. The reduction of cupric ions to a metal can only take place in an alkaline medium, preferably in a pH range between 12 and 13.

Such an alkaline bath is disclosed in United States Patent Specification 3,095,309, which bath is capable of depositing good, ductile copper on layers consisting of metal nuclei which may be obtained by chemical or photographic means and which nuclei catalyse the copper deposition. This copper plating bath contains an inorganic cyanide and/or an organic nitrile as a complexing agent.

United Kingdom Patent Specification 1,330,332 discloses a copper plating bath which contains as essential constituents a soluble copper salt, one or more complexing agents, formaldehyde and a polyoxyalkylene compound.

The stability of electroless copper plating solutions has always been a weak point. To improve it various measures have been tried such as filtering, adding a large quantity of methanol, passing oxygen through the solution and complexing cupric ions. United States Patent Specification 3,095,309 uses the addition of cyanide to complex cupric ions.

Netherlands Patent Application 7300599 which has been laid open to public inspection, proposes the addition of

compounds of the thionophosphate type to the copper plating solutions. A nitro group may *inter alia* be present as a substituent, such as, for example, in the compound diethyl-*p*-nitrophenylthionophosphate, which is known by the trade name Parathion. This type of compound is generally very poisonous, which is a great drawback for industrial use. However, toxicity is also a drawback of the above mentioned cyanide-containing bath.

During the investigations which led to the invention, it was found, that simple aromatic nitro-compounds are particularly effective for stabilising electroless copper plating solutions containing formaldehyde as a reducing agent.

The invention provides an aqueous alkaline electroless copper-plating bath containing cupric ions, a compound which forms complexes with cupric ions, alkali, formaldehyde or a compound which yields formaldehyde, and an addition consisting of a substituted aromatic nitro-compound having at least one of the following groups as a substituent: aldehyde, alkyl, sulphonic acid, hydroxyalkyl, α -hydroxyketoalkyl, *p*-amino, or an additional nitro group, and wherein the pH of the bath is in the range from 10 to 13.

It is advantageous if the copper plating bath according to the invention contains at least one polyalkylene oxidic compound containing at least 4 alkoxy groups. Such polyalkylene oxidic compounds are used in the solutions described in United Kingdom Patent Specification 1,330,332. It was found that an electroless copper-plating bath according to the invention had a considerably better selectivity for intensifying nuclear metal images than a similar bath containing no substituted aromatic nitro-compound.

Some embodiments of the invention will now be further described with reference to the following Examples.

EXAMPLES.

Various aromatic nitro-compounds were

added to the baths of the following two compositions.

Composition I.

7.5 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

5 85 g/l sodium potassium tartrate (Rochell salt)

15 g/l Na_2CO_3

12 g/l NaOH

10 36 ml/l formalin (solution 37% by weight) working temperature 25°C , pH of 12.3.

Composition II.

7.5 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

15 21 g/l tetrasodium salt of ethylenediamine-tetra-acetic-acid

3 g/l NaOH

7 ml/l formalin (solution 37% by weight)

2 g/l "TRITON (Trade Mark) QS 44" working temperature 70°C , pH of 12.2.

"TRITON QS 44" of Messrs. Rohm and Haas is an alkyl phenoxy polyethylene phosphate ester having a molecular weight of approximately 800 and containing approximately 8 ethoxy groups.

One of the following nitrobenzene derivatives was added to a quantity of each of compositions I and II, 0.1 g/l of the derivative being added to composition I and 1 g/l of the derivative being added to composition II and thereafter 10 ml/l of a solution of 2 g/l PdCl_2 . The Table below specifies the time in minutes after which the baths became unstable. These tests are accelerated tests used for evaluation of the compositions. The presence of the PdCl_2 provides decomposition nuclei. In the absence of the PdCl_2 addition, baths according to the invention were found to be stable for some days.

TABLE

Compound added	Composition I	Composition II
none	0 - 2	0 - 2
2-Cl-4-nitro-aniline	10 - 15	5 - 10
m-nitrobenzaldehyde	15 - 20	15 - 20
p-nitrotoluene	20 - 25	5 - 10
m-nitrobenzenesulphonic acid	20 - 25	5 - 10
o-nitrobenzaldehyde	25 - 30	25 - 30
m-dinitrobenzene	30 - 35	25 - 30
p-nitrobenzaldehyde	60 - 65	40 - 45

40 No improvement in stability was found when *inter alia* halogenized nitrobenzene, methoxylized nitrobenzene and unsubstituted nitrobenzene, were added. The deposition rates of the copper, that is to say 2 μm /hour for composition I and 4 μm /hour for the composition II at the specified working temperatures were not influenced by the addition.

WHAT WE CLAIM IS:—

50 1. An aqueous alkaline electroless copper-plating bath containing cupric ions, a compound which forms complexes with cupric ions, alkali, formaldehyde or a compound which yields formaldehyde, and an addition consisting of a substituted aromatic nitro-compound having at least one of the following groups as a

substituent:— aldehyde, alkyl, sulphonic acid, hydroxyalkyl, α -hydroxyketoalkyl, p-amino or an additional nitro group, and wherein the pH of the bath is in the range from 10 to 13.

2. An aqueous alkaline electroless copper-plating bath as claimed in Claim 1, containing at least one polyalkylene oxidic compound containing at least 4 alkoxy groups.

3. An aqueous alkaline electroless copper-plating bath containing a substituted aromatic nitro-compound, substantially as herein described with reference to any of the Examples and to the Table.

4. A product obtained by means of an aqueous alkaline electroless copper-plating bath as claimed in any preceding Claim.



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Composition I.

- 5 7.5 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
85 g/l sodium potassium tartrate (Rochell salt)
15 g/l Na_2CO_3
12 g/l NaOH
10 36 ml/l formalin (solution 37% by weight)
working temperature 25°C , pH of 12.3.

Composition II.

- 7.5 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
15 21 g/l tetrasodium salt of ethylenediamine-tetra-acetic-acid
3 g/l NaOH
7 ml/l formalin (solution 37% by weight)
2 g/l "TRITON (Trade Mark) QS 44"
working temperature 70°C , pH of 12.2.

"TRITON QS 44" of Messrs. Rohm and Haas is an alkyl phenoxy polyethylene phosphate ester having a molecular weight of approximately 800 and containing approximately 8 ethoxy groups.

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2. An aqueous alkaline electroless copper-plating bath as claimed in Claim 1, containing at least one polyalkylene oxidic compound containing at least 4 alkoxy groups.

3. An aqueous alkaline electroless copper-plating bath containing a substituted aromatic nitro-compound, substantially as herein described with reference to any of the Examples and to the Table.

4. A product obtained by means of an aqueous alkaline electroless copper-plating bath as claimed in any preceding Claim.



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