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PATENT SPECIFICATION

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(54) ELECTROLESS COPPER PLATING SOLUTIONS

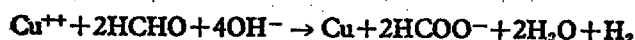
(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED of Abacus House, 33 Gutter Lane, London, EC2V 8AH, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and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

The invention relates to electroless aqueous copper plating solutions and to a method of preparing such solutions.

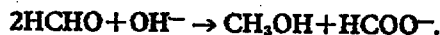
As a rule electroless copper plating solutions comprise cupric ions, one or more compounds which form a complex with cupric ions and a reducing agent which is usually formaldehyde or a compound which is capable of producing formaldehyde. With such a solution the reduction of cupric ions to metal can only take place in an alkaline medium preferably in the pH-range between 12 and 13.

United States Patent Specification No. 3,615,732 discloses such an alkaline solution by means of which good, ductile copper can be deposited on layers of metal nuclei which may have been obtained either chemically or photographically and which act as a catalyst for the electroless copper deposition. In accordance with this patent specification, the inclusion of hydrogen during the decomposition reaction of an electroless copper plating bath is prevented and the ductility of the deposited copper is improved by the addition of a compound which forms with formaldehyde an addition-product such as a sulphite, a bisulphite or a phosphite. An electroless copper plating bath described in that United States Patent Specification comprises as essential constituents a soluble cupric salt, alkali for adjusting the pH, one or more complexing agents for cupric ions, formaldehyde or a compound which is capable of producing formaldehyde and, preferably, also a polyoxyalkylene compound.

An annoying property of formaldehyde is that in an alkaline medium it takes part to side-reactions so that the greater part is lost for the reduction reaction from cupric ions to copper metal



An unwanted side-reaction is the so-called Cannizzaro reaction, in which formates are formed according to



The so-called aldol condensation takes place which also contributes to the loss of formaldehyde from the solution.

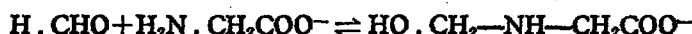
The above-mentioned formaldehyde addition products decompose substantially completely in an alkaline medium so that the disadvantages of the occurrence of the above-mentioned side-reactions remains. Consequently, when the copper plating baths are used continuously much more formaldehyde must be added than is in accordance with the reaction which is responsible for the copper deposition.

It is an object of the invention to provide a composition of the bath in which the unwanted reactions do not occur anymore or are reduced to such an extent that they are no longer annoying.

The invention provides an electroless aqueous copper plating solution comprising cupric ions, at least one cupric ion-complexing compound, alkali for adjusting the pH of the solution, formaldehyde or a compound capable of producing formaldehyde, and one or more salts of an aminoalkane carboxylic acid, of an aminoalkane sulphonic acid or of an aminoalkane phosphonic acid, which salt(s) contain(s) no

bivalent sulphur and have at least one free —NH_2 group predominantly in the form of an addition product with formaldehyde via said —NH_2 group. According to one aspect of the invention, the molar salt concentration of the solution is not greater than the molar formaldehyde concentration. The alkali may be an alkaline substance such as an alkali metal hydroxide or an alkali metal carbonate.

The addition compound discussed here is formed in the copper plating solution by adding an amino-acid and the formaldehyde as such. The compound may also be prepared separately, for example according to



at a pH of over 7.

The presence of the above-said addition product has in the first place the advantage that the undesired Cannizzaro reaction is reduced to a non-annoying level.

By way of illustration two experiments are discussed here. In the first experiment a solution of 1.5 mol/l formaldehyde-bisulphite compound to which NaOH is added so as to give a pH of 12.8 is heated for 5.5 hours at 52° C. In the second experiment a solution of 1.5 mol of the addition product glycine-formaldehyde to which NaOH is added so as to give a pH of 12.8 is heated at 60° C for 6.5 hours. In the first experiment 40% of the formaldehyde is converted into formate and in the second experiment less than 1%. The determination of formate is done by means of nuclear magnetic resonance (nmr) by measuring the formate proton. In these experiments the Cu^{++} has been omitted from the solution because the paramagnetic Cu^{++} is a disturbing factor in the nmr-determination.

During use the solution according to the invention is replenished by the addition of formaldehyde.

A further advantage of the solution according to the invention is a good quality of the copper deposited therefrom as regards ductility. That this is caused by the presence of amino-acids or addition products is the more surprising because in general hydrogen-containing compounds such as urea, pyridine or quaternary ammonium compounds give inferior copper deposits as regards appearance and ductility.

The increased stability of the reducing agent reduces the formation of by-products. Especially the fact that a smaller quantity of ionic by-products is formed is of very great importance for a production bath which is in continuous operation.

An additional advantage of the bath according to the invention is that the unpleasant smell of formaldehyde is substantially not noticeable.

A solution according to the invention contains one or more salts of aminoalkane-carboxylic, aminoalkanesulphonic or aminoalkanephosphonic acids defined above having at least one free —NH_2 group in the form of the addition compound with formaldehyde in which the grouping $\text{—NH—CH}_2\text{OH}$ is present.

Compounds with other nitrogen groups such as amides, amines, urea compounds or peptides show no effect or even impair the quality of the deposited copper. Amino-acids which contain bivalent sulphur must not be used because they result in poisoning of the copper surface.

It should be noted that, for example, in DT—OS 2,051,279 glycine is mentioned amongst a large number of complexing agents for cupric ions in electroless copper plating baths. However, in the copper plating solution according to the invention another complexing agent is invariably present, whilst besides that one or more salts of an aminoalkane-carboxylic acid, of an aminoalkanesulphonic acid, or of an aminoalkanephosphonic acid defined above, in a quantity preferably up to the stoichiometrical proportion with formaldehyde is added.

The presence in a solution according to the invention of an effective concentration of one or more soluble polyoxyalkylene compounds, which contain at least 4 alkoxy groups, as is known *per se* from United Kingdom Patent Specification No. 1,330,332 has an extra favourable effect in combination with the salt of an aminoalkane-carboxylic acid, or of an aminoalkanesulphonic acid, or of an aminoalkanephosphonic acid defined above.

A practically very interesting embodiment of the invention is an electroless copper plating solution having the tetrasodium salt of ethylenediaminetetra-acetic acid as a complexing agent for cupric ions and glycine to form an addition compound with formaldehyde.

The copper plating solution according to the invention is prepared in such a way that the salts of the aminoalkylcarboxylic acid, of the aminoalkane sulphonic acid, or of the aminoalkanephosphonic acid and the formaldehyde are added separately in

quantities wherein the salt preferably is, at most, molarly equal to the quantity of formaldehyde.

During use the quantity of formaldehyde gradually decreases but when the bath is replenished with a cupric salt this quantity must be brought to the original level again.

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

EXAMPLE I.

Glass plates, roughened on one side by means of carborundum paper were activated for electroless copper deposition by moving them first for 2 minutes at ambient temperature in a solution of 50 g stannous chloride and 10 ml of concentrated hydrochloric acid in 1 litre of deionised water, were washed for 15 seconds in running deionised water, were then sensitised by moving them for 1 minute in a solution of 0.25 g PdCl_2 and 10 ml of concentrated HCl in one litre of deionised water and were finally rinsed by moving them again for half a minute in running deionised water. These operations were repeated a second time wherein the glass plates were moved for 45 seconds in the stannous chloride solution and for 30 seconds in the PdCl_2 solution. Thereafter the glass plates were processed for 30 seconds in an aqueous solution at 50°C which contains per litre 0.10 mole NaOH and 0.10 mole formaldehyde and were immediately thereafter rinsed for 15 seconds in deionised water at 50°C . The plates nucleated in this manner were thereafter subjected to electroless plating in a solution which was heated to 60°C and which contained the following constituents per litre:

0.06 mole $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

0.066 mole tetrasodium salt of ethylenediaminetetra-acetic acid

0.15 mole hydroxymethylaminopotassium acetate (addition product of formaldehyde and glycine) and approximately 0.10 mole NaOH was used to adjust the pH of the solution to 12.5.

After $5\frac{1}{2}$ hours a thickness of approximately 13 microns of copper had been deposited on the glass plate. The ductility of the deposited copper layer was $2\frac{1}{2}$ bends. If instead of 0.15 mole of the addition product 0.15 mole of free formaldehyde was added (the pH was again 12.5), the solution was unstable and brittle copper was deposited on the glass plate.

EXAMPLE II.

Glass plates which had been nucleated in the manner described in Example I were plated at 50°C in a solution (A) which contained per litre:

0.06 mole $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

0.066 mole tetrasodium salt of ethylenediaminetetra-acetic acid approximately 0.10 mole NaOH was used to adjust the pH to 12.6

0.10% by weight of the polyoxyethylene compound "Triton" (Trade Mark) QS 44
0.15 mole hydroxymethylaminopotassium acetate.

"Triton" QS 44 is an anionic phosphate ester having approximately 8 ethylene oxide groups (molar weight approximately 800), and is supplied by Rohm and Haas Corporation.

The addition product is added in the form of a 3.5 mole aqueous solution having a pH of 12.8. After 6 hours approximately 11 microns of copper had been deposited on the glass plate. The ductility of the copper layer was 4 bends. For comparison a solution (B) was made in which the addition product was replaced by a concentration of free formaldehyde of 0.02 mol/l so that the rate of deposition during one hour had the same value and which, as regards the other constituents of the bath was identical to the above solution. With both solutions, each using a volume of 200 ml, one solution having an addition product of formaldehyde and glycine, the other having free formaldehyde, copper was deposited on glass plates which had been nucleated in the manner described in Example I (surface area 5.9 cm^2) at a temperature of 50°C for a working day of 6 hours. After each day the quantity of cupric ions used up was determined and the cupric ion concentration of the solution was restored to its original value. After the pH had been adjusted to the original value, copper was deposited on new nucleated glass plates. In this manner the exhaustion of the form-

aldehyde content of the solutions could be studied. The quantities of copper deposited per hour by the two solutions had the following values:

TABLE I

	solution A	solution B
1st day	1.3 mg/cm ²	1.3 mg/cm ²
2nd day	1.1 mg/cm ²	0.5 mg/cm ²
3rd day	1.1 mg/cm ²	0.15 mg/cm ²

EXAMPLE III.

Glass plates which had been nucleated using the method described in Example I were electrolessly copper plated at a temperature of 52° C in solutions which contained per litre the following constituents:

0.06 mole CuSO₄ · 5H₂O

0.066 mole tetrasodium salt of ethylenediaminetetra-acetic acid

NaOH was added to adjust the pH to the required value.

- A) varying concentrations in mole/l of hydroxymethylaminopotassium acetate, or
B) varying concentration in mole/l of free formaldehyde.

The quantities of copper deposited per hour were as follows:—

TABLE II'

Conc. A	pH 12.4	pH 12.6	Conc. B	pH 12.4
0.10	3.4 mg/cm ²	4.0 mg/cm ²	0.01	0.4 mg/cm ²
0.20	3.6 mg/cm ²	4.6 mg/cm ²	0.02	2.4 mg/cm ²
0.30	3.6 mg/cm ²	4.7 mg/cm ²	0.03	3.7 mg/cm ²
0.50	3.5 mg/cm ²	4.7 mg/cm ²	0.04	4.7 mg/cm ²

The results show that unlike the solutions prepared using free formaldehyde, the solutions prepared using hydroxymethylaminopotassium acetate have substantially stable rates of deposition over a wide range of concentrations of the formaldehyde source, which is of great importance for practical use.

EXAMPLE IV.

Glass plates which had been nucleated using the method described in Example I were electrolessly copper plated in solutions which contained the following constituents per litre:

A) 0.06 mole CuSO₄ · 5H₂O

0.066 mole tetrasodium salt of ethylenediaminetetra-acetic acid

0.10 mole NaOH used to adjust the pH.

B) solution A+0.13 mole addition product of β-alanine and formaldehyde (K-salt)

C) solution A+0.13 mole addition product of α-alanine and formaldehyde (K-salt)
+0.10% per weight of polyoxyethylene compound
" Triton " QS 30 (Rohn and Haas), an anionic acid phosphate ester,

D) solution A+0.10 mole addition product of serine and formaldehyde (K-salt)
+0.10% by weight " Triton " QS 30.

20

Some data as regards pH and temperature of the solutions and the results obtained are as follows:

TABLE III

	Solution B	Solution C	Solution D
pH	12.9	12.8	12.8
Temperature	60°C	52°C	52°C
Deposit thickness after 5 hours	9 microns	15 microns	13 microns
Ductility	>3 bends	1 bend	2 bends

EXAMPLE V.

5 Glass plates which had been nucleated by using the method described in Example I were plated in solutions having various concentrations of (free) formaldehyde and of glycine and which also contain the following constituents per litre: (temperature 52° C):

10 0.06 mole $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
0.066 mole tetrasodium salt of ethylenediaminetetra-acetic acid
0.10 mole NaOH to adjust the pH of the solution to a value of 12.8.
0.10% by weight of polyoxyethylene compound "Triton" QS 44
X mole (free) formaldehyde
Y mole glycine.

15 The pH of the solution was kept constant in all cases (approximately 12.8). The results are shown in Table IV.

TABLE IV

X	0.10	0.10	0.10	0.15	0.15	0.15
Y	—	0.05	0.10	0.05	0.10	0.15
Deposit thickness after 5 hours in microns	20	15	8	16	13	9
Ductility (bends)	brittle	1½	>3	½	1½	>3

EXAMPLE VI.

20 Glass plates which had been nucleated using the method described in Example I were electrolessly copper plated at a temperature of 52° C in a solution which contained per litre:

25 0.06 mole $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
0.066 mole ethylenediaminetetrasodium acetate
0.10 mole NaOH used to adjust the pH
0.15 mole hydroxymethylaminoethanesodium sulphonate (addition product of formaldehyde and 2-aminoethanesodium sulphonate).

After 6 hours approximately 13 microns of copper had been deposited which had a ductility of at least 2 bends.

EXAMPLE VII.

Glass plates which had been nucleated using the method described in Example I were electrolessly copper plated at a temperature of 50° C in a solution which contained the following constituents per litre:

- | | | |
|----|--|----|
| 5 | 0.02 mole $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | 5 |
| | 0.10 mole triethanolamine | |
| | 0.40 mole NaOH used to adjust the pH | |
| | 0.10 mole hydroxymethylaminopotassium acetate | |
| 10 | 0.20% per weight of polyalkaleneglycol "Pluronic" (Trade Mark) F 108 (manufactured by Wyandotte Chemical Corporation). | 10 |

After 5 hours 15 microns of copper had been deposited on the glass plate. The ductility of the deposit was 2 bends. If "Pluronic" F 108 was replaced by 0.025% by weight of a thio-ether ($\text{C}_{12}\text{H}_{25}-\text{S}-$) of "Pluronic" F 108 then the stability of the solution was increased whilst 12 microns of copper was deposited in 5 hours and this had a ductility of 4 bends.

WHAT WE CLAIM IS:—

- | | | |
|----|---|----|
| 1 | An electroless aqueous copper plating solution comprising cupric ions, at least one cupric ion-complexing compound, alkali for adjusting the pH of the solution, formaldehyde or a compound capable of producing formaldehyde, and one or more salts of an aminoalkanecarboxylic acid, of an aminoalkanesulphonic acid, or of an aminoalkanephosphonic acid, which salt(s) contain(s) no-bivalent sulphur and have at least one free $-\text{NH}_2$ group predominantly in the form of an addition product with formaldehyde via said $-\text{NH}_2$ group and in a quantity which is preferably at the utmost molarly equal to the quantity of formaldehyde present. | 20 |
| 25 | 2. An electroless aqueous copper plating solution as claimed in Claim 1, wherein the salt concentration (expressed in moles) of the solution is not greater than the formaldehyde concentration (expressed in moles). | 25 |
| 30 | 3. An electroless aqueous copper plating solution as claimed in Claim 1 or Claim 2, which contains an effective concentration of one or more soluble polyoxyalkylene compounds which contain at least 4 alkoxy groups. | 30 |
| 35 | 4. An electroless aqueous copper plating solution as claimed in any preceding Claim, which contains the tetrasodium salt of ethylenediaminetetra-acetic acid as a complexing agent for cupric ions and glycine as an aminoalkane carboxylic acid. | 35 |
| | 5. An electroless aqueous copper plating solution as claimed in Claim 1, substantially as herein described with reference to any of Examples I to VIII. | |
| | 6. A method of preparing an electroless aqueous copper plating solution as claimed in any of Claims 1 to 4, wherein the salt of the aminoalkanecarboxylic acid, of the aminoalkanesulphonic acid or of the aminoalkanephosphonic acid respectively and the formaldehyde are added as such during preparation of the solution. | |

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EXAMPLE VII.

Glass plates which had been nucleated using the method described in Example I were electrolessly copper plated at a temperature of 50° C in a solution which contained the following constituents per litre:

- 5 0.02 mole $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 5
0.10 mole triethanolamine
0.40 mole NaOH used to adjust the pH
0.10 mole hydroxymethylaminopotassium acetate
10 0.20% per weight of polyalkaleneglycol "Pluronic" (Trade Mark) F 108 (manufactured by Wyandotte Chemical Corporation). 10

15 After 5 hours 15 microns of copper had been deposited on the glass plate. The ductility of the deposit was 2 bends. If "Pluronic" F 108 was replaced by 0.025% by weight of a thio-ether ($\text{C}_{12}\text{H}_{25}-\text{S}-$) of "Pluronic" F 108 then the stability of the solution was increased whilst 12 microns of copper was deposited in 5 hours and this had a ductility of 4 bends. 15

WHAT WE CLAIM IS:—

- 20 1. An electroless aqueous copper plating solution comprising cupric ions, at least one cupric ion-complexing compound, alkali for adjusting the pH of the solution, formaldehyde or a compound capable of producing formaldehyde, and one or more salts of an aminoalkanecarboxylic acid, of an aminoalkanesulphonic acid, or of an aminoalkanephosphonic acid, which salt(s) contain(s) no-bivalent sulphur and have at least one free $-\text{NH}_2$ group predominantly in the form of an addition product with formaldehyde via said $-\text{NH}_2$ group and in a quantity which is preferably at the utmost molarly equal to the quantity of formaldehyde present. 20
- 25 2. An electroless aqueous copper plating solution as claimed in Claim 1, wherein the salt concentration (expressed in moles) of the solution is not greater than the formaldehyde concentration (expressed in moles). 25
- 30 3. An electroless aqueous copper plating solution as claimed in Claim 1 or Claim 2, which contains an effective concentration of one or more soluble polyoxyalkylene compounds which contain at least 4 alkoxy groups. 30
4. An electroless aqueous copper plating solution as claimed in any preceding Claim, which contains the tetrasodium salt of ethylenediaminetetra-acetic acid as a complexing agent for cupric ions and glycine as an aminoalkane carboxylic acid.
- 35 5. An electroless aqueous copper plating solution as claimed in Claim 1, substantially as herein described with reference to any of Examples I to VIII. 35
6. A method of preparing an electroless aqueous copper plating solution as claimed in any of Claims 1 to 4, wherein the salt of the aminoalkanecarboxylic acid, of the aminoalkanesulphonic acid or of the aminoalkanephosphonic acid respectively and the formaldehyde are added as such during preparation of the solution.

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