

[54] **ELECTROLESS DEPOSITION OF COPPER AND COPPER-TIN ALLOYS**
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[57] **ABSTRACT**
Electroless bath compositions for the deposition of copper or copper-tin alloys, said baths being devoid of formaldehyde or potassium heptagluconate and having less alkalinity than prior art baths, said baths providing highly adherent deposits to such substrates as steel, for example, and consisting of:
Copper sulfate·5H₂O
Di-sodium salt of Ethylenediamine tetra-acetic acid·2H₂O
Ammonium hydroxide (28 percent NH₃)
Dimethylamine borane
and if a copper-tin alloy deposit is desired, stannous chloride·2H₂O.

11 Claims, No Drawings

ELECTROLESS DEPOSITION OF COPPER AND COPPER-TIN ALLOYS

The invention described herein may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

This invention relates to electroless deposition and more particularly concerns improved bath compositions for the electroless deposition of copper and copper-tin alloys.

A principal object of the invention is to provide bath compositions yielding electroless copper or copper-tin alloy deposits which possess good bond strength to substrates such as steel.

This and other objects of the invention will become apparent as the invention is further described hereinafter.

Electroless copper plating baths of the prior art require the presence of formaldehyde, a reducing agent, the bath being very strongly alkaline and having a pH approaching 13. It is believed the strong alkalinity of these prior art baths promoted passivation of the steel, thus preventing attainment of good adherent deposits. Further, the use of diemthylamine borane, a reducing agent, hereinafter referred to as DMAB, in the prior art electroless copper plating baths required the presence of potassium heptagluconate, a complexing agent and stabilizer, which is not readily available and is relatively expensive compared to the salts used in the present invention.

We have discovered improved electroless copper plating bath compositions consisting of copper sulfate.5H₂O, disodium salt of ethylenediamine tetraacetic acid, hereinafter referred to as EDTA, ammonium hydroxide (28 percent NH₃) and DMAB; and improved electroless copper-tin plating bath compositions including stannous chloride.2H₂O to the above.

More specifically, improved bath compositions depicting our invention are shown below:

TABLE I

Electroless Copper Plating Bath Compositions		
Constituent	Preferred Concentration	Effective Range
Copper sulfate.5H ₂ O	2 g/l	0.5 - 3.0 g/l
Na ₂ C ₁₀ H ₁₄ O ₈ N ₂ .2H ₂ O	6 g/l	1.0 - 10.0 g/l
Ammonium hydroxide (28% NH ₃)	50 ml/l	5 - 150 ml/l
DMAB (C ₂ H ₆ NHBBH ₃)	4 g/l	0.5 - 10 g/l
pH	Approx. 10.7	8 - 11

TABLE II

Electroless Copper-Tin Plating Bath Compositions		
Constituent	Preferred Concentration	Effective Range
Copper sulfate.5H ₂ O	1 g/l	0.5 - 2.0 g/l
Stannous chloride.2H ₂ O	2 g/l	0.1 - 5.0 g/l
Na ₂ C ₁₀ H ₁₄ O ₈ N ₂ .2H ₂ O	6 g/l	1.0 - 10.0 g/l
NH ₄ OH (28% NH ₃)	50 ml/l	5 - 150 ml/l
DMAB	4 g/l	0.5 - 10 g/l

The above baths will normally be used at a maximum pH of about 10.7 and about 60C.

All solutions were prepared with reagent grade chemicals. DMAB however, was at least of 99 percent purity.

Specimens of steel, copper, and electroless nickel plated steel were prepared for electroless copper plating by alkaline cleaning, rinsing, immersing one minute in 50 percent (vol.) HCl at 25C and rinsing. Specimens of plastic, e.g., acrylonitrile-butadiene-styrene, were etched three minutes in 420 g/l chromic acid - 190 ml/l sulfuric acid (sp. gr. 1.84) at 57C. The plastic was rinsed and activated by one minute immersion in 5 g/l stannous chloride - 10 ml/l HCl (37 percent) at 25C, rinsing; one minute immersion in 0.1 g/l palladium chloride - 0.1 ml/l HCl (37 percent) at 25C, and rinsing. All specimens were immersed into an electroless DMAB-copper or copper-tin plating bath and examined for copper or copper-tin deposition.

The effect of copper concentration at 50 ± 1°C on deposition rate was determined with the disodium salt of EDTA present at a molar concentration double that of copper. Electroless copper deposition reached a maximum rate at about 4 g/l copper sulfate pentahydrate but the deposits were powdery, and at 0.5 g/l, the deposition rate was slow. Optimum copper concentration was determined to be about 2 g/l of the copper salt.

Ammonium hydroxide concentration of 5 to 150 ml/l had little effect on deposition rate. At the lower concentration, deposition rates decreased somewhat, while at the upper concentration of 150 ml/l, the deposition rate was substantially identical with the preferred concentration of about 50 ml/l. Ammonium hydroxide plays an important role in stabilizing our bath compositions, since baths at a given pH, using sodium hydroxide instead of ammonium hydroxide, were subject to decomposition with formation of spongy copper. Ammonium hydroxide is an effective complexing agent for the copper ions.

Effect of DMAB concentration on electroless copper deposition rate was determined at 50C with a solution consisting of 2 g/l CuSO₄.5H₂O, 6 g/l the disodium salt of EDTA, and 50 ml/l NH₄OH (28 percent NH₃). Deposition rates increased with increasing DMAB concentration up to about 4 g/l with no additional benefits when the preferred concentration was exceeded.

The disodium salt of EDTA chelates the copper salt in order to provide solution stability. When the disodium salt of EDTA is present in the bath at the lower concentration of only 1 g/l, instability of the bath results. When the upper concentration of 10 g/l is employed, the deposition rate will be suppressed. A concentration of about 6 g/l will yield the best deposits.

2 g/l of the tin salt was selected as the most economical concentration upon balancing of the amount of tin deposited at the lower concentration against the cost of the tin salt used at the higher concentration.

The effect of bath temperature from 30 to 80C on the deposition rate of copper and copper-tin deposits was determined from baths of the preferred compositions, the bath pH at room temperature being 10.7. The deposition rate increases with increasing temperature. At about 50C however, the rate increase is not as pronounced as would have been expected, which may be attributable to the relatively low metal ion concentration of the electroless copper or copper-tin plating baths. Deposit appearance was excellent from baths at 60C which produced copper deposits at the rate of 2.1 mg/cm² per hour, or 2.3 microns/hour, and copper-tin

deposits at about 0.7 mg/cm² per hour. Substantial increase in deposition rates could be obtained by employing solution agitation during plating.

The electroless copper and copper-tin deposits so formed possessed hardness of about 140 Knoop at 25 gram load, the copper deposit containing 98.6 weight percent copper by electrochemical analysis, and less than 0.1 weight percent boron through atomic absorption spectrophotometry. The copper-tin deposit is attractive, light colored, and contains 10.0 weight percent tin, 88.6 weight percent copper, and less than 0.1 weight percent boron. Deposits of copper or copper-tin exceeding about 12 microns thickness suffered from a tendency for nodules and dendrites to form, but additions to the baths of 1 mg/l gelatine and 1 mg/l sodium lauryl sulfate effectively minimized this condition.

The ability of our electroless copper and copper-tin plating baths to provide spontaneous deposition on various substrates was excellent, on steel, copper, electroless nickel plated steel and palladium-activated plastic. Adhesion to each of these substrates by the deposits was sufficient to resist separation by cellophane tape pull test. Steel panels, prepared for electroless copper plating by alkaline cleaning, rinsing, immersing one minute in 50 percent (vol.) HCl at 25C and then rinsing, as aforescribed, were subsequently electrolessly copper plated for about 7 minutes in our preferred bath composition. After being so plated, an additional electroplate of about 21 microns copper (connected to rectifier before immersion) from a proprietary acid copper plating bath at 25C at 3.2 amperes/dm² was applied. All specimens were then repeatedly bent to fracture and examined microscopically at the region of fracture. No evidence of adhesion failure was observed in any of the specimens. Prior art electrolessly deposited copper or steel substrates were not capable of withstanding this test or consistently withstanding the cellophane tape pull test.

There is set forth hereinbelow for purposes of illustration, examples of our deposits prepared with several bath compositions under varying conditions:

EXAMPLE I EXAMPLE II EXAMPLE III

Copper sulfate.5H ₂ O(g/l)	2	1	1
Stannous chloride.2H ₂ O(g/l)	—	4	4
The disodium salt of EDTA (g/l)	6	6	6
NH ₄ OH(28% NH ₃)(ml/l)	50	50	50
DMAB (g/l)	4	4	4
Substrate	Plastic*	Copper	Electroless Nickel**
Bath Temperature	60C	60C	60C
Bath pH	10.7	10.5	10.5
Deposition Time	10 min.	1 Hr.	1 Hr.
Thickness of Deposit (microns)	0.4	.8	.8
Deposit	Copper	Cu-Sn	Cu-Sn

*Palladium-activated, acrylonitrile-butadiene-styrene
**Electroless nickel plated steel.

Our copper and copper-tin electroless deposits, by virtue of their firm adhesion to various substrates, function as welcome alternatives to the conventional cyanide copper strike used to provide adhesion of copper on steel prior to high-speed acid-copper plating.

The copper deposit of Example I will find utility as an alternative to electroless nickel for plating plastic, and is expected to find widespread use as an effective means for applying strike deposits in highly recessed areas.

The copper-tin deposit (10.0 weight percent tin) of Example II promotes excellent retention solderability

and is decoratively similar to brass and bronze platings.

The copper-tin deposit (10.0 wt. percent tin) of Example III also provides excellent retention of solderability when a steel plate has been previously electroless nickel plated for corrosion resistance.

We wish it to be understood that we do not desire to be limited to the exact details described for obvious modifications will occur to a person skilled in the art.

We claim:

1. An electroless plating bath for providing a predominately copper deposit which is firmly adherent to various substrates, said bath being devoid of formaldehyde or potassium heptagluconate and comprising

0.5 to 3.0 g/l copper sulfate.5H₂O,
1.0 to 10.0 g/l disodium salt of EDTA,
5 to 150 ml/l NH₄OH(28 percent NH₃), and
0.5 to 10.0 g/l DMAB.

2. The bath as described in claim 1, said deposit comprising about 98.6 weight percent copper.

3. The bath as described in claim 1 further characterized by the inclusion of 0.1 to 5.0 g/l stannous chloride.2H₂O and said deposit comprising copper-tin, said tin being present in said deposit in an amount of about 10 weight percent, balance being substantially copper.

4. The bath as described in claim 1, said copper sulfate.5H₂O being present in an amount of 2 g/l, said disodium salt of EDTA being present in an amount of 6 g/l, said ammonium hydroxide (28 percent NH₃) being present in an amount of 50 ml/l, and said DMAB being present in an amount of 4 g/l.

5. The bath as described in claim 3, said copper sulfate.5H₂O being present in amount of 1 g/l, said stannous chloride being present in an amount of 2 g/l, said disodium salt of EDTA being present in an amount of 6 g/l, said ammonium hydroxide (28 percent NH₃) being present in amount of 50 ml/l, and said DMAB being present in an amount of 4 g/l.

6. The bath as described in claim 1 wherein said substrate is selected from the group consisting of steel, copper, electroless nickel plated steel, and palladium-activated plastic.

7. The bath as described in claim 4 wherein said substrate is selected from the group consisting of steel, copper, electroless nickel plated steel, and palladium-activated plastic.

8. The bath as described in claim 5 wherein said substrate is selected from the group consisting of steel, copper, electroless nickel plated steel, and palladium-activated plastic.

9. The bath as described in claim 1 wherein said copper sulfate.5H₂O is present in an amount of 2 g/l, said disodium salt of EDTA is present in an amount of 6 g/l, said NH₄OH (28 percent NH₃) is present in an amount

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of 50 ml/l, and said DMAB is present in an amount of 4 g/l, said substrate is palladium-activated acrylonitrile-butadiene-styrene, and said deposit is substantially all copper having a thickness of about 0.4 microns.

10. The bath as described in claim 3 wherein said copper sulfate.5H₂O is present in amount of 1 g/l, said stannous chloride is present in an amount of 4 g/l, said disodium salt of EDTA is present in an amount of 6 g/l, and NH₄OH (28 percent NH₃) is present in an amount

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of 50 ml/l, and said DMAB is present in an amount of 4 g/l, said substrate is copper, and said deposit comprises copper-tin, said tin being present in said deposit in an amount of about 10.0 weight percent, balance being substantially copper, and said copper-tin deposit having a thickness of about 0.8 microns.

11. The bath and deposit as described in claim 10, said substrate being electroless nickel plated steel.

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