

Description

The present invention relates to an additive for an acid electrolytic copperplating bath, to the process for its preparation and to its application to the copper-
5 plating of printed circuits.

Various compositions of acid copperplating baths for coating by electrolysis are known.

Thus, French Patent No. 1,255,271 describes acid copperplating baths comprising one or more basic color-
10 ants which may especially contain an ethenyl chromophor, amino compounds without a carbonyl group, a sulphonic organic acid or a water-soluble salt of this acid and which contains, in its molecule, at least one azido group, as additional brightening agent an organic compound which
15 has at least one carbon atom linked exclusively to a hetero atom, and which contains a hydrocarbon radical, linked through a sulphur and/or nitrogen atom and of which one hydrogen is replaced by a sulphonic acid group, a thioamide or isothioamide which contains a sulphonic acid group linked
20 to the nitrogen atom of the thioamide or the isothioamide group through a hydrocarbon radical, a thiourea derivative in which at least one nitrogen atom is replaced by an alkyl or anyl (sic) radical containing an ether, hydroxyl or carboxyl group.

25 Moreover, according to Belgian Patent No. 572,186, acid copperplating baths which have a content of organic sulphonic acids or of their water-soluble salts containing

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at least one azido group in the molecule, an additional content of sulphonic alkyl esters of N-mono or disubstituted dithiocarbonic acids or of their water-soluble salts, an additional content of 1,3,5-triazine-2,4,6-
5 tris-(mercaptoalkane-sulphonic) acid or of their water-soluble salts, and an additional content of agents which improve the ductility of the coats are known.

However, the particular additives described in these patents are not satisfactory, especially because
10 they degrade relatively rapidly during their use, their stability at temperatures greater than 25°C is low.

According to US Patent A-4,036,710, copper plating baths containing at least one compound chosen from the following are known:

- 15 (A) colorants containing triphenylmethane groups, for example crystal violet and
(B) sulphoalkylsulphides containing the S-alkyl-SO₃M group.

According to US Patent A-4,038,161, processes are
20 known for producing regular copper coats of the type according to which copper is electrolytically deposited from an aqueous acid electrolytic coating bath containing one or more copper salts which are soluble in the bath and a free acid, characterized in that a quantity sufficient to cause a regular
25 electrolytic deposition of copper of at least one organic level equalizing compound which is soluble in the bath and which is obtained by reacting one or more epihalohydrins

with one or more nitrogenous compounds chosen from the whole consisting of the following is added into the bath:

a) substituted pyridines of general formula:



5 in which R is a lower alkyl, a lower alkenyl, an alkylene-amine, a mercapto, a cyano, an alkylene-4-pyridyl, a -C(S)NH₂ or -CH = NOH group, or a group of formula -C(O)R' in which R' is a lower aryl or alkyl group or -N(Et)₂,

10 b) substituted pyridines of general formula:



in which R₂ is an amino, chloro or β-acrylic acid group,

- c) 2-vinylpyridine,
- d) 2-methyl-5-vinylpyridine,
- 15 e) quinoline or 3-aminoquinoline,
- f) isoquinoline, or
- g) benzimidazole.

The role of the colorants containing triphenyl-methane groups in electrolytic copperplating baths is known from the article CA vol. 82, no. 26, 30 June 1975, 20 pages 415-416.

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The Applicant Company has developed an additive and a process for an acid electrolytic copperplating bath which overcomes the disadvantages mentioned above and which especially has the following advantages:

- 5 a low degradability in the bath during the operation, leading to a significant increase in the period of use of a bath and to a low consumption of the product,
an excellent stability at temperatures greater than 25°C, leading to additive consumptions at these
10 temperatures which are two to three times lower than those required with the known additives,

the additive makes it possible to use a very wide range of current density, for example from 1 to 10 A/dm²,

- a very wide range of additive concentration can
15 be used without lowering the quality of the electrolytic deposition.

In effect, the present invention relates to a process for the preparation of an additive for an acid electrolytic copperplating bath, characterized in that it
20 comprises the following stages:

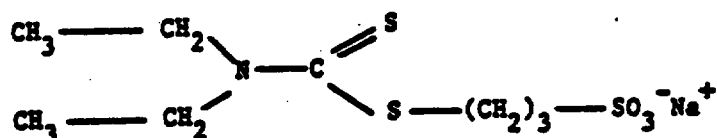
a) ω -(sodium-sulphate)-n-propyl N,N-diethyldithiocarbamate, a polyethylene glycol of average molecular weight between 6,000 and 20,000, crystal violet and sulphuric acid are mixed,

- 25 b) the mixture thus obtained is matured at a temperature of between approximately 58 and 70°C, and preferably 60 and 62°C, for a period of between 60 and 200

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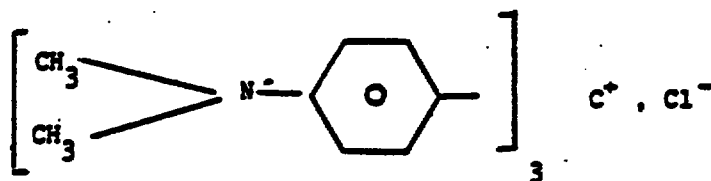
hours, and preferably 75 and 100 hours.

The ω-(sodium sulphonate)-n-propyl N,N-diethyl-dithiocarbamate has the formula:



5 The crystal violet consists of a variable composition mixture of hexamethyl-, pentamethyl- and tetramethylpararosanine hydrochlorides.

According to the invention, the crystal violet consisting of hexamethylparasoaniline (sic) hydrochloride of
10 the following formula is preferably employed:



The proportions of the constituents in the additive may vary within wide limits, a concentration of between 0.5 and 10 g/l, and preferably between 1 and 3 g/l
15 of the ω-(sodium sulphonate)-n-propyl N,N-diethyldithiocarbamate is suitable; a concentration of between 10 and 100 g/l, and preferably 15 and 20 g/l of polyethylene glycol is suitable; a concentration of between 0.1 and



1 g/l, and preferably 0.2 and 0.5 g/l of crystal violet is suitable and a concentration of between 0.1 and 0.2 N of sulphuric acid is suitable.

The present invention also relates to the process for the preparation of the additive. The process is characterized in that it consists of the following stages:

a) the four constituents making up the additive are mixed,

b) the mixture thus obtained is matured at a temperature of between approximately 58 and 70°C, and preferably between 60 and 62°C, for a period of between 60 and 200 hours, and preferably from 75 to 100 hours.

The mixing of the constituents which make up the additive is carried out in the proportions given above.

The additive thus prepared may be employed in the acid copperplating bath. The additive concentration in the bath may vary between approximately 2 and 100 ml/l, and preferably 3 and 50 ml/l.

In general, the metallization is carried out at temperatures less than 60° and with current densities varying from 0.5 to 10 A/dm². The range of current intensity which gives the best brightening effects varies depending on the proportions of the constituents of the additive. By the use of the additive according to the invention, the range of current intensity which gives the maximum brightening effect can be widened and the certainty of success in practice can be increased. As metal supports,

all kinds of metals usually destined for this use such as iron, copper, steel, zinc and other common metals or alloys may be used.

The acid copperplating baths in which the additives
5 according to the invention may be used mainly comprise copper sulphate, the concentration of which may vary between 50 and 250 g/l and sulphuric acid, the concentration of which may vary between 60 and 250 g/l.

The additive according to the invention has an
10 excellent chemical stability in acid baths, so that the latter remain capable of functioning even if the operation is carried out at relatively high bath temperatures.

The additive according to the invention may be used in copperplating operations.

15 The additive according to the present invention is particularly effective for carrying out the electrolytic copperplating of printed circuits and of parts made by electroforming.

This additive can also be used in combination with
20 other known agents, such as conducting salts, wetting agents or antiporous agents.

Thus, the additive according to the invention makes it possible to produce copper deposits which are bright, ductile, levelling and resistant to thermal shock.
25 It also makes it possible, because of its low degradability in the bath during the operation, to lead to a significant increase in the period of use of the bath.

Additionally, its excellent stability at temperatures greater than 25°C leads to an additive consumption at these temperatures which is three times lower than with additives used until now. Furthermore, it makes it possible to use a very wide range of current density and also a very wide range of concentration in the copperplating bath.

The thickness of the copper deposits obtained with the additive may vary within wide proportions; for example, depositions which have a thickness of between a few microns and 5 mm may be carried out.

The example below illustrates the invention without limiting its scope.

Example

15 Preparation of the additive

The following are introduced in sequence into a 200-litre glass-lined reactor:

186 litres of distilled water, 522 millilitres of H₂SO₄ having a concentration of 36 N,
20 65 g of crystal violet,
3,095 g of polyethylene glycol which has an average molecular weight of 12,000,
186 g of ω-(sodium sulphonate)-n-propyl N,N-di-ethylthiocarbamate.

25 The contents are stirred for approximately 2 hours, the temperature is then increased to 60°C in two hours; the mixture is matured at this temperature for 100 hours,

then cooled to the ambient temperature: approximately
187 litres of additive are thereby obtained.

Application

A bath having the following composition is lowered
5 into a 1,000-litre tank for the metallization of printed
circuits:

Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	75 g/l
Sulphuric acid	180 g/l
Chloride	50 mg/l

10 After performing an electrolysis for 10 hours at
1 ampere/dm² in order to remove the metal impurities,
5 litres of additive prepared according to the example
are added: the deposits obtained after this addition are
dried, ductile and without internal voltage - the structure
15 of the copper deposited is of fine grains and no cracking
appears in the deposit after the thermal shock test (10
second immersion in the solder at 290°C followed by im-
mersion in water).

The range of current density which can be used
20 extends from 1 to 10 A/dm² if it is desired only to obtain
a deposit which is bright and resistant to thermal shock,
and from 1 to 8 A/dm² if, in addition to these qualities,
it is desired to obtain a fine grain structure of copper.

The monitoring of the additive concentration in
25 the bath can easily be carried out using the Hull cell
test (Electroplating McGraw-Hill Book Company 1978 pages
148-150) under the following conditions:

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Intensity: 2 amperes

Duration: 5 minutes

Temperature: 22-24°C

Stirring: yes

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Electrolyte volume: 250 cm³

In the case of the 1,000-litre tank, 1-litre additions of the additive are made each time the width of the area burnt on the plate of the Hull cell reaches 10 mm. Under these conditions, for a temperature less than 26°C, the additive consumption will be of between 1 and 2 litres for 10,000 amperes/hour and the life period of the bath before regeneration with active charcoal will be greater than 1.5 million ampere x hour.

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Claims

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1. Process for the preparation of an additive for an acid electrolytic copperplating bath, characterized in that it comprises the following stages:

a) ω -(sodium sulphonate)-n-propyl N,N-diethyldithiocarbamate, a polyethylene glycol of average molecular weight between 6,000 and 20,000, crystal violet and sulphuric acid are mixed,

b) the mixture thus obtained is matured at a temperature of between approximately 58 and 70°C for a period of between 60 and 200 hours.

2. Process according to Claim 1, characterized in that concentration of ω -(sodium-sulphonate)-n-propyl N,N-diethyldithiocarbamate is of between 0.5 and 10 g/l, the concentration of polyethylene glycol is of between 10 and 100 g/l, the concentration of crystal violet is of between 0.1 and 1 g/l and the concentration of sulphuric acid is of between 0.1 and 0.5 N.

3. Electrolytic copperplating process characterized in that the additive prepared according to Claims 1 or 2 is used in a copperplating bath containing mainly copper sulphate, the concentration of which is of between 60 and 250 g/l, and sulphuric acid, the concentration of which is of between 60 and 250 g/l, the concentration of the additive in the bath is of between 2 and 100 m/l, the temperature of the bath is less than 60°C and the current density is of between 0.5 and 10 A/dm².



Claims (as printed)

1. Process for the preparation of an additive for an acidic electrolytic coppering bath, characterised in that it comprises the following stages:

a) ω -(sodium sulphonate)-n-propyl N,N-diethyldithiocarbamate, a polyethylene glycol of mean molecular weight between 6,000 and 20,000, crystal violet and sulphuric acid are mixed, and

b) the mixture thus obtained is ripened at a temperature of between 58 and 70 °C for a period of between 60 and 200 hours.

2. Process according to Claim 1, characterised in that the concentration of ω -(sodium sulphonate)-n-propyl N,N-diethyldithiocarbamate is between 0.5 and 10 g/l, the concentration of polyethylene glycol is between 10 and 100 g/l, the concentration of crystal violet is between 0.1 and 1 g/l and the concentration of sulphuric acid is between 0.1 and 0.5 N.

3. Electrolytic coppering process, characterised in that the additive prepared according to Claims 1 or 2 is employed in a coppering bath which principally contains copper sulphate of concentration between 50 and 250 g/l and sulphuric acid of concentration between 60 and 250 g/l, the concentration of the additive in the bath being between 2 and 100 ml/l, the bath temperature being less than 60 °C and the current density being between 0.5 and 10 A/dm².

Patentansprüche (as printed)

1. Verfahren zur Herstellung eines Additivs für ein Bad zur sauren elektrolytischen Verkupferung, dadurch gekennzeichnet, daß es aus folgenden Stufen besteht:

a) man mischt das N,N-diäthylthiocarbamat von Natrium-n-propyl- ω -sulfonat, ein Polyäthylenglykol eines mittleren Molekulargewichts zwischen 6 000 und 20 000, Kristall-violett, Schwefelsäure,

b) man läßt die so erhaltene Mischung bei einer Temperatur zwischen etwa 58 und 70 °C reifen während einer Zeitdauer zwischen 60 und 200 Stunden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Konzentration des N,N-diäthylthiocarbamats von Natrium-n-propyl- ω -sulfonat zwischen 0,5 und 10 g/l, die Konzentration an Polyäthylenglykol zwischen 10 und 100 g/l, die Konzentration des Kristallvioletts zwischen 0,1 und 1 g/l, und die Konzentration der Schwefelsäure zwischen 0,1 und 0,5 N beträgt.

3. Verfahren zur elektrolytischen Verkupferung, dadurch gekennzeichnet, daß man das nach den Ansprüchen 1 oder 2 hergestellte Additiv in einem Verkupferungsbad einsetzt, das hauptsächlich Kupfersulfat in einer Konzentration zwischen 50 und 250 g/l und Schwefelsäure in einer Konzentration zwischen 60 und 250 g/l enthält, die Konzentration des Additivs in dem Bad zwischen 2 und 100 ml/l liegt, die Badtemperatur unter 60 °C liegt und die Stromdichte zwischen 0,5 und 10 A/dm² beträgt.



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