

The invention relates to an acidic bath for the galvanic deposition of shiny, ductile and smooth copper coatings and to the use of this combination. The bath according to the invention can be used both for reinforcing the conductor paths of printed circuits and in the decorative sector.

It has long been known for organic substances to be added to galvanic copper baths in order to achieve shiny depositions. The numerous compounds already known for this purpose, such as, for example, thiourea, gelatins, molasses, coffee extract, "basic" dyestuffs and thiophosphoric acid esters, no longer have any practical significance, however, since the quality of the copper coatings obtained with them - more especially with regard to the uniform appearance, hardness and elongation at break - does not meet today's requirements.

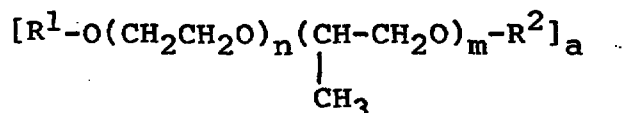
Prior art includes baths which contain a mixture of high molecular oxygen-containing compounds with organic, more especially aromatic thio compounds (DE-AS 1521062). These, however, produce unsatisfactory results with regard to metal scattering and/or smoothness.

To improve this, DE-AS 2039831 describes an acidic copper bath which, in addition to a polymeric oxygen-containing compound and a thio compound with a water-soluble group, also contains, in dissolved form, at least one dyestuff from the series of polymeric phenazonium compounds. Further works describe the combination of organic thio compounds and polymeric oxygen-containing compounds with other dyestuffs such as, for example, crystal-violet (EP-PS 071512) or phthalocyanine derivatives with apo-safranine (DE-PS 3420999) or a combination with amides (DE-PS 2746938).

Stability in the electrolyte is disadvantageous when using conventional oxygen-containing high-molecular compounds. In normal use, these said compounds slowly decompose during electrolysis to form the water-insoluble polymers, which become increasingly richer in the electrolyte, become attached to the walls as jellies and are finally deposited on the article itself, so that the article is subject to defects and thus becomes unusable. This decomposition is increased greatly if the bath temperature exceeds 28° C.

It is an object of this invention to avoid these disadvantages.

This object is achieved, according to the invention, by an acidic bath which contains at least one polyalkylene glycol dialkyl ether of the general formula



in which $n = 8 - 800$, preferably $14 - 90$, and $m = 0 - 50$, preferably $0 - 20$, R^1 is a low alkyl C_1 to C_4 , R^2 is an aliphatic chain or an aromatic residue and $a = 1$ or 2 .

The quantity in which the polyalkylene glycol dialkyl ethers can be added in order to achieve a distinct improvement in the copper deposition amounts substantially to between 0.005 and 30 g/litre; preferably between 0.02 and 8.0 g/litre. The relative molar mass can amount to between 500 and 35000 g/mol; preferably between 800 and 4000 g/mol.

The polyalkylene glycol dialkyl ethers are known per se or can be produced according to processes known per se by reacting polyalkylene glycols with an alkalising agent such as, for example, dimethyl sulphate or tert. butene.

Listed in Table 1 are examples of the polyalkylene glycol dialkyl ethers to be used according to the invention, as well as their preferred concentration of use:

Table 1

polyalkylene glycol dialkyl ethers	preferred concentration g/litre
dimethyl-polyethyleneglycol ethers	0.1 - 5.0
dimethyl-polypropyleneglycol ethers	0.05 - 0.1
di-tert.-butyl-polyethyleneglycol ethers	0.1 - 2.0
stearyl-monomethyl-polyethyleneglycol ethers	0.5 - 8.0

nonylphenyl-monomethyl-polyethyleneglycol	
ethers	0.5 - 6.0
polyethylene-polypropylene-dimethyl	
ethers (co- or block polymer)	0.02 - 5.0
octyl-monomethyl-polyalkylene	
ethers (co- or block polymer)	0.05 - 5.0
dimethyl-bis(polyalkyleneglycol) octylene	
ethers (co- or block polymer)	0.02 - 0.5
β -naphthol-monomethyl-polyethyleneglycol	
ethers	0.03 - 4.0

At least one thio compound with a water-solubilising group may be added to the compound according to the invention, in order to produce shiny depositions. Further additives, such as nitrogen-containing thio compounds, polymeric nitrogen compounds and/or polymeric phenazonium compounds may also be added to the bath.

These individual constituents of the copper bath according to the invention may be contained in the ready-to-use bath within the following concentration limits in a generally advantageous manner:

Conventional organic thio compounds

with water-soluble groups 0.0005 - 0.4 g/litre

preferably 0.001 - 0.15 g/litre

Listed in Table 2 are some conventional thio compounds with water-soluble groups as well as their preferred concentration of use:

Table 2

thio compounds	preferred concentration g/litre
3-mercaptopropane-1-sulphonic acid, sodium salt	0.002 - 0.1
thiophosphoric acid-O-ethyl-bis- (ω -sulphopropyl)-esters, disodium salt	0.01 - 0.15
thiophosphoric acid-tris- (ω -sulphopropyl)-esters, trisodium salt	0.02 - 0.15
thioglycol acid	0.001 - 0.005
ethylene dithiodipropylsulphonic acid, sodium salt	0.001 - 0.1

bis-(ω -sulphopropyl)-disulphide, disodium salt	0.001 - 0.05
bis-(ω -sulphopropyl)-sulphide, disodium salt	0.01 - 0.15
O-ethyl-dithiocarbonic acid-S- (ω -sulphopropyl)-esters, potassium salt	0.002 - 0.05
3(benzthiazolyl-2-thio)-propylsulphonic acid, sodium salt	0.005 - 0.1
bis-(ω -sulphohydroxypropyl)-disulphide, disodium salt	0.003 - 0.04
bis-(ω -sulphobutyl)-disulphide, disodium salt	0.004 - 0.04
bis-(p-sulphophenyl)-disulphide, disodium salt	0.004 - 0.04
methyl-(ω -sulphopropyl)-disulphide, disodium salt	0.007 - 0.08
methyl-(ω -sulphopropyl)-trisulphide, disodium salt	0.005 - 0.03

Conventional nitrogen-containing thio
compounds (so-called thiourea derivatives) and/or
polymeric phenazonium compounds and/or polymeric

nitrogen compounds

0.0001 - 0.50 g/litre

preferably

0.0005 - 0.04 g/litre

Table 3 contains examples of nitrogen-containing thio compounds (so-called thiourea derivatives) containing nitrogen, Table 4 contains examples of polymeric phenazonium compounds, and Table 5 contains examples of polymeric nitrogen compounds.

Table 3 nitrogen-containing thio compounds

N-acetylthiourea

N-trifluoroacetylthiourea

N-ethylthiourea

N-cyanoacetylthiourea

N-allylthiourea

o-tolylthiourea

N,N'-butylenethiourea

thiazolidine thiol(2)

4-thiazolidine thiol(2)

imidazolidine thiol(2) (N,N'-ethylenethiourea)

4-methyl-2-pyrimidine thiol

2-thiouracil

Table 4 polymeric phenazonium compounds

poly(6-methyl-7-dimethylamino-5-phenyl
phenazonium sulphate)
poly(2-methyl-7-diethylamino-5-phenyl
phenazonium chloride)
poly(2-methyl-7-dimethylamino-5-phenyl
phenazonium sulphate)
poly(5-methyl-7-dimethylamino-phenazonium
acetate)
poly(2-methyl-7-anilino-5-phenyl phenazonium
sulphate)
poly(2-methyl-7-dimethylamino-phenazonium
sulphate)
poly(7-methylamino-5-phenyl phenazonium
acetate)
poly(7-ethylamino-2,5-diphenyl phenazonium
chloride)
poly(2,8-dimethyl-7-diethylamino-5-p-tolyl
phenazonium chloride)
poly(2,5,8-triphenyl-7-dimethylamino-
phenazonium sulphate)
poly(2,8-dimethyl-7-amino-5-phenyl phenazonium
sulphate)

poly(7-dimethylamino-5-phenyl phenazonium
chloride)

Table 5 polymeric nitrogen compounds

polyethyleneimine
polyethyleneimide
polyacrylicacidamide
polypropyleneimine
polybutyleneimine
N-methylpolyethyleneimine
N-acetylpolyethyleneimine
N-butylpolyethyleneimine

The basic composition of the bath according to the invention can fluctuate within wide limits. Generally, an aqueous solution of the following composition is used:

copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	20	-	250 g/litre
preferably	60	-	80 g/litre
or	180	-	220 g/litre
sulphuric acid	50	-	350 g/litre

	preferably	180	-	220 g/litre
	or	50	-	90 g/litre
chloride ions		0.01	-	0.18 g/litre
	preferably	0.03	-	0.10 g/litre

Instead of copper sulphate, other copper salts may also be used, at least partially. The sulphuric acid may also be replaced, partially or wholly, by fluoroboric acid, methane sulphonic acid or other acids. The chloride ions are added as alkali chloride (e.g. sodium chloride) or in the form of hydrochloric acid p.a. The addition of sodium chloride may be wholly or partially eliminated if halogen ions are already contained in the additives.

Furthermore, conventional brightening agents, smootheners or wetting agents may also additionally be contained in the bath.

To produce the bath according to the invention, the individual constituents of the basic composition are added.

The operating conditions of the bath are as follows:

pH value < 1

temperature 15°C - 50°C,
preferably 25°C - 40°C

cath. current density 0.5 - 12 A/dm²,
preferably 2-7 A/dm²

The electrolyte movement is effected by blowing-in clean air at such a strong rate that the electrolyte surface undulates considerably.

Copper, having a content of between 0.02 and 0.067 % phosphorus, is used as the anode.

The following examples serve to illustrate the invention:

EXAMPLE 1

To a copper bath with the composition

200.0 g/litre copper sulphate (CuSO₄·5H₂O)

65.0 g/litre sulphuric acid

0.12 g/litre sodium chloride

are added, as brightening agents,

0.2 g/litre polyethyleneglycol,

0.01 g/litre bis-(ω -sulphopropyl)-
disulphide, disodium salt,

and 0.02 g/litre polymeric 7-dimethylamino-5-
phenyl-phenazonium-chloride.

A satisfactorily smoothened shiny copper coating is produced at an electrolyte temperature of 30° C with a current density of 4 A/dm² and movement caused by the blowing-in of air.

If the electrolyte is now subjected to a continuous loading of 500 Ah/l, whereby the brightening agents, used during the electrolysis, are supplemented to desired values, the electrolyte exhibits distinct jelly-like polymeric structures at the tank edge.

If, however, instead of the polyethyleneglycol, the compound according to the invention, polyethylene glycol dimethyl ether, is added to the electrolyte in the same quantity, the electrolyte exhibits no polymeric structures after the aging process.

EXAMPLE 2

To a copper bath with the composition

80 g/litre copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

180 g/litre conc. sulphuric acid

0.08 g/litre sodium chloride

are added, as brightening agents,

0.6 g/litre polypropyleneglycol,

0.02 g/litre 3-mercaptopropane-1-sulphonic
acid, sodium salt,

and 0.003 g/litre N-acetylthiourea.

Shiny depositions are produced at an electrolyte temperature of 30° C on scored copper laminate with a current density of 2 A/dm².

If the electrolyte is now subjected to a continuous loading of 500 Ah/l, whereby the brightening agents used during the electrolysis are supplemented to desired values, the electrolyte exhibits distinct jelly-like polymeric structures at the tank edge.

If, however, instead of the polyethyleneglycol, the compound according to the invention, polyethylene glycol dimethyl ether, is added to the electrolyte in the same quantity, the electrolyte exhibits no polymeric structures after the aging process.

EXAMPLE 3

To a copper bath with the composition

80 g/litre copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

200 g/litre conc. sulphuric acid

0.06 g/litre sodium chloride

are added, as brightening agents,

0.4 g/litre octylpolyalkyl ether and

0.01 g/litre bis-(ω -sulphopropyl)-sulphide,
disodium salt

and

0.01 g/litre polyacrylicacidamide.

Shiny depositions are produced at an electrolyte temperature of 30° C on scored copper laminate with a current density of 2 A/dm².

If the electrolyte is now subjected to a continuous loading of 500 Ah/l, whereby the brightening agents used during the electrolysis are supplemented to desired values, the electrolyte exhibits distinct jelly-like polymeric structures at the tank edge.

If, however, instead of the octylpolyalkylglycol, the compound according to the invention, octyl-

monomethyl-polyalkylglycol, is added to the electrolyte in the same quantity, the electrolyte exhibits no polymeric structures after the aging process.

EXAMPLE 4

A copper foil of 40 μm , which was separated from a copper bath with the composition

80 g/litre copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

200 g/litre conc. sulphuric acid

0.06 g/litre sodium chloride

exhibits an elongation at break of 4.2 %. After

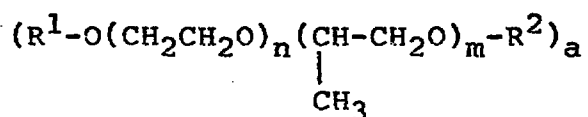
0.4 g/litre dimethyl-polyalkyl ether

was dissolved in the electrolyte, a foil which had been separated under the same conditions exhibits an elongation at break of 12.3 %.



CLAIMS

1. Aqueous, acidic bath for the galvanic deposition of shiny and smooth copper coatings, containing polyalkylene glycol dialkyl ethers of the general formula



in which $n = 8 - 800$, $m = 0 - 50$, R^1 is a low alkyl C_1 to C_4 , R^2 is an aliphatic chain or aromatic residue and $a=1$ or 2 .

2. Aqueous, acidic bath according to claim 1, containing polyalkylene glycol dialkyl ethers or mixtures thereof in concentrations of between 0.005 and 30 g/litre.

3. Aqueous, acidic bath according to claims 1 and 2, containing

dimethyl-polyethyleneglycol ethers,

di-tert.-butyl-polyethyleneglycol ethers,



stearyl-monomethyl-polyethyleneglycol ethers,
nonylphenyl-monomethyl-polyethyleneglycol ethers,
polyethylene-polypropylene-dimethylglycol ethers,
octyl-monomethyl-polyalkylene ethers,
dimethyl-bis(polyalkyleneglycol) octylene ethers
and/or

β -naphthol-monomethyl-polyethyleneglycol ethers.

4. Aqueous, acidic bath according to claims 1 to 3, additionally containing a thio compound or a mixture of a plurality of thio compounds.

5. Aqueous, acidic bath according to claim 4, containing

3-mercaptopropane-1-sulphonic acid, sodium salt,
thiophosphoric acid-O-ethyl-bis-(ω -sulphopropyl)-esters, disodium salt,

thiophosphoric acid-tris-(ω -sulphopropyl)-esters,
trisodium salt,

thioglycol acid,

ethylene dithiodipropylsulphonic acid, sodium salt,

bis-(ω -sulphopropyl)-disulphide, disodium salt,

bis-(ω -sulphopropyl)-sulphide, disodium salt,



0-ethyl-dithiocarbonic acid-S-(ω -sulphopropyl)-
esters, potassium salt,

3(benzthiazolyl-2-thio)-propylsulphonic acid, sodium
salt,

bis-(ω -sulphohydroxypropyl)-disulphide, disodium
salt,

bis-(ω -sulphobutyl)-disulphide, disodium salt,

bis-(p-sulphophenyl)-disulphide, disodium salt,

methyl-(ω -sulphopropyl)-disulphide, disodium salt
and/or

methyl-(ω -sulphopropyl)-trisulphide, disodium salt.

6. Aqueous, acidic bath according to claims 4 and
5, containing thio compounds in concentrations of
between 0.0005 and 0.4 g/litre.

7. Aqueous, acidic bath according to claims 1 to
6, characterised by an additional content of at least
one polymeric phenazonium compound.

8. Aqueous, acidic bath according to claim 7,
containing
poly(6-methyl-7-dimethylamino-5-phenyl phenazonium
sulphate),



poly(2-methyl-7-diethylamino-5-phenyl phenazonium
chloride),
poly(2-methyl-7-dimethylamino-5-phenyl phenazonium
sulphate),
poly(5-methyl-7-dimethylamino-phenazonium acetate),
poly(2-methyl-7-anilino-5-phenyl phenazonium
sulphate),
poly(2-methyl-7-dimethylamino-phenazonium sulphate),
poly(7-methylamino-5-phenyl phenazonium acetate),
poly(7-ethylamino-2,5-diphenyl phenazonium chloride),
poly(2,8-dimethyl-7-diethylamino-5-p-tolyl phenazonium
chloride),
poly(2,5,8-triphenyl-7-dimethylamino-phenazonium
sulphate),
poly(2,8-dimethyl-7-amino-5-phenyl phenazonium
sulphate) and/or
poly(7-dimethylamino-5-phenyl phenazonium chloride).

9. Aqueous, acidic bath according to claims 7 and 8, containing polymeric phenazonium compounds in concentrations of between 0.0001 and 0.5 g/litre.



10. Aqueous, acidic bath according to claims 1 to 6, characterised by an additional content of at least one thiourea derivative.

11. Aqueous, acidic bath according to claim 10, containing

N-acetylthiourea,

N-trifluoroacetylthiourea,

N-ethylthiourea,

N-cyanoacetylthiourea,

N-allylthiourea,

o-tolylthiourea,

N,N'-butylenethiourea,

thiazolidine thiol(2),

4-thiazolidine thiol(2),

imidazolidine thiol(2) (N,N'-ethylenethiourea),

4-methyl-2-pyrimidine thiol and/or

2-thiouracil.

12. Aqueous, acidic bath according to claims 10 and 11, containing thiourea derivative in concentrations of between 0.0001 and 0.5 g/litre.



13. Aqueous, acidic bath according to claims 1 to 6, characterised by an additional content of at least one polymeric nitrogen compound.

14. Aqueous, acidic bath according to claim 13, containing

polyethyleneimine,

polyethyleneimide,

polyacrylicacidamide,

polypropyleneimine,

polybutyleneimine,

N-methylpolyethyleneimine,

N-acetylpolyethyleneimine and/or

N-butylpolyethyleneimine.

15. Aqueous, acidic bath according to claims 13 and 14, containing polymeric nitrogen compounds in concentrations of between 0.0001 and 0.05 g/litre.

16. Aqueous, acidic bath, characterised by a content of polyalkylene glycol dialkyl ethers according to claims 1 to 3 and thio compounds according to claims 4 to 6.



17. Use of the bath according to at least one of claims 1 to 16 for reinforcing conductor paths of printed circuits.

18. Use of the bath according to at least one of claims 1 to 16 for the production of shiny and smooth copper coatings.