The invention relates to an acidic bath for the electrodeposition of shiny and smooth copper coatings and use thereof.

It has been known for a long time that specific organic substances can be added in small quantities to acidic, sulphuric acid copper electrolytes, which are mainly distributed, in order to achieve shiny copper coatings instead of a crystalline-matt deposition. For example, polyethylene glycol, thiourea, gelatin, molasses, coffee extract, "basic" dyestuffs and thiophosphoric acid esters are used for this purpose. However, such baths no longer have any practical significance, since the quality of the copper coatings obtained does not meet today's requirements. In consequence, either the coatings are too brittle or they have too little shine, or respectively they precipitate in a relief-like manner in specific current density ranges.

The addition of polyalkylimines in conjunction with organic thio compounds is known (DE-PS 1246347) and polyvinyl compounds mixed with oxygen-containing, high-molecular compounds and organic, more especially aromatic thio compounds are known (DE-AS 1521062). However, such copper electrolytes do not permit the use of higher cathodic current densities, and the deposited copper coatings, moreover, can only be nickel-plated after a previous intermediate treatment. Moreover, an acidic copper bath is described in the above-mentioned DE-AS 1521062 which also contains at least one substituted phenazonium compound in a dissolved state in additional to a polymeric, oxygen-containing compound with a hydrophilic group.

The usable current density for these monomeric

phenazonium compounds and the ageing behaviour are worthy of improvement. Furthermore, combinations of organic thio compounds and non-ionogenic wetting agents with other dyestuffs such as, for example, crystal violet (EP-PS 71512), amides (DE-PS 2746938), phthalocyanine derivatives with apo-saffronine (DE-PS 3420999) are known. Undefined conversion products of polyamines with benzyl chloride (DE-PS 2541897) or respectively epichlorohydrine (EU-PS 68807) or those with thio compounds and acrylic amide (EU-PS 107109) are also used instead of the dyestuff.

The baths known hitherto all produce irregular depositions; more especially the combination with nitrogen-containing thio compounds.

Progress was made with baths which contained polymeric phenazonium compounds (DE-PS 2039831); these are mainly used in combination with non-ionogenic wetting agents and organic sulphur compounds.

It is prior art in fact to add non-ionogenic wetting agents to the acidic copper baths, but the fine roughness was not eliminated thereby.

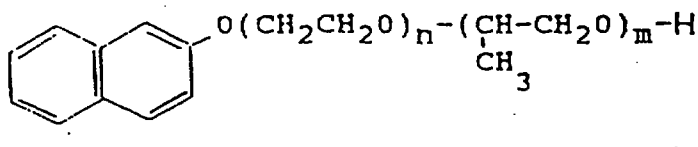
The use of ß-naphthol polyglycol ether as an addition for a copper bath is disclosed in DE-OS 37 21 985 (Example 2) and GB-A-2075063, but not in the combination with polymeric phenazonium compounds.

A fluoroborate bath is described in DE-PS 3104108, which contains ß-naphthol ethoxylate in combination with a phthalocyanine dyestuff. The electrolyte itself only exhibits a moderate smoothness compared with polymeric phenazonium compounds.

These baths are disadvantageous because, with a high degree of smoothness, there is a fine roughness (pittings, nodules) on the layer which is considerably detrimental to the decorative appearance, particularly of large-surface parts. This roughness is not produced by suspended particles in the electrolyte, but it is caused by a defective deposition in the cathodic double layer. This occurs particularly with nitrogen-containing sulphur compounds (so-called thiourea derivatives) and with phenazonium compounds.

An object of this invention is to overcome these described disadvantages and, moreover, not to impair the advantageous smoothness.

This object is achieved, according to the invention, by an acidic bath which includes at least one mixture comprising ß-naphthol alkoxylates of the general formula I



I

in which n = 0 - 50, preferably 10 - 25, and m = 0 - 50, preferably 0 - 10, n + m being ≥ 3, thiourea or thiourea derivative and polymeric phenazonium compound.

Particularly suitable as ß-naphthol alkoxylates of the general formula I are compounds of

Table 1

ß-naphthol-tetracosa(ethoxylate)	n= 24; m = 0
ß-naphthol-eicosa(ethoxylate)	n= 20; m = 0
ß-naphthol-octadeca(ethoxylate)	n= 18; m = 0
ß-naphthol-hexadeca(ethoxylate)	n= 16; m = 0
ß-naphthol-tetradeca(ethoxylate)	n= 14; m = 0
ß-naphthol-trideca(ethoxylate)	n= 13; m = 0
ß-naphthol-dodeca(ethoxylate)	n= 12; m = 0
ß-naphthol-deca(ethoxylate)	n= 10; m = 0
ß-naphthol-octa(ethoxylate)	n= 8; m = 0
ß-naphthol-hexa(ethoxylate)	n= 6; m = 0
ß-naphthol-tetracosa(propoxylate)	n= 0, m = 24
ß-naphthol-tetracosa(ethoxy)-mono(propoxylate)*)	n=24; m = 1-
ß-naphthol-octadeca(ethoxy)-di(propoxylate)*)	n= 20; m = 2
ß-naphthol-mono(propoxy)-tetracosa(ethoxylate)*)	n= 24; m = 1
ß-naphthol-di(propoxy)-octadeca(ethoxylate)*)	n= 20; m = 2

*) co- or block polymer

Thiourea and thiourea derivatives as well as S- and N-containing heterocyclic compounds are used as nitrogen-containing thio compounds.

Table 2 contains examples of nitrogen-containing thio compounds (so-called thiourea derivatives) or S- and N-containing heterocyclic compounds, and Table 3 contains examples of polymeric phenazonium compounds.

Table 2

thiourea

N-acetyl thiourea,
N-trifluoroacetyl thiourea
N-ethyl thiourea
N-cyanoacetyl thiourea
N-allyl thiourea
o-tolyl thiourea
N,N'-butylene thiourea
thiazolidine thiol(2)
4-thiazoline thiol (2)
imidazolidine thiol(2) (N,N'-ethylene thiourea)
4-methyl-2-pyrimidine thiol
2-thiouracil

Table 3

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)

Mixtures of the compounds listed in Tables 1, 2 and 3 are used for the solutions according to the invention.

The preferred quantity, in which the ß-naphthol ethoxylate needs to be added in order to achieve a distinct improvement in the copper deposition, is about 0.005 to 3 g/litre, preferably 0.01 to 0.25 g/litre.

ß-naphthol ethoxylates are known or may be produced according to methods known per se by converting ß-naphthol with ethylene oxide and/or propylene oxide.

The individual components of the copper bath according to the invention may generally be contained advantageously in the ready-for-use bath within the following limit concentrations:

Conventional oxygen-containing, high-molecular compounds	0.005 - 20 g/litre
preferably	0.01 - 5 g/litre
Conventional, organic thio compounds with hydrophilic groups	0.0005 - 0.2 g/litre
preferably	0.001 - 0.03 g/litre
Conventional nitrogen-containing thio compounds (so-called thio-urea derivatives) and/or polymeric phenazonium compounds	0.0001 - 0.50 g/litre
preferably	0.0005 - 0.04 g/litre

The basic composition of the bath according to the invention may vary within broad limits. An aqueous solution of the following composition is generally used:

Copper sulphate ($CuSO_4.5H_2O$)	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
Sodium chloride	0.02 - 0.25 g/litre
preferably	0.05 - 0.12 g/litre

Instead of copper sulphate, other copper salts may also be used, at least in part. Sulphuric acid may also be replaced partially or wholly by fluoroboric acid, methane sulphonic acid or other acids. The addition of sodium chloride may be eliminated wholly or partially when halogen ions are already contained in the additions.

Moreover, conventional polishers, smootheners or wetting agents may also additionally be included in the bath.

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

The operating conditions for the bath are as follows:

pH value: < 1

temperature: 15°C - 45°C, preferably 20°C - 30°C

cath.current density 0.5 - 12 A/dm^2, preferably 2-4 A/dm^2

The electrolyte movement is achieved by injecting air.

Copper, with a content of 0.02 to 0.067 % phosphorus, is used as the anode.

The invention also includes methods using the baths of the invention in accordance with the claims.

The following Examples serve to illustrate the invention:

EXAMPLE 1

0.2 g/litre polyethylene glycol,

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

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

are added as polishers to a copper bath of the composition

200.0 g/litre copper sulphate ($CuSO_4.5H_2O$)

65.0 g/litre sulphuric acid

0.2 g/litre sodium chloride.

At an electrolyte temperature of 27°C, a very smooth, shiny copper coating is obtained with a current density of 4 A/dm^2 and air injection, said coating exhibiting fine rough portions (pittings) on polished brass plate with an accurate appearance.

If 0.025 g/litre ß-naphthol alkoxylates of the general formula I with n = 12 and m = 0 is additionally added to the bath, the deposition is as shiny as a mirror and very smooth. No defects are found.

EXAMPLE 2

0.6 g/litre polypropylene glycol and

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

and 0.003 g/litre N-acetyl thiourea

are added as polishers to a copper bath of the composition

80 g/litre copper sulphate ($CuSO_4.5H_2O$)

180 g/litre conc. sulphuric acid

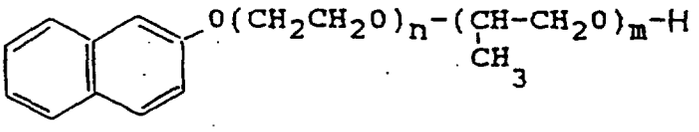
0.08 g/litre sodium chloride.

At an electrolyte temperature of 30°C, shiny depositions are obtained on scratched copper laminate with a current density of 2 A/dm^2, fine rough portions (pittings) being visible therein.

If 0.05 g/litre of the substance according to the invention of the general formula I with n = 24 and m = 0 is added to the bath, the copper coating is polished and does not contain any defects.

CLAIMS

1. Aqueous acidic bath for the electrodeposition of shiny and smooth copper coatings, including at least one mixture comprising ß-naphthol alkoxylate of the general formula I



I

in which n = 0-50 and m = 0 - 50, n + m being > 3; thiourea, thiourea derivative or S- and N-containing heterocyclic compounds and a polymeric phenazonium compound.

2. Bath according to claim 1, including as the ß-naphthol alkoxylate of the general formula I

ß-naphthol-tetracosa(ethoxylate)
ß-naphthol-eicosa(ethoxylate)
ß-naphthol-octadeca(ethoxylate)
ß-naphthol-hexadeca(ethoxylate)
ß-naphthol-tetradeca(ethoxylate)
ß-naphthol-trideca(ethoxylate)
ß-naphthol-dodeca(ethoxylate)
ß-naphthol-deca(ethoxylate)
ß-naphthol-octa(ethoxylate)
ß-naphthol-hexa(ethoxylate)
ß-naphthol-tetracosa(propoxylate)
ß-naphthol-tetracosa(ethoxy)-mono(propoxylate)
ß-naphthol-octadeca(ethoxy)-di(propoxylate)
ß-naphthol-mono(propoxy)-tetracosa(ethoxylate)
ß-naphthol-di(propoxy)-octadeca(ethoxylate)
or mixtures of these compounds.

3. Bath according to claim 1 or 2, including ß-naphthol alkoxylate of the general formula I in concentrations of between 0.005 and 3 g/litre.

4. Bath according to claim 1, including as the thiourea derivative or S- and N-containing heterocyclic compounds

N-acetyl thiourea,
N-trifluoroacetyl thiourea
N-ethyl thiourea
N-cyanoacetyl thiourea
N-allyl thiourea
o-tolyl thiourea
N,N'-butylene thiourea
thiazolidine thiol(2)
4-thiazoline thiol (2)
imidazolidine thiol(2) (N,N'-ethylene thiourea)
4-methyl-2-pyrimidine thiol
2-thiouracil
or mixtures of these compounds.

5. Bath according to claim 1 or 4, including thiourea or thiourea derivatives in concentrations of between 0.0001 and 0.5 g/litre.

6. Bath according to claim 1, including as the polymeric phenazonium compound

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)
or mixtures of these compounds.

7. Bath according to claim 1 or 6, including polymeric phenazonium compounds in concentrations of between 0.0001 and 0.5 g/litre.

8. Bath according to claim 1, characterised by an additional content of at least one oxygen-containing, high-molecular compound.

9. Bath according to claim 8, including as the oxygen-containing, high-molecular compounds

polyvinyl alcohol
carboxymethyl cellulose
polyethylene glycol
polypropylene glycol
stearic acid polyglycol ester
oleic acid polyglycol ester
stearyl alcohol polyglycol ether

nonyl phenol polyglycol ether
octonal polyalkylene glycol ether
octane diol-bis(polyalkylene glycol ether)
polyoxypropylene glycol
polyethylene-propylene glycol
or mixtures of these compounds.

10. Bath according to claim 9, including oxygen-containing, high-molecular compounds in concentrations of between 0.005 and 20 g/litre.

11. Bath according to claim 1, characterised by an additional content of an organic, nitrogen-free thio compound with water-soluble, hydrophilic groups.

12. Bath according to claim 11, including as the organic, nitrogen-free thio compound

3-mercaptopropane-1-sulphonic acid, sodium salt
thiophosphoric acid-o-ethyl-bis-(w-sulphopropyl)-ester, disodium salt
thiophosphoric acid-tris-(w-sulphopropyl)-ester, trisodium salt
ethylene dithiodipropyl sulphonic acid, sodium salt
di-n-propyl thioether-di-w-sulphonic acid, disodium salt
bis-(w-sulphopropyl)disulphide, disodium salt
bis(w-sulphohydroxypropyl)disulphide, disodium salt
bis(w-sulphobutyl)disulphide, disodium salt
methyl-(w-sulphopropyl)disulphide, sodium salt
methyl-(w-sulphobutyl)trisulphide, sodium salt
or mixtures of these compounds.

13. Bath according to claim 12, including the organic, nitrogen-free thio compounds with water-

soluble, hydrophilic groups in concentrations of between 0.0005 and 0.2 g/litre.

14. Use of the bath according to at least one of claims 1 to 13 for the electrodeposition of copper.