

[54] **ACID GALVANIC COPPER BATH**
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[58] **Field of Search**..... **204/52 R, 52 Y, 44; 106/1; 117/130 E**

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[57] **ABSTRACT**
Acid aqueous electrolytes for the deposition of bright, low-tension, ductile copper coatings containing organo selenium compounds are used.

5 Claims, No Drawings

ACID GALVANIC COPPER BATH

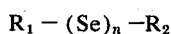
The invention relates to an acid aqueous electrolyte for the deposition of bright, low-tension, ductile copper coatings.

It is known that certain organic substances can be added in small quantities to acid copper electrolytes, particularly the most widely used sulfuric acid types, in order to obtain bright copper coatings instead of a crystalline, dull deposition. There have been proposed for this purpose chiefly organic thio compounds, such as thio-alkanosulfonic acids (German Pat. No. 1,037,801), derivatives of acid sulfur containing phosphorus derivatives (German Pat. No. 1,168,208, No. 1,196,464, No. 1,201,152), and organic sulfides containing at least one sulfonic acid in mixture or in chemical bond with a polyether (German Pat. application No. 1,521,062).

These thio compounds, however, often adversely affect the working of the acid electrolytes and the properties of the copper precipitates deposited therefrom. Thus, for example, in certain current density ranges the deposits turn out with black streaks due to the formation of copper sulfide, or there are deposited coatings having a high hardness or high internal macro tensions, which show an inferior corrosion behavior, especially under mechanical stresses. Many of the organic thio compounds, moreover, are very critical in their proportioning and must be added to the electrolyte in a very narrow concentration range if coatings with constant properties are to be obtained.

The problem underlying the invention herein, therefore, is to prevent the formation of black, streaky depositions and to make possible the precipitation of lustrous, low tension and ductile copper depositions of high anti-corrosion value over a wide current density range.

This problem is solved according to the present invention by using an acid aqueous copper electrolyte which is characterized by a content of at least one compound of the general formula



in which R_1 and R_2 are identical or different and represent possibly a mono- or multi-substituted aromatic, aliphatic, cycloaliphatic, araliphatic, or heterocyclic hydrocarbon radical, at least one of the two radicals containing a sulfonic acid group, or in which R_1 has the above-stated meaning and R_2 represents the cyanide or the sulfonic acid group and n is equal to 1 or 2, or the salts thereof.

Especially suitable for this invention are, as additions, those compounds wherein the above general formula, R_1 is phenyl, nitrophenyl, alkylphenyl, alkoxyphenyl, carboxyphenyl, carbmethoxyphenyl, dimethylaminophenyl, alkylmercaptophenyl, aminophenyl, alkyl containing preferably 2 to 8 carbon atoms, benzyl, phenoxyalkyl, sulfonlanyl, furyl, cyclohexylalkyl, pyridylalkyl, carboxyalkyl, dihydroxypropyl, sulfoalkyl containing preferably 2 to 6 carbon atoms, sulfophenyl, alkoxy-sulfophenyl, alkylmercapto-sulfophenyl, halogen-sulfophenyl, sulfonaphthyl, disulfonaphthyl or sulfophenyl-alkyl, R_2 represents sulfoalkyl containing preferably 2 to 6 carbon atoms, sulfophenyl, alkoxy-sulfophenyl, alkylmercapto-sulfophenyl, halogen-sulfophenyl, sulfonaphthyl, disulfonaphthyl or sulfophenylalkyl, and n is 1 or 2, or in which R_1 represents sulfoalkyl containing preferably 2 to 6 carbon atoms,

sulfophenyl, alkoxy-sulfophenyl, alkylmercaptosulfophenyl, halogen-sulfophenyl, sulfonaphthyl, disulfonaphthyl, sulfophenylalkyl, R_2 represents the cyanide or the sulfonic acid group, and n is the number 1.

The compounds to be used according to the invention are known in themselves or can be produced by methods known in themselves, as described for example in HOUBEN-WEYL "Methoden der organischen Chemie," volume 9 (1955), pages 972 - 1002 and pages 1,086 - 1,099.

Thus the alkyl- or aryl-selenoalkylsulfonic acids can be prepared by reaction of the respective alkali selenolates with sulfoalkyl halides.

The symmetrical sulfoalkyl- or sulfoaryl-diselenides are formed, for example, by hydrolysis of the respective selenoxyanates of the alkali-alkyl-selenosulfates.

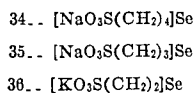
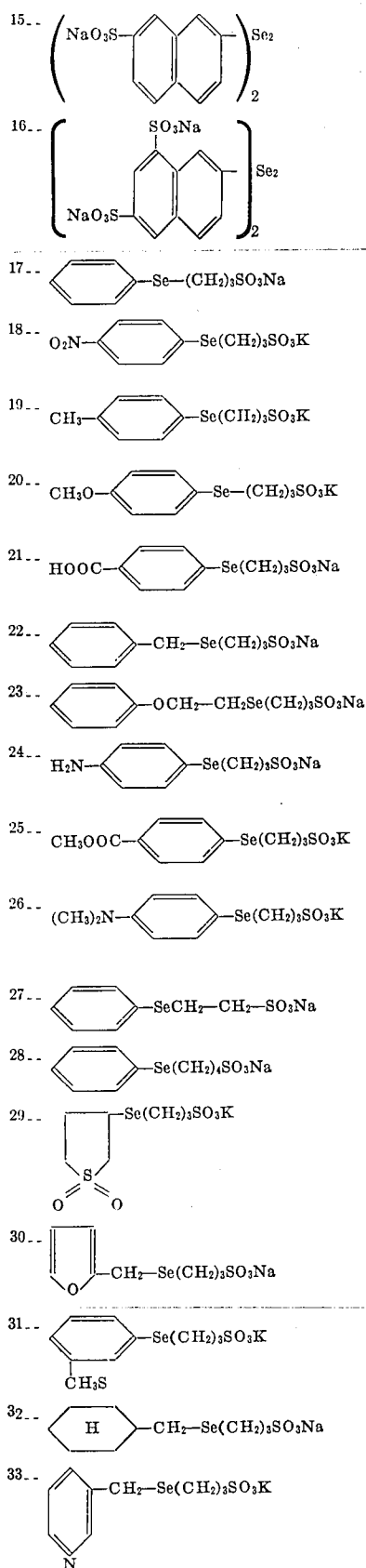
Alkylselenocyanates and, or, respectively, alkyl-selenosulfates are formed by reaction of alkyl halides with alkali-selenocyanates or selenosulfates.

Aromatic selenocyanates are formed by reaction of corresponding diazonium salts with alkali-selenocyanates.

The characterized compounds are used as such or better in the form of their salts, e.g. the alkali, ammonium or amino salts. As an example there may be named the sodium, potassium, ammonium and triethylammonium salt. The following table lists compounds to be used according to the invention:

TABLE I

1...	$[KO_3S(CH_2)_6]_2Se_2$	Di-(6-potassium-sulfohexyl)-diselenide.
2...	$[KO_3S(CH_2)_4]_2Se_2$	Di-(4-potassium-sulfobutyl)-diselenide.
3...	$[KO_3S(CH_2)_3]_2Se_2$	Di-(3-potassium-sulfopropyl)-diselenide.
4...	$[HO_3S(CH_2)_3]_2Se_2$	Di-(3-sulfopropyl)-diselenide.
5...	$[NH_4O_3S(CH_2)_3]_2Se_2$	Di-(3-ammonium-sulfopropyl)-diselenide.
6...	$[N(C_2H_5)_3HO_3S(CH_2)_3]_2Se_2$	Di-(3-triethylammonium-sulfopropyl)-diselenide.
7...	$[NaO_3S-\overset{\overset{CH_3}{ }}{CH}-CH_2-CH_2]_2Se_2$	Di-(3-methyl-3-sodiumsulfo-propyl)-diselenide.
8...	$[NaO_3S-CH_2-CH_2]_2Se_2$	Di-(2-sodium-sulfoethyl)-diselenide.
9...	$(NaO_3S-\text{C}_6\text{H}_4-CH_2)_2Se_2$	Di-(4-sodium-sulfophenyl)-diselenide.
10...	$(NaO_3S-\text{C}_6\text{H}_4)_2Se_2$	Di-(4-sodium-sulfophenyl)-diselenide.
11...	$(\text{SO}_3Na-\text{C}_6\text{H}_4)_2Se_2$	Di-(3-sodium-sulfophenyl)-diselenide.
12...	$(\text{SO}_3Na-\text{C}_6\text{H}_3(\text{CH}_3\text{O}))_2Se_2$	Di-(4-methoxy-3-sodiumsulfo-phenyl)-diselenide.
13...	$(\text{SO}_3Na-\text{C}_6\text{H}_3(\text{CH}_3\text{S}))_2Se_2$	Di-(5-methylmercapto-3-sodiumsulfo-phenyl)-diselenide.
14...	$(NaO_3S-\text{C}_6\text{H}_3(\text{Cl}))_2Se_2$	Di-(4-sodiumsulfo-3-chlor-phenyl)-diselenide.



Di-(7-sodium-sulfonaphthyl-2)-diselenide.

Di-(6,8-disodium-sulfonaphthyl-2)-diselenide.

-(phenylseleno)-propylsulfonate of sodium.

-(p-nitrophenylseleno)-propylsulfonate of potassium.

-(p-methylphenylseleno)-propylsulfonate of potassium.

-(p-methoxyphenylseleno)-propylsulfonate of potassium.

-(p-carboxyphenylseleno)-propylsulfonate of sodium.

-(benzylseleno)-propylsulfonate of sodium.

benzylseleno)-propylsulfonate of sodium.

-(4-aminophenylseleno)-propylsulfonate of sodium.

3-(p-carbomethoxyphenylseleno)-propylsulfonate of potassium.

3-(p-dimethylaminophenylseleno)-propylsulfonate of potassium.

2-(phenylseleno)-ethylsulfonate of sodium.

4-(phenylseleno)-butylsulfonate of sodium.

3-(sulfolanylseleno)-propylsulfonate of potassium.

3-(furylseleno)-propylsulfonate of sodium.

3-(m-methylmercaptophenylseleno)-propylsulfonate of potassium.

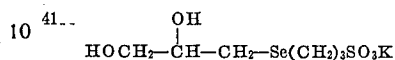
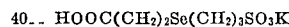
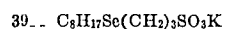
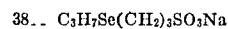
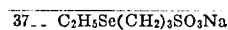
3-(cyclohexylmethylseleno)-propylsulfonate of sodium.

3-(3-pyridylmethylseleno)-propylsulfonate of potassium.

Bis(4-sodiumsulfo-butyl)-selenide.

Bis(3-sodiumsulfo-propyl)-selenide.

Bis(2-potassium-sulfoethyl)-selenide.



3-(ethylseleno)-propylsulfonate of sodium.

3-(propylseleno)-propylsulfonate of sodium.

3-(octylseleno)-propylsulfonate of potassium.

3-(2-carboxyethylseleno)-propylsulfonate of potassium.

3-(2,3-dihydroxypropylseleno)-propylsulfonate of potassium.

As additives to be used according to the invention there are suitable also those compounds which contain, besides a sulfo group-containing organic radical at the selenium atom, the cyanide or the sulfonic acid group. These seleno-cyanates or selenosulfates split in the highly acid copper electrolytes to diselenides, which then constitute what are actually the active compounds. The following table lists some such selenocyanates and seleno-sulfates

TABLE II

1. $\text{KO}_3\text{S}(\text{CH}_2)_6\text{SeCN}$	Omega-potassium-sulfohexylseleno-cyanate.
2. $\text{KO}_3\text{S}(\text{CH}_2)_4\text{SeCN}$	Omega-potassium-sulfobutylseleno-cyanate.
3. $\text{KO}_3\text{S}(\text{CH}_2)_2\text{SeCN}$	Omega-potassium-sulfoethylseleno-cyanate.
4. $\text{KO}_3\text{S}(\text{CH}_2)_2\text{SeCN}$	Omega-potassium-sulfoethylseleno-cyanate.
5. $\text{KO}_3\text{S}(\text{CH}_2)_6\text{SeSO}_3\text{K}$	Omega-potassium-sulfohexylseleno-sulfonate of potassium.
6. $\text{KO}_3\text{S}(\text{CH}_2)_4\text{SeSO}_3\text{K}$	Omega-potassium-sulfobutylseleno-sulfonate of potassium.
7. $\text{KO}_3\text{S}(\text{CH}_2)_2\text{SeSO}_3\text{K}$	Omega-potassium-sulfoethylseleno-sulfonate of potassium.
8. $\text{KO}_3\text{S}(\text{CH}_2)_2\text{SeSO}_3\text{K}$	Omega-potassium-sulfoethylseleno-sulfonate of potassium.
9.	p-(Sodiumsulfo)-benzylselenocyanate.
10.	p-(Sodiumsulfo)-phenylselenocyanate.
11.	p-(Sodiumsulfo)-benzylseleno-sulfonate of sodium.
12.	7-(sodiumsulfo)-2-naphthylseleno-cyanate.
13.	4-methoxy-3-sodium-sulfo-phenylseleno-cyanate.
14.	6,8-di-(sodiumsulfo)-2-naphthylseleno-cyanate.

As electrolyte for the deposition of copper coatings with the addition of the substances according to the invention a sulfuric acid copper sulfate solution of the following composition is generally used:

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Copper sulfate $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ 125 to 260 g/liter
Sulfuric acid H_2SO_4 20 to 85 g/liter.

Instead of copper sulfate, other copper salts may be used in toto or at least in part. The sulfuric acid may be replaced in part or entirely by fluoroboric acid, phosphoric acid and/or other acids. The electrolyte may be chloride-free or, and this is usually advantageous for improving the luster and the leveling, it may contain chlorides, such as alkali chlorides, or hydrochloric acid in quantities of from 0.001 to 0.2 g/liter.

The quantities in which the substances according to the invention must be added to the copper baths in order to achieve an improvement of the copper deposition are, surprisingly, very low and amount to about 0.0005 to 0.5 g/liter, preferably 0.0005 to 0.1 g/liter. With these additions one obtains a definite fining of the grain, in certain current density ranges even lustrous copper coatings.

The substances according to the invention are also especially suitable, in conjunction with other common luster-formers and/or wetting agents, for depositing high-luster coatings which show a great leveling of rugosities of the base material and yet are very ductile and possess a high extensibility.

As known additives which can be used together with the substances according to the invention there are suitable primarily oxygen-containing high-molecular compounds. The quantities of these substances that one adds to the copper electrolyte are about 0.01 to 20.0 g/liter, preferably 0.02 to 8.0 g/liter. Table III contains examples of oxygen-containing high-molecular compounds.

TABLE III

1. Polyvinyl alcohol
2. Carboxymethyl cellulose
3. Polyethylene glycol
4. Polypropylene glycol
5. Stearic acid polyglycol ester
6. Oleic acid polyglycol ester
7. Stearyl alcohol polyglycol ether
8. Nonylphenol-polyglycol ether
9. Reaction products of alkylene oxides with amines.

As additional compounds known in the art and which can be added to the copper electrolyte the following, for example, may be used:

Polymeric phenazonium compounds, polyalkylenamines, polyvinylamines, polyvinylimidazol, polyvinylpyrrolidone, phenazine dyes as well as the organic thio-compounds already mentioned.

The following examples will illustrate but not restrict the use of the substances according to the invention.

EXAMPLE 1

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	50 g/liter
Di-(3-potassiumsulfo- <i>propyl</i>)-diselenide	0.05 g/liter
Temperature: 25°C	
Current density: 4.0 A/dm ²	
Stock is mixed by agitation	

EXAMPLE 2

Copper fluoroborate ($\text{Cu}(\text{BF}_4)_2$)	300 g/liter
Fluoroboric acid	20 g/liter
2-(phenylseleno)-ethylsulfonate of sodium	0.3 g/liter
Temperature: 25°C	
Current density: 8.0 A/dm ²	
The electrolyte is agitated by injection of air	

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EXAMPLE 3

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	200 g/liter
Sulfuric acid, conc.	60 g/liter
Chloride ions	0.03 g/liter
Di-(3-sulfo- <i>propyl</i>)-diselenide	0.08 g/liter
Temperature: 22°C	
Current density: 4.0 A/dm ²	
Stock is stirred or agitated	

EXAMPLE 4

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	60 g/liter
Chloride ions	0.05 g/liter
Di-(3-potassiumsulfo- <i>propyl</i>)-diselenide	0.01 g/liter
Polypropylene glycol	0.5 g/liter
Temperature: 26°C	
Current density: 5.0 A/dm ²	
The stock is mixed by injection of air	

EXAMPLE 5

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	60 g/liter
Chloride ions	0.05 g/liter
Di-(4-sodiumsulfo- <i>phenyl</i>)-diselenide	0.03 g/liter
Monylphenol-polyglycol ether	4.0 g/liter
Temperature: 22°C; Current density: 4.0 A/dm ²	
Stock is agitated	

EXAMPLE 6

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	60 g/liter
Chloride ions	0.02 g/liter
Di-(4-methoxy-3-sodiumsulfo- <i>phenyl</i>)-diselenide	0.02 g/liter
Polyethylene glycol	0.2 g/liter
Temperature: 22°C	
Current density: 5.0 A/dm ²	
The mixture is treated by injection of air	

EXAMPLE 7

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	150 g/liter
Sulfuric acid, conc.	30 g/liter
Chloride ions	0.03 g/liter
3-(phenylseleno)-propylsulfonate of sodium	0.1 g/liter
Carboxymethyl cellulose	0.1 g/liter
Temperature: 22°C	
Current density: 3.0 A/dm ²	
The stock is agitated	

EXAMPLE 8

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	50 g/liter
Chloride ions	0.08 g/liter
3-(benzylseleno)-propylsulfonate of sodium	0.01 g/liter
omega-potassiumsulfohexylselenocyanate	0.02 g/liter
Polyethyleneglycol	0.01 g/liter
Temperature: 25°C	
Current density: 5.0 A/dm ²	
The mixture is treated by injection of air	

EXAMPLE 9

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	30 g/liter
Fluoroboric acid	10 g/liter
Chloride ions	0.05 g/liter
3-(p-carbomethoxyphenylseleno)-propylsulfonate of potassium	0.04 g/liter
Oleic acid polyglycol ester	1.0 g/liter
Temperature: 25°C	
Current density: 4.0 A/dm ²	
The stock is mixed by agitation or stirring	

EXAMPLE 10

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
Sulfuric acid, conc.	60 g/liter
Chloride ions	0.05 g/liter
3-(sulfolanyl-seleno)-propylsulfonate of potassium	0.06 g/liter
Stearyl alcohol polyglycol ether	1.5 g/liter
Temperature: 25°C	
Current density: 4.0 A/dm ²	
The stock is mixed by agitation or stirring	

EXAMPLE 11

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
3-(*m*-methylmercaptophenylseleno)-propylsulfonate
of potassium
Stearyl alcohol polyglycol ether
Temperature: 25°C
Current density: 4.0 A/dm²
The stock is mixed by stirring

EXAMPLE 12

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
Bis-(4-sodiumsulfoethyl)-selenide
omega-potassium sulfohexylselenosulfonate
of potassium
Polypropylene glycol
Temperature: 25°C
Current density: 5.0 A/dm²
The ingredients are mixed by injection of air

EXAMPLE 13

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
3-(ethylseleno)-propylsulfonate of sodium
Nonylphenol-polyglycol ether
Temperature: 25°C
Current density: 5.0 A/dm²
The stock is mixed by agitation

EXAMPLE 14

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
3-(octylseleno)-propylsulfonate of potassium
Polypropylene glycol
Temperature: 30°C
Current density: 5.0 A/dm²
The stock is mixed by stirring

EXAMPLE 15

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
omega-potassiumsulfoethylselenocyanate
Stearic acid polyglycol ester
Temperature: 25°C
Current density: 4.0 A/dm²
The ingredients are mixed by injection of air

EXAMPLE 16

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
omega-potassiumsulfoethylselenosulfonate
of potassium
Polyethylene glycol
Temperature: 25°C
Current density: 5.0 A/dm²
The ingredients are mixed by injection of air

EXAMPLE 17

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
omega-potassium sulfoethylselenosulfonate
of potassium
Nonylphenol polyglycol ether
Temperature: 25°C
Current density: 4.0 A/dm²
The ingredients are mixed by injection of air

EXAMPLE 18

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
Sulfuric acid, conc.
Chloride ions
p-(sodiumsulfo)-benzylselenocyanate
Nonylphenol-polyglycol ether
Temperature: 20°C
Current density: 3.0 A/dm²
The ingredients are mixed by injection of air

EXAMPLE 19

220 g/liter	Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	220 g/liter
60 g/liter	Sulfuric acid, conc.	60 g/liter
0.05 g/liter	Chloride ions	
	0.04 g/liter	
5	7-(sodiumsulfo)-2-naphthylseleno-cyanate	0.02 g/liter
0.02 g/liter	Stearyl alcohol polyglycol ether	1.5 g/liter
1.5 g/liter	Temperature: 25°C	
	Current density: 4.0 A/dm ²	
	The ingredients are mixed by injection of air	

EXAMPLE 20

220 g/liter	Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	200 g/liter
60 g/liter	Sulfuric acid, conc.	60 g/liter
0.05 g/liter	Chloride ions	0.04 g/liter
0.01 g/liter	4-methoxy-3-sodiumsulfo-phenyl-selenocyanate	0.06 g/liter
0.01 g/liter	Polyethylene glycol	0.6 g/liter
0.3 g/liter	Temperature: 25°C	
	Current density: 5.0 A/dm ²	
	The ingredients are mixed by injection of air	

What is claimed is:

1. In an acidic electrolyte for the electrodeposition of copper essentially consisting of water, sources of copper ions and of hydrogen ions, and a brightening composition in an amount sufficient to increase the luster of copper electrodeposited from said electrolyte, the improvement in said brightening composition which comprises at least one compound of the formula $\text{R}_1 - (\text{Se})_n - \text{R}_2$ or a salt thereof, the amount of said compound or salt being between 0.0005 g and 0.5 g per liter of said electrolyte, in said formula R_1 and R_2 being identical or different, R_1 being a radical of mono- or multi-substituted aromatic, aliphatic, cycloaliphatic, araliphatic, or heterocyclic hydrocarbon, R_2 being a radical of a mono- or multi-substituted aromatic, aliphatic, cycloaliphatic, araliphatic, or heterocyclic hydrocarbon, cyano or the sulfonic acid group, at least one of said R_1 and R_2 containing a sulfonic acid group, and n being 1 or 2.

2. In an electrolyte as set forth in claim 1, the amount of said at least one compound being not more than 0.1 g per liter of said electrolyte.

3. In an electrolyte as set forth in claim 1, said sources having respective anionic moieties selected from the group consisting of sulfate, fluoborate, and phosphate.

4. Electrolyte according to claim 1, wherein R_1 is phenyl, nitrophenyl, alkylphenyl, alkoxyphenyl, carboxyphenyl, carbmethoxyphenyl, dimethylaminophenyl, alkylmercaptophenyl, aminophenyl, alkyl containing from 2 to 8 carbon atoms, benzyl, phenoxy-alkyl, sulfolanyl, furyl, cyclohexylalkyl, pyridylalkyl, carboxyalkyl, dihydroxypropyl, sulfoalkyl containing 2 to 6 carbon atoms, sulfophenyl, alkoxy-sulfophenyl, alkylmercapto-sulfophenyl, halogen-sulfophenyl, sulfonaphthyl, di-sulfonaphthyl or sulfophenyl-alkyl, R_2 is sulfoalkyl containing 2 to 6 carbon atoms, sulfophenyl, alkoxy-sulfophenyl, alkylmercapto-sulfophenyl, halogen-sulfophenyl, sulfonaphthyl, disulfonaphthyl or sulfophenylalkyl.

5. An electrolyte according to claim 1, wherein R_1 is sulfoalkyl containing 2 to 6 carbons atoms, sulfophenyl, alkoxy-sulfophenyl, alkylmercapto-sulfophenyl, halogen-sulfophenyl, sulfonaphthyl, disulfonaphthyl, sulfonphenylalkyl, R_2 is the cyanide or the sulfonic acid group, and n is the number 1.