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(54) Method for producing matt copper deposits

(57) The present invention relates to a method for deposition of a matt copper coating wherein a first copper layer is deposited from an aqueous copper electrolyte which does not contain an organic compound comprising divalent sulfur. A second copper layer is then deposited onto the first copper layer from an aqueous copper electrolyte comprising a first and a second water soluble sulfur-containing additive wherein the first water soluble sulfur-containing compound is an alkyl sulfonic acid derivative and the second water soluble sulfur-containing additive is an aromatic sulfonic acid derivative. The method provides copper layers with a homogeneous and adjustable matt appearance for decorative applications.

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Description

Field of the Invention

[0001] The present invention relates to a method for deposition of matt copper deposits in the field of decorative coatings.

Background of the Invention

[0002] Matt copper coatings in the field of decorative coatings are required as a surface finish for e.g. sanitary equipment. Another application of matt copper coatings is to replace matt nickel layers ("satin nickel") as an intermediate layer in decorative multilayer coating systems which becomes more demanding due to the toxicity of nickel.

[0003] A homogeneous matt appearance is required for decorative metal layers. The homogeneity of the matt appearance can easily be achieved on substrates which have no complex shape because the current density distribution during electroplating of matt copper layers is within a narrow range. However, in cases where the substrate to be coated has a complex shape, the current density during electroplating is within a wide range. Typical substrates having a complex shape which are to be coated with a matt copper coating are for example shower heads and automotive interior parts.

[0004] Another requirement for matt copper layers is that their matt level should be adjustable in order to be able to manufacture copper layers having different matt levels.

[0005] Plating bath compositions comprising at least one polyglycerine compound for producing matt copper layers during manufacture of printed circuit boards are disclosed in US 2004/0020783 A1. It is neither possible to obtain a homogeneously matt copper deposit on a substrate having a complex shape nor to adjust the matt level of such a copper deposit when using the electrolyte disclosed therein.

Objective of the Invention

[0006] It is the objective of the present invention to provide a method for depositing copper layers which have a homogeneous and adjustable matt appearance, especially on substrates having a complex shape.

Summary of the Invention

[0007] This objective is solved by a method for deposition of a matt copper coating, comprising, in this order, the steps

a. Providing a substrate,

b. Depositing a first copper layer onto the substrate from a first aqueous electrolyte comprising a source of copper ions, at least one acid and at least one polyether compound wherein said first electrolyte does not contain an organic compound comprising divalent sulfur
and

c. Depositing a second copper layer onto the first copper layer from a second aqueous electrolyte comprising a source of copper ions, at least one acid, a first water soluble sulfur-containing additive selected from the group consisting of alkyl sulfonic acid derivatives and a second water soluble sulfur-containing additive selected from the group consisting of aromatic sulfonic acid derivatives.

[0008] The copper coatings obtained by the method according to the present invention have a homogeneous matt appearance on substrates having a complex shape. Furthermore, the matt appearance of the copper coating can be adjusted during deposition of the individual copper layers.

Detailed Description of the Invention

[0009] The method for deposition of a matt copper coating comprises deposition of two individual copper layers onto a substrate from two individual copper electrolytes which are herein denoted first electrolyte from which the first copper layer is deposited and second electrolyte from which the second copper layer is deposited onto the first copper layer.

[0010] The first electrolyte comprises a source of copper ions, at least one acid and at least one polyether compound. The first electrolyte does not contain an organic compound comprising divalent sulfur, e.g., sulfides, disulfides, thioles, and derivatives thereof.

[0011] Copper ions are added to the first electrolyte in the form of a water-soluble copper salt or an aqueous solution thereof. Preferably, the source of copper ions is selected from copper sulfate and copper methane sulfonate. The

concentration of copper ions in the first electrolyte preferably ranges from 15 to 75 g/l, more preferably from 40 to 60 g/l.

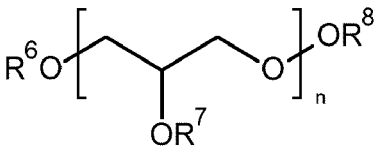
[0012] The at least one acid in the first electrolyte is selected from the group comprising sulfuric acid, fluoro boric acid and methane sulfonic acid. The concentration of the at least one acid in the first electrolyte preferably ranges from 20 to 400 g/l and more preferably from 40 to 300 g/l.

[0013] In case sulfuric acid is used as the acid, it is preferably added in form of a 50 to 96 wt.-% solution. More preferably, sulphuric acid is added to the first electrolyte as a 50 wt.-% aqueous solution of sulfuric acid.

[0014] The at least one polyether compound in the first electrolyte is selected from the group consisting of polyalkylene ethers and polyglycerine compounds.

[0015] Suitable polyalkylene ethers are selected from the group consisting of polyethylene glycol, polypropylene glycol, stearylalcoholpolyglycolether, nonylphenolpolyglycolether, octanolpolyalkylenglcolether, octanediol-bis-(polyalkylenglycolether), poly(ethylenglycol-ran-propylenglycol), poly(ethylenglycol)-block-poly(propylenglycol)-block-poly(ethylenglycol) and poly-(propylenglycol)-block-poly(ethylenglycol)-block-poly(propylenglycol).

[0016] Suitable polyglycerine compounds are selected from the group consisting of poly(1,2,3-propantriol), poly(2,3-epoxy-1-propanol) and derivatives thereof which are represented by formulae (1), (2) and (3):

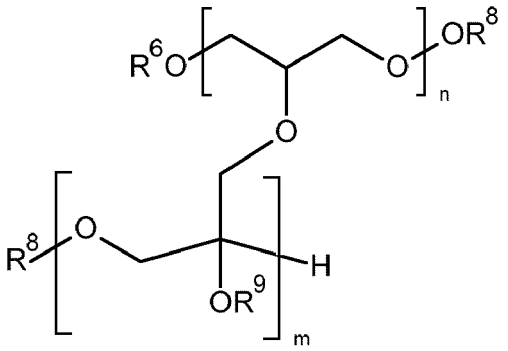


(1)

wherein

n is an integer from 1 to 80, preferably from 2 to 30;

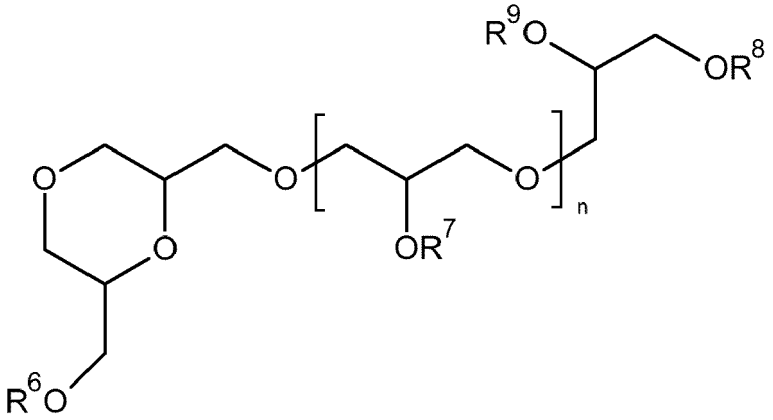
R^6, R^7 and R^8 are identical or different and are selected from the group consisting of hydrogen, alkyl, acyl, phenyl and benzyl, wherein alkyl preferably is linear or branched C_1 to C_{18} alkyl and acyl preferably is R^{10}-CO, wherein R^{10} is linear or branched C_1 to C_{18} alkyl, phenyl or benzyl; alkyl phenyl and benzyl in formula (1) may be substituted;



(2)

wherein

n is an integer >1, m is an integer >1 with the provisio n + m is ≤30;
R^6, R^7, R^8 and R^9 are identical or different and are selected from the group consisting of hydrogen, alkyl, acyl, phenyl and benzyl, wherein alkyl preferably is linear or branched C_1 to C_{18} alkyl and acyl preferably is R^{10}-CO, wherein R^{10} is linear or branched C_1 to C_{18} alkyl, phenyl or benzyl; alkyl phenyl and benzyl in formula (2) may be substituted;



(3)

wherein

n is an integer from 1 to 80; preferably from 2 to 20;

and wherein R^6, R^7 are selected from the group consisting of hydrogen, alkyl, acyl, phenyl and benzyl, wherein alkyl preferably is linear or branched C_1 to C_{18} alkyl and acyl preferably is R^{10}-CO, wherein R^{10} is linear or branched C_1 to C_{18} alkyl, phenyl or benzyl; alkyl phenyl and benzyl in formula (3) may be substituted.

[0017] Polyglycerine compounds are produced according to known methods. Indications on the conditions of production are disclosed in the following publications for example: Cosmet. Sci. Technol. Ser., glycerines, page 106 and US 3,945,894. Further details on the syntheses of polyglycerine compounds according to formulae (1), (2) and (3) are disclosed in US 2004/0020783 A1.

[0018] Most preferably, the at least one polyether compound in the first electrolyte is selected from compounds according to formulae (1), (2) and (3).

[0019] The concentration of the at least one polyether compound or all polyether compounds together in case more than one polyether compound is added preferably ranges from 0.005 g/l to 20 g/l, more preferably from 0.01 g/l to 5 g/l.

[0020] During operation, the temperature of the first electrolyte is preferably adjusted to a value in the range of from 30 to 60°C, more preferably from 40 to 50 °C.

[0021] The current density applied to the substrate during copper deposition from the first aqueous electrolyte preferably ranges from 0.5 to 5 A/dm^2, more preferably from 1 to 3 A/dm^2.

[0022] Optionally, the substrate is rinsed with water before depositing the second copper layer from the second electrolyte.

[0023] Copper ions are added to the second electrolyte as a water-soluble copper salt or an aqueous solution thereof. Preferably, the source of copper ions is selected from copper sulfate and copper methane sulfonate. The concentration of copper ions in the second electrolyte preferably ranges from 15 to 75 g/l, more preferably from 40 to 60 g/l.

[0024] The at least one acid in the second electrolyte is selected from the group comprising sulfuric acid, fluoro boric acid and methane sulfonic acid. The concentration of the at least one acid in the second electrolyte preferably ranges from 20 to 400 g/l and more preferably from 40 to 300 g/l.

[0025] In case sulfuric acid is used as the acid, it is added in form of a 50 to 96 wt.-% solution. Preferably, sulfuric acid is added as a 50 wt.-% aqueous solution of sulfuric to the second electrolyte.

[0026] The second electrolyte further comprises a first water-soluble sulfur-containing additive and a second water-soluble sulfur-containing additive.

[0027] The first water-soluble sulfur-containing compound is an alkyl sulfonic acid derivative. Preferably, the alkyl sulfonic acid derivative comprises divalent sulfur. The second water-soluble sulfur-containing compound is an aromatic sulfonic acid derivative. Preferably, the aromatic sulfonic acid derivative comprises divalent sulfur.

[0028] The first sulfur-containing additive is more preferably selected from the group consisting of compounds according to formulae (4) and (5):

$$R^1S\text{-}(CH_2)_n\text{-}SO_3R^2 \quad (4)$$

$$R^3SO_3\text{-}(CH_2)_m\text{-}S\text{-}S\text{-}(CH_2)_m\text{-}SO_3R^3 \quad (5)$$

wherein

R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium, more preferably R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, sodium and potassium;

n is an integer from 1 to 6, more preferably n is an integer from 2 to 4;

R^2 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium, more preferably, R^2 is selected from the group consisting of hydrogen, sodium and potassium;

R^3 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium, more preferably R^3 is selected from the group consisting of hydrogen, sodium, potassium and

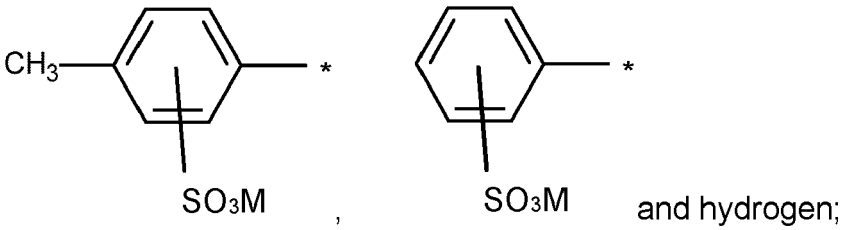
m is an integer from 1 to 6, more preferably m is an integer from 2 to 4.

[0029] The concentration of the first sulfur-containing additive in the second electrolyte preferably ranges from 0.0001 to 0.05 g/l, more preferably from 0.0002 to 0.025 g/l.

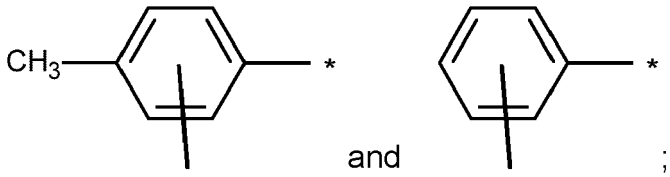
[0030] The second sulfur-containing additive in the second electrolyte is more preferably selected from the group consisting of compounds according to formulae (6) and (7):

$$R^4S_yX\text{-}SO_3M \quad (6)$$

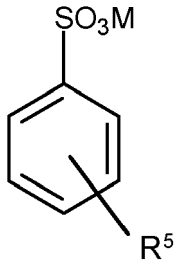
wherein R^4 is selected from the group consisting of



X is selected from the group consisting of



y is an integer from 1 to 4 and M is selected from the group consisting of hydrogen, sodium, potassium and ammonium; and



(7)

wherein R^5 is selected from the group consisting of hydrogen, SH and SO_3M and M is selected from the group consisting

of hydrogen, sodium, potassium and ammonium.

[0031] Most preferably, the second sulfur-containing additive is selected from compounds according to formula (6).

[0032] The concentration of the second sulfur-containing additive in the second electrolyte preferably ranges from 0.005 to 1 g/l, more preferably from 0.01 to 0.25 g/l.

[0033] Optionally, the second electrolyte further comprises one or more carrier additive selected from the group consisting of polyvinylalcohol, carboxymethylcellulose, polyethylene glycol, polypropylene glycol, stearic acid polyglycolester, alkoxylated naphtoles, oleic acid polyglycolester, stearylalcoholpolyglycolether, nonylphenolpolyglycolether, octanolpolyalkylenglycolether, octanediol-bis-(polyalkylenglycolether), poly(ethylenglycol-ran-propylenglycol), poly(ethylenglycol)-block-poly(propylenglycol)-block-poly(ethylenglycol) and poly(propylenglycol)-block-poly(ethylenglycol)-block-poly(propylenglycol).

[0034] The concentration of the optional carrier additive in the second electrolyte preferably ranges from 0.005 g/l to 5 g/l, more preferably from 0.01 g/l to 3 g/l.

[0035] During operation, the temperature of the second electrolyte is preferably adjusted to a value in the range of from 20 to 50 °C, most preferably of from 25 to 30°C.

[0036] The current density applied to the substrate during copper deposition from the second aqueous electrolytes preferably ranges from 0.5 to 5 A/dm^2, more preferably from 1 to 3 A/dm^2.

[0037] The matt level of the copper surface may be tailored by adjusting the thicknesses of the first and second copper layer by simple experimentation. A more matt appearance may be achieved with a thinner second copper layer, whereas a less matt appearance may be achieved with a thicker second copper layer.

[0038] The following examples further illustrate the present invention.

Examples

[0039] Substrates:

Both ABS (acrylnitrile-butadiene-styrol-copolymer) and brass substrates having a complex shape were used throughout all examples.

The ABS substrates were etched in chromic acid, activated with a palladium containing colloid and metallised by electroless plating of nickel from an acidic hypophosphite-based electrolyte prior to copper deposition.

The brass substrates were degreased prior to deposition of copper.

[0040] Test methods:

The matt appearance of copper coatings was tested by visual inspection of the copper plated substrates throughout all examples.

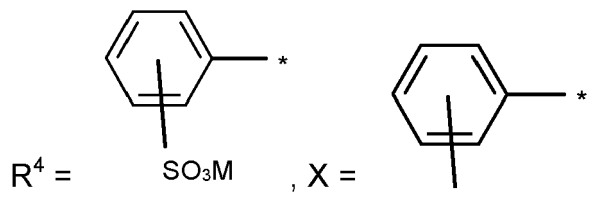
Example 1 (comparative)

[0041] Copper was deposited on ABS and brass substrates having a complex shape from an aqueous acidic electrolyte comprising 80 g/l $CuSO_4$ - $5H_2O$, 240 g/l sulfuric acid, and 1 g/l of a mixture of polyglycerin compounds according to formula (1) with n = 2 to 7.

[0042] A homogenous, strongly matt copper surface was obtained which is too matt for decorative applications.

Example 2 (comparative)

[0043] Copper was deposited on ABS and brass substrates having a complex shape from an aqueous acidic electrolyte comprising 80 g/l $CuSO_4 \cdot 5H_2O$, 240 g/l sulfuric acid, and 0.5 mg/l of a first sulfur-containing additive according to formula (5) with m = 3 and R^3 = sodium, 80 mg/l of a second sulfur-containing additive according to formula (6) with



y=2and

[0044] M = sodium and 200 mg/l polyethylene gylcol.

[0045] The copper surface obtained has a homogenous technical gloss which is not desired for decorative applications.

Example 3 (comparative)

[0046] A first layer of copper was deposited onto ABS and brass substrates having a complex shape from the electrolyte used in example 2. Thereon, a second copper layer was deposited from the electrolyte used in example 1.

[0047] A homogenous, strongly matt copper surface was obtained which is too matt for decorative applications.

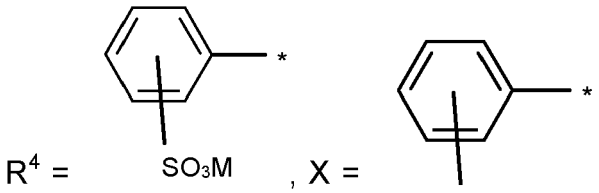
Example 4 (comparative)

[0048] A first copper layer was deposited onto ABS and brass substrates having a complex shape from the electrolyte used in example 1. Next, a second copper layer was deposited thereon from a second electrolyte comprising 80 g/l $CuSO_4 \cdot 5H_2O$, 240 g/l sulfuric acid, and 0.5 mg/l of a sulfur-containing additive according to formula (5) with m = 3 and R^3 = sodium. The second electrolyte did not contain a second sulfur-containing additive selected from compounds according to formulae (6) and (7).

[0049] The resulting copper surface has a non-homogeneous matt appearance which is not acceptable for decorative applications.

Example 5 (comparative)

[0050] A first copper layer was deposited onto ABS and brass substrates having a complex shape from the electrolyte used in example 1. Next, a second copper layer was deposited thereon from a second electrolyte comprising 80 g/l $CuSO_4 \cdot 5H_2O$, 240 g/l sulfuric acid, and 80 mg/l of a sulfur-containing additive according to formula (6) with



y=2andM= sodium. The second electrolyte did not contain a first sulfur-containing additive selected from compounds according to formulae (4) and (5).

[0051] The copper surface obtained has a matt appearance with burnt areas (shady black appearance) which is not acceptable for decorative applications.

Example 6

[0052] The first copper layer was deposited onto the ABS and brass substrates from the electrolyte used in Example 1. The second copper layer was deposited thereon from the electrolyte used in Example 2.

[0053] The copper surface obtained has a homogeneous matt appearance which is desired for decorative applications.

Example 7

[0054] The first copper layer was deposited from a first electrolyte comprising 80 g/l $CuSO_4 \cdot 5H_2O$, 240 g/l sulfuric acid, and 1 g/l polyethylene glycol. The second copper layer was deposited thereon from the electrolyte used in Example 2.

[0055] The copper surface obtained has a homogeneous matt appearance which is desired for decorative applications.

Table 1: First and second electrolytes used in Examples 1 to 6.

	Example 1*	Example 2*	Example 3*	Example 4*	Example 5*	Example 6	Example 7
First electrolyte	Containing mix of polyglycines according to formula (1); No additive with divalent sulfur	none	Containing additives with divalent sulfur according to formula (5) and (6)	Containing mix of polyglycines according to formula (1); No additive with divalent sulfur	Containing mix of polyglycines according to formula (1); No additive with divalent sulfur	Containing mix of polyglycines according to formula (1); No additive with divalent sulfur	Containing polyethylene-glycol; No additive with divalent sulfur
Second electrolyte	none	Containing additives with divalent sulfur according to formula (5) and (6)	Containing mix of polyglycines according to formula (1); No additive with divalent sulfur	Containing additive with divalent sulfur according to formula (5); No additive acc. to formula (6)	Containing additive with divalent sulfur according to formula (6); No additive acc. to formula (5)	Containing additives with divalent sulfur according to formula (5) and (6)	Containing additives with divalent sulfur according to formula (5) and (6)
Optical appearance**	-	-	-	-	-	+	+
* comparative examples; ** + = good; -: not sufficient							

Claims

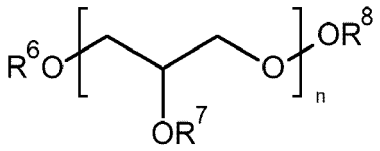
1. A method for deposition of a matt copper coating comprising, in this order, the steps

a. Providing a substrate,
b. Depositing a first copper layer onto the substrate from a first aqueous electrolyte comprising a source of copper ions, at least one acid and at least one polyether compound wherein said first electrolyte does not contain an organic compound comprising divalent sulfur
and
c. Depositing a second copper layer onto the first copper layer from a second aqueous electrolyte comprising a source of copper ions, at least one acid, a first water soluble sulfur-containing additive selected from the group consisting of alkyl sulfonic acid derivatives and a second water soluble sulfur containing additive selected from the group consisting of aromatic sulfonic acid derivatives.

2. The method for deposition of a matt copper coating according to claim 1 wherein the at least one polyether compound in the first electrolyte is selected from the group consisting of polyalkylene glycoles and polyglycerines.

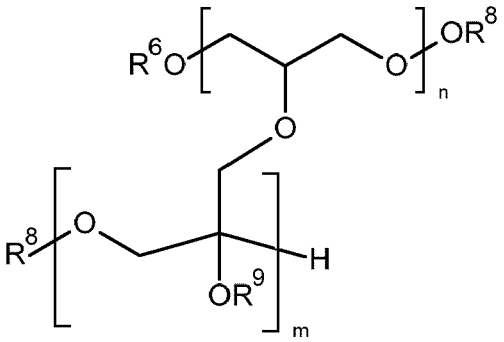
3. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the at least one polyether compound in the first electrolyte is selected from the group consisting of poly(1,2,3-propantriol), poly (2,3-epoxy-1-propanol) and derivatives thereof.

4. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the at least one polyether compound in the first electrolyte is selected from the group consisting of compounds according to formulae (1), (2) and (3):



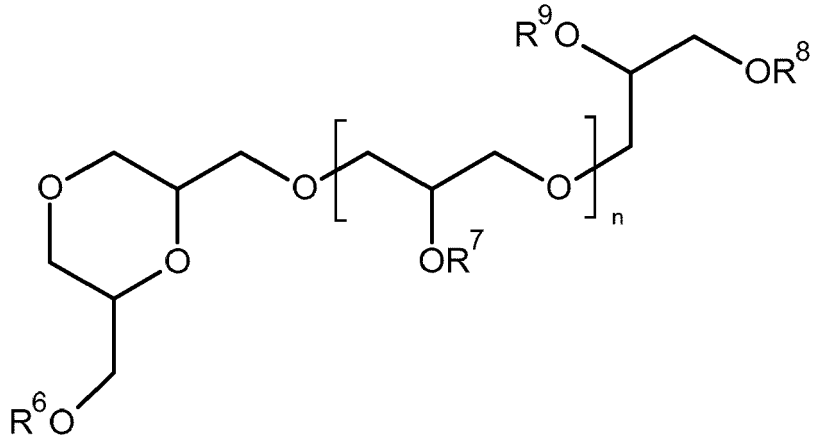
(1)

wherein n is an integer from 1 to 80;



(2)

wherein n is an integer >1, m is an integer >1 with the provisio n + m is ≤30;



(3)

wherein n is an integer from 1 to 80;
and wherein
R^6, R^7, R^8 and R^9 are identical or different and are selected from the group comprising hydrogen, alkyl, acyl, phenyl and benzyl.

5. The method for deposition of a matt copper coating according to claim 4 wherein the molecular weight of the compounds according to formulae (1), (2) and (3) ranges from 160 to 6000 g/mol.

6. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the concentration of the at least one polyether compound in the first electrolyte ranges from 0.005 g/l to 5 g/l.

7. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the first water soluble sulfur-containing additive in the second electrolyte is selected from the group consisting of compounds according to formulae (4) and (5):

$$R^1S\text{-}(CH_2)_n\text{-}SO_3R^2 \quad (4)$$
$$R^3SO_3\text{-}(CH_2)_m\text{-}S\text{-}S\text{-}(CH_2)_m\text{-}SO_3R^3 \quad (5)$$

wherein

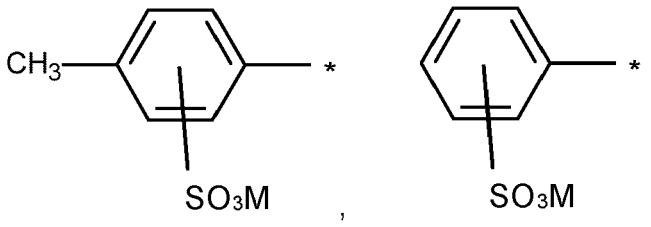
R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,
n ranges from 1 to 6,
R^2 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,
R^3 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium and
m ranges from 1 to 6.

8. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the concentration of the first water soluble sulfur-containing additive in the second electrolyte ranges from 0.0001 to 0.05 g/l.

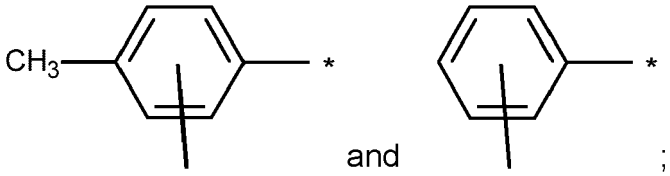
8. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the second water soluble sulfur-containing additive in the second electrolyte is selected from the group consisting of compounds according to formulae (6) and (7):

$$R^4S_y\text{-}X\text{-}SO_3M \quad (6)$$

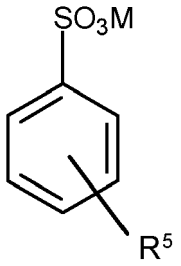
wherein R^4 is selected from the group consisting of



and hydrogen
X is selected from the group consisting of



y is an integer from 1 to 4 and M is selected from the group consisting of hydrogen, sodium, potassium and ammonium; and



(7)

wherein R^5 is selected from the group consisting of H, SH and SO_3M and M is selected from the group consisting of hydrogen, sodium, potassium and ammonium.

9. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the concentration of the second water soluble sulfur-containing additive in the second electrolyte ranges from 0.005 to 1 g/l.

10. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the second electrolyte further comprises at least one carrier additive.

11. The method for deposition of a matt copper coating according to claim 10 wherein the at least one carrier additive selected from the group consisting of polyvinylalcohol, carboxymethylcellulose, polyethylene glycol, polypropylene glycol, stearic acid polyglycolester, alkoxylated naphtoles, oleic acid polyglycolester, stearylalcoholpolyglycolether, nonylphenolpolyglycolether, octanolpolyalkylenglycolether, octanediol-bis-(polyalkylenglycolether), poly-(ethyleneglycol-ran-propylenglycol), poly(ethylenglycol)-block-poly-(propyleneglycol)-block-poly(ethylenglycol) and poly (propylenglycol)-block-poly(ethylenglycol)-block-poly(propylenglycol).

12. The method for deposition of a matt copper coating according to claims 10 and 11 wherein the concentration of the at least one carrier additive in the second electrolyte ranges from 0.005 g/l to 5 g/l.

Europäisches Patentamt
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EUROPEAN SEARCH REPORT

Application Number
EP 12 15 2390

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	JP 8 134689 A (KANEHIRO METALIZING YK) 28 May 1996 (1996-05-28) * abstract *	1-12	INV. C25D3/38 C25D5/10
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A	US 2004/154926 A1 (SUN ZHI-WEN [US] ET AL) 12 August 2004 (2004-08-12) * page 4, paragraph 33 - page 5; claim 1 *	1-12	
A	US 2005/045485 A1 (SHIH CHIEN-HSUEH [TW] ET AL) 3 March 2005 (2005-03-03) * page 3, paragraphs 25,26; claims 1,2,15 *	1-12	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	24 May 2012	Gault, Nathalie

CATEGORY OF CITED DOCUMENTS

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