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(54) **Method for producing matt copper deposits**

Verfahren zur Herstellung von matten Kupferablagerungen

Procédé de production de dépôts de cuivre mate

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EP 2 620 529 B1

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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.

[0006] A dull plating method is disclosed in JP 8 134689 wherein a copper plating layer is first deposited by barrel electroplating, roughened by "emery power" and then a non-lustrous copper or nickel plating layer is deposited thereon.

[0007] A multiple chemistry electrochemical plating method is disclosed in US 2004/0154926 A1 wherein a first copper layer is deposited from a first solution followed by electroplating a second copper layer from a second solution thereon.

[0008] A method to improve copper electrochemical deposition is disclosed in US 2005/0045485 A1 wherein a first copper layer is deposited from a plating bath comprising a antiforming agent followed by electroplating a second copper layer thereon.

Objective of the Invention

[0009] 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

[0010] 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.

wherein a current density is applied to the substrate during step b. and c.

[0011] The copper coatings obtained by the method according to the present invention have a homogeneous matt appearance on substrates having a complex shape.

[0012] Furthermore, the matt appearance of the copper coating can be adjusted during deposition of the individual copper layers.

Detailed Description of the Invention

[0013] 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.

[0014] 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.

[0015] 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.

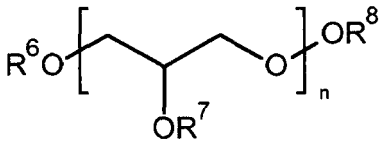
[0016] The at least one acid in the first electrolyte is selected from the group comprising sulfuric acid, fluoro boric acid and methane sulfonic acid. The concentration of the at least one acid in the first electrolyte preferably ranges from 20 to 400 g/l and more preferably from 40 to 300 g/l.

[0017] 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.

[0018] The at least one polyether compound in the first electrolyte is selected from the group consisting of polyalkylene ethers and polyglycerine compounds.

[0019] Suitable polyalkylene ethers are selected from the group consisting of polyethylene glycol, polypropylene glycol, stearylalcoholpolyglycolether, nonylphenolpolyglycolether, octanolpolyalkylenglcolether, octanediol-bis-(polyalkyleng-lycolether), poly(ethylenglycol-*ran*-propylenglycol), poly(ethylenglycol)-*block*-poly(propylenglycol)-*block*-poly(ethyleng-lycol) and poly-(propylenglycol)-*block*-poly(ethylenglycol)-*block*-poly(propylenglycol).

[0020] 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):

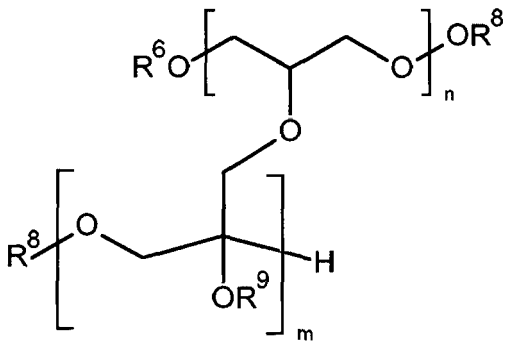


(1)

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;

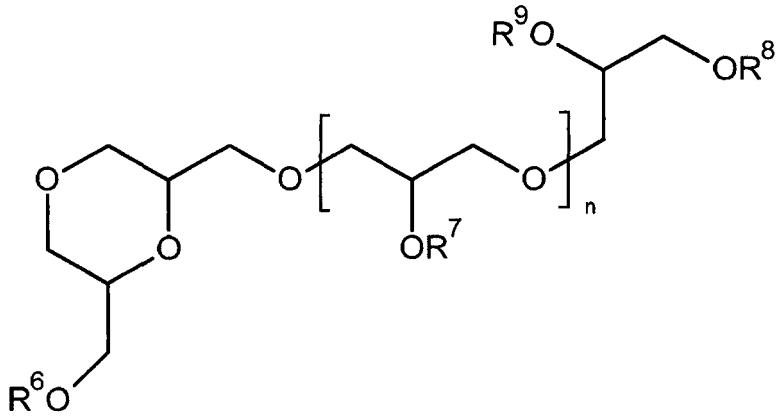


(2)

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.

[0021] 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.

[0022] Most preferably, the at least one polyether compound in the first electrolyte is selected from compounds according to formulae (1), (2) and (3).

[0023] 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.

[0024] 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.

[0025] 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.

[0026] Optionally, the substrate is rinsed with water before depositing the second copper layer from the second electrolyte.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] The second electrolyte further comprises a first water-soluble sulfur-containing additive and a second water-soluble sulfur-containing additive.

[0031] 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.

[0032] The first sulfur-containing additive is more preferably selected from the group consisting of compounds according to formulae (4) and (5):

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

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

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

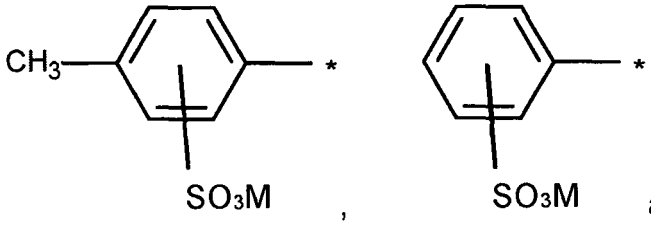
m is an integer from 1 to 6, more preferably m is an integer from 2 to 4.

[0033] 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.

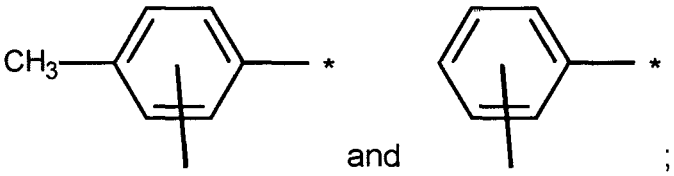
[0034] The second sulfur-containing additive in the second electrolyte is more preferably selected from the group consisting of compounds according to formulae (6) and (7):

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

wherein R^4 is selected from the group consisting of

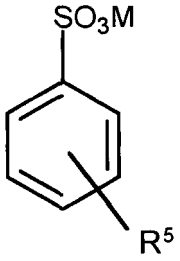


and hydrogen;
X is selected from the group consisting of



;

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 hydrogen, SH and SO_3M and M is selected from the group consisting of hydrogen, sodium, potassium and ammonium.

[0035] Most preferably, the second sulfur-containing additive is selected from compounds according to formula (6).

[0036] 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.

[0037] 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).

[0038] 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.

[0039] 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.

[0040] 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.

[0041] 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.

[0042] The following examples further illustrate the present invention.

Examples

Substrates:

[0043] Both ABS (acrylnitrile-butadiene-styrol-copolymer) and brass substrates having a complex shape were used throughout all examples.

[0044] 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.

[0045] The brass substrates were degreased prior to deposition of copper.

Test methods:

[0046] The matt appearance of copper coatings was tested by visual inspection of the copper plated substrates throughout all examples.

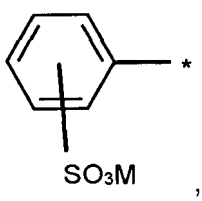
Example 1 (comparative)

[0047] 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 1 g/l of a mixture of polyglycerin compounds according to formula (1) with n = 2 to 7.

[0048] A homogenous, strongly matt copper surface was obtained which is too matt for decorative applications.

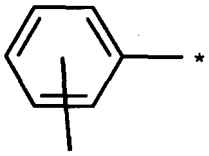
Example 2 (comparative)

[0049] 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 R^4 =



,

X=



y=2and M = sodium and 200 mg/l polyethylene gylcol.

[0050] The copper surface obtained has a homogenous technical gloss which is not desired for decorative applications.

Example 3 (comparative)

[0051] 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.

[0052] A homogenous, strongly matt copper surface was obtained which is too matt for decorative applications.

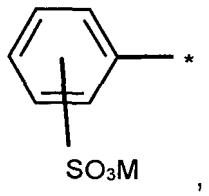
Example 4 (comparative)

[0053] 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 $CuSO_4$ $5H_2O$, 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).

[0054] The resulting copper surface has a non-homogeneous matt appearance which is not acceptable for decorative applications.

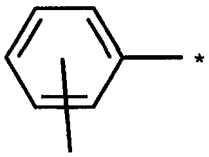
Example 5 (comparative)

[0055] 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 R^4 =



,

X =



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

[0056] The copper surface obtained has a matt appearance with burnt areas (shady black appearance) which is not acceptable for decorative applications.

Example 6

[0057] 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.

[0058] The copper surface obtained has a homogeneous matt appearance which is desired for decorative applications.

Example 7

[0059] 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.

[0060] 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

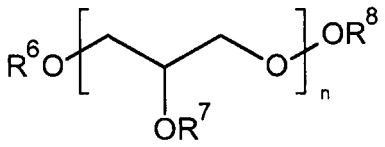
1. A method for deposition of a matt copper coating comprising, in this order, the steps

   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
   wherein a current density is applied to the substrate during step b. and c.

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.

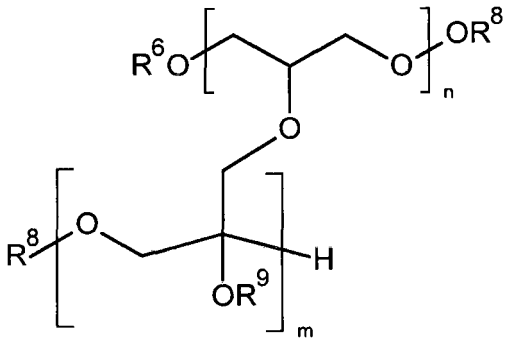
3. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the at least one polyether compound in the first electrolyte is selected from the group consisting of poly(1,2,3-propantriol), poly(2,3-epoxy-1-propanol) and derivatives thereof.

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):



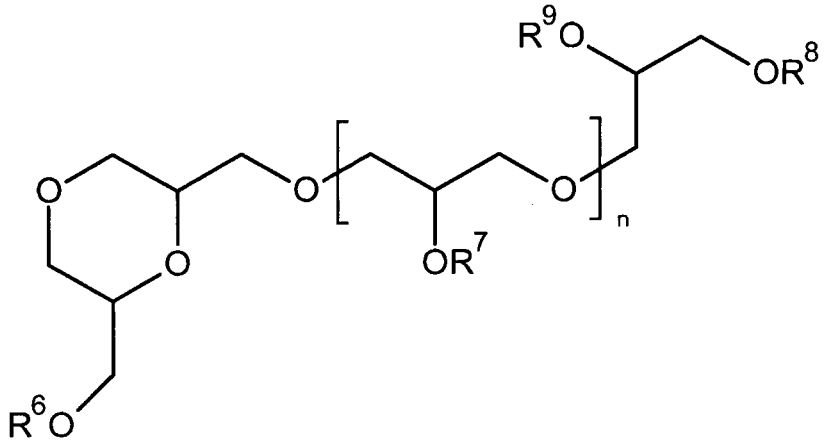
(1)

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):

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

$$R^3SO_3\text{-}(CH^2)_m\text{-}S\text{-}S\text{-}(CH_2)_m\text{-}SO_3R^3 \qquad (5)$$

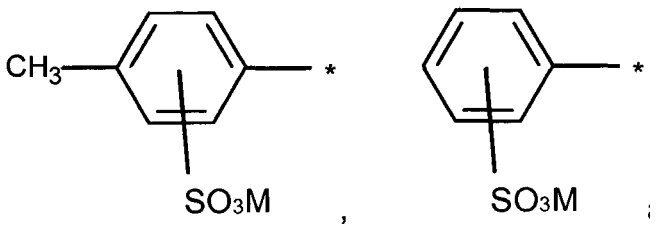
wherein
R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,
n ranges from 1 to 6,
R^2 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,
R^3 is selected from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

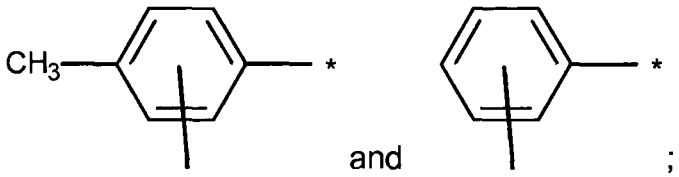
9. The method for deposition of a matt copper coating according to any of the foregoing claims wherein the second water soluble sulfur-containing additive in the second electrolyte is selected from the group consisting of compounds according to formulae (6) and (7):

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

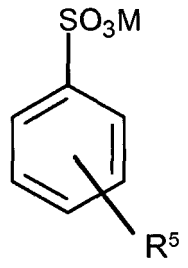
wherein R^4 is selected from the group consisting of



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.

10. 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.

11. 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.

12. The method for deposition of a matt copper coating according to claim 11 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).

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

Patentansprüche

1. Verfahren zum Abscheiden einer matten Kupferbeschichtung, umfassend, in dieser Reihenfolge, die Schritte

a. Bereitstellen eines Substrats,

b. Abscheiden einer ersten Kupferschicht aus einem ersten wässrigen Elektrolyten, der eine Quelle von Kupferionen, wenigstens eine Säure und wenigstens eine Polyetherverbindung umfasst, auf das Substrat, wobei der erste Elektrolyt keine organische Verbindung, die zweiwertigen Schwefel umfasst, enthält

und

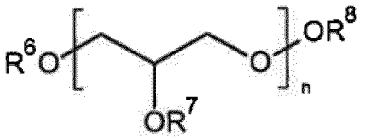
c. Abscheiden einer zweiten Kupferschicht aus einem zweiten wässrigen Elektrolyten, der eine Quelle von Kupferionen, wenigstens eine Säure, einen ersten wasserlöslichen Schwefel-enthaltenden Zusatzstoff, ausgewählt aus der Gruppe bestehend aus Alkylsulfonsäurederivaten, und einen zweiten wasserlöslichen Schwefel-enthaltenden Zusatzstoff, ausgewählt aus der Gruppe bestehend aus aromatischen Sulfonsäurederivaten, umfasst, auf die erste Kupferschicht,

wobei bei den Schritten b. und c. eine Stromdichte an das Substrat angelegt wird.

2. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß Anspruch 1, wobei die wenigstens eine Polyetherverbindung in dem ersten Elektrolyten ausgewählt ist aus der Gruppe bestehend aus Polyalkylenglycolen und Polyglycerinen.

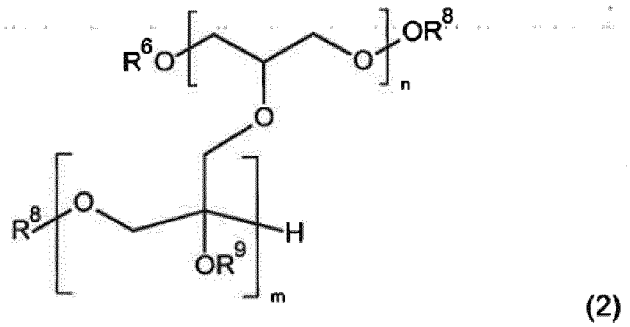
3. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei die wenigstens eine Polyetherverbindung in dem ersten Elektrolyten ausgewählt ist aus der Gruppe bestehend aus Poly(1,2,3-propantriol), Poly(2,3-epoxy-1-propanol) und Derivaten davon.

4. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei die wenigstens eine Polyetherverbindung in dem ersten Elektrolyten ausgewählt ist aus der Gruppe bestehend aus Verbindungen gemäß den Formeln (1), (2) und (3):



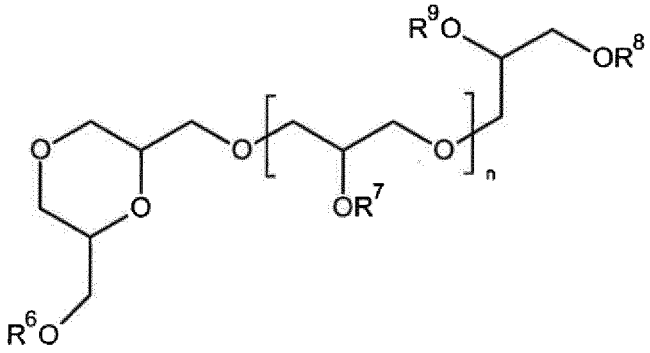
(1)

wobei n eine ganze Zahl von 1 bis 80 ist;



(2)

wobei n eine ganze Zahl > 1 ist, m eine ganze Zahl > 1 ist, mit der Maßgabe, dass $n + m \leq 30$;



(3)

wobei n eine ganze Zahl von 1 bis 80 ist;
und wobei
R^6, R^7, R^8 und R^9 gleich oder verschieden sind und ausgewählt sind aus der Gruppe umfassend Wasserstoff, Alkyl, Acyl, Phenyl und Benzyl.

5. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß Anspruch 4, wobei das Molekulargewicht der Verbindungen gemäß den Formeln (1), (2) und (3) im Bereich von 160 bis 6000 g/mol liegt.

6. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei die Konzentration der wenigstens einen Polyetherverbindung in dem ersten Elektrolyten im Bereich von 0,005 g/l bis 5 g/l liegt.

7. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei der erste wasserlösliche Schwefel-enthaltende Zusatzstoff in dem zweiten Elektrolyten ausgewählt ist aus der Gruppe bestehend aus Verbindungen gemäß den Formeln (4) und (5):

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

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

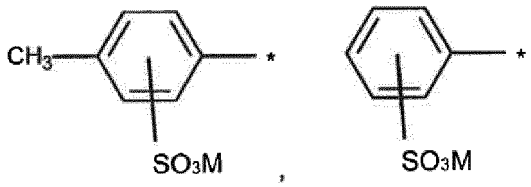
wobei
R^1 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Methyl, Ethyl, Propyl, Butyl, Lithium, Natrium, Kalium und Ammonium,
n im Bereich von 1 bis 6 liegt,
R^2 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Methyl, Ethyl, Propyl, Butyl, Lithium, Natrium, Kalium und Ammonium,
R^3 ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Methyl, Ethyl, Propyl, Butyl, Lithium, Natrium, Kalium und Ammonium und
m im Bereich von 1 bis 6 liegt.

8. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei die Konzentration des ersten wasserlöslichen Schwefel-enthaltenden Zusatzstoffs in dem zweiten Elektrolyten im Bereich von 0,0001 bis 0,05 g/l liegt.

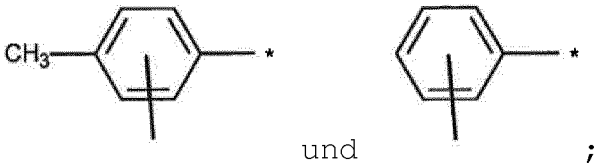
9. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei der zweite wasserlösliche Schwefel-enthaltende Zusatzstoff in dem zweiten Elektrolyten ausgewählt ist aus der Gruppe bestehend aus Verbindungen gemäß den Formeln (6) und (7):

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

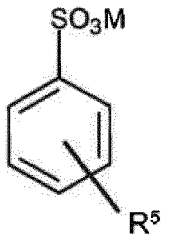
wobei R^4 ausgewählt ist aus der Gruppe bestehend aus



und Wasserstoff;
X ausgewählt ist aus der Gruppe bestehend aus



y eine ganze Zahl von 1 bis 4 ist und M ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Natrium, Kalium und Ammonium; und



(7)

wobei R^5 ausgewählt ist aus der Gruppe bestehend aus H, SH und SO_3M, und M ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, Natrium, Kalium und Ammonium.

10. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei die Konzentration des zweiten wasserlöslichen Schwefel-enthaltenden Zusatzstoffs in dem zweiten Elektrolyten im Bereich von 0,005 bis 1 g/l liegt.

11. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß einem der vorstehenden Ansprüche, wobei der zweite Elektrolyt ferner wenigstens einen Träger-Zusatzstoff umfasst.

12. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß Anspruch 11, wobei der wenigstens eine Träger-Zusatzstoff ausgewählt ist aus der Gruppe bestehend aus Polyvinylalkohol, Carboxymethylcellulose, Polyethylenglycol, Polypropylenglycol, Stearinsäurepolyglycolester, alkoxylierten Naphtolen, Oleinsäurepolyglycolester, Stearylalkoholpolyglycolether, Nonylphenolpolyglycolether, Octanolpolyalkylenglycolether, Octandiolbis(polyalkylenglycolether), Poly(ethylenglycol-*ran*-propylenglycol), Poly(ethylenglycol)-*block*-poly(propylenglycol)-*block*-poly(ethylenglycol) und Poly(propylenglycol)-*block*-poly(ethylenglycol)-*block*-poly(propylenglycol).

13. Verfahren zum Abscheiden einer matten Kupferbeschichtung gemäß Ansprüchen 11 und 12, wobei die Konzentration des wenigstens einen Träger-Zusatzstoffs in dem zweiten Elektrolyten im Bereich von 0,005 g/l bis 5 g/l liegt.

Revendications

1. Procédé de dépôt d'un revêtement de cuivre mat comprenant, dans cet ordre, les étapes consistant à

a. se procurer un substrat,
b. déposer une première couche de cuivre sur le substrat à partir d'un premier électrolyte aqueux comprenant

une source d'ions cuivre, au moins un acide et au moins un composé de polyéther, ledit premier électrolyte ne contenant pas de composé organique comprenant du soufre divalent, et

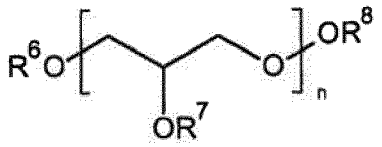
c. déposer une deuxième couche de cuivre sur la première couche de cuivre à partir d'un deuxième électrolyte aqueux comprenant une source d'ions cuivre, au moins un acide, un premier additif contenant du soufre hydrosoluble choisi dans le groupe constitué par les dérivés alkyliques d'acide sulfonique et un deuxième additif contenant du soufre hydrosoluble choisi dans le groupe constitué par les dérivés aromatiques d'acide sulfonique,

dans lequel une densité de courant est appliquée au substrat pendant l'étape b et c.

2. Procédé de dépôt d'un revêtement de cuivre mat selon la revendication 1 dans lequel l'au moins un composé de polyéther dans le premier électrolyte est choisi dans le groupe constitué par les polyalkylène glycols et les polyglycérines.

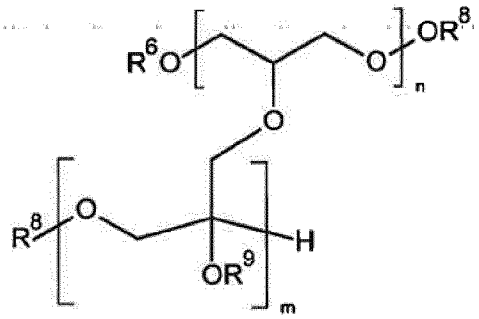
3. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel l'au moins un composé de polyéther dans le premier électrolyte est choisi dans le groupe constitué par le poly(1,2,3-propanetriol), le poly(2,3-époxy-1-propanol) et les dérivés de ceux-ci.

4. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel l'au moins un composé de polyéther dans le premier électrolyte est choisi dans le groupe constitué par les composés répondant aux formules (1), (2) et (3) :



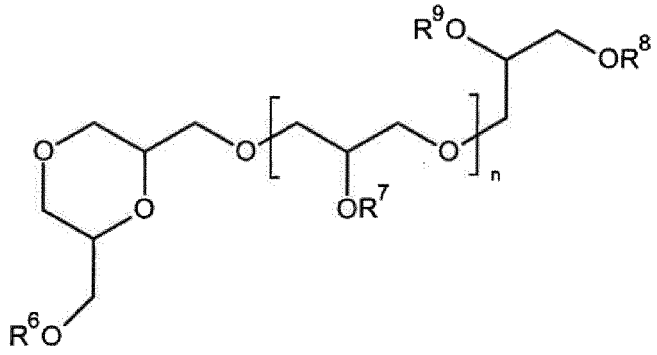
(1)

dans laquelle n est un entier de 1 à 80 ;



(2)

dans laquelle n est un entier > 1 et m est un entier > 1, à condition que n+m soit ≤ 30 ;



(3)

dans laquelle n est un entier de 1 à 80 ;

et dans lesquelles
R^6, R^7, R^8 et R^9 sont identiques ou différents et sont choisis dans le groupe comprenant l'hydrogène et les groupes alkyle, acyle, phényle et benzyle.

5. Procédé de dépôt d'un revêtement de cuivre mat selon la revendication 4 dans lequel le poids moléculaire des composés répondant aux formules (1), (2) et (3) va de 160 à 6000 g/mol.

6. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel la concentration de l'au moins un composé de polyéther dans le premier électrolyte va de 0,005 g/l à 5 g/l.

7. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel le premier additif contenant du soufre hydrosoluble dans le deuxième électrolyte est choisi dans le groupe constitué par les composés répondant aux formules (4) et (5) :

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

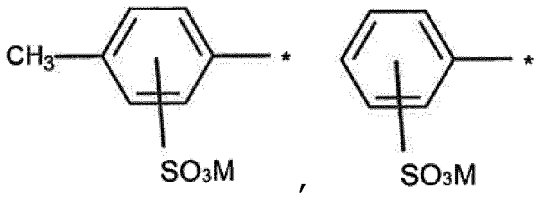
dans lesquelles
R^1 est choisi dans le groupe constitué par l'hydrogène, le méthyle, l'éthyle, le propyle, le butyle, le lithium, le sodium, le potassium et l'ammonium,
n va de 1 à 6,
R^2 est choisi dans le groupe constitué par l'hydrogène, le méthyle, l'éthyle, le propyle, le butyle, le lithium, le sodium, le potassium et l'ammonium,
R^3 est choisi dans le groupe constitué par l'hydrogène, le méthyle, l'éthyle, le propyle, le butyle, le lithium, le sodium, le potassium et l'ammonium, et
m va de 1 à 6.

8. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel la concentration du premier additif contenant du soufre hydrosoluble dans le deuxième électrolyte va de 0,0001 à 0,05 g/l.

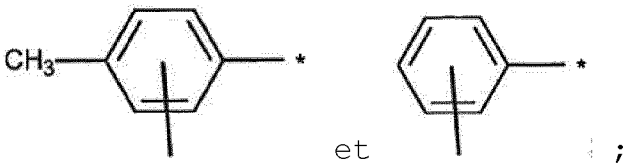
9. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel le deuxième additif contenant du soufre hydrosoluble dans le deuxième électrolyte est choisi dans le groupe constitué par les composés répondant aux formules (6) et (7) :

$$R^4S_y\ X\text{-}SO_3 \quad (6)$$

dans laquelle R^4 est choisi dans le groupe constitué par

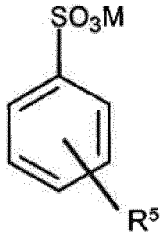


et l'hydrogène ;
X est choisi dans le groupe constitué par



y est un entier valant de 1 à 4 ; et

M est choisi dans le groupe constitué par l'hydrogène, le sodium, le potassium et l'ammonium ; et



(7)

dans laquelle R^5 est choisi dans le groupe constitué par H, SH et SO_3M et M est choisi dans le groupe constitué par l'hydrogène, le sodium, le potassium et l'ammonium.

10. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel la concentration du deuxième additif contenant du soufre hydrosoluble dans le deuxième électrolyte va de 0,005 à 1 g/l.

11. Procédé de dépôt d'un revêtement de cuivre mat selon l'une quelconque des revendications précédentes dans lequel le deuxième électrolyte comprend en outre au moins un additif de support.

12. Procédé de dépôt d'un revêtement de cuivre mat selon la revendication 11 dans lequel l'au moins un additif de support est choisi dans le groupe constitué par l'alcool polyvinylique, la carboxyméthylcellulose, le polyéthylène glycol, le polypropylène glycol, l'ester de polyglycol d'acide stéarique, les naphtoles alcoxylés, l'ester de polyglycol d'acide oléique, l'éther de polyglycol d'alcool stéarylique, l'éther de polyglycol de nonylphénol, l'éther de polyalkylène glycol d'octanol, le bis-(éther de polyalkylène glycol) d'octanediol, le poly(éthylène glycol-*ran*-propylène glycol), le poly(éthylène glycol)-*bloc*-poly(propylène glycol)-*bloc*-poly(éthylène glycol) et le poly(propylène glycol)-bloc-poly(éthylène glycol)-*bloc*-poly(propylène glycol).

13. Procédé de dépôt d'un revêtement de cuivre mat selon les revendications 11 et 12 dans lequel la concentration de l'au moins un additif de support dans le deuxième électrolyte va de 0,005 g/l à 5 g/l.

REFERENCES CITED IN THE DESCRIPTION

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