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(54) Electrolyte and method for the deposition of a matt metal layer

(57) This invention relates to an electrolyte as well as a method for the deposition of a matt metal layer on a substrate surface. In particular, the invention relates to an electrolyte which has a low concentration of the deposition metal and a method to deposit a matt metal layer by using such electrolytes. The inventive electrolyte for the deposition of a matt metal layer of a metal of the group consisting of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, In, Sn, Sb, Te, Re, Pt, Au, Tl, Bi, or an alloy of these metals on a substrate surface, wherein the electrolyte forms an emulsion and/or dispersion by the addition of an unsubstituted polyalkylene oxide or an derivate of an substituted or unsubstituted polyalkylene oxide, or a wetting agent, wherein the wetting agent is a fluorated or perfluorated wetting agent or an polyalkylene oxide substituted quaternary ammonium compound, is characterized in that the electrolyte comprises at least one halogenide, sulphate, or sulfonate of an element of the group consisting of sodium, potassium, aluminium, magnesium, or boron.

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Description

[0001] This invention relates to an electrolyte as well as a method for the deposition of a matt metal layer on a substrate surface. In particular, the invention relates to an electrolyte which has a low concentration of the deposition metal and a method to deposit a matt metal layer by using such electrolytes.

[0002] In general, it is the intention when depositing metal layers on substrate surfaces to gain a plain and glossy metal layer on the substrate surface. The metal layer deposited may have functional properties, which properties can optimise the substrate surface for the later proposal, or decorative effects should be obtained. According to the intended use of the substrate, sometimes it is preferred to have a non-glossy, matt or so-called pearlbrite metal layer on the substrate surface. On one side, this intention can be based on the optical appearance of the deposit, on the other side matt or so-called pearlbrite deposits have specific technical properties, like for example to be non-glare, which properties may be desirable for technical or decorative use. The application area for such a matt or pearlbrite metal layers is, for example, jewellery industry, fitting industry, automotive industry, as well as optical or fine mechanical industry. Especially in these areas non-glare metal layers are desired. In the area of jewellery industry, the deposition of matt or pearlbrite metal layers of non-allergic or low allergic metals is requested. The same is true for the application of matt or pearlbrite metal layers in the area of kitchen machinery and kitchen implements.

[0003] In the field of optical or fine mechanical industry the deposition of matt or pearlbrite metal layers of different metals is of interest due to the different features which come along with the different metals, thus the substrate surface can be adapted to the later technical use. In this concern, for example, the ductility, the hardness, the corrosion resistance, or comparable mechanical properties of the substrate surface can be optimised.

[0004] The international patent application WO 2007/076898 discloses an electrolyte as well as a method for the deposition of matt metal layers, especially of the metals vanadium, chrome, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, palladium, silver, indium, tin, antimony, tellurium, rhenium, platinum, gold, thallium, bismuth, or alloys of these. For the deposition of these metals on a substrate surface, according to WO 2007/076898, which is incorporated as reference, an emulsion and/or dispersion is formed in the electrolyte by addition of an emulsion agent and/or dispersion agent, or a wetting agent.

[0005] A drawback of the electrolyte as well as the method known from the state of the art is that sometimes it is difficult to gain even deposits on the substrate surface. Thus, it is the object of this invention to optimise the electrolyte as well as the method known from the state of the art.

[0006] This object is solved by an electrolyte for the deposition of a matt metal layer of a metal of the group consisting of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, In, Sn, Sb, Te, Re, Pt, Au, Tl, Bi, or an alloy of these metals on a substrate surface, wherein the electrolyte comprises a substituted or unsubstituted polyalkylene oxide or a derivate of a substituted or unsubstituted polyalkylene oxide, or a wetting agent, wherein the wetting agent is fluorated or perfluorated, or is a quaternary ammonium compound substituted with a polyalkalylene oxide, for building an emulsion and/or dispersion in the electrolyte, **characterised in that** the electrolyte comprises at least one halogenide, sulphate, or sulfonate of an element of the group consisting of sodium, potassium, aluminium, magnesium, or boron. In an embodiment, a methanesulfonate of sodium, potassium, or magnesium is preferred. In another embodiment, aluminium sulphate and/or boron tetrafluoride is preferred.

[0007] Surprisingly it was found that the addition of soluble compounds of heavy cations, especially of an alkaline halogenide or alkaline earth halogenide, an alkaline sulphate or alkaline earth sulphate, or an alkaline sulfonate or alkaline earth sulfonate as well as aluminium sulphate, aluminium chloride, or boron tetrafluoride, alone or in combination, is capable to overcome the drawbacks known from the state of the art. These compounds can be used to increase the density of the electrolyte in the inventive way.

[0008] By increasing the density of the electrolyte, the cloud point is exceeded, which effect is to be avoided by normal plating electrolytes, but here leads to the desired matt effect of the deposited metal layer. The addition of the mentioned inert compounds which do not comprise any depositable metal cations increases the density so that a matt metal layer is deposited even at a very low concentration of plating metal in the electrolyte.

[0009] According to the invention, the electrolyte may comprise density increasing compound within a concentration in the range of from 10% to 100% by weight of the concentration of the metal to be deposited. Preferably, the alkali compound or alkaline earth compound is comprised in the inventive electrolyte in a range between 20% to 60% by weight of the concentration of the metal to be deposited.

[0010] Furthermore, it was surprisingly found that the addition of a surface active wetting agent to the inventive electrolyte is possible. The addition of a surface active wetting agent supports the even deposition of metal layers further. To the electrolytes known from the state of the art the addition of surface active wetting agents was not possible since those surface active wetting agents would influence the formation of an emulsion and/or dispersion in the electrolyte, thereby influencing the matt or pearlbrite effect of the electrolyte. If surface active wetting agents were added to the electrolytes known from the state of the art, the deposited metal layers turned to be glossy instead of being non-glare.

[0011] In the inventive electrolyte, the addition of surface active wetting agents is possible without influencing

the matt effect of the electrolyte.

[0012] The surface active wetting agent which can be added to the inventive electrolyte may be a wetting agent of the group consisting of alkyl sulphates, sulfosuccinic acid, and betaines.

[0013] The surface active wetting agent may be comprised in the inventive electrolyte in a concentration between 0,01 mol/l and 100 mol/l, preferably between 0,1 mol/l and 10 mol/l.

[0014] In a preferred embodiment, the density increasing compound in the inventive electrolyte is sodium sulphate, magnesium sulphate, or aluminium sulphate.

[0015] In terms of the method, the object of the invention is solved by a method for the electrolytic deposition of a matt metal layer on a substrate surface, which matt metal layer is deposited from an electrolyte forming an emulsion and/or dispersion by conducting a current between a cathodic contacted substrate surface and an anode, which method is **characterised in that** 10 to 50% by weight of the metal to be deposited comprised in the electrolyte is substituted by at least on density increasing halogenide, sulphate, or sulphonate of an element of the group consisting of sodium, potassium, aluminium, magnesium, or boron.

[0016] It is the inventive idea to substitute some of the concentration of the metal to be deposited in the electrolyte by a density increasing compound, thereby reducing the concentration of the metal to be deposited and increasing the density of the electrolyte.

[0017] By doing so, on one hand, due to the less amount of metal to be deposited in the electrolyte an economic benefit is gained, since less deposition metal has to be used to formulate the electrolyte. On the other hand, due to the addition of an alkali compound and/or alkaline earth compound, the density of the electrolyte is increased, which leads to a more even deposition of the metal on the substrate surface. Furthermore, it was found that due to the increased density of the electrolyte, the addition of a surface active wetting agent is possible without influencing the matt appearance of the deposited metal layer in an unintended way.

[0018] The invention is described further in terms of examples, while the subject matter of the invention is not limited to these examples.

Examples

Example 1:

[0019] From a Watts-type electrolyte comprising:

190 g/l nickel sulphate 6aq
40 g/l boric acid
30 g/l nickel chloride 6aq
5 g/l sodium saccharinate and
300 g/l magnesium sulphate 7aq
3 mg/l PEG 10.000

a matt nickel layer was deposited in 10 minutes at a temperature of 52° C and a current density of 5 A/dm^2. The pH-value of the electrolyte was about 4,2. The substrate to be plated was moved through the electrolyte at a speed of 2 m/min. The structure of the matt nickel layer deposited was identical to the structure of a matt nickel layer deposited from an electrolyte comprising 3 mg/l of a polyethylenglycol having an average molecular weight of 10.000 g/mol, which electrolyte comprises:

440 g/l nickel sulphate 6aq
40 g/l boric acid
30 g/l nickel chloride 6aq
5 g/l sodium saccharinate and
3 mg/l PEG 10.000

Example 2:

[0020] From a Watts-type electrolyte comprising:

190 g/l nickel sulphate 6aq
40 g/l boric acid
30 g/l nickel chloride 6aq
5 g/l sodium saccharinate and
300 g/l magnesium sulphate 7aq
3 mg/l PEG 10.000

a matt nickel layer was deposited in 10 minutes at a temperature of 52° C and a current density of 5 A/dm^2. The pH-value of the electrolyte was about 4,2. The substrate to be plated was moved through the electrolyte at a speed of 2 m/min. The structure of the matt nickel layer deposited was identical to the structure of a matt nickel layer deposited from an electrolyte comprising 3 mg/l of a polyethylenglycol having an average molecular weight of 10.000 g/mol, which electrolyte comprises:

440 g/l nickel sulphate 6aq
40 g/l boric acid
30 g/l nickel chloride 6aq
5 g/l sodium saccharinate and
3 mg/l PEG 10.000

Example 3:

[0021] From a Sn/Co-electrolyte comprising:

120 g/l sodium gluconate
50 g/l cobalt (II) sulphate 7aq
25 g/l tin (II) sulphate
260 g/l sodium sulphate and
1 mg/l PEG 35.000

in 5 minutes at a temperature of 45°C and a current density of 0,5 A/dm^2 a very fine matt layer of a tin-cobalt alloy was deposited. The pH-value of the electrolyte was about 8,4 and the substrate to be plated was moved through the electrolyte at a speed of 2 m/min. The deposited very

fine matt layer was identical to a layer deposited from an electrolyte comprising

120 g/l sodium gluconate
100 g/l cobalt(II) sulphate 7aq
50 g/l tin (II) sulphate
1 mg/l PEG 35.000.

[0022] The above embodiments clearly show that the inventive addition of an alkali compound or alkaline earth compound to an electrolyte composition known from the state of the art enables the reduction of the plating metal concentration in the electrolyte, without influencing the plating result. This enables plating electrolytes having a very low concentration of plating metal which gives great economic benefit.

Example 4:

[0023] From a Ni-electrolyte comprising:

225 g/l nickel sulphate 7aq
50 g/l nickel chloride
40g/l boric acid
225 g/l magnesium sulphate 7aq
2,6 g/l sodium benzoic acid sulphonimide
1,5 mg/l polyethylenglycol-methylether and
1,8 mg/l sodium-2-propen-sulphonate

on a substrate surface a matt nickel layer was deposited in 10 min. at a current density of 5 A/dm^2 and a temperature of 55°C, which layer has the same properties than a layer deposited under the same conditions by from an electrolyte comprising 550 g/l nickel sulphate and no magnesium sulphate.

Example 5:

[0024] From a Sn/Co-electrolyte comprising:

120 g/l sodium gluconate
50 g/l cobalt (II) sulphate 7aq
25 g/l tin (II) sulphate
120 g/l aluminium sulphate and
1 mg/l PEG 35.000

in 5 minutes at a temperature of 45°C and a current density of 0,5 A/dm^2 a very fine matt layer of a tin-cobalt alloy was deposited. The pH-value of the electrolyte was about 8,4 and the substrate to be plated was moved through the electrolyte at a speed of 2 m/min. The deposited very fine matt layer was identical to a layer deposited from an electrolyte comprising

120 g/l sodium gluconate
100 g/l cobalt(II) sulphate 7aq
50 g/l tin (II) sulphate
1 mg/l PEG 35.000.

[0025] The above embodiments clearly show that the inventive addition of a density increasing compound to an electrolyte composition known from the state of the art enables the reduction of the plating metal concentration in the electrolyte, without influencing the plating result. This enables plating electrolytes having a very low concentration of plating metal which gives great economic benefit.

Claims

1. Electrolyte for the deposition of a matt metal layer of a metal of the group consisting of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, In, Sn, Sb, Te, Re, Pt, Au, Tl, Bi, or an alloy of these metals on a substrate surface, wherein the electrolyte forms an emulsion and/or dispersion by the addition of an unsubstituted polyalkylene oxide or an derivate of an substituted or unsubstituted polyalkylene oxide, or a wetting agent, wherein the wetting agent is a fluorated or perfluorated wetting agent or an polyalkylene oxide substituted quaternary ammonium compound, **characterized in that** the electrolyte comprises at least one halogenide, sulphate, or sulfonate of an element of the group consisting of sodium, potassium, aluminium, magnesium, or boron.

2. Electrolyte according to claim 1, wherein the electrolyte comprises a compound of the group consisting of sodium methanesulfonate, potassium methanesulfonate, magnesium methanesulfonate, aluminium sulphate, or a boron tetrafluoride.

3. Electrolyte according to claim 1 or 2, wherein the electrolyte comprises at least one surface active wetting agent.

4. Electrolyte according to one of the preceding claims, wherein the alkali compound or alkaline earth compound is comprised in the electrolyte in a concentration within the range between 10% and 100% by weight of the concentration of the metal to be deposited.

5. Electrolyte according to one of the claims 3 or 4, wherein the surface active wetting agent is a wetting agent of the group consisting of alkyl sulphates, sulfo-succinic acid, and betaines.

6. Electrolyte according to one of the claims 3 to 5, wherein the surface active wetting agent is comprised in the electrolyte in a concentration within the range of 0,01 mol/l and 100 mol/l, preferably between 0,1 mol/l and 10 mol/l.

7. Electrolyte according to one of the preceding claims, wherein the electrolyte comprises sodium sulphate

and/or magnesium sulphate.

8. Method for the electrolytic deposition of a matt metal layer on a substrate surface from an electrolyte forming an emulsion and/or dispersion, by conducting a current between a cathodic contacted substrate surface and an anode, **characterized in that** in the electrolyte, between 10% and 50% by weight of the metal to be deposited is substituted by at least one halogenide, sulphate, or sulfonate of an element of the group consisting of sodium, potassium, aluminium, magnesium, or boron.

9. A method according to claim 8, wherein a surface active wetting agent is added to the electrolyte.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 01 2262

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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
Munich	23 December 2008	Zech-Agarwal, Nicole

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EUROPEAN SEARCH REPORT

Application Number
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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
Munich	23 December 2008	Zech-Agarwal, Nicole

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X : particularly relevant if taken alone
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