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(54) METHOD FOR ELECTRODEPOSITING A DARK CHROMIUM LAYER, SUBSTRATE COMPRISING SAME, AND ELECTROPLATING BATH THEREOF

(57) The present invention relates to a method for electrodepositing a dark chromium layer on a substrate, a respective electroplating bath for depositing such a dark chromium layer, and a respective substrate comprising said dark chromium layer. The electroplating bath comprises colloidal particles containing the chemical element aluminum. The substrate comprising said dark chromium layer is primarily suited for decorative purposes.

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Description

Field of the Invention

[0001] The present invention relates to a method for electrodepositing a dark chromium layer on a substrate, a respective electroplating bath for depositing such a dark chromium layer, and a respective substrate comprising said dark chromium layer. The electroplating bath comprises colloidal particles containing the chemical element aluminum. The substrate comprising said dark chromium layer is primarily suited for decorative purposes.

Background of the Invention

[0002] From the very beginning of chromium coatings, a high interest in dark chromium coatings was observable due to its great appeal for decorative applications.

[0003] Beginning with even dark hexavalent chromium coatings, the focus today significantly shifted to trivalent chromium coatings due to a higher environmental acceptance. Since some years the demand for dark trivalent chromium coatings is more and more increasing, for example for decorative automotive parts. However, a very dark color tone might be perceived as too cold in some cases such that slight color tone modifications are often demanded to create a variety of dark tones, serving various decorative purposes. Typically, the degree of dark tones varies significantly depending on deposition parameters as well as bath ingredients.

[0004] There is an ongoing demand to provide a dark chromium layer, which allows a fine-tuning in either a slightly more warmer color tone or a sightly more darker color tone. It is desired to have adjustment means that allow such a fine-tuning in an easy to handle way.

[0005] In principle, dark trivalent chromium layers are known.

[0006] US 2011/155286 A1 refers to a composition for a chemical conversion treatment comprising trivalent chromium ions and optionally inorganic silica sol or an alumina sol.

[0007] JP 5890394 B2 refers to a chromium plating solution containing trivalent chromium and ceramic particles.

[0008] RU 2231581 C1 refers to a chromium electrolyte containing trivalent chromium ions and Al2O3 powder.

[0009] US 2012/312694 A1 refers to an aqueous acidic trivalent chromium electrolyte comprising trivalent chromium ions and colloidal silica.

Objective of the Invention

[0010] It is the objective of the present invention to provide a method for electrodepositing a dark chromium layer, which starts with a base darkness but in addition to that providing (I) a further reduced darkness and (II) at the same time a high measure of flexibility in the electroplating bath to slightly vary the degree of the further reduced darkness to a specific target darkness by lowering or increasing the brightness L* (according to the L*a*b* color space system) according to the required specification. Furthermore, this flexibility preferably allows to return to the base darkness without discarding the electroplating bath.

Summary of the Invention

[0011] These objectives are solved by a method for electrodepositing a dark chromium layer on a substrate, the method comprising the steps

(a) providing the substrate,

(b) providing an aqueous trivalent chromium electroplating bath comprising

  (i) trivalent chromium ions,

  (ii) one or more than one complexing agent for said trivalent chromium ions,

  (iii) colloidal particles containing the chemical element aluminum,

  (iv) a first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, and

  (v) optionally a second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below being different from (iv),

(c) contacting the substrate with said electroplating bath and applying an electrical current such that the dark chromium layer is electrolytically deposited on the substrate.

[0012] Own experiments have shown (see examples below in the text) that by means of colloidal particles containing the chemical element aluminum a further reduced darkness is obtained, which is primarily expressed by a further reduced L* value compared to a respective electroplating bath not comprising said colloidal particles. This is in particular the case if the aqueous trivalent chromium electroplating bath comprises said first sulfur-containing compound, most preferably methionine. However, own experiments have also shown that this effect does not necessarily occur with colloidal particles not comprising aluminum, e.g. colloidal silica.

[0013] Another great benefit of the method of the present invention is that the aqueous trivalent chromium electroplating bath comprises a combination of (iii) and (iv). Most preferably, both act as darkening agents in the context of the present invention. However, they both vary significantly in their nature. Wherein (iii) is formed of particles, (iv) is preferably a soluble compound. This means that (iii) can be adapted in its concentration by either adding such colloidal particles or by partially (or fully) removing them from the electroplating bath. Most preferably such a removal is accomplished by physical/mechanical separation means, for example filtration. This typically allows a fine-tuning of the brightness L*, depending on the amount present. Such a removal typically does not significantly affect the presence of (iv). In other words, the total concentration of (iii) is preferably reversibly adapted by physical means without affecting the total concentration of (iv). This allows a great variety of dark color tones with ideally the same base electroplating bath.

Detailed Description of the Invention

[0014] Very preferably, the dark chromium layer is a decorative chromium layer. Typical applications are automotive parts, most preferably for the interior of a car. The electroplating bath utilized in the method of the present invention is very suitable in order to obtain such a dark chromium layer, most preferably such a dark chromium layer as defined throughout the present text.

[0015] The dark chromium layer in the context of the present invention is defined by the L*a*b* color system, preferably as introduced in 1976 by the Commission Internationale de l'Eclairage, if not stated otherwise.

[0016] In step (a) of the method of the present invention, a substrate is provided.

[0017] Preferred is a method of the present invention, wherein the substrate comprises a non-metallic substrate, preferably comprises a plastic substrate.

[0018] Preferred is a method of the present invention, wherein the non-metallic substrate, preferably the plastic substrate, comprises acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene styrene - polycarbonate (ABS-PC), polypropylene (PP), polyamide (PA), polyurethane (PU), polyepoxide (PE), polyacrylate, polyetherimide (PEI), a polyetherketone (PEK), mixtures thereof, and/or composites thereof; preferably acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene styrene - polycarbonate (ABS-PC), polyamide (PA), polyurethane (PU), polyepoxides (PE), polyacrylate, mixtures thereof, and/or composites thereof. Such plastic substrates are often used in decorative applications such as automotive parts, in particular ABS and ABS-PC.

[0019] Preferred is a method of the present invention, wherein the substrate, preferably the non-metallic substrate, more preferably the plastic substrate, comprises at least one metal layer (most preferably in addition). Preferably, the at least one metal layer comprise a copper or copper alloy layer and/or a nickel or nickel alloy layer.

[0020] In some other cases, a method of the present invention is preferred, wherein the substrate is a metallic substrate, preferably comprising iron, copper, nickel, aluminum, zinc, mixtures thereof, and/or alloys thereof. A very preferred metallic substrate comprising iron is steel. A mixture thereof preferably includes composites.

[0021] Preferred is a method of the present invention, wherein after step (a) and prior to step (c) the method of the present invention includes step

(a1) pre-treating the substrate, preferably cleaning the substrate, most preferably degreasing and/or pickling the substrate.

[0022] Preferably, the degreasing comprises an electrolytic degreasing.

[0023] Preferably, the pickling comprises a contacting with an acid, preferably an inorganic acid.

[0024] Step (a1) is preferably followed by a water rinse.

[0025] In step (b) of the method of the present invention, said aqueous trivalent chromium electroplating bath is provided.

[0026] Said electroplating bath comprises water, preferably at least 55 vol.-% or more is water, based on the total volume of the electroplating bath, more preferably 65 vol.-% or more, even more preferably 75 vol.-% or more, yet even more preferably 85 vol.-% or more, still more preferably 90 vol.-% or more, most preferably 95 vol.-% or more. Most preferably, water is the only solvent.

[0027] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is acidic, preferably having a pH ranging from 1.5 to 5.0, more preferably from 2.1 to 4.6, even more preferably from 2.4 to 4.2, yet more preferably from 2.7 to 3.8, most preferably from 3.0 to 3.5. The pH is preferably adjusted with hydrochloric acid, sulfuric acid, ammonia, potassium hydroxide, and/or sodium hydroxide.

[0028] The aqueous trivalent chromium electroplating bath comprises (i), trivalent chromium ions.

[0029] Preferred is a method of the present invention, wherein in said electroplating bath the trivalent chromium ions have a total concentration ranging from 5 g/L to 35 g/L, based on the total volume of the electroplating bath, preferably from 6 g/L to 32 g/L, more preferably from 7 g/L to 29 g/L, even more preferably from 8 g/L to 26 g/L, yet even more preferably from 9 g/L to 23 g/L, most preferably from 10 g/L to 22 g/L.

[0030] Preferably, the trivalent chromium ions are from a trivalent chromium salt, preferably from an inorganic chromium salt and/or an organic chromium salt, most preferably from an inorganic chromium salt. A preferred inorganic chromium salt comprises chloride and/or sulfate anions, preferably sulfate anions. A very preferred inorganic chromium salt is basic chromium sulfate. A preferred organic chromium salt comprises carboxylic acid anions, preferably formate, acetate, malate, and/or oxalate anions.

[0031] Preferred is a method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the trivalent chromium ions together with optional iron ions (regarding iron ions, which are optional but preferred in some cases, see text below) represent 80 mol-% or more of all transition metal ions in the aqueous trivalent chromium electroplating bath, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably 90 mol-% or more, more preferably 93 mol-% or more, even more preferably 96 mol-% or more, most preferably 98 mol-% or more.

[0032] The aqueous trivalent chromium electroplating bath comprises (ii), one or more than one complexing agent for said trivalent chromium ions.

[0033] Such compounds keep the trivalent chromium ions in solution. Preferably, the one or more than one complexing agent is not a compound of (iv) and (v) is therefore preferably different therefrom.

[0034] Preferred is a method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the one or more than one complexing agent comprises an organic acid and/or salts thereof, preferably an organic carboxylic acid and/or salts thereof, most preferably an organic carboxylic acid comprising one, two, or three carboxylic groups and/or salts thereof.

[0035] The organic carboxylic acid and/or salts thereof (preferably also the organic carboxylic acid comprising one, two, or three carboxylic groups and/or salts thereof) are preferably substituted with a substituent or unsubstituted. A preferred substituent comprises an amino group and/or a hydroxyl group. Preferably, the substituent does not comprise a SH moiety and/or a SCN moiety. More preferably, the one or more than one complexing agent for said trivalent chromium ions is not a sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below.

[0036] More preferably, the organic carboxylic acid and/or salts thereof (preferably also the organic carboxylic acid comprising one, two, or three carboxylic groups and/or salts thereof) comprise amino carboxylic acids (preferably alpha-amino carboxylic acids), hydroxyl carboxylic acids, and/or salts thereof. Preferred (alpha-) amino carboxylic acids comprise glycine, aspartic acid, and/or salts thereof. Preferably, the amino carboxylic acids (preferably alpha-amino carboxylic acids, respectively) is not a compound according to (iv), more preferably is not a sulfur-containing amino carboxylic acid (preferably is not a sulfur-containing alpha-amino carboxylic acid, respectively), most preferably is not methionine. It is in particularly preferred that the one or more than one complexing agent is distinct from (iv) und (v).

[0037] More preferred is a method of the present invention, wherein the one or more than one complexing agent comprises formic acid, acetic acid, oxalic acid, tartaric acid, malic acid, citric acid, glycine, aspartic acid, and/or salts thereof, preferably formic acid, acetic acid, oxalic acid, tartaric acid, malic acid, citric acid, and/or salts thereof, more preferably formic acid, acetic acid, oxalic acid, tartaric acid, malic acid, and/or salts thereof, even more preferably formic acid, acetic acid, and/or salts thereof, most preferably formic acid and/or salts thereof.

[0038] Preferred is a method of the present invention, wherein the one or more than one complexing agent has a total concentration ranging from 5 g/L to 200 g/L, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably ranging from 8 g/L to 150 g/L, more preferably ranging from 10 g/L to 100 g/L, even more preferably from 12 g/L to 75 g/L, yet even more preferably ranging from 15 g/L to 50 g/L, most preferably ranging from 20 g/L to 35 g/L.

[0039] The aqueous trivalent chromium electroplating bath comprises (iii), colloidal particles containing the chemical element aluminum.

[0040] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is a colloidal suspension, preferably a sol. This is due to the presence of said colloidal particles, which are preferably correspondingly small.

[0041] Preferred is a method of the present invention, wherein said colloidal particles comprise nano-particles, preferably are nano-particles. Preferably, the colloidal particles containing the chemical element aluminum have a particle size of less than 1000 nm, preferably of less than 500 nm, more preferably at least 90% of the colloidal particles have a particle size of less than 500 nm, most preferably at least 90% of the colloidal particles have a particle size of less than 150 nm.

[0042] Preferred is a method of the present invention, wherein said colloidal particles have an average particle diameter D_{50} of 100 nm or less, preferably of 80 nm or less, more preferably of 60 nm or less, even more preferably of 50 nm or less, most preferably of 40 nm or less, very most preferably of 30 nm or less, even most preferably of 25 nm or less, based on volume.

[0043] More preferred is a method of the present invention, wherein said colloidal particles comprise at least particles with a particle size of 100 nm or less, preferably of 80 nm or less, more preferably of 60 nm or less, even more preferably of 50 nm or less, most preferably of 40 nm or less, very most preferably of 30 nm or less, even most preferably of 20 nm or less.

[0044] Preferred is a method of the present invention, wherein said colloidal particles are present in a total amount ranging from 0.05 g/L to 15 g/L, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably from 0.1 g/L to 12 g/L, more preferably from 0.5 g/L to 10 g/L, even more preferably from 1.0 g/L to 8 g/L, most preferably from 1.5 g/L to 6 g/L, even most preferably from 1.9 g/L to 4 g/L.

[0045] More preferred is a method of the present invention, wherein said colloidal particles comprise aluminum oxide.

[0046] Most preferred is a method of the present invention, wherein said colloidal particles comprise Al_2O_3, preferably substantially consist of Al_2O_3. Most preferably, these are the only colloidal particles in the aqueous trivalent chromium electroplating bath.

[0047] The aqueous trivalent chromium electroplating bath comprises (iv), a first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below. Preferably, acids, salts, isoforms, and betaines thereof are included. However, sulfate anions are not counted among (iv) and (v).

[0048] Optionally, the aqueous trivalent chromium electroplating bath comprises (v), a second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below being different from (iv). Again, this preferably includes acids, salts, isoforms, and betaines thereof.

[0049] In some cases, a method of the present invention is preferred, wherein the aqueous trivalent chromium electroplating bath comprises (iv) and (v). Thus, in this case, (v) is not optional.

[0050] Generally preferred is a method of the present invention, wherein the first and the optional second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below comprises a divalent sulfur atom. They are preferably inorganic or organic.

[0051] In some cases, preferably the first sulfur-containing compound comprises one or more than one organic sulfur-containing compound (preferably as described throughout the text), wherein preferably the second sulfur-containing compound comprises one or more than one inorganic sulfur-containing compound (preferably as described throughout the text).

[0052] More generally preferred is a method of the present invention, wherein the first and the optional second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below is selected from the group consisting of (including its salts)

(1) 2-(2-Hydroxy-ethylsulfanyl)-ethanol,

(2) Thiazolidine-2-carboxylic acid,

(3) Thiodiglycol ethoxylate,

(4) 2-Amino-3-ethylsulfanyl-propionic acid,

(5) 3-(3-Hydroxy-propylsulfanyl)-propan-1-ol,

(6) 2-Amino-3-carboxymethylsulfanyl-propionic acid,

(7) 2-Amino-4-methylsulfanyl-butan-1-ol,

(8) 2-Amino-4-methylsulfanyl-butyric acid,

(9) 2-Amino-4-ethylsulfanyl-butyric acid,

(10) 3-Carbamimidoylsulfanyl-propane-1-sulfonic acid,

(11) 3-Carbamimidoylsulfanyl-propionic acid,

(12) Thiomorpholine,

(13) 2-[2-(2-Hydroxy-ethylsulfanyl)-ethylsulfanyl]-ethanol,

(14) 4,5-Dihydro-thiazol-2-ylamine,

(15) Thiocyanic acid,

(16) 2-Amino-4-methanesulfinyl-butyric acid,

(17) 1,1-Dioxo-1,2-dihydro-1 lambda*6*-benzo[d]isothiazol-3-one,

(18) Prop-2-yne-1-sulfonic acid,

(19) Methanesulfinylmethane, and

(20) 2-(1,1,3-Thoxo-1,3-dihydro-1lambda*6*-benzo[d]isothiazol-2-yl)-ethanesulfonic acid

[0053] Also generally preferred is a method of the present invention, wherein (iv) and (v) together have a total concentration ranging from 16 mmol/L to 1150 mmol/L, based on the total volume of the electroplating bath, preferably from 45 mmol/L to 1000 mmol/L, more preferably from 80 mmol/L to 900 mmol/L, even more preferably from 120 mmol/L to 800 mmol/L, yet even more preferably from 150 mmol/L to 700 mmol/L, most preferably from 180 mmol/L to 650 mmol/L. This most preferably applies to all sulfur-containing compounds having a sulfur atom with an oxidation number of +5 or below in the aqueous trivalent chromium electroplating bath (i.e. a total concentration over all such compounds).

[0054] Particularly preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath comprises (iv) in a total concentration ranging from 15 mmol/L to 750 mmol/L, based on the total volume of the electroplating bath, preferably from 40 mmol/L to 650 mmol/L, more preferably from 70 mmol/L to 600 mmol/L, even more preferably from 100 mmol/L to 550 mmol/L, yet even more preferably from 120 mmol/L to 500 mmol/L, most preferably from 140 mmol/L to 470 mmol/L.

[0055] Particularly preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath comprises (v) in a total concentration ranging from 1 mmol/L to 400 mmol/L, based on the total volume of the electroplating bath, preferably from 5 mmol/L to 350 mmol/L, more preferably from 10 mmol/L to 300 mmol/L, even more preferably from 20 mmol/L to 250 mmol/L, yet even more preferably from 30 mmol/L to 200 mmol/L, most preferably from 40 mmol/L to 180 mmol/L.

[0056] Preferred is a method of the present invention, wherein (iv) has a higher molar concentration than (v). In some cases, preferred is a method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the molar ratio of (iv) to (v) is more than 1, preferable 1.1 or more, most preferably 1.2 or more. Most preferably, said first sulfur-containing compound has the highest concentration of sulfur containing compounds having a sulfur atom with an oxidation number of +5 or below.

[0057] In some cases, more preferred is a method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the molar ratio of (iv) to (v) is ranging from 1.05 to 15, preferably from 1.10 to 12, more preferably from 1.15 to 10, even more preferably from 1.20 to 9, most preferably from 1.25 to 8. Again, most preferably, said first sulfur-containing compound has the highest concentration of sulfur containing compounds having a sulfur atom with an oxidation number of +5 or below.

[0058] In some cases, preferred is a method of the present invention, wherein the first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below and being different from (iv) comprises a nitrogen atom, more preferably comprises an amino group, most preferably comprises an amino acid.

[0059] Preferably, said amino acid comprises an alpha-amino acid having a sulfur atom with an oxidation number of +5 or below, most preferably a proteinogenic amino acid having a sulfur atom with an oxidation number of +5 or below. Most preferably this comprises methionine and cysteine.

[0060] In some cases, more preferred is a method of the present invention, wherein the first sulfur-containing compound comprises methionine. The aforementioned molar ratios most preferably apply, if the first sulfur-containing compound comprises methionine. However, in other cases a method of the present invention is preferred, wherein the second sulfur-containing compound comprises methionine instead of the first one.

[0061] Preferred is a method of the present invention, wherein methionine has a total concentration ranging from 100 mmol/L to 500 mmol/L, based on the total volume of the electroplating bath, preferably from 110 mmol/L to 450 mmol/L, more preferably from 120 mmol/L to 400 mmol/L, even more preferably from 130 mmol/L to 350 mmol/L, yet even more preferably from 140 mmol/L to 300 mmol/L, most preferably from 150 mmol/L to 250 mmol/L. However, in some cases it is preferred that methionine even has a lower total concentration, preferably ranging from 15 mmol/L to 100 mmol/L, more preferably from 20 mmol/L to 80 mmol/L.

[0062] In some cases, preferred is a method of the present invention, wherein the second sulfur-containing compound comprises an inorganic sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, preferably comprises thiocyanate anions. However, in some other cases a method of the present invention is preferred, wherein the first sulfur-containing compound comprises thiocyanate anions instead of the second one. In the context of the present invention, thiocyanate anions (i.e. SCN^-) are considered to be inorganic, wherein organic compounds comprising a thiocyanate moiety are considered to be organic thiocyanates. Preferably, thiocyanate anions are present through a thiocyanate salt (e.g. potassium, sodium, ammonium thiocyanate) and/or through thiocyanic acid.

[0063] Preferred is a method of the present invention, wherein thiocyanate anions have a total concentration ranging from 1 mmol/L to 400 mmol/L, based on the total volume of the electroplating bath, preferably from 3 mmol/L to 350 mmol/L, more preferably from 5 mmol/L to 300 mmol/L, even more preferably from 8 mmol/L to 250 mmol/L, yet even more preferably from 12 mmol/L to 200 mmol/L, most preferably from 15 mmol/L to 180 mmol/L.

[0064] Preferably, the aqueous trivalent chromium electroplating bath comprises further compounds or preferably does not contain particular compounds as outlined in the following.

[0065] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath further comprises Fe(II) ions, preferably in a concentration ranging from 0.1 mmol/L to 10 mmol/L, based on the total volume of the electroplating bath, preferably from 0.4 mmol/L to 8 mmol/L, more preferably from 0.8 mmol/L to 6 mmol/L, even more preferably from 1.2 mmol/L to 5 mmol/L, most preferably from 1.5 mmol/L to 4.5 mmol/L. In many cases, said Fe(II) ions positively affect the electroplating performance. Furthermore, in some cases it is preferred that the dark chromium layer comprises iron.

[0066] Preferred is a method of the present invention, wherein in step (b) the aqueous trivalent chromium electroplating bath further comprises sulfate anions, preferably in a concentration ranging from 0.2 mol/L to 1.3 mol/L, based on the total volume of said electroplating bath, more preferably from 0.3 mol/L to 1.1 mol/L, even more preferably from 0.4 mol/L to 1.0 mol/L, yet even more preferably from 0.5 mol/L to 0.9 mol/L, most preferably from 0.6 mol/L to 0.8 mol/L. Preferably, sulfate ions are present due to the source of trivalent chromium ions, e.g. basic chromium sulfate. Sulfate ions excellently contribute to the conductivity of said electroplating bath.

[0067] Preferred is a method of the present invention, wherein in step (b) the aqueous trivalent chromium electroplating bath further comprises halogen anions, preferably halogen anions in a total concentration ranging from 0.1 mol/L to 6 mol/L, based on the total volume of said electroplating bath, more preferably in a total concentration ranging from 0.5 mol/L to 5 mol/L, even more preferably from 1 mol/L to 4.5 mol/L, yet even more preferably from 1.5 mol/L to 4.2 mol/L, most preferably from 2 mol/L to 3.9 mol/L.

[0068] More preferred is a method of the present invention, wherein the halogen anions comprise chloride anions, preferably in a total concentration ranging from 0.5 mol/L to 5 mol/L, based on the total volume of said electroplating bath, more preferably from 0.8 mol/L to 4.7 mol/L, even more preferably from 1.3 mol/L to 4.5 mol/L, yet even more preferably from 1.8 mol/L to 4 mol/L, most preferably from 2.3 mol/L 3.7 mol/L. Chloride ions are preferably from a chloride salt and/or hydrochloric acid, preferably from sodium chloride, potassium chloride, ammonium chloride, chromium chloride (at least as a part of all chloride ions), and/or mixtures thereof. Typically, chloride ions are present as the anion of a conductivity salt. A very preferred conductivity salt is ammonium chloride, sodium chloride and potassium chloride, ammonium chloride being preferred most.

[0069] Preferred is a method of the present invention, wherein in step (b) the halogen anions comprise bromide anions, in some cases preferably in addition to chloride anions. Bromide ions typically avoid an anodic formation of undesired hexavalent chromium species. Preferably, the bromide ions have a concentration ranging from 3 g/L to 20 g/L, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably ranging from 4 g/L to 18 g/L, more preferably ranging from 5 g/L to 16 g/L, even more preferably ranging from 6 g/L to 14 g/L, most preferably ranging from 7 g/L to 12 g/L. Bromide ions are preferably from a bromide salt, preferably from sodium bromide, potassium bromide, ammonium bromide, and/or mixtures thereof. Preferably, the bromide ions are also present if sulfate ions are utilized in the aqueous trivalent chromium electroplating bath.

[0070] Preferred is a method of the present invention, wherein in step (b) the aqueous trivalent chromium electroplating bath further comprises ammonium ions.

[0071] Preferred is a method of the present invention, wherein in step (b) the aqueous trivalent chromium electroplating bath further comprises one or more than one pH buffer compound. Most preferably, the one or more than one pH buffer compound is distinct (i.e. different) from (ii). This preferably means that the one or more than one pH buffer compound does not comprise a carboxylic acid, preferably does not comprise an organic acid.

[0072] In many cases a method of the present invention is preferred, wherein in the aqueous trivalent chromium electroplating bath the one or more than one pH buffer compound comprises a boron-containing compound, preferably boric acid and/or a borate, most preferably boric acid. A preferred borate is sodium borate.

[0073] Generally preferred is method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the one or more than one pH buffer compound has a total concentration ranging from 30 g/L to 250 g/L, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably ranging from 35 g/L to 200 g/L, more preferably ranging from 40 g/L to 150 g/L, even more preferably ranging from 45 g/L to 100 g/L, most preferably ranging from 50 g/L to 75 g/L. This even more preferably applies to said boron-containing compound, yet even more preferably to said boric acid together with said borate, most preferably to said boric acid. Most preferably the one or more than one pH buffer compound comprises boric acid but no borate. Thus, most preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath comprises boric acid, preferably in a total amount concentration ranging from 35 g/L to 90 g/L, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably from 40 g/L to 80 g/L, more preferably from 50 g/L to 70 g/L, most preferably from 56 g/L to 66 g/L.

[0074] However, in some other cases the aqueous trivalent chromium electroplating bath does not explicitly comprise a distinct pH buffer compound. Rather, the one or more than one complexing agent for said trivalent chromium ions are present in such an amount and selected in such a way that they do not only serve as complexing agent for the trivalent chromium ions but additionally serve as pH buffer compound. In the context of the present invention this is less preferred but possible.

[0075] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, ions and/or compounds comprising zinc. Preferably, the dark chromium layer is substantially free of, preferably does not comprise, zinc.

[0076] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is not a conversion treatment composition. In other words, the aqueous trivalent chromium electroplating bath is not suitable for conversion coatings and/or for applying on a zinc or zinc alloy layer. In yet even other words, the method of the present invention is not a conversion coating method.

[0077] Preferred is a method of the present invention, wherein the substrate is substantially free of, preferably does not comprise, a zinc and zinc alloy layer.

[0078] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, fluoride ions. Preferably, the dark chromium layer is substantially free of, preferably does not comprise, fluorine.

[0079] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, phosphate anions, more preferably is substantially free of, preferably does not comprise, phosphorous-containing compounds. Preferably, the dark chromium layer is substantially free of, preferably does not comprise, phosphorous.

[0080] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, sulfite anions.

[0081] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, a compound comprising chromium with an oxidation number +6. Thus, said electroplating bath is substantially free of, preferably does not comprise, hexavalent chromium. This in particular means that hexavalent chromium is at least not intentionally added to the aqueous trivalent chromium electroplating bath.

[0082] In some cases, preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, ions and/or compounds comprising cobalt. Preferably, the dark chromium layer is substantially free of, preferably does not comprise, cobalt. However, in other cases a method of the present invention is preferred, wherein the aqueous trivalent chromium electroplating bath comprises ions and/or compounds comprising cobalt. Preferably, the dark chromium layer comprises cobalt. Although cobalt is environmental questionable, it provides an additional darkening effect in some cases.

[0083] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, a soluble aluminum compound (including salts thereof), preferably does not comprise dissolved aluminum ions.

[0084] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, nickel ions. In some cases, a typical Ni-contamination of up to 150 ppm is observed, which is basically acceptable and therefore considered as substantially free of nickel ions. Thus, in some cases it is preferred that the nickel ions have a concentration ranging from 0 ppm to 200 ppm, based on the total weight of the aqueous trivalent chromium electroplating bath, preferably from 1 ppm to 150 ppm, most preferably from 2 ppm to 100 ppm. However, most preferably the aqueous trivalent chromium electroplating bath is free of nickel. Preferably, the dark chromium layer is substantially free of, preferably does not comprise, nickel.

[0085] It is generally preferred to avoid environmental questionable nickel and cobalt species. This generally leads to less complicated wastewater treatment and bath disposal. In addition, neither nickel nor cobalt is generally needed to obtain a dark color tone.

[0086] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is substantially free of, preferably does not comprise, a sulfamic acid and salts thereof.

[0087] In step (c) of the method of the present invention, the substrate is contacted with the aqueous trivalent chromium electroplating bath and an electrical current is applied such that a dark chromium layer is electrolytically deposited on the substrate.

[0088] Preferred is a method of the present invention, wherein the electrical current in step (c) is a direct current, preferably in a range from 3 A/dm^2 to 30 A/dm^2, more preferably from 4 A/dm^2 to 25 A/dm^2, even more preferably from 5 A/dm^2 to 20 A/dm^2, most preferably from 6 A/dm^2 to 18 A/dm^2.

[0089] Preferred is a method of the present invention, wherein in step (c) at least one anode is utilized. The at least one anode is preferably selected from the group consisting of graphite anodes, precious metal anodes, and mixed metal oxide anodes (MMOs).

[0090] Preferred precious metal anodes comprise platinized titanium anodes and/or platinum anodes.

[0091] Preferred mixed metal oxide anodes comprise platinum oxide coated titanium anodes and/or iridium oxide coated titanium anodes.

[0092] Preferred is a method of the present invention, wherein the dark chromium layer electrolytically deposited in step (c) has a layer thickness ranging from 0.05 μm to 1 μm, preferably from 0.1 μm to 0.8 μm,more preferably from 0.125 μm to 0.6 μm, most preferably from 0.15 μm to 0.5 μm.

[0093] Preferred is a method of the present invention, wherein in step (c) the contacting is carried out for 1 minute to 20 minutes, preferably for 2 minutes to 15 minutes, more preferably from 3 minutes to 10 minutes.

[0094] Preferred is a method of the present invention, wherein in step (c) the contacting is carried out at a temperature ranging from 20°C to 60°C, preferably from 25°C to 52°C, more preferably from 30°C to 45°C.

[0095] In step (c) of the method of the present invention a dark chromium layer is electrolytically deposited (i.e. it is an electroplated chromium layer) on the substrate, preferably with a lightness value L* according to the L*a*b* color-space system of 60 or less, more preferably of 58 or less, even more preferably of 56 or less, yet even more preferably of 53 or less, most preferably 51 or less.

[0096] More preferred is a method of the present invention, wherein in step (c) the dark chromium layer has, according to the L*a*b color system, a L* value ranging from 45 to 59, preferably from 47 to 55, most preferably from 49 to 53. Most preferably, the dark chromium layer comprises the chemical element aluminum. This means that said colloidal particles are preferably incorporated into the dark chromium layer.

[0097] Preferred is a method of the present invention, wherein in step (c) the dark chromium layer has a a* value, according to the L*a*b color system, ranging from -0.5 to +3.0, preferably from 0 to 2.5, more preferably from +0.3 to +2, most preferably from +0.5 to 1.5.

[0098] Preferred is a method of the present invention, wherein the dark chromium layer has a b* value, according to the L*a*b color system, ranging from +3.1 to +7, preferably from 3.5 to 6.5, more preferably from +4 to +6, most preferably from +4.5 to 5.5.

[0099] Preferred is a method of the present invention further comprising prior to step (c) at least one metal plating step to deposit at least one metal or metal alloy layer, most preferably at least one nickel plating step to deposit at least one nickel or nickel alloy layer. In many cases two or even three such metal plating steps are preferably involved.

[0100] Most preferably, the at least one nickel or nickel alloy layer comprises at least one bright-nickel layer and/or (preferably or) at least one satin nickel layer, most preferably at least one bright-nickel layer.

[0101] More preferred is a method of the present invention, wherein the at least one nickel or nickel alloy layer comprises at least one semi-bright nickel layer, preferably at least one semi-bright-nickel layer in addition to said at least one bright-nickel layer and/or said at least one satin nickel layer. The at least one semi-bright nickel layer is preferably optionally. Most preferably (if applied) the at least one semi-bright nickel layer is deposited prior to said at least one bright-nickel layer and/or said at least one satin nickel layer.

[0102] Also preferred is a method of the present invention, wherein the at least one nickel or nickel alloy layer comprises at least one MPS nickel layer, preferably at least one MPS nickel layer in addition to said at least one bright-nickel layer and/or said at least one satin nickel layer, most preferably at least one MPS nickel layer in addition to said at least one bright-nickel layer and/or said at least one satin nickel layer, and further to said at least one semi-bright nickel layer. In the context of the present invention MPS denotes that the MPS nickel layer comprises non-conductive micro-particles, which cause micro-pores in a subsequent chromium layer, preferably in the dark chromium layer. The at least one MPS nickel layer is preferably optionally.

[0103] In some cases, a method of the present invention is preferred, wherein the MPS nickel layer is adjacent to the dark chromium layer.

[0104] In other cases a method of the present invention is preferred wherein the dark chromium layer is adjacent to the at least one bright-nickel layer and/or the at least one satin nickel layer, which is in many cases preferred, most preferably in combination with the at least one bright-nickel layer.

[0105] Preferably, the dark chromium layer is part of a layer stack.

[0106] The present invention furthermore relates to an aqueous trivalent chromium electroplating bath comprising

(i) trivalent chromium ions,

(ii) one or more than one complexing agent for said trivalent chromium ions,

(iii) colloidal particles containing the chemical element aluminum,

(iv) a first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, and

(v) optionally a second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below being different from (iv).

[0107] Preferably, the aforementioned regarding the method of the present invention, in particular relating to the aqueous trivalent chromium electroplating bath utilized in the method of the present invention, applies likewise to the aqueous trivalent chromium electroplating bath of the present invention, most preferably features described as particularly preferred.

[0108] Furthermore, the present invention also relates to a substrate comprising a dark chromium layer, wherein the dark chromium layer comprises the chemical element aluminum and has, according to the L*a*b color system, a L* value of 60 or less, preferably of 58 or less, more preferably of 56 or less, even more preferably of 53 or less, most preferably 51 or less.

[0109] Preferably, the aforementioned regarding the method of the present invention, in particular relating to the dark chromium layer obtained by the method of the present invention, applies likewise to the substrate of the present invention, most preferably features described as particularly preferred. This most preferably applies to the appearance and ingredients of the dark chromium layer mentioned before, explicitly or implicitly, in relation to the method of the present invention.

[0110] Very preferred is a substrate of the present invention, wherein the dark chromium layer comprises the chemical element aluminum and has, according to the L*a*b color system, a L* value ranging from 45 to 59, preferably from 47 to 55, most preferably from 49 to 53.

[0111] Particularly preferred is a substrate of the present invention, wherein the dark chromium layer has a a* value ranging from -0.5 to +3.0, preferably from 0 to 2.5, more preferably from +0.3 to +2, most preferably from +0.5 to 1.5.

[0112] Particularly preferred is a substrate of the present invention, wherein the dark chromium layer has a b* value ranging from +3.1 to +7, preferably from 3.5 to 6.5, more preferably from +4 to +6, most preferably from +4.5 to 5.5.

[0113] Most preferred is a substrate of the present invention, wherein the dark chromium layer is substantially free of, preferably does not comprise, cobalt. In contrast, in other cases it is preferred, wherein the dark chromium layer comprises cobalt.

[0114] Most preferred is a substrate of the present invention, wherein the dark chromium layer is substantially free of, preferably does not comprise, nickel.

[0115] Preferably, the dark chromium layer is not the only metal layer between the dark chromium layer and the substrate.

[0116] Preferred is a substrate of the present invention, wherein the substrate comprises at least one nickel layer or nickel alloy layer under the dark chromium layer.

[0117] Preferred is a substrate of the present invention, wherein said at least one nickel layer or nickel alloy layer comprises at least one bright-nickel layer or at least one satin nickel layer. This is in many cases most preferred.

[0118] Preferred is a substrate of the present invention, wherein said at least one nickel layer or nickel alloy layer comprises at least one semi-bright nickel layer, preferably at least one semi-bright-nickel layer in addition to said at least one bright-nickel layer and/or said at least one satin nickel layer. The at least one semi-bright nickel layer is preferably optionally. Most preferably the at least one semi-bright nickel layer is the nickel layer (of all nickel layers) closest to the substrate.

[0119] Preferred is a substrate of the present invention, wherein said at least one nickel layer or nickel alloy layer comprises at least one MPS nickel layer, preferably at least one MPS nickel layer in addition to said at least one bright-nickel layer and/or said at least one satin nickel layer, most preferably at least one MPS nickel layer in addition to said at least one bright-nickel layer, and/or said at least one satin nickel layer, and further to said at least one semi-bright nickel layer. In the context of the present invention MPS denotes micro porous.

[0120] Preferred is a substrate of the present invention, wherein said at least one MPS nickel layer faces on the one side the dark chromium layer and on the other side said at least one bright-nickel layer or said at least one satin nickel layer.

[0121] Preferred is a substrate of the present invention, wherein said at least one semi-bright nickel layer is under said at least one bright-nickel layer or said at least one satin nickel layer.

[0122] Even more preferred is a substrate of the present invention, wherein the dark chromium layer is part of a layer stack, the layer stack comprising, along a direction from the dark chromium layer to the substrate (adjacent or not adjacent):

(i) the dark chromium layer,

(ii) optionally, at least one MPS nickel layer,

(iii) at least one bright-nickel layer and/or (preferably or) at least one satin nickel layer, and

(iv) optionally, at least one semi-bright nickel layer.

[0123] The aforementioned particular features regarding the substrate of the present invention preferably apply likewise to the method of the present of the present invention if not yet stated otherwise.

[0124] In some cases, the layer stack preferably comprises a sealer layer and/or an anti-fingerprint layer, most preferably on the dark chromium layer. If both is applied, preferably the sealer layer is applied first, followed by the anti-fingerprint layer, which preferably forms the very outermost layer.

[0125] The spirit of the present invention is further illustrated in the following examples without limiting the scope of the invention as herein defined in the claims.

Examples

(a) Providing the substrate:

[0126] For the following examples copper panels (99 mm x 70 mm) were used as a substrate, primarily for mimicking plastic substrates deposited with a copper layer.

[0127] In a first step the substrate was cleaned by electrolytic degreasing with Uniclean® 279 (product of Atotech), 100 g/L at room temperature (RT). Afterwards the copper panels were pickled with 10 % H_2SO_4 by volume and rinsed with water.

[0128] In a second step, the cleaned and rinsed substrate was subjected to nickel plating to obtain a bright nickel layer on top of the copper panel (parameters: 10 min at 4 A/dm^2; Makrolux® NF electrolyte; product of Atotech).

(b) Providing the aqueous trivalent chromium electroplating bath

[0129] The following aqueous trivalent chromium base electroplating bath was used:

128 g/L	Basic chromium sulfate
46 g/L	Formic acid
60 g/L	Boric acid
12 g/L	Ammonium bromide
100 g/L	Ammonium chloride
110 g/L	Potassium chloride
25-45 g/L	Methionine
0.1 g/L	Sodium diamyl sulphosuccinate

[0130] Further ingredients and amounts are summarized in Tables 1 and 2 below. In Table 1, "E" refers to examples according to the present invention, wherein in Table 2 "CE" refers to comparative examples not according to the present invention.

[0131] The final pH value was about 3.

[0132] In all examples according to the present invention (i.e. E1 to E11), aluminum oxide nanoparticles were used with a particle size D_{50} of 25 nm (Nanobyk-3603; BYK-Chemie GmbH). For comparative examples either no particles at all or SiO_2 nanoparticles with a particle size of 20 nm were used (ThermoFisher; 43110; concentration at least 40%).

(c) Contacting the substrate with said electroplating bath

[0133] Electroplating was carried out in a Hull Cell having a graphite anode and the substrate installed as the cathode. An electrical current of 5 A was applied to the aqueous trivalent chromium electroplating bath for 3 minutes, the bath having a temperature of about 35 °C for all examples (including comparative examples).

[0134] As a result, a respective dark chromium layer was deposited on top of the nickel-plated copper panel. Afterwards, the substrate having the dark chromium layer was rinsed with water.

[0135] The color according to the L*a*b* color space system was determined with a colorimeter (Konica Minolta CM-700 D spectrophotometer). Calibration was done with black and white standard. Color determination was done at an area in the center of the substrate. The measuring area is located 1 cm from the left edge and 2 cm from the lower edge (the left edge pointing to the anode).

Table 1: Summary of compositions and results according to the invention

No.	Al-nanoparticles [g/L]	Fe(II) [mmol/L]	Methionine [g/L]	L*; a*; b*
E1	1	2	30**	49.9; +1.0; +5.6
E2	1.7	2	30**	49.5; +0.9; +5.6
E3	2.3	2	30**	48.9; +0.9; +5.7
E4	1	2	25	56.0; +0.3; +2.6
E5	1.7	2	25	55.3; +0.4; +2.9
E6	2.3	2	25	55.2; +0.3; +3.1
E7	1	4	25	57.6; +0.1; +1.9
E8	1.7	4	25	56.6; +0.2; +2.3
E9	2.3	4	25	55.7; +0.3; +2.8
E10	1	4	43*	53.9; +0.5; +4.0
E11	2.3	4	43*	52.1; +0.7; +4.7
* additionally containing about up to 20 g/L of a thioglycol ** additionally containing about up to 20 g/L of a thioglycol and thiocyanate anions				

Table 2: Summary of compositions and results of comparative examples

No.	SiO_2-nano- particles [ml/L]	Fe(II) [mmol/L]	Methionine [g/L]	L*; a*; b*
CE1	0	2	30**	55.8; +0.4; +3.2
CE2	2	2	30**	55.2; +0.4; +3.3
CE3	3	2	30**	55.3; +0.4; +3.3
CE4	4	2	30**	56.2; +0.4; +3.2
CE5	0	2	25	61.7; -0.3; 0
CE6	0	4	25	61.6; -0.1; +0.4
CE7	0	4	43*	58.9; +0.2; +1.3
* additionally containing about up to 20 g/L of a thioglycol ** additionally containing about up to 20 g/L of a thioglycol and thiocyanate anions				

[0136] Comparative examples CE1 and CE5 to CE7 show conditions without any particles but rather only containing organic coloring agents such as methionine. Interestingly, the presence of silica nanoparticles does not significantly lower the L* value (compare CE1 vs. CE2 to CE4); at least not for a methionine-containing plating bath. In these cases, the L* value remained more or less at 55. Nevertheless, all obtained chromium layers are already dark.

[0137] However, upon adding colloidal particles containing the chemical element aluminum, in particular aluminum oxide nanoparticles, a significant further decrease of the L* value is observed (i.e. a further darkening). In detail: CE1 (L* 55.8) => E1 to E3 (L* 48.9 to 49.9; at least reduced by about 10%); CE5 (L* 61.7) => E4 to E6 (L* 55.2 to 56.0; at least reduced by about 9%); CE6 (L* 61.6) => E7 to E9 (L* 55.7 to 57.6; at least reduced by about 6%); and CE7 (L* 58.9) => E10 and E11 (L* 52.1 to 53.9; at least reduced by about 8%).

[0138] In each scenario, i.e. in each comparative example and its corresponding inventive example the L* value was reduced between about 6% and 10%.

[0139] As also shown in tables 1 and 2, throughout all examples, the a* value remains basically constant. However, adding colloidal particles containing the chemical element aluminum significantly affects the b* value, which basically always increases. In detail: CE1 (b* +3.2) => E1 to E3 (b* about +5.6); CE5 (b* 0) => E4 to E6 (b* +2.6 to +3.1); CE6 (b* +0.4) => E7 to E9 (b* +1.9 to +2.8); and CE7 (b* +1.3) => E10 and E11 (b* +4.0 to +4.7). Thus, with colloidal particles containing the chemical element aluminum a warmer, brownish color tone is obtained.

[0140] The dark chromium layer obtained with the invention is glossy.

Claims

1. A method for electrodepositing a dark chromium layer on a substrate, the method comprising the steps

    (a) providing the substrate,
    (b) providing an aqueous trivalent chromium electroplating bath comprising

        (i) trivalent chromium ions,
        (ii) one or more than one complexing agent for said trivalent chromium ions,
        (iii) colloidal particles containing the chemical element aluminum,
        (iv) a first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, and
        (v) optionally a second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below being different from (iv),

    (c) contacting the substrate with said electroplating bath and applying an electrical current such that the dark chromium layer is electrolytically deposited on the substrate.

2. The method of claim 1, wherein the aqueous trivalent chromium electroplating bath is a colloidal suspension, preferably a sol.

3. The method of claim 1 or 2, wherein said colloidal particles comprise nano-particles, preferably are nano-particles.

4. The method of any one of the aforementioned claims, wherein said colloidal particles have an average particle diameter D_{50} of 100 nm or less, preferably of 80 nm or less, more preferably of 60 nm or less, even more preferably of 50 nm or less, most preferably of 40 nm or less, very most preferably of 30 nm or less, even most preferably of 25 nm or less, based on volume.

5. The method of any one of the aforementioned claims, wherein said colloidal particles comprise at least particles with a particle size of 100 nm or less, preferably of 80 nm or less, more preferably of 60 nm or less, even more preferably of 50 nm or less, most preferably of 40 nm or less, very most preferably of 30 nm or less, even most preferably of 20 nm or less.

6. The method of any one of the aforementioned claims, wherein said colloidal particles are present in a total amount ranging from 0.05 g/L to 15 g/L, based on the total volume of the aqueous trivalent chromium electroplating bath, preferably from 0.1 g/L to 12 g/L, more preferably from 0.5 g/L to 10 g/L, even more preferably from 1.0 g/L to 8 g/L, most preferably from 1.5 g/L to 6 g/L, even most preferably from 1.9 g/L to 4 g/L.

7. The method of any one of the aforementioned claims, wherein said colloidal particles comprise aluminum oxide.

8. The method of any one of the aforementioned claims, wherein said colloidal particles comprise Al_2O_3, preferably substantially consist of Al_2O_3.

9. The method of any one of the aforementioned claims, wherein the first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below and being different from (iv) comprises a nitrogen atom, more preferably comprises an amino group, most preferably comprises an amino acid.

10. The method of any one of the aforementioned claims, wherein the first sulfur-containing compound comprises methionine.

11. The method of any one of the aforementioned claims, wherein the second sulfur-containing compound comprises an inorganic sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, preferably comprises thiocyanate anions.

12. An aqueous trivalent chromium electroplating bath comprising

    (i) trivalent chromium ions,
    (ii) one or more than one complexing agent for said trivalent chromium ions,
    (iii) colloidal particles containing the chemical element aluminum,

(iv) a first sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, and
(v) optionally a second sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below being different from (iv).

13. A substrate comprising a dark chromium layer, wherein the dark chromium layer comprises the chemical element aluminum and has, according to the L*a*b color system, a L* value of 60 or less, preferably of 58 or less, more preferably of 56 or less, even more preferably of 53 or less, most preferably 51 or less.

14. The substrate according to claim 13, wherein the dark chromium layer has a a* value ranging from -0.5 to +3.0, preferably from 0 to 2.5, more preferably from +0.3 to +2, most preferably from +0.5 to 1.5.

15. The substrate according to claim 14, wherein the dark chromium layer has a b* value ranging from +3.1 to +7, preferably from 3.5 to 6.5, more preferably from +4 to +6, most preferably from +4.5 to 5.5.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 17 8841

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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	30 November 2021	Suárez Ramón, C

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X : particularly relevant if taken alone
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