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(54) METHOD FOR ADJUSTING THE BRIGHTNESS L* OF AN ELECTROPLATED CHROMIUM LAYER

(57) The present invention relates to a method for adjusting the brightness L* of an electroplated chromium layer, in particular of a dark electroplated chromium layer. The method includes an aqueous trivalent chromium electroplating bath comprising colloidal particles and/or agglomerates thereof and a step of fully or partially removing same with optionally adding colloidal particles.

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Description

Field of the Invention

[0001] The present invention relates to a method for adjusting the brightness L* of an electroplated chromium layer, in particular of a dark electroplated chromium layer. The method includes an aqueous trivalent chromium electroplating bath comprising colloidal particles and/or agglomerates thereof and a step of fully or partially removing same with optionally adding colloidal particles.

Background of the Invention

[0002] From the very beginning of chromium layers an interest in dark chromium layers was observable. Beginning with dark hexavalent chromium layers, the focus today significantly shifted to trivalent chromium layers due to a higher environmental acceptance.

[0003] Typically, each chromium layer, in particular dark chromium layers, are characterized by color values referenced to the L*a*b* color-space system. While the value L* defines the brightness (or sometimes also referred to as lightness), values a* and b* define the color of a respective chromium layer. While a L* value of 100 defines a diffuse white, a L* value of 0 is a deep black. Values for a* and b* can be positive and negative, wherein a* values describe the colors green (negative) and red (positive), while b* values describe the colors blue (negative) and yellow (positive). A combination of a* and b* with 0 describes a neutral grey color, turning into a deep neutral black the lower the L* value (e.g. of 50 or below).

[0004] Depending on the chemical composition of a respective aqueous trivalent chromium electroplating bath and/or its deposition parameters a huge variety of L*a*b* values are generated with more or less varying values. The more pronounced these variations are the more obvious is an optical difference between two electroplated chromium layers.

[0005] Sadly, in many cases an obvious optical difference between two electroplated chromium layers is not acceptable. In many cases this means that a process with its specific chemistry cannot easily exchanged with another process because very often such slight but obvious optical differences are obtained in production.

[0006] First attempts to adjust the brightness and color, respectively, of electroplated chromium layers are known already.

[0007] For example, WO 2017/053655 A1 refers to a flexible color adjustment for dark Cr(III) platings, disclosing an electroplating bath comprising sulfur containing compounds having a concentration, which is adjusted by filtering the bath through an activated carbon filter. However, such attempts have the drawback that a removal is not sufficiently specific and other compounds are removed as well, which should remain in the bath. Furthermore, such sulfur containing compounds cannot easily re-used and often are lost, which is not acceptable from the cost-perspective. In addition, since various compounds are affected by an activated carbon filter, the concentration of remaining compounds is often unclear and sophisticated analysis are need in order to determine them accurately.

[0008] US 2012/312694 A1 refers to an aqueous acidic trivalent chromium electrolyte comprising a dispersion of colloidal silica. However, US'694 is silent regarding a flexible or reversible color adjustment.

[0009] US 2019/301038 A1 refers to an electroplating bath configured to precipitate a black trivalent chromium layer, wherein the electroplating bath comprises a nanodiamond and a thiocyanate ion. However, also US'038 is silent regarding a flexible or reversible color adjustment.

[0010] US 2013/213813 A1 refers to a method of adjusting and controlling the color of trivalent chromium deposits. However, US'813 is silent regarding a removal of colloidal particles.

[0011] There is therefore an ongoing demand to provide improved methods for adjusting/adapting the brightness and color, respectively, of electroplated chromium layers.

Objective of the Invention

[0012] Since mostly all aqueous trivalent chromium electroplating baths comprise organic compounds, it is a primary object of the present invention to provide a method for effectively adjusting the brightness L* without affecting the concentration of such organic compounds, most preferably neither those who are mainly responsible for a dark color nor those who are not involved in a coloring.

[0013] It was furthermore an objective of the present invention to provide a method, which allows a reversible and easy to handle adjustment.

[0014] It was also an objective of the present invention to provide a method which allows a fine tuning of a certain brightness in order to easily harmonize the brightness to the brightness of a another electroplated chromium layer such that optical differences are at least minimized or even completely avoided.

Summary of the Invention

[0015] These objectives are solved by the present invention, i.e. by a method for adjusting the brightness L* of an electroplated chromium layer, the method comprising the steps

(a) providing a 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 and/or agglomerates thereof, and

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

(c) contacting the substrate with said electroplating bath and applying an electrical current such that a chromium layer is electrolytically deposited on the substrate with a lightness value L1* according to the L*a*b* color-space system,

(d) treating the aqueous trivalent chromium electroplating bath obtained from step (c) such that a treated aqueous trivalent chromium electroplating bath results, by

(d1) removing fully or partially said colloidal particles and/or said agglomerates thereof,
and optionally

(d2) adding colloidal particles,

(e) contacting another substrate with the treated aqueous trivalent chromium electroplating bath and applying an electrical current such that a chromium layer is electrolytically deposited on the another substrate with a lightness value L2* according to the L*a*b* color-space system,
wherein L2* is higher or lower than L1*.

[0016] As shown below in the example section, the present invention nicely allows an adaptation to slightly different L* values. This allows a harmonization to achieve an indistinguishable brightness.

[0017] Preferably, the method of the present invention primarily refers to a decorative electroplated chromium layer.

Detailed Description of the Invention

[0018] In step (a) of the method of the present invention, a substrate is provided.

[0019] Preferred is a method of the present invention, wherein the substrate comprises a non-metallic substrate, preferably comprises a plastic substrate.

[0020] 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.

[0021] 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.

[0022] 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.

[0023] Preferably, the degreasing comprises an electrolytic degreasing.

[0024] Preferably, the pickling comprises a contacting with an acid, preferably an inorganic acid.

[0025] Step (a1) is preferably followed by a water rinse.

[0026] In step (b) of the method of the present invention, said aqueous trivalent chromium electroplating bath is provided.

[0027] 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.

[0028] 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.

[0029] The aqueous trivalent chromium electroplating bath comprises (i), trivalent chromium ions.

[0030] 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.

[0031] 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.

[0032] 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.

[0033] The aqueous trivalent chromium electroplating bath comprises (ii), one or more than one complexing agent for said trivalent chromium ions.

[0034] 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 is therefore preferably different from (iv).

[0035] 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.

[0036] 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.

[0037] 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).

[0038] 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.

[0039] 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.

[0040] The aqueous trivalent chromium electroplating bath comprises (iii), colloidal particles and/or agglomerates thereof.

[0041] Preferably, the aqueous trivalent chromium electroplating bath comprises at least said colloidal particles. This means, either with or without agglomerates thereof.

[0042] Preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath is a colloidal suspension. This is due to the presence of said colloidal particles.

[0043] Preferred is a method of the present invention, wherein the colloidal particles comprise one or more than one chemical element selected from the group consisting of silicon, aluminum, and carbon, preferably silicon and aluminum, most preferably the colloidal particles comprise the chemical element aluminum.

[0044] Generally preferred is a method of the present invention, wherein the colloidal particles comprise nano-particles, preferably are nano-particles. Preferably, the colloidal particles 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.

[0045] Preferred is a method of the present invention, wherein said colloidal particles comprise nano-particles, preferably are nano-particles.

[0046] 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.

[0047] 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. Most preferably, a particle size of 100 nm is not exceeded.

[0048] Preferred is a method of the present invention, wherein the colloidal particles comprising the chemical element silicon, comprise silica, preferably are silica colloidal particles.

[0049] Preferred is a method of the present invention, wherein the colloidal particles comprising the chemical element aluminum, comprise aluminum oxide, preferably are aluminum oxide colloidal particles.

[0050] Most preferred is a method of the present invention, wherein said colloidal particles comprise aluminum oxide, preferably are aluminum oxide colloidal particles.

[0051] Preferred is a method of the present invention, wherein the colloidal particles comprising the chemical element carbon, comprise nanodiamonds, preferably are nanodiamond colloidal particles.

[0052] Preferred is a method of the present invention, wherein in step (b) or after step (d2) said colloidal particles are present in a total amount ranging from 0.05 g/L to 100 g/L, based on the total volume of the respective aqueous trivalent chromium electroplating bath, preferably from 0.1 g/L to 80 g/L, more preferably from 0.25 g/L to 60 g/L, even more preferably from 0.5 g/L to 45 g/L, most preferably from 0.75 g/L to 35 g/L, even most preferably from 1 g/L to 20 g/L.

[0053] The aqueous trivalent chromium electroplating bath comprises (iv), one or more than one 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).

[0054] In some cases, a method of the present invention is preferred, wherein said one or more than one sulfur-containing compound comprises a divalent sulfur atom.

[0055] Generally preferred is a method of the present invention, wherein in step (b) the aqueous trivalent chromium electroplating bath comprises (iv) in a total concentration ranging from 1 mmol/L to 1150 mmol/L, based on the total volume of said electroplating bath, preferably from 16 mmol/L to 900 mmol/L, more preferably from 30 mmol/L to 800 mmol/L, even more preferably from 70 mmol/L to 700 mmol/L, most preferably from 110 mmol/L to 595 mmol/L. This preferably applies likewise to the treated aqueous trivalent chromium electroplating bath obtained in step (d).

[0056] In some cases, preferred is a method of the present invention, wherein (iv) comprises at least one inorganic sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below. However, in other cases a method of the present invention is preferred, wherein (iv) comprises at least one organic sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below.

[0057] Preferred is a method of the present invention, wherein (iv) comprises thiocyanate anions. 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) or through thiocyanic acid.

[0058] Particularly preferred is a method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the 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. This preferably applies likewise to the treated aqueous trivalent chromium electroplating bath obtained in step (d).

[0059] Preferred is a method of the present invention, wherein (iv) comprises at least a sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below and additionally comprising a nitrogen atom, preferably additionally comprising an amino group, more preferably (iv) comprises at least an amino acid having a sulfur atom with an oxidation number of +5 or below, most preferably (iv) comprises at least methionine.

[0060] Preferably, the amino acid having a sulfur atom with an oxidation number of +5 or below 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.

[0061] Preferred is a method of the present invention, wherein in the aqueous trivalent chromium electroplating bath the at least one sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below and additionally comprising a nitrogen atom (preferably the at least an amino acid having a sulfur atom with an oxidation number of +5 or below, more preferably said alpha-amino acids) has a total concentration ranging from 10 mmol/L to 550 mmol/L, based on the total volume of the electroplating bath, preferably from 30 mmol/L to 480 mmol/L, more preferably from 60 mmol/L to 410 mmol/L, even more preferably from 80 mmol/L to 350 mmol/L, yet even more preferably from 100 mmol/L to 280 mmol/L, most preferably from 130 mmol/L to 200 mmol/L. This preferably applies likewise to the treated aqueous trivalent chromium electroplating bath obtained in step (d).

[0062] Particularly preferred is a method of the present invention, wherein the aqueous trivalent chromium electroplating bath comprises

- an inorganic sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below, preferably thiocyanate anions,
  and/or (preferably and)

- a sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below and additionally comprising a nitrogen atom, preferably an amino acid having a sulfur atom with an oxidation number of +5 or below, most preferably methionine.

[0063] Thus, in some cases, a method of the present invention is preferred, wherein the aqueous trivalent chromium electroplating bath comprises two or more than two compounds of (iv), most preferably thiocyanate anions and methionine.

[0064] In some cases, a method of the present invention is even more preferred, wherein the aqueous trivalent chromium electroplating bath comprises one or more than one of the following compounds (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-1lambda*6*-benzo[d]isothiazol-3-one,

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

(19) Methanesulfinylmethane,

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

[0065] Preferably, the aqueous trivalent chromium electroplating bath comprises further compounds or preferably does not contain particular compounds as outlined in the following.

[0066] Preferred is a method of the present invention, wherein in step (b), and preferably additionally in step (e), 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 said 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 4 mmol/L, most preferably from 1.5 mmol/L to 2.5 mmol/L.

[0067] Preferred is a method of the present invention, wherein said concentration of Fe(II) ions applies likewise to the treated aqueous trivalent chromium electroplating bath. Most preferably, in general and if not stated otherwise, concentrations given for the aqueous trivalent chromium electroplating bath (e.g. certain chemical compounds or ions) apply likewise to the treated aqueous trivalent chromium electroplating bath obtained after step (d); except for (iii). In many cases, said Fe(II) ions positively affect the electroplating performance. Furthermore, in some cases it is preferred that the chromium layer comprises iron.

[0068] Preferred is a method of the present invention, wherein in step (b), and preferably additionally in step (e), 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.

[0069] Generally, in the context of the present invention, preferably additionally in step (e) denotes that it preferably applies likewise to the treated aqueous trivalent chromium electroplating bath utilized in step (e).

[0070] Preferred is a method of the present invention, wherein in step (b), and preferably additionally in step (e), 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.

[0071] 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.

[0072] Preferred is a method of the present invention, wherein in step (b), and preferably additionally in step (e), the halogen anions comprise bromide 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.

[0073] Preferred is a method of the present invention, wherein in step (b), and preferably additionally in step (e), the aqueous trivalent chromium electroplating bath further comprises ammonium ions.

[0074] Preferred is a method of the present invention, wherein in step (b), and preferably additionally in step (e), 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.

[0075] 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.

[0076] 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.

[0077] 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.

[0078] 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 chromium layer is substantially free of, preferably does not comprise, zinc.

[0079] 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.

[0080] 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.

[0081] 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 chromium layer is substantially free of, preferably does not comprise, fluorine.

[0082] 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 chromium layer is substantially free of, preferably does not comprise, phosphorous.

[0083] 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.

[0084] 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.

[0085] 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 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 chromium layer comprises cobalt. Although cobalt is environmental questionable, it provides a darkening effect in some cases.

[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 soluble aluminum compound (including salts thereof), preferably does not comprise dissolved aluminum ions.

[0087] 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.

[0088] 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.

[0089] 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.

[0090] 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 said chromium layer is electrolytically deposited on the substrate.

[0091] Preferred is a method of the present invention, wherein the electrical current in step (c) and preferably additionally in step (e) 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.

[0092] Preferred is a method of the present invention, wherein in step (c) and preferably additionally in step (e) 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).

[0093] Preferred precious metal anodes comprise platinized titanium anodes and/or platinum anodes.

[0094] Preferred mixed metal oxide anodes comprise platinum oxide coated titanium anodes and/or iridium oxide coated titanium anodes.

[0095] Preferred is a method of the present invention, wherein the chromium layer electrolytically deposited in step (c) and preferably additionally in (e) 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.

[0096] Preferred is a method of the present invention, wherein in step (c) and preferably additionally in (e) 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.

[0097] Preferred is a method of the present invention, wherein in step (c) and preferably additionally in (e) 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.

[0098] In step (c) of the method of the present invention a chromium layer is electrolytically deposited (i.e. it is an electroplated chromium layer) on the substrate with a lightness value L1* according to the L*a*b* color-space system.

[0099] Preferred is a method of the present invention, wherein the electroplated chromium layer is dark, preferably black. This means it is a dark, respectively a black, electroplated chromium layer. This generally applies preferably also to the electroplated chromium layer obtained in step (e).

[0100] Preferred is a method of the present invention, wherein L1* is 55 or less, preferably 53 or less, more preferably 51 or less, even more preferably 50 or less, most preferably 49 or less.

[0101] Preferred is a method of the present invention, wherein the electroplated chromium layer obtained in step (c) has an a1* value, preferably ranging from -1.5 to +3, preferably ranging from -1 to +2.5, most preferably ranging from -0.5 to +2. Preferably, the a1* value is at least positive.

[0102] Preferred is a method of the present invention, wherein the electroplated chromium layer obtained in step (c) has a value b1*, according to the L*a*b* color-space system.

[0103] Preferred is a method of the present invention, wherein b1* is ranging from +4 to +7, preferably from +4.5 to +6.5.

[0104] 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.

[0105] 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.

[0106] 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.

[0107] 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.

[0108] In some cases, a method of the present invention is preferred, wherein the MPS nickel layer is adjacent to the chromium layer, preferably the dark chromium layer.

[0109] In other cases a method of the present invention is preferred wherein the chromium layer, preferably 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.

[0110] Preferably, the chromium layer, more preferably the dark chromium layer, is part of a layer stack.

[0111] In step (d) of the method of the present invention the aqueous trivalent chromium electroplating bath obtained from step (c) is treated such that a treated aqueous trivalent chromium electroplating bath is resulting. The treatment includes steps

(d1) removing fully or partially said colloidal particles and/or said agglomerates thereof,
and optionally

(d2) adding colloidal particles.

[0112] In some cases, a method of the present invention is preferred, wherein said method comprises step (d1) and step (d2). In other words, step (d2) is not optional but indeed carried out.

[0113] Step (d) is the essential steps in the method of the present invention. The primary goal of step (d) is to alter the over-all content of the colloidal particles and agglomerates thereof (if agglomerates are formed) in order to slightly change the lightness value L1*.

[0114] Preferably, step (d1) is carried out to various extends; the removal is either fully or partly. The extent of removal depends on the desired effect on L1* (further details see examples below) in order to achieve the required adaptation in the lightness.

[0115] Thus, the method of the present invention is preferably a method for adjusting the brightness L*, preferably within a range for L* of ±10 units, preferably of ±7 units. This is most preferably referenced to L1*.

[0116] As shown in the examples below, by carrying out step (d), b*1 might change, too, although this is not necessarily always the case. Thus, preferred is a method of the present invention, wherein not only the brightness L1* is adjusted but additionally the color by adjusting b1*, most preferably within the ranges defined for b1* as defined above.

[0117] In step (d1) said colloidal particles and/or said agglomerates are removed. Preferred is a method of the present invention, wherein in step (d1) the removing is carried out by filtration, centrifugation, and/or sedimentation, most preferably filtration.

[0118] Most preferably, the removing comprises a mechanical removing, preferably sufficient to remove only particles, preferably colloidal particles.

[0119] Preferably, the filtration utilizes a filter membrane, preferably for mechanical filtration.

[0120] More preferably, the filtration utilizes a paper filter.

[0121] In some cases, a method of the present invention is preferred, wherein the filtration does not utilize activated coal. Although particles are typically removed with high efficiency, own experiments have shown that activated coal in many cases also binds (and therefore removes) organic compounds, which is primarily not desired.

[0122] By carrying out step (d1), typically the lightness is at least slightly increasing in a subsequent plating step (see examples).

[0123] In step (d2) of the method of the present invention, colloidal particles are added. Preferably, step (d2) is carried out to various extends; the addition may vary to the extent how much alteration in the lightness is desired/required (further details see examples below. Most importantly, step (d2) depends on the removal carried out in step (d1). For example, if in step (d1) too much of the colloidal particles and/or agglomerates was removed, such an undesired loss can be compensated in step (d2) and, thus, the desired lightness can be achieved. However, if by empirical observation the extent of removal carried out in step (d1) is clearly defined, there might be no need for carrying out step (d2).

[0124] In some cases, a method of the present invention is preferred, wherein the colloidal particles added in step (d2) are at least partly those removed in step (d1), for example carried out in one of previous steps (d1). In contrast, in other cases it is preferred that the added colloidal particles are new/fresh colloidal particles.

[0125] In some cases, a method of the present invention is preferred, wherein the colloidal particles added in step (d2) are of the same kind (e.g. same particle size, etc.) as those removed in step (d1), most preferably of same chemistry and same kind. In other words, the colloidal particles added in step (d2) correspond to the colloidal particles present in the aqueous trivalent chromium electroplating bath provided in step (b). However, it is not excluded that in some cases the kind and/or chemistry is preferably different from what was removed in step (d1) and, thus, present in the aqueous trivalent chromium electroplating bath provided in step (b).

[0126] Preferably, the colloidal particles added in step (d2) are added under mixing, preferably stirring and/or agitation.

[0127] As a result of steps (d1) and, optionally, (d2) a treated aqueous trivalent chromium electroplating bath is obtained.

[0128] In step (e) of the method of the present invention, another substrate is contacted with the treated aqueous trivalent chromium electroplating bath and an electrical current is applied such that a chromium layer is electrolytically deposited on the another substrate with a lightness value L2* according to the L*a*b* color-space system. Typically, the lightness obtained in step (e) will be different from the lightness obtained in step (c).

[0129] Preferably, the aforementioned regarding step (c) applies likewise to step (e). Most preferably, step (e) is, regarding the deposition parameters, a repetition of step (c).

[0130] Preferred is a method of the present invention, wherein L2* is higher than L1*. This is typically the result expected after step (d1) is carried out.

[0131] More preferred is a method of the present invention, wherein L2* is more than 55, preferably more than 53, more preferably more than 51, even more preferably more than 50, most preferably more than 49. In many cases, dark/black electrolytically deposited chromium layers typically have a lightness L* ranging from 49 or below to 55. Thus, it is very desirable to have means available allowing a fine-tuning of the lightness in order to adapt to the lightness of a chromium layer deposited from e.g. another trivalent chromium electroplating bath.

[0132] Preferred is a method of the present invention, wherein the electroplated chromium layer obtained in step (e) has an a2* value, preferably ranging from -1.5 to +3, preferably ranging from -1 to +2.5, most preferably ranging from -0.5 to +2. Preferably, the a2* value is at least positive.

[0133] Preferred is a method of the present invention, wherein the electroplated chromium layer obtained in step (e) has a value b2*, according to the L*a*b* color-space system. Preferably, b2* is lower than b1*, most preferably if L2* is higher than L1*.

[0134] 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:

[0135] For the following examples copper panels (100 mm x 70 mm) were used as a substrate, primarily for mimicking a plastic substrate with a copper layer thereon.

[0136] 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 vol.-% H_2SO_4 and subsequently rinsed with water.

[0137] 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; UniBrite 2002, product of Atotech).

(b) Providing the aqueous trivalent chromium electroplating bath

[0138] The following aqueous trivalent chromium 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 g/L	Methionine
2 g/L	Potassium Thiocyanate
3 ml/L	Aluminum oxide nanoparticle dispersion, 40%, D_{50}=25 nm (NANOBYK-3603, BYK-Chemie GmbH)
2 mmol/L	Fe(II) ions

[0139] The final pH value was 3.5.

(c) Contacting the substrate with said electroplating bath

[0140] 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. Agitation was achieved via air agitation.

[0141] As a result, a respective dark electroplated chromium layer was deposited on top of the nickel-plated copper panel. Afterwards, the substrate having the dark electroplated chromium layer was rinsed with water and the L*a*b* values, according to the L*a*b* color-space system, were determined (Konica Minolta CM-700 D spectrophotometer; CIE standard illuminator D65 and 10° standard observer). Calibration was done with black and white standard. Color determination was done at an area located 1 cm from the left edge and 2 cm from the lower edge (the left edge pointing to the anode), typically known as a high current density measuring point. Thus, L1* was obtained.

[0142] The values obtained are summarized below in Table 1.

(d) Filtering the aqueous trivalent chromium electroplating bath

[0143] The aqueous trivalent chromium electroplating bath utilized in step (c) was filtered twice with a Whatman filter (Grade 597) such that basically all nanoparticles were removed.

(e) Contacting another substrate with the filtered electroplating bath

[0144] Electroplating was repeated and carried out as described above for step (c) with another substrate but as defined in step (a) above.

[0145] Color determination was repeated as described above in step (c). Thus, L2* was obtained.

[0146] Subsequently, a new portion of nanoparticles (3 ml/L) was added to the aqueous trivalent chromium electroplating bath utilized in step (e) after plating was finished in order to obtain an aqueous trivalent chromium electroplating bath with fresh colloidal particles.

[0147] After that, steps (c) to (e) were repeated in a so called "second run" with yet another substrate.

Table 1: Summary of color values according to the L*a*b* color-space system

Method step	L*	a*	b*
(c)	48.2 (=L1*)	+1.0	+6.2
(e)	52.5 (=L2*)	+0.7	+4.8
"Second run"			
(c)	49.6 (=L1*)	+1.0	+6.2
(e)	53.4 (=L2*)	+0.7	+4.7

[0148] As shown in Table 1, the method of the present invention is suitable for adjusting the brightness L* of an electroplated chromium layer, in particular of a dark electroplated chromium layer.

[0149] The example described above includes a basically full removal of the colloidal particles and potential agglomerates thereof. Thus, the maximum and minimum values for L*, a*, and b* shown in Table 1 basically represent the overall possible shift for these values. However, upon partial removal, for example by filtering only a partial volume of the aqueous trivalent chromium electroplating bath, less drastic changes are obtained (data not shown).

[0150] This allows an adaptive adjustment of the brightness L* in order to meet a specific brightness. Such an adaptive adjustment is advantageous to harmonize brightnesses from different product batches or to harmonize a brightness of a first product with a brightness of a second product but providing a very similar overall brightness. This can be achieved by utilizing dedicated amounts of (iii) obtained by an individual removal thereof.

[0151] Table 1 furthermore shows that values for a* and b* can be nicely regained in the "second run".

[0152] On the one hand Table 1 shows that the brightness L* significantly increases upon removal of the colloidal nanoparticles. On the other hand, initial values can be basically regained if colloidal particles are again added. Thus, the method of the present invention provides a reversible adjustment.

[0153] This means, the method of the present invention allows use of an aqueous trivalent chromium electroplating bath with and without said colloidal particles such that different brightness values can be obtained. This is an advantage because different specific electroplating baths for individual brightnesses are no longer required. Instead, a single electroplating bath can be used for slightly different brightnesses.

Claims

1. A method for adjusting the brightness L* of an electroplated chromium layer, the method comprising the steps

(a) providing a 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 and/or agglomerates thereof, and
- (iv) one or more than one sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below,

(c) contacting the substrate with said electroplating bath and applying an electrical current such that a chromium layer is electrolytically deposited on the substrate with a lightness value L1* according to the L*a*b* color-space system,
(d) treating the aqueous trivalent chromium electroplating bath obtained from step (c) such that a treated aqueous trivalent chromium electroplating bath results, by

- (d1) removing fully or partially said colloidal particles and/or said agglomerates thereof,
- and optionally
- (d2) adding colloidal particles,

(e) contacting another substrate with the treated aqueous trivalent chromium electroplating bath and applying an electrical current such that a chromium layer is electrolytically deposited on the another substrate with a lightness value L2* according to the L*a*b* color-space system,
wherein L2* is higher or lower than L1*.

2. The method of claim 1, wherein the colloidal particles comprise one or more than one chemical element selected from the group consisting of silicon, aluminum, and carbon, preferably silicon and aluminum, most preferably the colloidal particles comprise the chemical element aluminum.

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 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.

5. The method of any one of the aforementioned claims, wherein the colloidal particles comprising the chemical element silicon, comprise silica, preferably are silica colloidal particles.

6. The method of any one of the aforementioned claims, wherein the colloidal particles comprising the chemical element aluminum, comprise aluminum oxide, preferably are aluminum oxide colloidal particles.

7. The method of any one of the aforementioned claims, wherein the colloidal particles comprising the chemical element carbon, comprise nanodiamonds, preferably are nanodiamond colloidal particles.

8. The method of any one of the aforementioned claims, wherein in step (b) or after step (d2) said colloidal particles are present in a total amount ranging from 0.05 g/L to 100 g/L, based on the total volume of the respective aqueous trivalent chromium electroplating bath, preferably from 0.1 g/L to 80 g/L, more preferably from 0.25 g/L to 60 g/L, even more preferably from 0.5 g/L to 45 g/L, most preferably from 0.75 g/L to 35 g/L, even most preferably from 1 g/L to 20 g/L.

9. The method of any one of the aforementioned claims, wherein (iv) comprises thiocyanate anions.

10. The method of any one of the aforementioned claims, wherein (iv) comprises at least a sulfur-containing compound having a sulfur atom with an oxidation number of +5 or below and additionally comprising a nitrogen atom, preferably additionally comprising an amino group, more preferably (iv) comprises at least an amino acid having a sulfur atom with an oxidation number of +5 or below, most preferably (iv) comprises at least methionine.

11. The method of any one of the aforementioned claims, wherein L1* is 55 or less, preferably 53 or less, more preferably 51 or less, even more preferably 50 or less, most preferably 49 or less.

12. The method of any one of the aforementioned claims, wherein said method comprises step (d1) and step (d2).

13. The method of any one of the aforementioned claims, wherein in step (d1) the removing is carried out by filtration, centrifugation, and/or sedimentation.

14. The method of any one of the aforementioned claims, wherein L2* is higher than L1*.

15. The method of any one of the aforementioned claims, wherein L2* is more than 55, preferably more than 53, more preferably more than 51, even more preferably more than 50, most preferably more than 49.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 17 8856

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
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