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(54) ELECTROPLATING BATH FOR DEPOSITING A BLACK ALLOY, METHOD FOR THE ELECTROCHEMICAL DEPOSITION OF A BLACK ALLOY ON A SUBSTRATE, A BLACK ALLOY AND AN ARTICLE COATED WITH SUCH BLACK ALLOY

(57) The present invention relates to an electroplating bath for depositing a black alloy, a method for the electrochemical deposition of a black alloy on a substrate, a black alloy and an article at least partly coated with the black alloy.

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Description

[0001] The present invention relates to an electroplating bath for depositing a black alloy, a method for the electrochemical deposition of a black alloy on a substrate, a black alloy and an article at least partly coated with the black alloy.

[0002] The black alloy according to the present invention contains at least gold, ruthenium and antimony and is preferably free of nickel. Iron and cobalt can optionally be also contained.

[0003] In the electrodeposition field of furniture, jewellery, fashion goods, differently coloured gold alloys are used in order to target many different colour coordinates, by changing alloy composition and electrolytes composition necessary to obtain such alloys. However, black coloured gold alloys are not common in gold electroplating and normally they are obtained by electroplating nickel together with gold and other metals.

Different black electrodeposited precious metals can be used instead of gold, such as black ruthenium, black rhodium, black platinum or black palladium, but their properties are not comparable to black gold alloys deposits. In particular due to the low electroplating efficiency of black ruthenium, rhodium and platinum it is impossible to obtain a uniform deposition in many applications, especially with barrel electroplating. Furthermore, black gold alloys are preferred with respect for example to black palladium layer because of the more yellowish aspect of the black gold deposit and for the fact that being softer, it is possible to use black gold alloys deposit for special vintage vibro-finishing.

[0004] Gold alloy electroplating is a common topic in literature, as it has been always the base for obtaining different gold colour deposits.

[0005] JP S63-250487 A describes a plating solution obtained by adding 4 to 450 g/L alkali hydroxide as a blackening agent to an Au-Ni alloy plating solution to adjust the pH to 3 to 6. The use of Nickel is nowadays restricted due to allergenic properties of this alloying metal.

[0006] JP 2015-157966 A discloses a black-tone gold alloy plating film consisting of a gold/palladium alloy deposited on a cathode substrate by an electrolytic reduction of a plating solution containing a sulphurous acid gold salt and dinitrodiammine palladium under specified conditions and a black thin film which is formed on the outermost layer of the gold/palladium alloy at the rate-determining stage of the reduction reaction and contains palladium nitrosyl. However, the use of palladium drastically increases the price of the final alloy.

[0007] TW201319328 A1 refers to a gold plating solution containing a gold cyanide salt, an inorganic acid salt, and a carboxylate group, and is characterized in that either antimony or antimonid is added to the solution. It is preferable that the antimony concentration is 10 to 100 mg/L in terms of a metal.

[0008] CN 101255509 A relates to a production process of colour gold jewellery, comprising the following steps: cleaning the gold jewellery with ultrasonic to remove the grease on the surface; washing the detergent on the gold jewellery with water, and removing grease by electrochemical method; water washing; acid washing with sulphuric acid; plating germanium on the surface of the gold jewellery; water washing the plated gold jewellery to wash away plating solution; locally coating insulating paint on the gold jewellery according to the needed pattern; removing grease attached during the coating process by electrolysis; plating gold or gold-copper alloy on the gold jewellery by electrolysis; dropping off the insulating paint; and water washing and drying. By plating black nails, gold or gold-copper alloy outside the colour gold jewellery, multicolour gold jewellery having black, yellow and red or white and the above three colours alternating pattern is formed, which changes the tradition that gold jewellery is only silvery white, in addition, since the plating layer is composed of nail or noble metal, the value of gold jewellery is remained.

[0009] EP 2 781 629 A1 refers to a solution for the electrodeposition of a gold alloy and the alloy derived therefrom having defined colour coordinates in the range of L: 65 to 75, a: 6 to 9 and b: 10 to 20. The solution comprises a gold salt, an iron salt and a vanadium salt, and optionally one or more salts of other metals selected from cobalt, palladium, ruthenium, for modulating the end colour shades; and optionally small amounts of tellurium, gallium or bismuth salts as sparkling aids and grain refiners.

[0010] US 4,199,417 relates to an aqueous alkaline bath composition for electroplating a black metallic co-deposit on ferrous and non-ferrous substrates comprised of an antimony-containing compound; a copper nickel or zinc compound, and a strong base. However, all the described electrodeposited alloys refer to non-precious metal deposits, not suitable for the jewellery and fashion good application due to poor corrosion resistance.

[0011] KR 2001-0008252 relates to an Au alloy and a method for coloring lustrous black color. These are provided not only to create variegated designs but also to produce high value-added ornaments by adding black color to an Au alloy which is originally in five colors of red, yellow, grass green, white, and purple colors. 5 to 65 wt% of one metal selected from the group consisting of Au, Cu, Fe, Co, and Ti is contained in an Au alloy. The Au alloy is heat-treated in the oxidation state that is in an atmospheric pressure, higher or lower than an oxygen partial pressure at a temperature of melting point of an Au alloy or less. The heat treated Au alloy is cooled in air, water or oil so that all or part of surface region of Au alloy processed goods is colored with glossy black color. JP-H4-193924 A relates to a method to color the surface layer part of an undermentioned worked product into bright grayish black or black by forming a gold alloy, where specific additive quantities of Cu, Fe, Co, etc., are added to Au, into a worked product and subjecting this worked product to heating at a temperature not higher than the melting point and to cooling. One or more kinds among 3 to 40 %, by weight, Cu, 3 to 40 % Fe, 3 to 40 % Co, 1 to 10 % Ti, 0.5 to 15 % Sn, 0.2 to 10 % V, 0.2 to 10 % Mn, 1 to 10 % Cr, 0.2 to 5% W, 0.2 to 5% Mo, 0.2 to 5% Nb, 0.2 to 15% Hf, 0.2 to 15% Ta, 0.2 to 15% Zr, 0.2 to 15% Y, 0.2 to 15% Re, 0.2 to 15% Ge, 0.5 to 10% Zn, and 0.2 to 10% rare earth metal are added to pure Au or a gold alloy having a composition in which platinum group elements, Ag, Ni, etc., are added and which has Au content of ≥ 38 %; A semiworked product or perfect worked product of this gold alloy is heated at a temperature not higher than its melting point in the air, etc., and cooled. By this method, the whole or a part of the surface layer part of the gold worked product can be colored into bright grayish black or black.

[0012] JP-H3-100158 A refers to a method to color an Au alloy containing specific ratios of Ag, Ni, platinum group elements, Cu, Fe, Co, and Ti to black having brightness by subjecting the above- mentioned alloy to a heating treatment at the temperature below the melting point of the alloy, then cooling the alloy. One or more kinds of the platinum group elements (Pt, Pd, Rh, Ir, Ru, and Os) are incorporated into pure Au, Au-Ag alloy, Au-Ni alloy or Au-Ag-Ni alloy containing ≥38 wt.-% Au and ≥1 kinds of Cu, Fe, Co, and Ti are added at 3 to 35 % thereto. The total content of the elements exclusive of the Au are required not to exceed 65 %. This Au alloy is subjected to the heating treatment at the temperature below the melting point of the alloy in the atmosphere or in an oxidation atmosphere higher or lower than the oxygen partial pressure of the atmosphere. The alloy is thereafter cooled with air, water or oil is thereby blackened in the whole or part of the surface layer of the alloy. This method does not require special raw materials and treating devices.

[0013] FR 2 353 656 A1 relates to an additive mixture for Au(alloy) electroplating bath contains organic water-soluble nitro compound(s). (I) of the formula $R(NO_2)$ n (where n = 1-4; R is a 1 to 15C alkyl, aryl or heterocyclic group, optionally substituted by a group containing C,H,O,N, and/or S) and water-soluble As, Sb, Bi, Tl or Se compound(s). (II). The addition of Tl-sulphate and Sodiumtrinitrobenzenesulphonate to an acid Au cyanide bath gave homogeneous fine-grained pure Au plating of silky lustre and allowed high power operation (up to 2.5 A/dm^2 instead of under 0.5 A/dm^2 without the additives). Used especially in acid, neutral or alkaline Au cyanide or sulphite baths.

[0014] Starting herefrom, one object of the present invention is to overcome the disadvantages of the alloys known from the prior art and the provision of an electroplating bath allowing to deposit an alloy with increased darkness and hardness, allowing to adapt the darkness and to obtain alloy layers for decorative purposes, having a variety of darkness levels, being corrosion resistant, abrasion resistant, non-allergenic and that can be applied by various methods like barrel and rack application and that can be used as final uniform black layer or for vintage vibro-finishing.

[0015] This object is achieved by the electroplating bath for depositing a black alloy according to claim 1 which comprises the following ingredients or consists of these ingredients.

a) at least one source of gold ions;

b) at least one source of ruthenium ions; and

c) at least one source of antimony ions as darkening agent.

[0016] The dependent patent claims 2 to 9 relate to advantageous embodiments of the electroplating bath according to the invention.

[0017] In addition, a method for depositing a black alloy on a substrate is provided according to patent claim 9. The dependent claims 10 and 11 relate to preferred embodiments of the method according to the invention.

[0018] Furthermore, patent claim 12 relates to a black gold alloy and the dependent claims 13 to 16 relate to preferred embodiments of this black gold alloy.

[0019] In addition, claim 17 relates to an article at least partly coated with the black gold alloy.

Quantity data

[0020] The black alloys according to the present invention comprise components (A) to (C) and optionally (D) and (E), the proviso applies thereby that components (A) to (E) add up in total to 100 % by weight. The set ranges of the quantity data for the individual components (A) to (E) should be understood such that, within the prescribed ranges, an arbitrary quantity can be selected for each of the individual components, provided the strict proviso is fulfilled that the sum of all the components (A) to (E) produces 100 % by weight.

[0021] The deposit formed from an electroplating bath according to the present invention may also comprise compounds formed from non-metallic ingredients contained in the bath, e.g. sulphur compounds. Preferably the deposit comprises not more than 5 wt.-% compounds formed from non-metallic ingredients.

[0022] The electroplating bath according to the present invention comprises at least one specific compound for the components a) to c) and optionally d) to h) in a specific concentration. In case that more than one specific compound for a component is present in the electroplating bath, the range for the specific concentration has to be met by the sum of these specific compounds.

[0023] For the purpose of the present the composition of the black alloy may be determined by electron microscope analysis, preferably with an energy dispersive X-ray spectroscopy detector (SEM-EDX, SEM: Leo 1430 VP, EDX: Bruker Quantax 200). Furthermore the concentration of components a) to h) in an electroplating bath may be determined by atomic absorbtion spectroscopy, preferably on a Agilent 55AA (from Agilent technologies) by applying standards for calibration of each element as available from Merck.

Black alloy

[0024] A black alloy in the gist of the present invention is an alloy having a L value in CIE Lab colour coordinates below 50, preferably below 45 and more preferably in the range from 38 to 45, whereby the L-value may be determined according to UNI EN ISO 8654:2018 on a Minolta CM-503i spectrophotometer.

Substantially free of nickel

[0025] The electroplating bath according to the present invention is substantially free of nickel sources. According to the present invention substantially free of nickel sources means that nickel sources are contained in a concentration below 20 mg/L, preferably below 10 mg/L and more preferably below 5 mg/L.

[0026] Most preferably the electroplating bath is totally free of nickel sources.

[0027] Where the term "comprising" is used in the present description and claims, it does not exclude other elements. For the purposes of the present invention, the term "consisting of" is considered to be a preferred embodiment of the term "comprising of". If hereinafter a group is defined to comprise at least a certain number of embodiments, this is also to be understood to disclose a group, which preferably consists only of these embodiments.

Electroplating bath

[0028] According to one preferred embodiment of the present invention the electroplating bath additionally comprises ingredients selected from the group consisting of d) a source of iron ions, e) a source of cobalt ions, f) sulphur compounds, g) condutive salts, h) complexing agents and mixtures thereof.

[0029] In another preferred embodiment of the present invention the electroplating bath comprises:

a) 0,3 to 5 g/L, preferably 0,3 to 1 g/L, more preferably 0,3 to 0,7 g/L and most preferably 0,4 to 0,6 g/L gold ions and/or

b) 0,1 to 10 g/L, preferably 0,1 to 2 g/L, more preferably 0,2 to 1 g/L and most preferably 0,3 to 0,5 g/L ruthenium ions and/or

c) 0,25 to 10 g/L, preferably 0,25 to 2 g/L, more preferably 0,3 to 1 g/L and most preferably 0,3 to 0,6 g/L antimony ions.

[0030] According to another preferred embodiment of the present invention the electroplating bath further comprises:

d) at least one source of iron ions, preferably from 0 to 0,4 g/L, more preferably 0,15 to 0,25 g/L and most preferably 0,2 to 0,25 g/L and/or

e) at least one source of cobalt ions, preferably from 0 to 0,27 g/L, more preferably 0,05 to 0,25 g/L and most preferably 0,1 to 0,25 g/L and/or

f) at least one sulphur compound, preferably from 0,05 to 30 g/L, more preferably 0,1 to 20 g/L and most preferably 0,1 to 15 g/L and/or

g) at least one conductive salt, preferably from 70 to 120 g/L, more preferably 80 to 90 g/L and most preferably 90 g/L and/or

h) at least one complexing agent, preferably from 50 to 150 g/L, more preferably 80 to 120 g/L and most preferably 100 g/L

[0031] According to one preferred embodiment of the present invention the at least one source of gold ions a) is selected from the group consisting of gold potassium cyanide complexes, preferably gold(III) potassium cyanide, gold(I) potassium cyanide, gold(III)chloride, sodium gold(I) sulphite, ammonium gold(I) sulphite and mixtures thereof and more preferably is gold(III) potassium cyanide.

[0032] A further preferred embodiment of the present invention provides that the at least one source of ruthenium ions b) is a ruthenium(III) complex, preferably selected from the group consisting of ruthenium sulfamate, ruthenium oxalate, ruthenium gluconate, ruthenium chloride, ruthenium sulphate, ruthenium ammonium sulfamate, ruthenium potassium oxalate, ruthenium sodium gluconate and mixtures thereof and more preferably is a mixed complex with ruthenium ammonium sulfamate and potassium oxalate, or ruthenium ammonium sulfamate and sodium gluconate.

[0033] According to another preferred embodiment of the present invention the at least one source of antimony ions c) is an antimony(III)-compound, preferably selected from the group consisting of antimony trioxide, antimony(III) chloride, antimony(III) acetate, antimony(III) sulphate and mixtures thereof or an antimony(V)-compound preferably selected from the group consisting of antimony(v) chloride, antimony(V) oxide and mixtures thereof, wherein antimony(III) compounds are preferred and most preferred is antimony trioxide in a media having a pH-value > 10 and/or antimony(III) chloride in a media having a pH-value > 10.

[0034] A further preferred embodiment of the present invention provides that the at least one source of iron ions d) is an iron(III)-salt and preferably is selected from the group consisting of iron(III) sulphate, iron(III) chloride, iron(III) citrate, iron(III) nitrate, iron(III) pyrophosphate, iron(III) oxalate, iron(III) acetate, iron(III) ammonium citrate, iron(III) ammonium sulphate and mixtures thereof and preferably is iron(III) sulphate or iron(III) citrate.

[0035] According to another preferred embodiment of the present invention the at least one source of cobalt ions e) is selected from the group consisting of cobalt(II) sulphate, cobalt(II) acetate, cobalt(II) oxalate, cobalt(II) chloride, cobalt(II) bromide, ammonium cobalt(II) sulphate, cobalt(II) thiocyanate, cobalt(II) phosphate and mixtures thereof and preferably is cobalt(II) acetate.

[0036] A further preferred embodiment of the present invention provides that the at least one sulphur compound f) is selected from the group consisting of ammonium thiocyanate, thiourea, thiourea derivatives, preferably N,N'-diethylthiourea, 1,2-methoxyphenyl-2-thiourea, 4-nitrophenyl-2-thiourea, heterocyclic compounds containing sulphur, preferably thiohydantoin, imidazolidinethione, 2-mercaptothiazoline, mercaptobenzothiazole, diammonium dithioglycolate, disodium 2,5-dimercapto-1,3,4-thiadizole, sulphur compounds of the general formula R^1-S-R^2 wherein R^1 and R^2 are each independently alkyl or aryl residues with 1 to 6 carbon atoms and more preferably is ammonium thiocyanate.

[0037] According to a further preferred embodiment of the present invention the at least one conductive salt g) is selected from the group consisting of potassium sulphate, sodium sulphate, ammonium sulphate, ammonium sulfamate, potassium oxalate and mixtures thereof and preferably is potassium citrate.

[0038] Another preferred embodiment of the present invention provides that the at least one complexing agent h) is selected from the group consisting of sodium gluconate, potassium acetate, potassium citrate, ammonium citrate, sodium potassium tartrate, sodium or potassium malate and mixtures thereof and preferably is sodium gluconate.

[0039] Another preferred embodiment of the present invention provides that the electroplating bath consists of compounds a), b), c), f), g) and h) and the concentration of these compounds is preferably as follows:

a) 0,4 to 0,6 g/L (as Au(III) ions);
b) 0,2 to 0,5 g/L (as Ru(III) ions);
c) 0,3 to 0,6 g/L (as Sb(III) or Sb(V) ions);
f) 10 to 20 g/L;
g) 80 to 100 g/L; and
h) 90 to 110 g/L.

[0040] Another preferred embodiment of the present invention provides that the electroplating bath consists of compounds a), b), c), d), f), g) and h) and the concentration of these compounds is preferably as follows:

a) 0,4 to 0,6 g/L (as Au(III) ions);
b) 0,2 to 0,5 g/L (as Ru(III) ions);
c) 0,3 to 0,6 g/L (as Sb(III) or Sb(V) ions);
d) 0,2 to 0,4 g/L (as Fe(III) ions);
f) 10 to 20 g/L;
g) 80 to 100 g/L; and
h) 90 to 110 g/L.

[0041] Another preferred embodiment of the present invention provides that the electroplating bath consists of compounds a), b), c), e), f), g) and h) and the concentration of these compounds is preferably as follows:

a) 0,4 to 0,6 g/L (as Au(III) ions);
b) 0,2 to 0,5 g/L (as Ru(III) ions);
c) 0,3 to 0,6 g/L (as Sb(III) or Sb(V) ions);

e) 0,05 to 0,15 g/L; (as Co(II) ions)
f) 10 to 20 g/L;
g) 80 to 100 g/L; and
h) 90 to 110 g/L.

[0042] Another preferred embodiment of the present invention provides that the electroplating bath has a pH-value in the range from 6 to 10, preferably from 6,5 to 8,5, more preferably from 7 to 8 and most preferably from 7,5 to 8.

[0043] According to a further preferred embodiment of the present invention the black alloy has a L-value in the range from 35 to 50, preferably from 35 to 45 and more preferably from 38 to 45.

[0044] A further preferred embodiment of the present invention provides that the black alloy has a a-value in the range from 0 to 3, preferably from 0 to 2,5 and more preferably from 1 to 2.

[0045] According to another preferred embodiment of the present invention the black alloy has a b-value in the range from 5 to 10, preferably from 5 to 8 and more preferably from 5 to 6,5.

[0046] A further preferred embodiment of the present invention provides that the L-value of the black alloy is in the range from 38 to 45, the a-value is in the range from 1 to 2 and the b-value is in the range from 5 to 6,5.

[0047] Another preferred embodiment of the present invention provides that the electroplating bath has a temperature in the range from 30 to 50°C, preferably from 35 to 40°C and more preferably of 35°C.

[0048] According to a further preferred embodiment of the present invention the electroplating bath comprises 80 to 100 g/L potassium citrate, 90 to 110 g/L sodium gluconate, 0,45 to 0,55 g/L Au(III) ions as gold(III) potassium cyanide salt, 0,35 to 45 g/L Ru(III) ions as ruthenium oxalate complex, 10 to 20 g/L ammonium thiocyanate and 0,4 to 0,6 g/L Sb(III) as antimony(III) oxide pre-complexed with potassium hydroxide.

According to another preferred embodiment of the present invention the electroplating bath comprises 80 to 100 g/L potassium citrate, 90 to 110 g/L sodium gluconate, 0,45 to 0,55 g/L Au(III) as gold(III) potassium cyanide salt, 0,25 to 0,35 g/L Ru(III) as ruthenium oxalate complex, 0,2 to 0,3 g/L Fe(III) as iron(III) sulphate, 10 to 20 g/L ammonium thiocyanate and 0,3 to 0,5 g/L Sb(III) as antimony(III) oxide pre-complexed with potassium hydroxide.

[0049] Another preferred embodiment of the present invention provides that the electroplating bath comprises 80 to 100 g/L potassium citrate, 90 to 110 g/L sodium gluconate, 0,45 to 0,55 g/L Au(III) as gold(III) potassium cyanide salt, 0,3 to 0,4 g/L Ru(III) as ruthenium oxalate complex, 0,05 to 0,15 g/L Co(II) as cobalt(II) acetate, 10 to 20 g/L ammonium thiocyanate and 0,4 to 0,6 g/L Sb(III) as antimony(III) oxide pre-complexed with potassium hydroxide.

Method for the electrochemical deposition of a black alloy

[0050] The inventive method for the electrochemical deposition of a black alloy on a substrate comprises the following steps:

(i) providing a substrate;

(ii) providing an electroplating bath as defined above;

(iii) contacting the substrate and the electroplating bath;

(iv) contacting at least a part of an anode with the electroplating bath;

(v) applying a voltage across the substrate and the anode; and

(vi) electroplating a black alloy deposit on the substrate.

[0051] In the method according to the present invention the substrate may act as cathode.

[0052] According to a preferred embodiment of the method according to the present invention step (iv) is carried out at a current density from 0,5 to 5 A/dm^2, preferably from 1 to 4 A/dm^2 and more preferably from 1 to 3 A/dm^2.

[0053] Another preferred embodiment of the present invention provides that step (iv) and preferably subsequent steps are carried out at a temperature of the electroplating bath from 30°C to 50°C, preferably from 35 to 40°C and more preferably of 35°C.

[0054] According to another preferred embodiment of the method according to the present invention the substrate is selected from the group consisting of bronze, brass, Zamack, alpacca, copper alloy, tin alloy, steel and mixtures thereof, and preferably further electroplated with copper, preferably in a thickness of 10 to 30 μm, white bronze, preferably in a thickness of 2 to 3 μm, and then palladium in a thickness of 0,5 to 1,0 μm and/or gold in a thickness of 0,2 to 0,3 μm.

Black alloy

[0055] The black alloy according to the present invention comprises the following compounds or consists of these compounds:

(A): 45 to 95 weight-% gold;

(B): 4 to 30 weight-% antimony;

(C): 1 to 15 weight-% ruthenium;

(D) 0 to 5 weight-% iron; and

(E) 0 to 5 weight-% cobalt;

wherein compounds (A) to () add up to 100 weight-%.

[0056] It is preferred that the black alloy according to the present invention can comprise up to 5 weight-% sulphur, preferably 0,1 to 5 weight-%, more preferably 0,5 to 2 weight-% and most preferably 1 to 1,5 weight-% sulphur.

[0057] According to a preferred embodiment of the present invention the black alloy comprises the following compounds:

(A): 55 to 87 weight-%, preferably 60 to 83 weight-% gold;
(B): 10 to 20 weight-%, preferably 10 to 18 weight-% antimony;
(C): 3 to 15 weight-%, preferably 5 to 15 weight-% ruthenium;
(D) 0 to 5 weight-%, preferably 1 to 3 weight-% iron; and
(E) 0 to 5 weight-%, preferably 1 to 4 weight-% cobalt;

wherein compounds (A) to (E) add up to 100 weight-%.

[0058] According to another preferred embodiment of the present invention the black alloy comprises or consists of the following compounds:

(A): 60 to 86 weight-%, preferably 73,5 to 84,5 weight-% gold;
(B): 10 to 20 weight-%, preferably 10 to 18 weight-% antimony;
(C): 3 to 15 weight-%, preferably 3 to 5 weight-% ruthenium;
(D) 1 to 5 weight-%, preferably 2,5 to 3,5 weight-% iron; and

wherein compounds (A) to (D) add up to 100 weight-%.

[0059] According to a further preferred embodiment of the present invention the black alloy comprises the following compounds or consists of the following compounds:

(A): 60 to 84 weight-%, preferably 66,5 to 75,5 weight-% gold;
(B): 12 to 20 weight-%, preferably 15 to 19 weight-% antimony;
(C): 2 to 15 weight-%, preferably 6 to 10 weight-% ruthenium;
(E) 2 to 5 weight-%, preferably 3,5 to 4,5 weight-% cobalt;

wherein compounds (A) to (C) and (E) add up to 100 weight-%.

[0060] Another preferred embodiment of the present invention provides that the black alloy has a L-value in the range from 35 to 50, preferably from 35 to 45 and more preferably from 38 to 45.

[0061] According to another preferred embodiment of the present invention the black alloy has a a-value in the range from 0 to 3, preferably from 0 to 2.5 and more preferably from 1 to 2.

[0062] A further preferred embodiment of the present invention provides that the black alloy has a b-value in the range from 5 to 10, preferably from 5 to 8 and more preferably from 5 to 6,5.

[0063] According to another preferred embodiment of the present invention the black alloy has an antimony release determined according to UNI EN 16711-2;2015 that is below 30 mg antimony per kg alloy, preferably below 25 mg antimony per kg alloy and more preferably below 20 mg antimony per kg alloy.

[0064] The black alloy according to the present invention is most preferably manufactured by the method as described above and in claims 8 to 10.

Article

[0065] The invention further relates to an article at least partially coated with the black alloy as described above and according to one of claims 11 to 14.

[0066] According to a preferred embodiment of the present invention the article is selected from a field selected from the group consisting of jewellery, luxury goods, fashion, leather goods, watch industry and spectacle frames.

Use

[0067] The present invention further relates to the use of the electroplating bath according to the present invention for electrodepositing a black alloy.

[0068] Another aspect of the present invention refers to the use of the black alloy according to the invention in the field selected from the group consisting of jewellery, luxury goods, fashion, leather goods, watch industry and spectacle frames.

[0069] The subject according to the invention is intended to be explained in more detail with reference to the subsequent examples without wishing to restrict said subject to the specific embodiments shown here.

1 Measuring methods

[0070] Within the scope of this application, the following measuring methods have been used.

Color coordinates

[0071] Color coordinates have been determined according to UNI EN ISO 8654:2018 on a Minolta CM-503i spectrophotometer. As illuminant daylight D65 (6500K) with an included reflective component (sci) has been used. The observer was set at standard (10°) and the measurements have been done in the color space CIE L*a*b*. The instrument has been calibrated before the measurement with a black (L = 0) and with a white (L = 100) standard.

Antimony Release

[0072] The extraction tests have been performed according to UNI EN 16711-2:2015 and the amount of released antimony has been determined by ICP-MS.

Alloy composition

[0073] The composition of the alloy has been determined by electron microscope analysis with an energy dispersive X-ray spectroscopy detector (SEM-EDX, SEM: Leo 1430 VP, EDX: Bruker Quantax 200)

Thickness of the deposit

[0074] The thickness of the deposit has been determined by X-ray fluorescence on a Fischerscope X-Ray XAN 222 from Helmut Fischer applying a gold foil from Oxford as standard for the calibration.

Corrosion Resistance

[0075] The corrosion resistance has been tested according to the following standards.

Synthetic Sweat 24 h (NFS 80-772)

[0076] The performance of a sample placed in a steam room at 55°C ± 5°C in contact for 24 hours with a synthetic sweat solution, in order to simulate the performance of the deposit when it is in contact with human sweat, has been observed. Artificial sweat is a solution composed of lactic acid (5 %), sodium chloride (10 %) and demineralized water (85 %).

Climatic Chamber 96 h (UNI EN ISO 4611)

[0077] In this test the sample has been placed in a chamber with controlled temperature and relative humidity, for a fixed time (96 hours). It has been checked if some change in colour occurs and/or formation of stains and/or oxidation spots is observed. A temperature of 40°C and 93% of relative humidity were used as defined in UNI EN ISO 4611. The climatic chamber machine that has been used is model MKF 115 from Binder.

Climatic Chamber in contact with Leather 96 h

[0078] This test has been performed as the UN EN ISO 4611 test for 96 hours, with the only difference that the sample has been placed in contact with leather in the same temperature and relative humidity controlled chamber, preventively sealed in a glass desiccator, to avoid dispersion of the chemicals released by the leather into the climatic chamber machine. The aim is to check the oxidation resistance of the sample to the chemicals released by the leather. The climatic chamber machine that has been used is model MKF 115 from Binder. Corrosion resistance of the part has been checked on the face that was in contact with leather. Typical corrosion signs are dark spots, oxidation regions and change in colour.

Sulphurous anhydride SO_2 8h

[0079] The aim of this test is to check the resistance of the sample to a strongly oxidant sulphurous anhydride containing atmosphere, to simulate for example the air pollution in a city. Sulphurous anhydride has been generated by reaction of sodium thiosulphate with sulphuric acid in a sealed chamber with specific inner volume in relation to the sample surface. The test has been conducted for 8 hours at 30°C.

[0080] For the synthetic sweat 24 h (NFS 80-772) test, the climatic chamber 96 h (UNI EN ISO 4611), the climatic chamber in contact with leather 96 h test and the sulphurous anhydride SO_2 8h test the following rating has been used.

0: POSITIVE, No sign of alteration and/or color change, test PASSED;
1: LIMIT, some minor sign of alteration and/or local color change;
2: NEGATIVE, extensive oxidation, dark spot, change in color on almost the total surface of the tested parts, test NOT PASSED.

Abrasion test

[0081] The abrasion test has been conducted according to UNI EN ISO 23160 "Watch cases and accessories -- Tests of the resistance to wear, scratching and impacts". The abrasion test has been conducted on a machine called TURBULA form the WAB Group by placing the parts in the presence of ceramic abrading material (spherical or cylindrical chips from Rosier, dimensions according to UNI EN ISO 23160), inside the rotating and vibrating machine (rotation speed 72 rpm).

2 Starting materials

[0082] The materials used in the electroplating baths according the examples are compiled in table 1.

Components	Provider/Manufacturer
Potassium Citrate CAS: 866-84-2	Provider: Toscochimica Manufacturer: Lianyungang Shuren Kechuang Food Additive Co Ltd - MADE IN CHINA
Sodium Gluconate CAS: 527-07-1	Provider: Toscochimica Manufacturer: ROQUETTE - MADE IN ITALY
Gold(III) potassium cyanide salt (58 % gold) CAS: 14263-59-3	Metalor
Ruthenium trichloride complex CAS: 14898-67-0 (x-hydrate)	Safimet
Ammonium thiocyanate CAS: 1762-95-4	Sigma Aldrich
Antimony(III) oxide CAS: 1309-64-4	Sigma Aldrich

(continued)

Components	Provider/Manufacturer
Sulphuric acid (5 %) CAS: 7664-93-9	Sigma Aldrich
Potassium hydroxide CAS: 1310-58-3	Brenntag
Iron(III) sulphate CAS: 10028-22-5	Sigma Aldrich
Cobalt(II) acetate CAS: 71-48-7 (anhydrous) 6147-53-1 (tetra-hydrate)	Brenntag

[0083] As substrates brass panels (5.0 X 3.5 cm x 0.3 cm thickness) from Ossian have been used on which the following layers in the order given below have been plated.

Acidic copper (10 to 30 µm)

[0084] Acidic Copper is a commercial product from Coventya named CUBRAC 440. The solution is composed of:

Copper Sulphate:	220 g/L
Sulphuric Acid:	65g/L
Chloride content:	100 ppm
Cubrac 440 base:	8 mL/L
Cubrac 440 leveller:	0.2 mL/L
Cubrac 440 brightener:	0.4 mL/L

White bronze (approximately 2 µm)

[0085] Also white bronze is a commercial product from Coventya, named Auralloy 450 LF, it is a Cu-Sn-Zn, lead-free alloy plated from a cyanide based plating solution. The composition of the ternary alloy is in the follwoging range (wt.-%):

Cu:	51-55%
Sn:	28-31%
Zn:	14-19%.

[0086] The solution is composed of the following commercial products:

AURALLOY 450 LF PAE	
AURALLOY 450 LF BRIGHTENER:	3 to5 mL/L
AURALLOY 450 LF SURFACT:	1,5 to 3 mL/L

Gold (0,2 to 0,3 µm) or palladium (approximately 0,5 to 1,0 µm)

[0087] The gold underlayer has been prepared from a generic acidic gold bath. The Coventya reference for this acidic Gold underlayer is Aurane 793.

[0088] The palladium underlayer has been prepared from a generic alkaline ammonia based Palladium alloy bath. The Coventya reference for this process is Decomet 460 NF.

[0089] Examples 1 to 3 have been conducted twice, one trial has been carried out with a substrate having a gold layer and another trial has been conducted using a substrate having a palladium layer.

[0090] The palladium layer has been used to avoid the interference of gold during the detection of the content of gold in the black alloy deposited on the substrate.

3 Examples

Example 1 (inventive)

[0091] For Working Example 1 the following electroplating bath has been prepared.

90 g/L	Potassium citrate
100 g/L	Sodium gluconate
0,50 g/L	Au (III) as Gold(III) potassium cyanide salt
0,40 g/L	Ru(III) as Ruthenium oxalate complex
15 g/L	Ammonium thiocyanate
0,5 g/L	Sb (III) as Antimony(III) oxide pre-complexed with potassium hydroxide (the final solution has an antimony concentration of 80 g/L as Sb metal, and a potassium hydroxide concentration of 250 g/L, completed with demineralized water up to 1 L of final volume)

[0092] The pH-value of the electroplating bath has been adjusted to 7,5 using sulphuric acid (5 %).

[0093] Electroplating from the bath described above has been carried out on the substrate described in chapter 2 above, using the following conditions.

[0094] pH: 7,5
Temperature of the electroplating bath: 35°C
Current density: 3 A/dm^2
Plating time: 3 minutes

[0095] A fully uniform black deposit has been obtained, the black deposit had the following color coordinates.

[0096] L: 46
a: 2
b: 6,5

[0097] The composition of the alloy given below has been determined by electron microscope analysis with energy dispersive X-ray spectroscopy detector.

[0098] Au: 69 wt.-%
Sb: 17,5 wt.-%
Ru: 11,5 wt.-%
S: 2 wt.-%

[0099] Moreover, the substrate coated with the black alloy passed the following corrosion tests as described in detail in chapter 1 above.

[0100] Synthetic Sweat 24h (NFS 80-772).
Climatic Chamber 96h (UNI EN ISO 4611).
Climatic Chamber in contact with Leather 96h.
Sulphurus anhydride SO$_2$ 8h.

[0101] All tests have been passed with the rating 0.

[0102] The abrasion test as described in chapter 1 above has been conducted and it took approximately 20 minutes to remove the Au-Ru-Sb deposit completely. Hence, the substrate coated with the black alloy shows a good abrasion resistance and a vintage vibro-finishing could be obtained.

Example 2 (inventive)

[0103] For Working Example 2 the following electroplating bath has been prepared.

90 g/L	Potassium citrate
100 g/L	Sodium gluconate
0,50 g/L	Au (III) as Gold(III) potassium cyanide salt
0,30 g/L	Ru(III) as Ruthenium oxalate complex
0,25 g/L	Iron(III) sulphate
15 g/L	Ammonium thiocyanate
0,40 g/L	Sb(III) as Antimony(III) oxide pre-complexed with potassium hydroxide (the final solution has an antimony concentration of 80 g/L as Sb metal, and a potassium hydroxide concentration of 250 g/L, completed with demineralized water up to 1 L of final volume)

[0104] The pH-value of the electroplating bath has been adjusted to 7,5 with sulphuric acid (5 %).

[0105] Electroplating from the bath described above has been carried out on the substrate described in chapter 2 above, using the following conditions.

[0106] pH: 7,5
Temperature of the electroplating bath: 35°C
Current density: 3 A/dm^2
Plating time: 3 minutes

[0107] A fully uniform black deposit has been obtained, the black deposit had the following color coordinates.

[0108] L: 38
a: 1,7
b: 5,5

[0109] The presence of iron further reduces the L-value of the deposit.

[0110] The composition of the alloy given below has been determined by electron microscope analysis with energy dispersive X-ray spectroscopy detector.

[0111] Au: 78 wt.-%
Sb: 13,5 wt.-%
Ru: 3,5 wt.-%
Fe: wt.-3 %
S: 2 wt.-%

[0112] Moreover, the substrate coated with the black alloy passed the following corrosion test as described in detail in chapter 1 above.

[0113] Synthetic Sweat 24h (NFS 80-772).
Climatic Chamber 96h (UNI EN ISO 4611).
Climatic Chamber in contact with Leather 96h.
Sulphurus anhydride SO_2 8h.

[0114] All tests have been passed with the rating 0.

[0115] The abrasion test as described in chapter 1 above has been conducted and it took approximately 15 minutes to remove the Au-Ru-Sb-Fe deposit completely. Hence, the deposit is softer than the deposit according to Example 1 and a vintage vibro-finishing could be obtained.

[0116] Additionally, the substrate coated with the black alloy shows a good abrasion resistance and a vintage vibro-finishing could be obtained.

[0117] Moreover, an antimony release test has been carried out with the alloy obtained from the bath according to Working Example 2. The results are summarized below.

Application	Application time [minutes]	Total thickness of the alloy [micrometers]	Antimony release [mg/kg]
Rack application	3	0,1	< 1,00
Barrel application	10	0,1	23
Barrel application + vibro-finishing	10	0,1	19,6
Barrel application + vibro-finishing with transparent epoxy lacquer	10	0,1	2,3

[0118] Rack and Barrel application refers to different deposition techniques. In rack plating the parts are fixed to metal racks with screws or wires, in order to be immersed into the plating solution. Rack plating is preferred for delicate parts that would be damaged in the rotation produced by the barrel. Rack plating is also used for large components.

[0119] Barrel plating is performed by placing the parts into a plastic barrel that have a wire contact in order to conduct electrical current to the samples. The barrel is immersed into the plating solution and its rotation permits uniform plating of the parts.

[0120] Vibro-finishing means that the plated object is placed in a vibrating machine with different kinds of abrading material (ceramic, wood, glass, etc...), in order to partly remove the final deposit and to give an old (vintage) aspect to the parts.

[0121] All the results both from barrel and rack application are below the limit of OEKO TEX STANDARD 100, that is fixed to 30 mg/kg for antimony release.

Example 3 (inventive)

[0122]

90 g/L	Potassium citrate
100 g/L	Sodium gluconate
0,50 g/L	Au(III) as Gold(III) potassium cyanide salt
0,35 g/L	Ru(III) as Ruthenium oxalate complex
0,10 g/L	Co(II) as Cobalt(II) acetate
15 g/L	Ammonium thiocyanate
0,50 g/L	Sb(III) as Antimony(III) oxide pre-complexed with potassium hydroxide(the final solution has an antimony concentration of 80 g/L as Sb metal, and a potassium hydroxide concentration of 250 g/L, completed with demineralized water up to 1 L of final volume)

[0123] The pH-value of the electroplating bath has been adjusted to 8,0 with sulphuric acid (5 %).

[0124] Electroplating from the bath described above has been carried out on the substrate described in chapter 2 above, using the following conditions.

[0125] pH: (8.0)
Temperature of the electroplating bath: 35°C
Current density: 3 A/dm^2
Plating time: 3 minutes

[0126] A fully uniform black deposit has been obtained, the black deposit had the following color coordinates.

[0127] L: 44
a: 2,0
b: 6,0

[0128] The composition of the alloy given below has been determined by electron microscope analysis with energy dispersive X-ray spectroscopy detector.

[0129] Au: 69 wt.-%
Sb: 17,5 wt.-%
Ru: 7,5 wt.-%
Co: 4 wt.-%
S: 2 wt.-%

[0130] Moreover, the substrate coated with the black alloy passed the following corrosion test as described in detail in chapter 1 above.

[0131] Synthetic Sweat 24h (NFS 80-772).
Climatic Chamber 96h (UNI EN ISO 4611).
Climatic Chamber in contact with Leather 96h.
Sulphurus anhydride SO_2 8h.

[0132] All tests have been passed with the rating 0.

[0133] The abrasion test as described in chapter 1 above has been conducted and it took approximately 30 minutes to remove the Au-Ru-Sb-Co deposit completely. Hence, the deposit is harder then the ones according to Examples 1 and 2 and the deposit is suited as uniform layer.

Further studies

[0134] The inventors carried out further studies to investigate the effect of the concentration of the alloying metals and ammonium thiocyanate in the electroplating bath on the colour coordinates of the obtained alloy. Furthermore, the effect of the temperature and the pH-value of the electroplating bath has been investigated. The plating bath according to example 2 has been applied for these tests.

[0135] The results are summarized in Figures 1 to 8.

[0136] In particular Gold increases the L value and increases also the a and b values. Antimony decreases the L value and Ruthenium does not affect the L value, so much but decreases a and b values. Iron decreases the L value, and also a and b values. Cobalt increases the L value, but the a and b values are not significantly changed. Cobalt increases also the hardness and abrasion resistance of the deposit.

[0137] Increasing pH-value of the electroplating bath promotes gold deposition and increases L, a and b values. A similar effect is observed when the temperature of the plating solution is increased. Decreasing the pH-value of the plating solution retards the deposition of gold, but increases the antimony content in the final alloy which results in a decrease of the L value.

[0138] Ammonium thiocyanate slightly decreases the L value. However, ammonium thiocyanate has a positive effect in combination with antimony. An excess of thiocyanate (>50 g/L) resulted in no more uniform deposition, with bluish regions on the low current density areas of the panel.

Claims

1. An electroplating bath for depositing a black alloy comprising or consisting of the following ingredients:

a) at least one source of gold ions;
b) at least one source of ruthenium ions; and
c) at least one source of antimony ions as darkening agent.

2. The electroplating bath according to claim 1,
characterized in that the electroplating bath comprises

a) 0,3 to 5 g/L, preferably 0,3 to 1 g/L, more preferably 0,3 to 0,7 g/L and most preferably 0,4 to 0,6 g/L gold ions and/or
b) 0,1 to 10 g/L, preferably 0,1 to 2 g/L, more preferably 0,2 to 1 g/L and most preferably 0,3 to 0,5 g/L ruthenium ions and/or
c) 0,25 to 10 g/L, preferably 0,25 to 2 g/L, more preferably 0,3 to 1 g/L and most preferably 0,3 to 0,6 g/L antimony ions.

3. The electroplating bath according to any of claims 1 or 2,
characterized in that the electroplating bath further comprises

d) at least one source of iron ions, preferably from 0 to 0,4 g/L, more preferably 0,15 to 0,25 g/L and most preferably 0,2 to 0,25 g/L and/or
e) at least one source of cobalt ions, preferably from 0 to 0,27 g/L, more preferably 0,05 to 0,25 g/L and most preferably 0,1 to 0,25 g/L and/or
f) at least one sulphur compound, preferably from 0,05 to 30 g/L, more preferably 0,1 to 20 g/L and most preferably 0,1 to 15 g/L and/or
g) at least one conductive salt, preferably from 70 to 120 g/L, more preferably 80 to 90 g/L and most preferably 90 g/L and/or
h) at least one complexing agent, preferably from 50 to 150 g/L, more preferably 80 to 120 g/L and most preferably 100 g/L

and mixtures thereof.

4. The electroplating bath according to any one of claims 1 to 3,
characterized in that
the at least one source of gold ions a) is selected from the group consisting of gold potassium cyanide complexes, preferably gold(III) potassium cyanide, gold(I) potassium cyanide, gold(III)chloride, sodium gold(I) sulphite, ammonium gold(I) sulphite and mixtures thereof and more preferably is gold(III) potassium cyanide; and/or
the at least one source of ruthenium ions b) is a ruthenium(III) complex, preferably selected from the group consisting of ruthenium sulfamate, ruthenium oxalate, ruthenium gluconate, ruthenium chloride, ruthenium sulphate, ruthenium ammonium sulfamate, ruthenium potassium oxalate, ruthenium sodium gluconate and mixtures thereof and more preferably is a mixed complex with ruthenium ammonium sulfamate and potassium oxalate, or ruthenium ammonium sulfamate and sodium gluconate; and/or
the at least one source of antimony ions c) is an antimony(III)-compound, preferably selected from the group consisting of antimony trioxide, antimony(III) chloride, antimony(III) acetate, antimony(III) sulphate and mixtures thereof or an antimony(V)-compound preferably selected from the group consisting of antimony(v) chloride, antimony(V) oxide and mixtures thereof, wherein antimony(III) compounds are preferred and most preferred is antimony trioxide in a media having a pH-value > 10 and/or antimony(III) chloride in a media having a pH-value > 10.

5. The electroplating bath according to any one of claims 3 or 4,

characterized in that
the at least one source of iron ions d) is an iron(III)-salt and preferably is selected from the group consisting of iron(III) sulphate, iron(III) chloride, iron(III) citrate, iron(III) nitrate, iron(III) pyrophosphate, iron(III) oxalate, iron(III) acetate, iron(III) ammonium citrate, iron(III) ammonium sulphate and mixtures thereof and preferably is iron(III) sulphate or iron(III) citrate; and/or
the at least one source of cobalt ions e) is selected from the group consisting of cobalt(II) sulphate, cobalt(II) acetate, cobalt(II) oxalate, cobalt(II) chloride, cobalt(II) bromide, ammonium cobalt(II) sulphate, cobalt(II) thiocyanate, cobalt(II) phosphate and mixtures thereof and preferably is cobalt(II) acetate and/or
the at least one sulphur compound f) is selected from the group consisting of ammonium thiocyanate, thiourea, thiourea derivatives, preferably N,N'-diethylthiourea, 1,2-methoxyphenyl-2-thiourea, 4-nitrophenyl-2-thiourea, heterocyclic compounds containing sulphur, preferably thiohydantoin, imidazolidinethione, 2-mercaptothiazoline, mercaptobenzothiazole, diammonium dithioglycolate, disodium 2,5-dimercapto-1,3,4-thiadiazole, sulphur compounds of the general formula R^1-S-R^2 wherein R^1 and R^2 are each independently alkyl or aryl residues with 1 to 6 carbon atoms and more preferably is ammonium thiocyanate; and/or
the at least one conductive salt g) is selected from the group consisting of, potassium sulphate, sodium sulphate, ammonium sulphate, ammonium sulfamate, potassium oxalate and mixtures thereof and preferably is potassium citrate; and/or
the at least one complexing agent h) is selected from the group consisting of sodium gluconate, potassium acetate, potassium citrate, ammonium citrate, sodium potassium tartrate, sodium or potassium malate and mixtures thereof and preferably is sodium gluconate.

6. The electroplating bath according to any of claims 1 to 5, **characterized in that** the electroplating bath has a pH-value in the range from 6 to 10, preferably 6,5 to 8,5, more preferably 7 to 8 and most preferably from 7,5 to 8.

7. The electroplating bath according to any of claims 1 to 6, **characterized in that** the electroplating bath is substantially free of nickel sources.

8. The electroplating bath according to any one of claims 1 to 7, **characterized in that** the electroplating bath has a temperature in the range from 30 to 50°C, preferably from 35 to 40°C and more preferably of 35°C.

9. A method for the electrochemical deposition of a black alloy on a substrate comprising the following steps:

(i) providing a substrate;
(ii) providing an electroplating bath as defined in any one of claims 1 to 7;
(iii) contacting the substrate and the electroplating bath;
(iv) contacting at least a part of an anode with the electroplating bath;
(v) applying a voltage across the substrate and the anode; and
(vi) electroplating a black alloy deposit on the substrate.

10. The method according to claim 9,
characterized in that step (iv) is carried out at a current density from 0.5 to 5 A/dm^2, preferably from 1 to 4 A/dm^2 and more preferably from 1 to 3 A/dm^2; and/or at a temperature of the electroplating bath from 30°C to 50°C, preferably from 35 to 40°C and more preferably of 35°C.

11. The method according to claim 9 or 10,
characterized in that the substrate is selected from the group consisting of bronze, brass, Zamack, alpacca, copper alloy, tin alloy, steel and mixtures thereof, and preferably further electroplated with copper, preferably in a thickness of 10 to 30 μm, white bronze, preferably in a thickness of 2 to 3 μm, and then palladium in a thickness of 0,5 to 1,0 μm and/or gold in a thickness of 0,2 to 0,3 μm.

12. A black alloy comprising the following compounds or consisting of these compounds:

(A): 45 to 95 weight-% gold;
(B): 4 to 30 weight-% antimony;
(C): 1 to 15 weight-% ruthenium;
(D) 0 to 5 weight-% iron; and
(E) 0 to 5 weight-% cobalt;

wherein compounds (A) to (E) add up to 100 weight-%.

13. The black alloy according to claim 12,
characterized in that the black alloy comprises the following compounds:

(A): 55 to 87 weight-%, preferably 70 to 85 weight-% gold;
(B): 10 to 20 weight-%, preferably 10 to 18 weight-% antimony;
(C): 3 to 15 weight-%, preferably 5 to 15 weight-% ruthenium;
(D) 0 to 5 weight-%, preferably 0 to 3 weight-% iron; and
(E) 0 to 5 weight-%, preferably 0 to 4 weight-% cobalt;

wherein compounds (A) to (E) add up to 100 weight-%.

14. The black alloy according to claim 12 or 13,
characterized in that the black alloy comprises up to 5 weight-% sulphur, preferably 0,1 to 5 weight-%, more preferably 0,5 to 2 weight-% and most preferably 1 to 1,5 weight-% sulphur.

15. The black alloy according to claim 12 to 14,
characterized in that
the black alloy has a L-value in the range from 35 to 50, preferably from 35 to 45 and more preferably from 38 to 45; and/or
the black alloy has a a-value in the range from 0 to 3, preferably from 0 to 2.5 and more preferably from 1 to 2; and/or
the black alloy has a b-value in the range from 5 to 10, preferably from 5 to 8 and more preferably from 5 to 6,5.

16. The black alloy according to any one of claims 12 to 15,
characterized in that the antimony release of the black alloy determined according to UNI EN 16711-2;2015 is below 30 mg antimony per kg alloy, preferably below 25 mg antimony per kg alloy and more preferably below 20 mg antimony per kg alloy.

17. Article at least partially coated with the black alloy according to one of claims 12 to 16 for use as jewellery, luxury goods, fashion, leather goods, watch industry and spectacle frames.

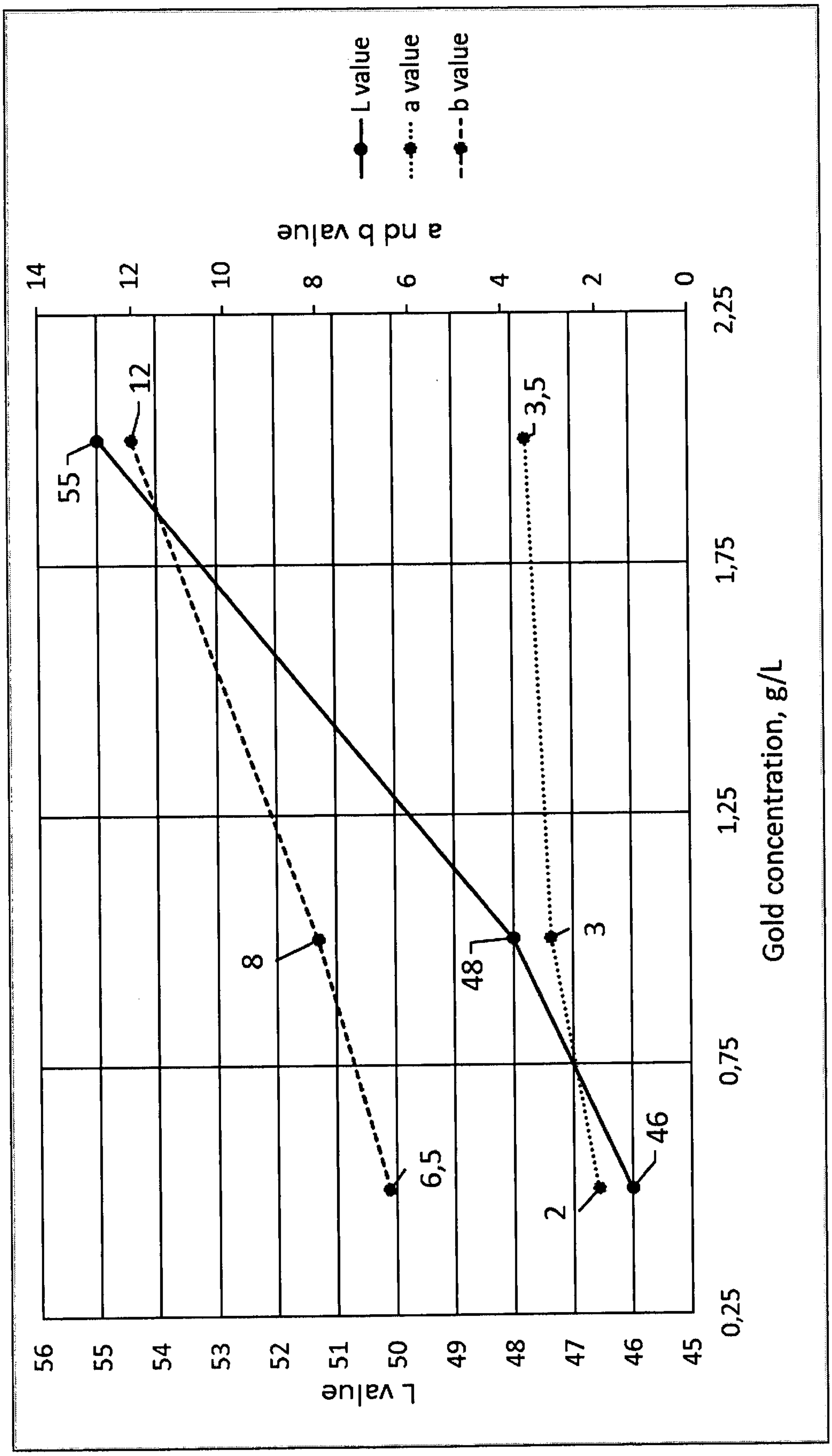
L value
56
55
54
53
52
51
50
49
48
47
46
45
a nd b value
14
12
10
8
6
4
2
0
Gold concentration, g/L
0,25
0,75
1,25
1,75
2,25
L value
a value
b value
55
12
3,5
48
8
3
46
6,5
2

Fig. 1

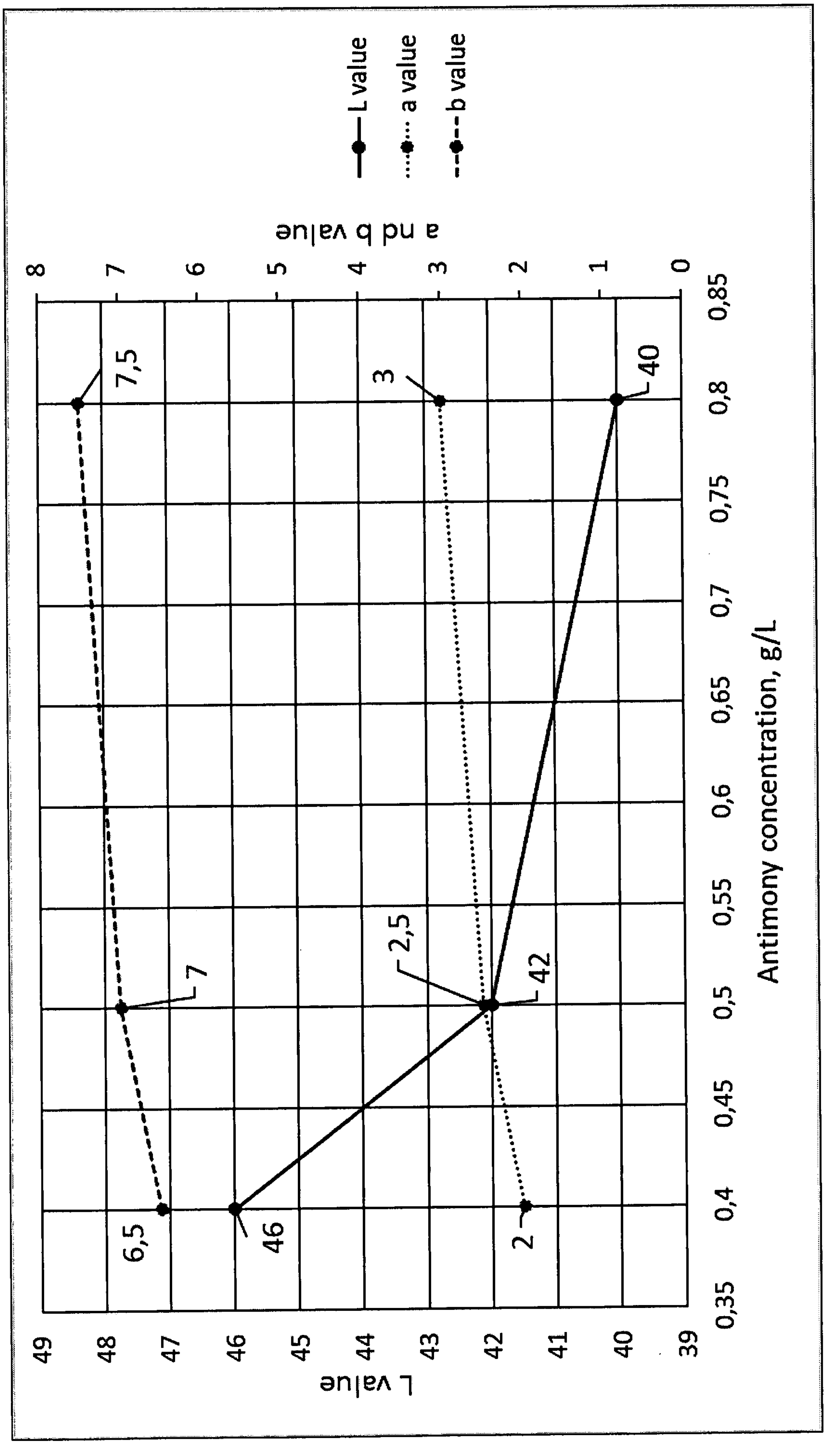
L value
a nd b value
Antimony concentration, g/L
0,35
0,4
0,45
0,5
0,55
0,6
0,65
0,7
0,75
0,8
0,85
39
40
41
42
43
44
45
46
47
48
49
0
1
2
3
4
5
6
7
8
L value
a value
b value
46
6,5
2
7
2,5
42
7,5
3
40

Fig. 2

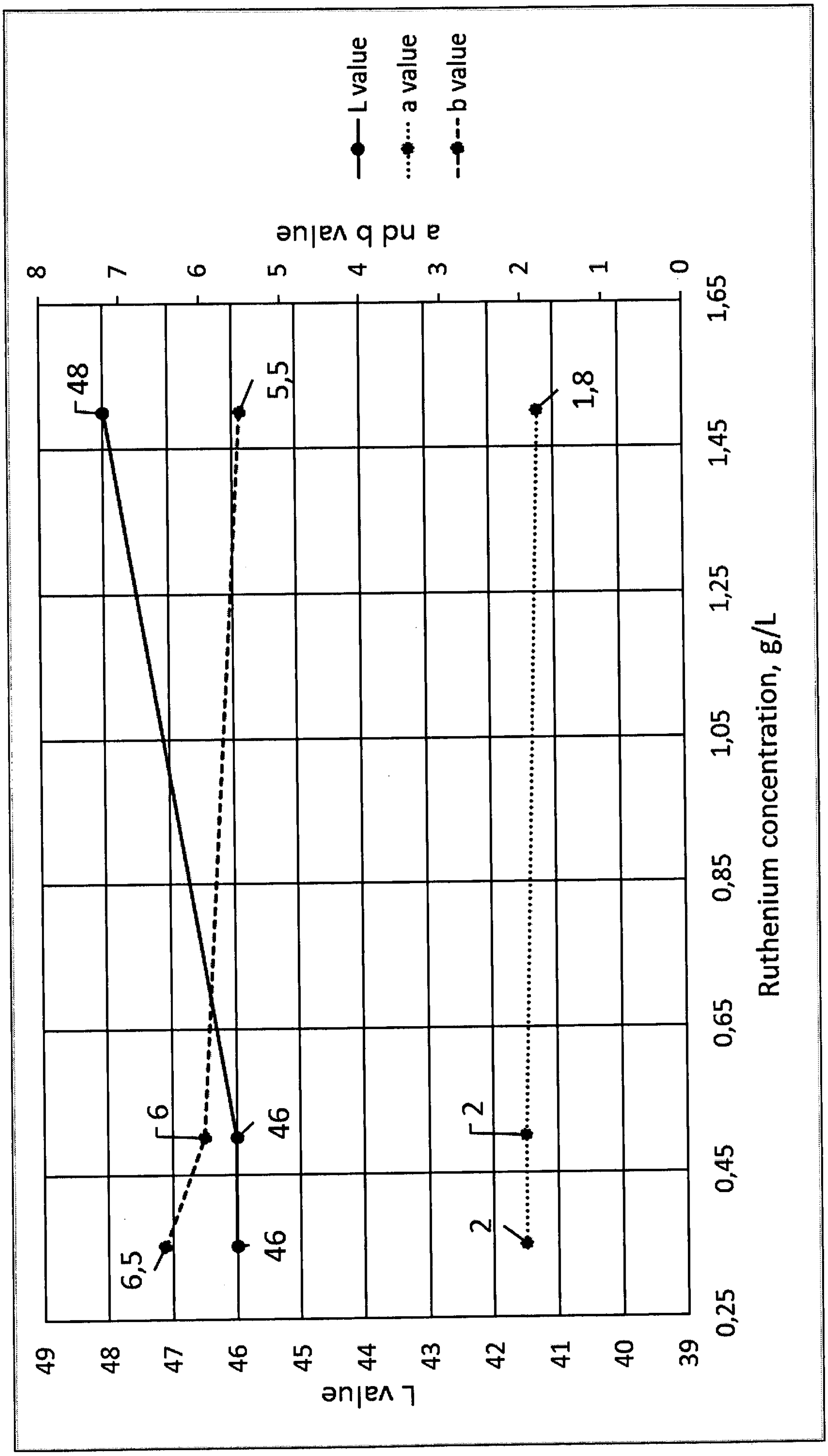
L value
a value
b value
a nd b value
8
7
6
5
4
3
2
1
0
L value
49
48
47
46
45
44
43
42
41
40
39
0,25
0,45
0,65
0,85
1,05
1,25
1,45
1,65
Ruthenium concentration, g/L
48
5,5
1,8
6
46
2
6,5
46
2

Fig. 3

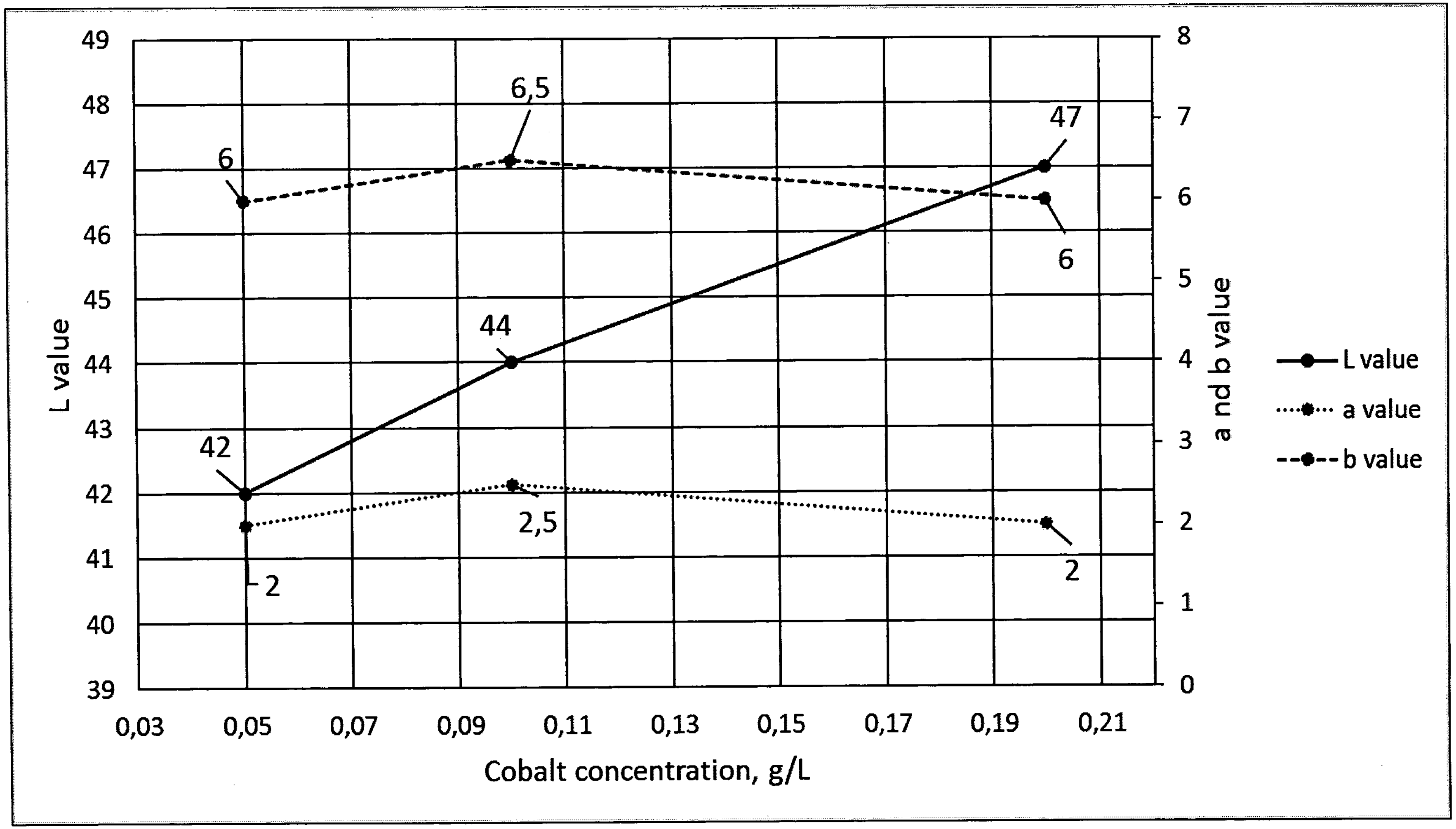
49
48
47
46
45
44
43
42
41
40
39
L value
8
7
6
5
4
3
2
1
0
a nd b value
0,03
0,05
0,07
0,09
0,11
0,13
0,15
0,17
0,19
0,21
Cobalt concentration, g/L
6
6,5
47
6
44
42
2,5
2
2
L value
a value
b value

Fig. 4

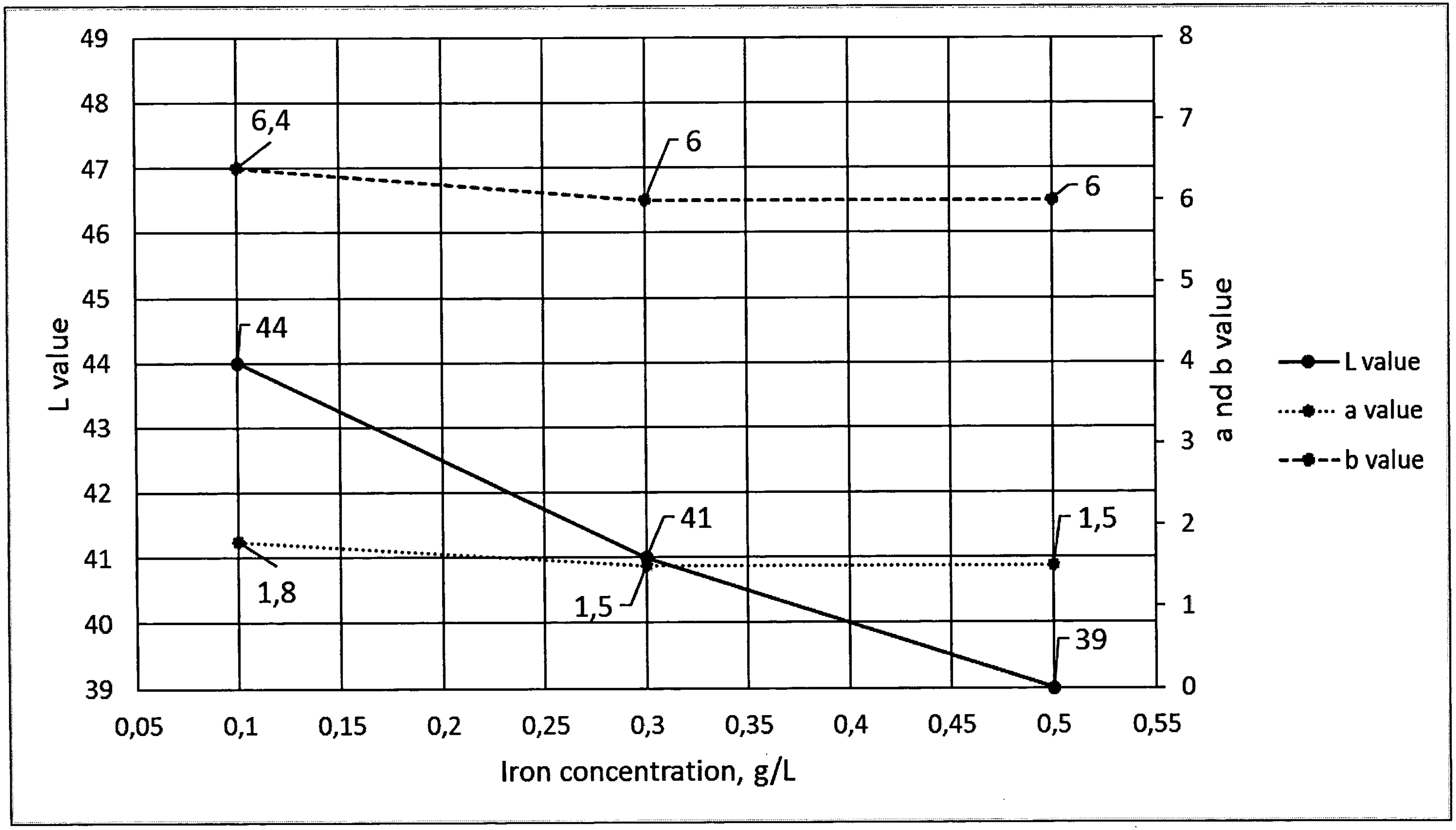
L value
49
48
47
46
45
44
43
42
41
40
39
a nd b value
8
7
6
5
4
3
2
1
0
0,05
0,1
0,15
0,2
0,25
0,3
0,35
0,4
0,45
0,5
0,55
Iron concentration, g/L
6,4
6
6
44
41
39
1,8
1,5
1,5
L value
a value
b value

Fig. 5

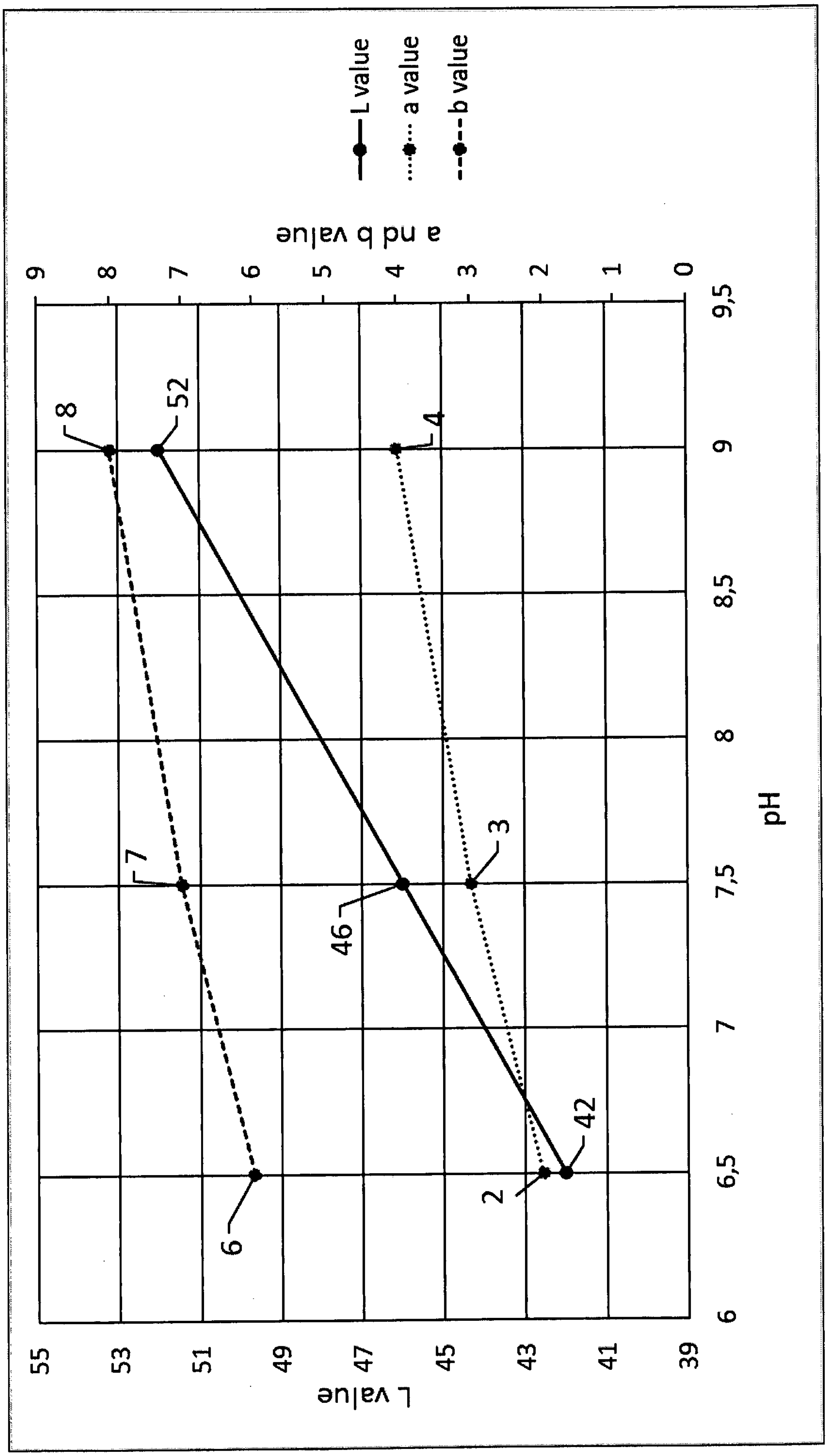
L value
55
53
51
49
47
45
43
41
39
a nd b value
9
8
7
6
5
4
3
2
1
0
pH
6
6,5
7
7,5
8
8,5
9
9,5
L value
a value
b value
52
46
42
8
7
6
4
3
2

Fig. 6

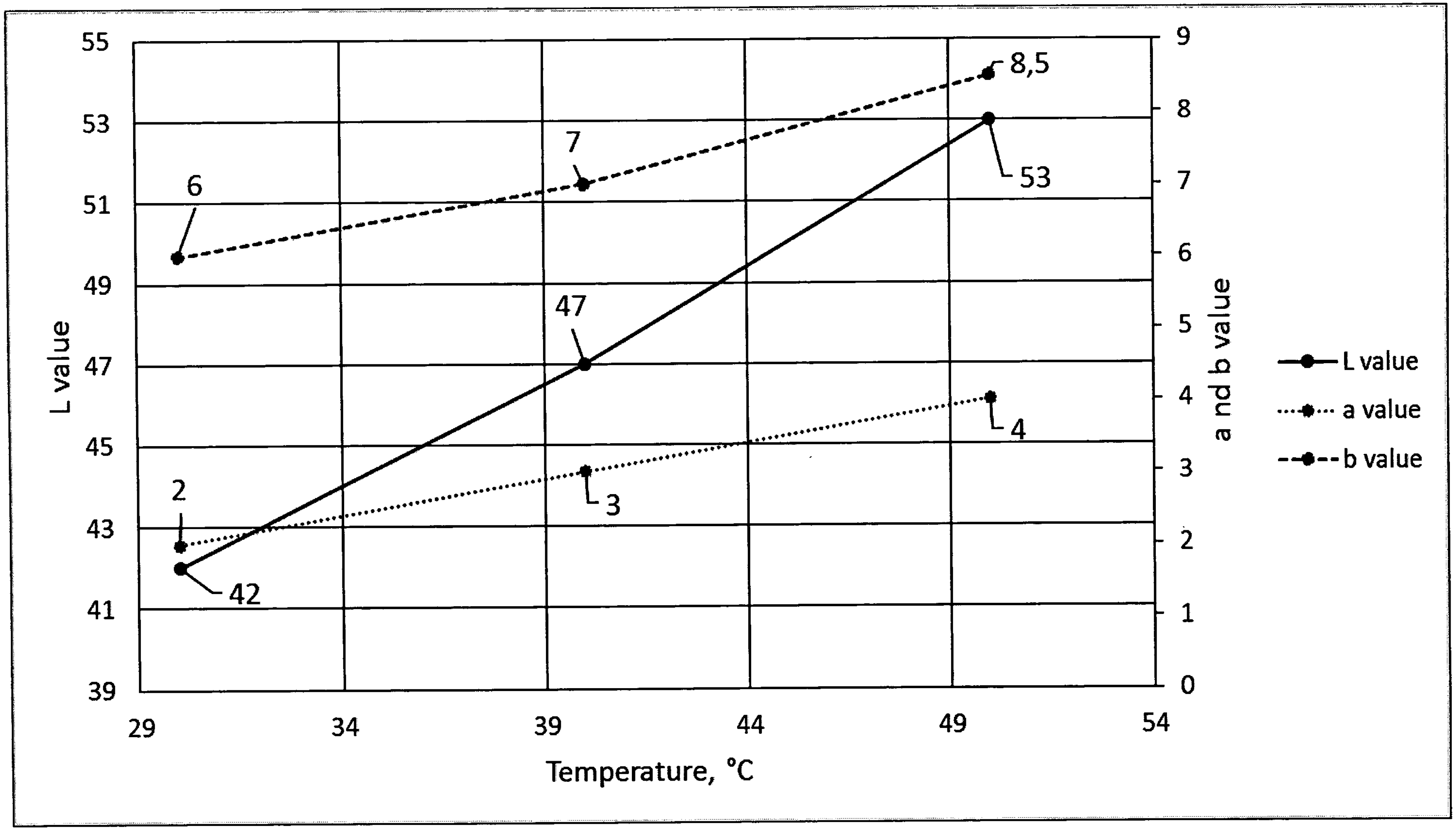
55
53
51
49
47
45
43
41
39
L value
29
34
39
44
49
54
Temperature, °C
9
8
7
6
5
4
3
2
1
0
a nd b value
6
7
8,5
47
53
42
2
3
4
L value
a value
b value

Fig. 7

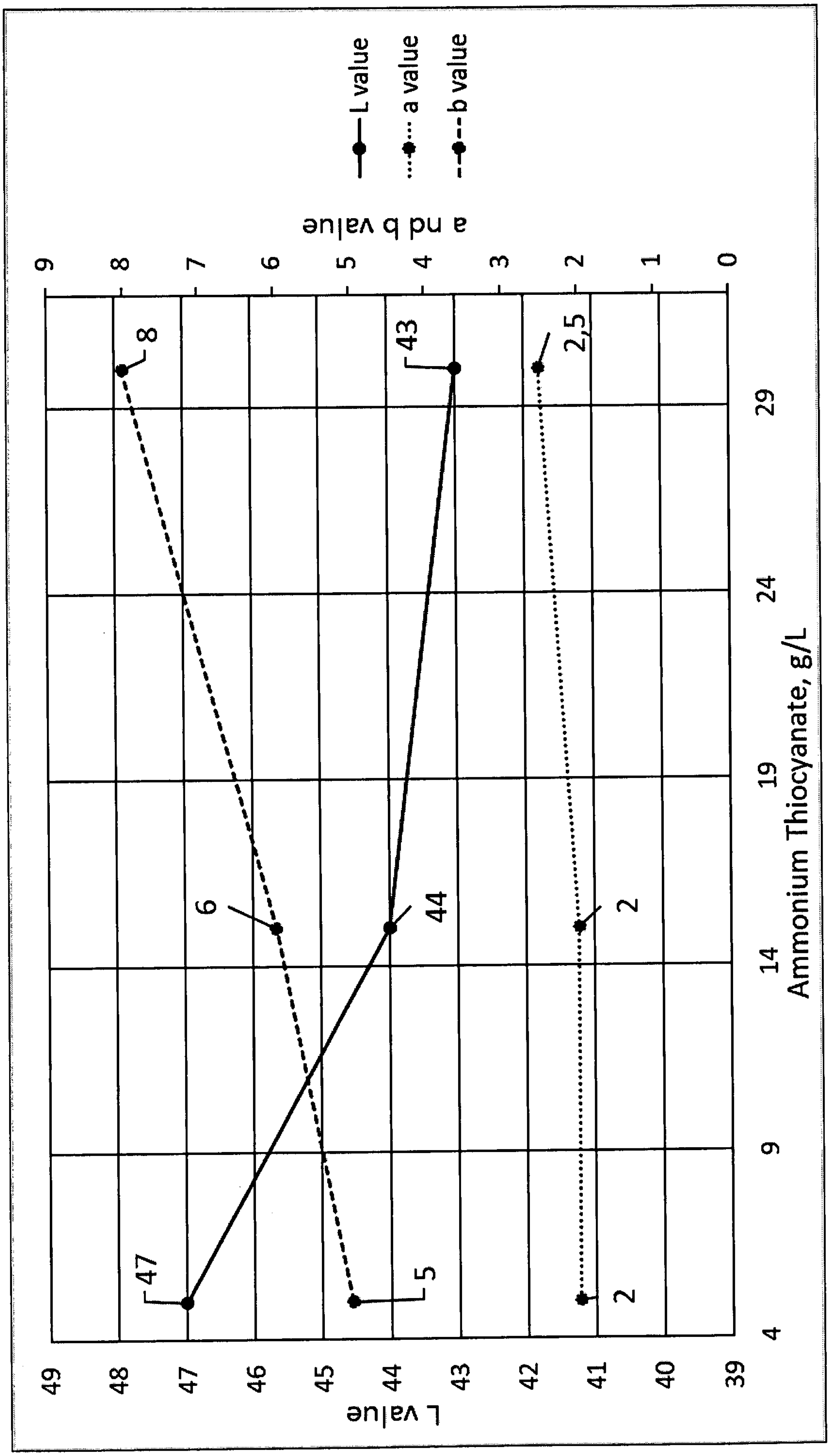
L value
a nd b value
Ammonium Thiocyanate, g/L
39
40
41
42
43
44
45
46
47
48
49
0
1
2
3
4
5
6
7
8
9
4
9
14
19
24
29
L value
a value
b value
47
44
43
5
6
8
2
2
2,5

Fig. 8

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EUROPEAN SEARCH REPORT

Application Number
EP 18 18 7270

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Place of search	Date of completion of the search	Examiner
The Hague	4 February 2019	Crottaz, Olivier

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