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(54) Solution for the electrodeposition of a gold alloy and the alloy derived therefrom

(57) The present invention discloses a solution for the electrodeposition of a gold alloy and the alloy derived therefrom having defined colour coordinates in the range of (L: 65-75; a: 6-9; b: 10-20). 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.

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the field of solutions for electrodeposition of metal alloys and derived alloys; in particular, it relates to a solution for the electrodeposition of a gold alloy and to the alloy derived therefrom having defined colour coordinates in the range of (L: 65-75; a: 6-9; b: 10-20).

PRIOR ART

[0002] The metal alloys obtained by electrodeposition are widely used in various production sectors, both for the physical qualities thereof and for the specific aesthetic nature thereof.

[0003] Coloured alloys, obtained by the electrodeposition of metals, both individually and alloyed together, are found to be of interest for this second purpose; these alloys are put to practical use in various fields: furniture, clothing, jewellery, and in general any sectors requiring articles having specific aesthetic properties. Coloured Gold alloys are found to be among the most used since they make it possible to obtain a vast range of colours and shades depending on the formulation used and the working conditions applied to obtain them.

[0004] Thus far, with galvanic gilding baths, it is possible to obtain the entire range of colours and shades of the colours white, yellow, pink and even green; however, brown colours are difficult to obtain under simple conditions and using chemically stable solutions.

[0005] There is therefore an interest in the formulation of chemically stable galvanic baths which are easy to manage and handle and can be used for the electrodeposition of brown gold alloys having colour coordinates in the range of: (L: 65-75; a: 6-9; b: 10-20) and having a shiny and coherent deposit.

SUMMARY OF THE INVENTION

[0006] The present invention solves the above problems by way of an aqueous solution for the electrodeposition of a Gold alloy; said solution comprising a Gold (Au) salt, an Iron (Fe) salt and a Vanadium (V) salt, and optionally one or more salts of other metals suitably selected among the Cobalt (Co), Palladium (Pd), Ruthenium (Ru) salts, for modulating the end colour shades; and optionally further comprising small amounts of one of more Tellurium (Te), Gallium (Ga) or Bismuth (Bi) salts, as sparkling aids and grain refiners.

[0007] The alloy derived from the aforementioned solution has colour coordinates in the range of: (L: 65-75; a: 6-9; b: 10-20).

[0008] The invention also further relates to a gold alloy having colour coordinates in the range of: (L: 65-75; a: 6-9; b: 10-20), said alloy, which can be obtained from the aforementioned solution, having the following percentage composition by weight:

- Au 86-91 %;
- Fe 6-8%
- V 4-6%
- Co, Pd, Ru or mixtures thereof 0-0.5%. Te, Ga, Bi or mixtures thereof are not alloyed, but merely serve as sparkling aids.

[0009] The invention also relates to a method for the electrodeposition of a gold alloy as disclosed above using the aforementioned solution.

DETAILED DESCRIPTION OF THE INVENTION

[0010] For the purposes of the present invention, a solution for electrodeposition is a galvanic bath and the solvent used is water.

[0011] The solution preferably contains a suitable buffer system, one or more complexing agents which guarantee stability of the metals in solution in addition to modulating the alloying thereof, and a surfactant which also acts as a sparkling aid.

[0012] The Gold salt may be Gold chloride, Gold sulphite, potassium Dicyanoaurate, potassium Tetracyanoaurate, ammonium Cyanoaurate or a combination thereof.

[0013] Preferably, the concentration of Gold as a metal is in the range of 0.5 to 3 g/L, more preferably from 0.7 to 1.8 g/L, the most suitable concentration for obtaining the desired triplet of colour coordinates in the range of interest (L: 65-75; a: 6-9; b:10-20) being selected from time to time.

[0014] The metals which are alloyed with the Gold are primarily Iron and Vanadium, introduced into the solution in the form of the most common salts thereof, such as, for Iron, by way of non-limiting example, Iron sulphate, Iron carbonate, Iron acetate, Iron citrate and Iron chloride, depending on the selected buffer system and on the stability of the selected salt in the environment of the solution, and for Vanadium, by way of non-limiting example, Vanadium Oxychloride, Vanadium Oxytriethoxide, Vanadium Oxytripropoxide, Vanadium Oxyfluoride, Vanadium Oxide, Sodium Vanadium Oxide, Vanadium halide.

[0015] The concentrations of the aforementioned metals are in the range of 0.2 g/L to 1 g/L, the most suitable concentration of each of these for obtaining the desired triplet of colour coordinates in the range of interest (L: 65-75; a: 6-9; b:10-20) being selected from time to time.

[0016] These metals are used so as to obtain a reduction in the values of the colour coordinates a and b with respect to the typical values for a 24 kt Gold deposits (L = 84-85; a = 6-8; b = 30-31); the amounts added for each individual metal bring about a corresponding effect on these coordinates in relation to the concentration. The other metals which may be introduced into the solution as salts for modulating the colour shades are Cobalt, Palladium, Ruthenium and mixtures thereof, these also being introduced into the solution in the form of the most common salts thereof, such as, by way of non-limiting example, sulphate, carbonate, acetate, citrate and chloride, depending on the selected buffer system and on the stability of the selected salt in the environment of the solution.

[0017] The concentrations of each of these metals are in the range of 0.005 to 0.5 g/L, the most suitable concentration of each of these for obtaining the desired triplet of colour coordinates in the range of interest (L: 65-75; a: 6-9; b:10-20) being selected from time to time.

[0018] These metals are used so as to obtain a modulation of the values of the colour coordinates a and b with respect to the typical values for a 24 kt Gold deposits (L = 84-85; a = 6-8; b = 30-31); the amounts added for each individual metal bring about a corresponding effect on these coordinates in relation to the concentration. In particular, it has been found that:

- Ruthenium reduces the L coordinate;
- Palladium and Cobalt increase the L coordinate;

[0019] It has further been found that Tellurium, Gallium and Bismuth or combinations thereof improve the homogeneity of the colour of the deposit and refine the grain of the deposit: they are introduced into the solution in the form of the soluble salts thereof or stable complexes thereof in the working conditions of the solution, in amounts for each metal in the range of 0.005 - 0.015 g/L as a metal.

[0020] The pH of the solution is not a critical parameter apart from for the stability in solution of the selected metals, and may be between 7 and 10, more preferably between 7.5 and 9.5, and is regulated using sodium or potassium hydroxide or using inorganic acids such as, by way of non-limiting example, sulphuric acid, phosphoric acid, formic acid.

[0021] In working conditions, the pH is kept stable by way of a buffer system selected among the acid/salt pairs of acids such as gluconic, oxalic, citric, tartaric, malonic, malic, phosphoric and sulphamic acid *inter alia,* which serve as complexing agents for the metals in solution, promoting the stability thereof, in addition to guaranteeing pH stability.

[0022] The salts of the aforementioned acids may be sodium or potassium salts or salts of other alkali and alkaline earth metals which are soluble in the conditions of the solution.

[0023] The concentrations of the acids and the salts thereof are in the range of 30 g/L to 170 g/L, more favourable of 50 g/L to 130 g/L.

[0024] It is also favourable to introduce one or more complexing agents into the solution, in concentrations of between 20 and 50 g/L, such as ethylenediaminetetraacetic acid, etidronic acid, nitrilotriacetic acid, ethylenediamine tetra methylenephosphonic acid, nitrilotrismethylenediphosphonic acid, in the form of the free acid or in the form of a salt.

[0025] The selection of the form of the complexing agent, the concentration and the composition of the eventual mixture is determined by the colour coordinates in the range of interest (L: 65-75; a: 6-9; b: 10-20) which it is desired to obtain.

[0026] The surfactant is selected from the sodium salts of the alkylsulphonates and alkylphosphonates which are soluble and stable at the working pH of the invention, and is used in an amount of no more than 1 g/L, introduced as a pre-diluted aqueous solution to avoid solubility problems.

[0027] The temperature and current density applied to the solution are parameters which influence the colour coordinates, and therefore have to be applied within particular intervals and modulated on the basis of the colour coordinates which it is desired to obtain in the range of interest (L: 65-75; a: 6-9; b: 10-20).

[0028] The preferred working temperature of the solution is in the range of 35 to 45°C; an increase in temperature leads to an increase in Gold in the deposit and thus raises the a and b coordinates.

[0029] The preferred current density is in the range of 0.5 A/dm^2 to 3 A/dm^3; an increase in applied current density initially leads to an alteration to the colour and subsequently to the appearance of burns and localised inhomogeneities of the deposit.

[0030] The duration of application of the current does not influence the colour, but in relation to a colouring bath the deposition times may typically be up to 2 minutes of application.

[0031] A better understanding of the invention may be gained from the following practical examples.

EXPERIMENTAL PART

Example No. 1

[0032] The following aqueous solution was prepared:

Citric Acid 30 g/L
Potassium Citrate 90 g/L
HEDP tetrasodium 7 g/L
Gold 1 g/L introduced as Potassium Dicyanoaurate
Iron 0.6 g/L introduced as Iron Citrate
Vanadium 0.6 g/L introduced as Vanadium Oxychloride
Tellurium 0.005 g/L introduced as Tellurium Oxide
Sodium Lauryl Ether 0.1 mL/L of the 10% w/v solution

[0033] A sheet of copper of size 10 × 10 cm, on which a layer of 24 kt Gold having colour coordinates (L = 84.8; a = 7.7; b = 30.2) had previously been deposited, was plated with the above-disclosed solution in the laboratory under the following working conditions:

pH 8
45 °C

0.8 A/dm^2
1 minute

[0034] The sheet was then rinsed in demineralised water and dried in an oven at 85°C for 30 minutes, then left to cool to room temperature.

[0035] The colour coordinates obtained were measured and found to be:

L: 72; a: 7.3; b: 15.2

[0036] From electron microscope analysis, the alloy was found to have the following average % composition by weight:

Au 89.4 %
Fe 6.65 %
V 3.95 %
Te did not alloy.

Claims

1. A solution for the electrodeposition of a gold alloy having color coordinates in the range between: L: 65-75; a: 6-9; b: 10-20; said solution comprising a Gold (Au) salt, an Iron (Fe) salt and a Vanadium (V) salt, and optionally one or more salts of other metals suitably selected among the Cobalt (Co), Palladium (Pd), Ruthenium (Ru) salts, for modulating the end color shades; and optionally further comprising small amounts of one of more Tellurium (Te), Gallium (Ga) or Bismuth (Bi) salts, as sparkling aids and grain refiners.

2. A solution according to claim 1, wherein Gold as a metal is in the range between 0.5 and 3 g/L.

3. A solution according to claim 1, wherein Fe and V as metals are provided in concentrations in the range between 0.2 and 1 g/L, respectively.

4. A solution according to claim 1, wherein Co, Pd and Ru, if provided, are each provided in concentrations in the range between 0.005 and 0.5 g/L, wherein the concentrations are referred to the metal in solution.

5. A solution according to claim 1, wherein Te, Ga, Bi or combinations thereof are introduced in the solution in the form of soluble salts thereof or stable complexes thereof in the working conditions of the solution, in amounts for each metal in the range between 0.005 and 0.015 g/L as a metal.

6. A solution according to any one of claims 1-5, having a buffered pH in the range between 7 and 10.

7. A solution according to any one of claims 1-9, comprising one or more complexing agents in concentrations in the range between 20 and 50 g/L.

8. A solution according to any one of the preceding claims, wherein a surfactant agent is provided in amounts of no more than 1 g/L.

9. A method for the electrodeposition of a gold alloy having color coordinates in the range: L: 65-75; a: 6-9; b: 10-20; said method comprising the use of a solution according to any one of the preceding claims.

10. A gold alloy, obtained according to the method of claim 12, said alloy having color coordinates in the range: L: 65-75; a: 6-9; b: 10-20 and having the following percentage composition by weight:

Au	86-91 %;
Fe	6-8%
V	4-6%
Co, Pd, Ru or mixtures thereof	0-0.5%.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 16 0514

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 4 075 065 A (KORBELAK ALEXANDER ET AL) 21 February 1978 (1978-02-21) * abstract * * column 1, line 50 - column 2, line 58 * * claim 2 * -----	1-4,7-9	INV. C25D3/62
Y	GB 2 306 508 A (ENTHONE OMI [CH]; ENTHONE OMI INC [US]) 7 May 1997 (1997-05-07) * abstract * * page 1, line 30 - page 3, line 33 * * page 5, lines 3-19 * * table 1 * -----	1-3,7-9	
Y	GB 2 323 853 A (ENTHONE OMI [CH]; ENTHONE OMI INC [US]) 7 October 1998 (1998-10-07) * abstract * * page 2, line 14 - page 3, line 27 * -----	1-3,5, 7-9	
Y	US 3 502 548 A (LYONS ERNEST H JR) 24 March 1970 (1970-03-24) * abstract * * claims 1,2,5 * -----	1-3,7-9	
Y	WO 02/068728 A1 (WIELAND DENTAL & TECHNIK GMBH [DE]; RUEBEL SUSANNE [DE]; STUEMKE MANFR) 6 September 2002 (2002-09-06) * abstract * * claims 1-6,13-18 * -----	1-3,5, 7-9	
A	US 3 904 493 A (LOSI SALVATORE ET AL) 9 September 1975 (1975-09-09) * abstract * * column 7, line 37 - column 8, line 17 * * columns 9,10; table 1 * -----	1-10	

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TECHNICAL FIELDS SEARCHED (IPC)
C25D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	9 July 2014	Haering, Christian

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 14 16 0514

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	GB 1 325 352 A (SEL REX CORP) 1 August 1973 (1973-08-01) * page 1, lines 44-88 * * claims 1,6,7,9,10,11,12 * -----	1-10	
A	US 3 475 292 A (SHOUSHANIAN HRANT H) 28 October 1969 (1969-10-28) * column 2, lines 10-20 * * claim 1 * -----	1-10	
A	US 3 990 954 A (FOULKE DONALD G ET AL) 9 November 1976 (1976-11-09) * abstract * * column 2, lines 41-59 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)
	The present search report has been drawn up for all claims		

1

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 14 16 0514

09-07-2014

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4075065 A	21-02-1978	NONE	
GB 2306508 A	07-05-1997	NONE	
GB 2323853 A	07-10-1998	NONE	
US 3502548 A	24-03-1970	NONE	
WO 02068728 A1	06-09-2002	AU 2002308221 A1	12-09-2002
		BR 0207724 A	23-03-2004
		CA 2438207 A1	06-09-2002
		CN 1494606 A	05-05-2004
		JP 4183240 B2	19-11-2008
		JP 2004527653 A	09-09-2004
		US 2004065225 A1	08-04-2004
		WO 02068728 A1	06-09-2002
US 3904493 A	09-09-1975	CH 555894 A	15-11-1974
		DE 2340462 A1	28-02-1974
		ES 417762 A1	16-06-1976
		FR 2253106 A1	27-06-1975
		GB 1447058 A	25-08-1976
		IT 994135 B	20-10-1975
		NL 7311108 A	12-02-1974
		US 3904493 A	09-09-1975
GB 1325352 A	01-08-1973	AT 310522 B	10-10-1973
		BE 754151 A1	31-12-1970
		CA 978136 A1	18-11-1975
		CH 506628 A	30-04-1971
		DE 2039157 A1	18-02-1971
		ES 382607 A1	16-10-1972
		FR 2060092 A1	11-06-1971
		GB 1325352 A	01-08-1973
		JP S4923976 B1	19-06-1974
		NL 7011357 A	10-02-1971
US 3475292 A	28-10-1969	BE 741892 A	04-05-1970
		DE 1621180 A1	19-05-1971
		GB 1134615 A	27-11-1968
		US 3475292 A	28-10-1969
US 3990954 A	09-11-1976	CA 1032108 A1	30-05-1978
		US 3990954 A	09-11-1976

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82