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(54) **Alloys for jewellery for making nickel-free white gold objects.**

(57) The present invention relates to the use of gallium Ga as a whitening element for the production of white gold alloys which are free of nickel Ni. Said use may be applied both during the direct production of the gold alloy and during the prior production of a specific master alloy.

In general, the invention is intended for the production of white gold alloys whose gold Au content, as a

weight relative to the total weight of the white gold alloy, is within the range $31 \% \leq \text{Au} \leq 92 \%$. The quantity of gallium Ga used, as a weight relative to the total weight of the white gold alloy, is within the range $1,4 \% \leq \text{Ga} \leq 30,0 \%$.

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Description

[0001] The present invention relates to the use of gallium on its own or combined with other elements as a whitening element in white gold alloys for nickel-free jewellery.

[0002] Therefore, the present invention relates to the use of gallium either directly in white gold alloys or in the master alloys for their production.

[0003] In the present invention the term white gold objects refers in particular to precious objects (such as jewellery, coins and medals) obtained both using precision casting processes and through mechanical working.

[0004] There is strong market demand for the production of white gold jewellery and said demand extends to practically all karat weights between 8 - 9 and 21 - 22 karats.

[0005] As regards methods for assessing the whiteness of an alloy, at present two colour examination methods are mainly used, the "Cielab" method (with coordinates a^* , b^* and L^*) and the "Yellowness Index" method (with YI index).

[0006] In the Cielab method, the L^* coordinate represents the lightness of the colour ($L^* = 0$ indicates black whilst $L^* = 100$ indicates white), the a^* coordinate represents the position of the colour between red/magenta and green (negative values indicate a tendency towards green whilst positive values indicate a tendency towards magenta) and the b^* coordinate indicates the position of the colour between yellow and blue (negative values indicate blue whilst positive values indicate yellow).

[0007] If the Cielab method is used, a white gold alloy is considered sufficiently white that it does not require a final rhodium plating treatment when its Cielab colour coordinates are: $0 < a < 2$; $0 < b < 9$.

[0008] If, instead the colour coordinates are $2 < a < 3.5$ and $9 < b < 14$, the colour is considered white but the items must be subjected to a final rhodium plating treatment.

[0009] For colour coordinates $a > 3.5$ and $b > 14$ the colour of the alloy is considered not white.

[0010] As regards the Yellowness Index (YI) method, its assessment is derived from a calculation (known and therefore not indicated) based on the use of the Cielab coordinates indicated above.

[0011] Based on this index, a gold alloy has a "premium white" colour, that is to say, which does not require further rhodium plating treatments if the YI value is less than 19. Instead, if the YI value is between 19 and 24.5, the alloy belongs to the "standard white" category and a rhodium plating treatment may or may not be necessary depending on requirements. Finally, if the YI value is between 24.5 and 32, the white gold alloy belongs to the "off white" category and a final rhodium plating treatment is necessary.

[0012] As is known, white gold is produced by inserting in an alloy metals that have a whitening effect, that is to say, with the capacity to cancel out the typical yellow

colour of gold.

[0013] The metal currently most used for this purpose is nickel, which as well as having high level whitening properties, is available on the market at a relatively low cost.

[0014] However, the problem of allergies caused by nickel has been known of for several years. Public opinion has demonstrated growing concern regarding the problem of allergies to nickel and the European Union issued a directive regulating the use of nickel which was subsequently adopted by member states.

[0015] The alternative to nickel is currently palladium, although since it is a precious metal its cost is significantly higher. Therefore, at present the use of palladium is limited to the production of high-end jewellery.

[0016] Only for low karat weights (8 - 9 kt) the alternative to nickel and palladium may be silver. However, this must be added in considerably high quantities due to its limited whitening power.

[0017] It should also be noticed that recent studies also highlighted the fact that palladium, always considered the safe alternative to nickel, can also potentially cause allergic contact dermatitis.

[0018] For the above reasons, over the years alternatives to nickel and palladium for production of white gold were sought, but without convincing results. The various metals tested over the years included chromium and manganese, whose reactivity against the refractories and casting systems used in the goldsmith's sector have so far made them unsuitable for use.

[0019] Finally, it should be remembered that, over the years many gold alloys having various colours have been developed, including gallium amongst the various elements of which they consist. For example, reference is made to patents DE 44 23 646, DE 43 20 928 and DE 34 14 128.

[0020] However, up to now, no indication has ever been provided regarding the possibility of using gallium as a whitening element for making white gold alloys.

[0021] In particular, with reference to the patents indicated above, when references are made in them to white gold alloys, said effect is never obtained by adding gallium, but always by adding other known whitening elements.

[0022] The features and advantages of the present invention are more apparent in the detailed description below, with reference to several preferred, non-limiting embodiments of the present invention.

[0023] As indicated, the core of the present invention consists of having identified gallium (in specific concentrations) as an innovative whitening element for making white gold alloys.

[0024] Gallium (whose chemical symbol is Ga, with atomic number 31 and atomic weight 69.7) is a silvery coloured metal, with a melting point of around 29.76°C. Its use for making jewellery is known. Thanks to its low melting point gallium is used to make solders. In some special applications gallium also gives alloys hardening

properties.

[0025] Many tests carried out by the Applicant have shown that gallium has extremely high level whitening properties, in line with what can normally be obtained using nickel and palladium.

[0026] The present invention is particularly important if one considers that the whitening effect is visible in particular at high karat weights, especially in 18 karat gold alloys.

[0027] For example, additions of around 5 - 6% of gallium to 18 kt gold alloys allow a whitening intensity to be obtained which is comparable to that obtainable with similar concentrations of nickel.

[0028] Moreover, in many applications the effect of melting temperature reduction allows a reduction in the casting temperature with consequent positive effects on precision casting with stones set in wax, zinc vaporisation and wear of the casting equipment.

[0029] There is also the possibility of adding gallium to alloys containing palladium. In this way it is possible to significantly reduce the quantity of palladium whose function is no longer that of guaranteeing the whitening effect.

[0030] As already indicated, the present invention may be applied both in the production of white gold alloy by simultaneously mixing all of the elements, and in the prior production of a master alloy intended to be mixed with the gold to obtain the white gold alloy only at a later stage. The master alloy comprises all of the elements of which the gold alloy consists except gold, and therefore allows easy preparation of the white gold alloy by simply weighing and mixing the master alloy and the gold.

[0031] Moreover, as indicated, the present invention relates both to alloys which are free of nickel Ni only, and, in the preferred embodiment, alloys which are free of both nickel Ni and palladium Pd.

[0032] In accordance with the present invention, the use of gallium as a whitening element is intended for the production of white gold alloys whose gold Au content, as a weight relative to the total weight of the white gold alloy, is within the range $31 \% \leq \text{Au} \leq 92 \%$.

[0033] With reference to white gold alloy, gallium Ga is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $1.4 \% \leq \text{Ga} \leq 30.0 \%$ or within the range $3 \% \leq \text{Ga} \leq 30.0 \%$.

[0034] In particular, when the white gold alloy has a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73 \% \leq \text{Au} \leq 77 \%$ (and preferably 75 %, that is to say, a content of 750 thousandths of the total), in accordance with the present invention the gallium Ga is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $3.1 \% \leq \text{Ga} \leq 12 \%$.

[0035] In contrast, when the white gold alloy has a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $57 \% \leq \text{Au} \leq 60 \%$ (and preferably 58.5 %, that is to say, a content of 585 thousandths of the total), in accordance with the present in-

vention the gallium Ga is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $1.4 \% \leq \text{Ga} \leq 20 \%$ or within the range $3 \% \leq \text{Ga} \leq 20 \%$ (and in some cases greater than 6.1 %).

[0036] Finally, when the white gold alloy has a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $36 \% \leq \text{Au} \leq 39 \%$ (and preferably 37.5 %, that is to say, a content of 375 thousandths of the total), in accordance with the present invention the gallium Ga is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $4 \% \leq \text{Ga} \leq 20 \%$.

[0037] Studies by the Applicant surprisingly allowed it to be ascertained that the whitening effect of gallium is enhanced when, in the gold alloy, to assist the whitening effect of the gallium Ga, silver Ag is used, in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Ag} \leq 60.0 \%$.

[0038] In particular, when white gold alloys have a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73 \% \leq \text{Au} \leq 77 \%$, and preferably equal to 75 %, in accordance with the present invention, in addition to gallium Ga, silver Ag is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Ag} \leq 22.0 \%$.

[0039] Similarly, in white gold alloys with a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $57 \% \leq \text{Au} \leq 60 \%$, and preferably equal to 58.5 %, silver Ag is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Ag} \leq 40.1 \%$ (eventually limited to 40.0 %), whilst in white gold alloys with a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $36 \% \leq \text{Au} \leq 39 \%$, and preferably equal to 37.5 %, silver Ag is preferably used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Ag} \leq 60.0 \%$.

[0040] Another improvement brought by the present invention is combining the use of gallium as a whitening element, assisted or not by silver, with the use of zinc Zn. The Applicant found that adding zinc to gallium improves the white shade of the white gold alloy. It was ascertained that the addition of zinc allows the improvement of white alloys obtained by adding gallium, directing their shades of colour even more precisely towards a pure white colour.

[0041] Said result may generally be obtained by adding zinc Zn in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Zn} \leq 30 \%$.

[0042] In particular, in white gold alloys with a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73 \% \leq \text{Au} \leq 77 \%$, and preferably equal to 75 %, in accordance with the present invention, in addition to gallium Ga, zinc Zn is used in a

quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Zn} \leq 7 \%$.

[0043] Similarly, in white gold alloys with a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $57 \% \leq \text{Au} \leq 60 \%$, and preferably equal to 58.5 %, zinc Zn is used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Zn} \leq 21 \%$, whilst in white gold alloys with a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $36 \% \leq \text{Au} \leq 39 \%$, and preferably equal to 37.5 %, zinc Zn is used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0.01 \% \leq \text{Zn} \leq 20 \%$.

[0044] As regards the other elements which may be part of the white gold alloys in which the whitening element consists of gallium, said alloys may, in general, contain one or more of the following elements, where the quantities are always expressed as a weight relative to the total weight of the white gold alloy:

copper Cu in a quantity of > 0 and $\leq 40.0 \%$;
indium In, tin Sn, silicon Si, chromium Cr and cobalt Co, each in a quantity of > 0 and $\leq 3.0 \%$;
manganese Mn in a quantity of > 0 any $\leq 2.9 \%$;
germanium Ge in a quantity of > 0 any $\leq 5.0 \%$; and
boron B, iridium Ir, ruthenium Ru, rhenium Re and molybdenum Mo, each in a quantity of > 0 and $\leq 0.5 \%$.

[0045] As indicated, although in the preferred embodiments of the present invention gallium is used as a whitening element in white gold alloys free of both nickel and palladium, in general it is also advantageously applied in all alloys which are free only of nickel.

[0046] However, in this case palladium may be present in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0 \% < \text{Pd} \leq 7.5 \%$.

[0047] When the present invention is implemented in the prior production of a master alloy, it is important to know the quantities of the various elements, and of the gallium in particular, relative to the composition of the master alloy.

[0048] In general, in master alloys gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $3.5 \% \leq \text{Ga} \leq 80 \%$ or within the range $6.4 \% \leq \text{Ga} \leq 80 \%$.

[0049] In contrast, in particular, when the master alloy is intended for the production of white gold alloys having a percentage gold content of between 73 % and 77 %, gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $12.4 \% \leq \text{Ga} \leq 48 \%$.

[0050] Similarly, when the master alloy is intended for the production of white gold alloys having a percentage gold content of between 57 % and 60 %, gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $3.5 \% \leq \text{Ga} \leq 48.2 \%$.

% or within the range $7.2 \% \leq \text{Ga} \leq 48.2 \%$.

[0051] Finally, when the master alloy is intended for the production of white gold alloys having a percentage gold content of between 36 % and 39 %, gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $6.4 \% \leq \text{Ga} \leq 32 \%$.

[0052] The same applies relative to the other elements which assist the action of the gallium, that is to say, silver and zinc.

[0053] In general, silver Ag and zinc Zn may be present in quantities, as a weight relative to the total weight of the master alloy, respectively within the range $0.01 \% \leq \text{Ag} \leq 96.5 \%$ (eventually limited to 93.6 %) and the range $0 \% \leq \text{Zn} \leq 60 \%$.

[0054] More specifically, when the master alloy is intended for the production of white gold alloys having a percentage gold content of between 73 % and 77 %, silver Ag is preferably used in a quantity, as a weight relative to the total weight of the master alloy, within the range $0.01 \% \leq \text{Ag} \leq 87.6 \%$, whilst zinc Zn is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $0.01 \% \leq \text{Zn} \leq 28 \%$.

[0055] In contrast, when the master alloy is intended for the production of white gold alloys having a percentage gold content of between 57 % and 60 %, silver Ag is preferably used in a quantity, as a weight relative to the total weight of the master alloy, within the range $0.01 \% \leq \text{Ag} \leq 96.5 \%$ (eventually limited to 92.8 %), and zinc Zn is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $0.01 \% \leq \text{Zn} \leq 50.6 \%$.

[0056] Finally, when the master alloy is intended for the production of white gold alloys having a percentage gold content of between 36 % and 39 %, silver Ag is preferably used in a quantity, as a weight relative to the total weight of the master alloy, within the range $0.01 \% \leq \text{Ag} \leq 93.6 \%$ and zinc Zn is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $0.01 \% \leq \text{Zn} \leq 32 \%$.

[0057] As regards the other possible elements of which the alloy consists, indicated above, with reference to the master alloy they may be present, as a weight relative to the total weight of the master alloy, in the following quantities:

copper Cu in the range $0 \% \leq \text{Cu} \leq 90 \%$;
indium In in the range $0 \% \leq \text{In} \leq 15 \%$;
tin Sn in the range $0 \% \leq \text{Sn} \leq 15 \%$;
silicon Si in the range $0 \% \leq \text{Si} \leq 15 \%$;
chromium Cr in the range $0 \% \leq \text{Cr} \leq 15 \%$;
manganese Mn in the range $0 \% \leq \text{Mn} \leq 15 \%$;
germanium Ge in the range $0 \% \leq \text{Ge} \leq 15 \%$;
cobalt Co in the range $0 \% \leq \text{Co} \leq 15 \%$;
iridium Ir in the range $0 \% \leq \text{Ir} \leq 2 \%$;
ruthenium Ru in the range $0 \% \leq \text{Ru} \leq 2 \%$;
rhenium Re in the range $0 \% \leq \text{Re} \leq 2 \%$;
molybdenum Mo in the range $0 \% \leq \text{Mo} \leq 2 \%$.

[0058] Finally, in accordance with what is indicated above, the master alloy may be free of palladium Pd, or may contain palladium in a quantity, as a weight relative to the total weight of the master alloy, within the range $0\% < \text{Pd} \leq 30\%$.

[0059] As indicated, gallium may be used as a whitening element both in alloys which are free only of nickel, and in alloys which are also free of palladium, always giving excellent results.

[0060] Below are several examples of both white gold alloys using conventional whitening elements, and white gold alloys made in accordance with the present invention, that is to say, in which the whitening element used is gallium.

[0061] For each alloy the whiteness values measured and calculated both with the Cielab method and with the Yellowness Index method are also provided.

[0062] A comparison between the whiteness values of the conventional alloys and those disclosed by the invention allows the validity of gallium as a whitening element to be established.

EXAMPLES

[0063] In the examples, all of the compositions are expressed as weights in thousandths.

[0064] For each alloy, both the Cielab coordinates measured and the YI value consequently calculated are also provided.

[0065] Moreover, for each example the value

$$C = \sqrt{a^{*2} + b^{*2}} \quad \text{is also provided, indicating}$$

the overall level of colour of the alloy. The lower the c value, the higher the level of alloy whiteness. *

1.1. Reference examples for 750 fineness white gold alloys containing nickel as the primary whitening element

Example 1.1.0.

[0066]

Au	750
Zn	40
Ni	70
Cu	140

Cielab colour coordinates: $a^* = 1.6$; $b^* = 11$; $c = 11.1$; $L^* = 81.5$, YI = 24.1

Example 1.1.1.

[0067]

Au	750
Zn	30
Ni	50
Cu	170

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Cielab coordinates: $a^* = 2.6$; $b^* = 11.8$; $c = 12.1$; $L^* = 86.2$, YI = 25.3

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1.2. Reference examples for 750 fineness white gold alloys containing gallium as the primary whitening agent

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[0068] In examples 1.2.0, 1.2.1, 1.2.2 the three 750 (18 kt) gold alloy formulations have the same basic composition, but differ in terms of the gallium content (and, obviously, in a corresponding inverse fashion, the copper content, this being the element which completes the alloy). The noticeable whitening effect which can be obtained by increasing the gallium concentration is clearly visible.

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Example 1.2.0.

[0069]

Au	750
Zn	20
Ga	90
Ag	12.5
Cu	127.5

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Cielab colour coordinates: $a^* = 1.6$; $b^* = 11.7$; $c = 11.8$, $L^* = 84.4$, YI = 22.7.

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Example 1.2.1.

[0070]

Au	750
Zn	20
Ga	135
Ag	12.5
Cu	82.5

40

45

Cielab colour coordinates: $a^* = 0.4$; $b^* = 4.8$; $c = 4.8$, $L^* = 85.2$, YI = 11.1

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Example 1.2.3.

[0071]

Au	750
Zn	20
Ga	180
Ag	12.5
Cu	37.5

55

Cielab colour coordinates: $a^* = 0.1$; $b^* = 2.9$; $c = 2.9$, $L^* = 85.5$, $YI = 7.2$

Example 1.2.4.

[0072]

Au	750
Zn	37.5
Ga	90
Ag	0
Cu	122.5

Cielab colour coordinates: $a^* = 1.6$; $b^* = 11.2$; $c = 11.3$, $L^* = 85.6$, $YI = 23.5$

[0073] In example 1.2.4 the formulation was changed compared with example 1.2.0, increasing the zinc content in the alloy by 87 %. A comparison of the colour coordinates for the two formulations shows how the whitening effect of zinc is negligible.

Example 1.2.5.

[0074]

Au	750
Zn	37.5
Ga	90
Ag	75
Cu	47.5

Cielab colour coordinates: $a^* = 0.8$; $b^* = 8.8$; $c = 8.8$, $L^* = 85.5$, $YI = 18.7$

[0075] In example 1.2.5 silver was added to the previous formulation 1.2.4. In this case, the silver contributed to further whitening of the alloy obtained, although to a noticeably lesser extent than can be obtained by adding similar quantities of gallium (see example 1.2.3). In any case, it is interesting to notice that, whilst the addition of silver to alloys containing nickel as the primary whitening element contributes less to improvement of the white colour, the addition of silver in the presence of gallium gives a more accentuated whitening effect. This condition was detected in particular in 750 fineness gold alloys.

[0076] The whitening effect of gallium is also evident to such a degree that its removal from the previous formulation (the other elements being the same with the exception of the copper compensator element) resulted in a clear yellowing of the alloy ($a^* = 3$; $b^* = 20.8$; $c = 21$; $L^* = 86.3$; $YI = 40.12$), further confirming the whitening effect of gallium and the inability of silver on its own to act as an autonomous decolourant agent at high karat weights.

[0077] In the following examples, zinc and silver were added on each occasion in such a way as to adjust, according to the objectives, the physical - mechanical prop-

erties and the aspects linked to the cost of the materials used.

Example 1.2.6.

[0078]

Au	750
Zn	37.5
Ga	60
Ag	105
Cu	47.5

Cielab colour coordinates: $a^* = 0.3$; $b^* = 13.1$; $c = 13.1$, $L^* = 85.2$, $YI = 25.8$

Example 1.2.7.

[0079]

Au	750
Zn	37.5
Ga	50
Ag	115
Cu	47.5

Cielab colour coordinates: $a^* = 0.01$; $b^* = 15.5$; $c = 15.5$; $L^* = 85.2$, $YI = 23.1$

[0080] In this example it is interesting to notice how, although coordinate b^* is worse, the visual impact is that of a noticeably white colour. This is due to the extremely low a^* values (red component of the colour); which as is well-known strike the sensitivity of the retina to a greater extent than coordinate b^* (yellow component of the colour).

Example 1.2.8.

[0081]

Au	750
Zn	37.5
Ga	70
Ag	95
Cu	47.5

Cielab colour coordinates: $a^* = 0.5$; $b^* = 11.2$; $c = 11.2$; $L^* = 86.3$, $YI = 23.1$

Example 1.2.9.

[0082]

Au	750
Zn	75

(continued)

Ga	50
Ag	75
Cu	50

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Cielab colour coordinates: $a^* = 0.6$; $b^* = 13.0$; $c = 13.0$;
 $L^* = 86.8$; $YI = 25.8$

2.1. Reference examples for 585 fineness white gold alloys containing nickel as the primary whitening agent

Example 2.1.0.

[0083]

Au	585
Zn	60
Ni	60
Cu	295

Cielab colour coordinates: $a^* = 2.2$; $b^* = 12.3$; $c = 12.5$;
 $L^* = 85.3$; $YI = 26.0$

Example 2.1.1.

[0084]

Au	585
Zn	48
Ni	87
Cu	280

Cielab colour coordinates: $a^* = 1.8$; $b^* = 9.7$; $c = 9.9$; $L^* = 85.4$; $YI = 21.1$

2.2. Reference examples for 585 fineness white gold alloys containing gallium as the primary whitening agent

Example 2.2.1.

[0085]

Au	585
Zn	100
Ga	62
Ag	62
Cu	191

Cielab colour coordinates: $a^* = 1.2$; $b^* = 14.1$; $c = 14.2$;
 $L^* = 86.6$; $YI = 28.2$

Example 2.2.2.

[0086]

Au	585
Zn	62
Ga	100
Ag	175
Cu	78

Cielab colour coordinates: $a^* = 0.3$; $b^* = 6.7$; $c = 6.8$; $L^* = 87$; $YI = 13.6$

Example 2.2.3.

[0087]

Au	585
Ga	2.075
Ag	39.425

Cielab color coordinates: $a^* = -2.58$; $b^* = 12.41$; $c = 12.68$; $L^* = 92.75$; $YI = 20.88$.

Example 2.2.4.

[0088]

Au	585
Ga	2.905
Ag	38.595

Cielab color coordinates: $a^* = -2.34$; $b^* = 11.96$; $c = 12.19$;
 $L^* = 92.17$; $YI = 20.4$.

3.1. Reference examples for 375 fineness white gold alloys containing nickel as the primary whitening agent

Example 3.1.0.

[0089]

Au	375
Zn	100
Ni	130
Cu	395

Cielab colour coordinates: $a^* = 0.7$; $b^* = 8.4$; $c = 8.4$; $L^* = 85.5$; $YI = 17.9$

Example 3.1.1.

[0090]

Au	375
Zn	130
Ni	65

(continued)

Cu 430

Cielab colour coordinates: $a^* = 0.6$; $b^* = 11.6$; $c = 11.6$;
 $L^* = 85.4$; $YI = 23.4$

3.2. Reference examples for 375 fineness white gold alloys containing gallium as the primary whitening agent

Example 3.2.1.

[0091]

Au	375
Zn	125
Ga	62
Ag	50
Cu	388

Cielab colour coordinates: $a^* = 1.1$; $b^* = 17.5$; $c = 17.5$;
 $L^* = 87.8$; $YI = 33.8$

Example 3.2.2.

[0092]

Au	375
Zn	94
Ga	150
Ag	262
Cu	119

Cielab colour coordinates: $a^* = 0.4$; $b^* = 5.1$; $c = 5.1$; $L^* = 82.3$; $YI = 11.1$.

[0093] The present invention brings important advantages.

[0094] Thanks to the present invention it was possible to identify an innovative whitening agent, gallium, which can be used as an alternative to conventional whitening agents (nickel, palladium) with equivalent if not better results.

[0095] Moreover, gallium is a safe element, since, although it has been used for many years in the goldsmith's sector, no cases of allergic contact dermatitis have ever been reported relative to it.

[0096] In addition, gallium, like nickel and unlike palladium, is not a precious metal, therefore the cost linked to implementation of the invention is relatively limited.

[0097] Further advantages are obtained when in addition to gallium silver and/or zinc are also used, since said elements allow respectively improvement of the whiteness of the alloy and improvement of its shade.

Claims

1. Use of gallium Ga as a whitening element for the production of white gold alloys which are free of nickel Ni.
2. Use of gallium Ga according to claim 1, for white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $31 \% \leq Au \leq 92 \%$.
3. Use of gallium Ga according to claim 2, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within one of the ranges $1,4 \% \leq Ga \leq 30,0 \%$ and $3 \% \leq Ga \leq 30,0 \%$.
4. Use of gallium Ga according to claim 3, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73 \% \leq Au \leq 77 \%$, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $3,1 \% \leq Ga \leq 12 \%$.
5. Use of gallium Ga according to claim 4, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, equal to 75% .
6. Use of gallium Ga according to claim 3, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $57 \% \leq Au \leq 60 \%$, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within one of the ranges $1,4 \% \leq Ga \leq 20 \%$, $3,1 \% \leq Ga \leq 20 \%$ and $6,1 \% \leq Ga \leq 20 \%$.
7. Use of gallium Ga according to claim 6, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, equal to $58,5 \%$.
8. Use of gallium Ga according to claim 3, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $36 \% \leq Au \leq 39 \%$, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $4 \% \leq Ga \leq 20 \%$.
9. Use of gallium Ga according to claim 8, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, equal to $37,5 \%$.
10. Use of gallium Ga according to claim 3, for the pro-

duction of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73 \% \leq \text{Au} \leq 77 \%$, and preferably equal to 75 %, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $3.1 \% \leq \text{Ga} \leq 12 \%$, and **in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the white gold alloy, respectively within the range $0.01 \% \leq \text{Ag} \leq 22.0 \%$ and within the range $0.01 \% \leq \text{Zn} \leq 7 \%$.

11. Use of gallium Ga according to claim 3, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $57 \% \leq \text{Au} \leq 60 \%$, and preferably equal to 58.5 %, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within one of the ranges $1.4 \% \leq \text{Ga} \leq 20 \%$, $3.1 \% \leq \text{Ga} \leq 20 \%$ and $6.1 \% \leq \text{Ga} \leq 20 \%$, wherein at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the white gold alloy, respectively within one of the ranges $0.01 \% \leq \text{Ag} \leq 40.0 \%$ and $0.01 \% \leq \text{Ag} \leq 40.1 \%$, and within the range $0.01 \% \leq \text{Zn} \leq 21 \%$.
12. Use of gallium Ga according to claim 3, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $36 \% \leq \text{Au} \leq 39 \%$, and preferably equal to 37.5 %, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $4 \% \leq \text{Ga} \leq 20 \%$, and **in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the white gold alloy, respectively within the range $0.01 \% \leq \text{Ag} \leq 60.0 \%$ and $0.01 \% \leq \text{Zn} \leq 20 \%$.
13. Use of gallium Ga according to any of the claims from 2 to 9, **characterised in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the white gold alloy, respectively within the range $0.01 \% \leq \text{Ag} \leq 60.0 \%$ and within the range $0.01 \% \leq \text{Zn} \leq 30 \%$.
14. Use of gallium Ga according to any of the claims from 2 to 12, for the production of white gold alloys

also comprising, as a weight relative to the total weight of the white gold alloy, one or more of the following elements:

- 5 copper Cu in a quantity of > 0 and $\leq 40.0 \%$;
indium In, tin Sn, silicon Si, chromium Cr and cobalt Co, each in a quantity of > 0 and $\leq 3.0 \%$;
manganese Mn in a quantity of > 0 any $\leq 2.9 \%$;
germanium Ge in a quantity of > 0 any $\leq 5.0 \%$;
10 and
boron B, iridium Ir, ruthenium Ru, rhenium Re and molybdenum Mo, each in a quantity of > 0 and $\leq 0.5 \%$.

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15. Use of gallium Ga according to claim 14, for the production of white gold alloys which are free of palladium Pd.
- 20 16. Use of gallium Ga according to claim 14, for the production of white gold alloys also comprising palladium in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0 \% < \text{Pd} \leq 7.5 \%$.
- 25 17. Use of gallium Ga according to any of the claims from 2 to 12, for the production of white gold alloys which are free of palladium Pd.
- 30 18. Use of gallium Ga according to any of the claims from 2 to 12, for the production of white gold alloys also comprising palladium in a quantity, as a weight relative to the total weight of the white gold alloy, within the range $0 \% < \text{Pd} \leq 7.5 \%$.
- 35 19. Use of gallium Ga according to claim 1, for the production of a master alloy intended for production of a white gold alloy by mixing with gold Au.
- 40 20. Use of gallium Ga according to claim 19, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within one of the ranges $3.5 \% \leq \text{Ga} \leq 80 \%$ and $6.4 \% \leq \text{Ga} \leq 80 \%$.
- 45 21. Use of gallium Ga according to claim 20, for the production of master alloys used to produce white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73 \% \leq \text{Au} \leq 77 \%$, and preferably equal to 75 %, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $12.4 \% \leq \text{Ga} \leq 48 \%$.
- 50 22. Use of gallium Ga according to claim 20, for the production of master alloys used to produce white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the

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range $57\% \leq \text{Au} \leq 60\%$, and preferably equal to 57.5 %, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within one of the ranges $3.5\% \leq \text{Ga} \leq 48.2\%$ and $7.2\% \leq \text{Ga} \leq 48.2\%$.

23. Use of gallium Ga according to claim 20, for the production of master alloys used to produce white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $36\% \leq \text{Au} \leq 39\%$, and preferably equal to 37.5 %, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the master alloy, within the range $6.4\% \leq \text{Ga} \leq 32\%$.

24. Use of gallium Ga according to claim 21, **characterised in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the master alloy, respectively within the range $0.01\% \leq \text{Ag} \leq 87.6\%$ and $0.01\% \leq \text{Zn} \leq 28\%$.

25. Use of gallium Ga according to claim 22, **characterised in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the master alloy, respectively within one of the ranges $0.01\% \leq \text{Ag} \leq 96.5\%$ and $0.01\% \leq \text{Ag} \leq 92.8\%$ and within the range $0.01\% \leq \text{Zn} \leq 50.6\%$.

26. Use of gallium Ga according to claim 23, **characterised in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is used in a quantity, as a weight relative to the total weight of the master alloy, respectively within the range $0.01\% \leq \text{Ag} \leq 93.6\%$ and $0.01\% \leq \text{Zn} \leq 32\%$.

27. Use of gallium Ga according to any of the claims from 19 to 23, **characterised in that** at least one between silver Ag, to assist the whitening effect of the gallium Ga, and zinc Zn, to improve the white shade of the final white gold alloy, is also used in a quantity, as a weight relative to the total weight of the master alloy, respectively within one of the ranges $0.01\% \leq \text{Ag} \leq 96.5\%$ and $0.01\% \leq \text{Ag} \leq 93.6\%$ and within the range $0\% \leq \text{Zn} \leq 60\%$.

28. Use of gallium Ga according to any of the claims from 19 to 26, for the production of master alloys for producing white gold alloys also comprising, as a weight relative to the total weight of the master alloy,

one or more of the following elements:

copper Cu in the range $0\% \leq \text{Cu} \leq 90\%$;
indium In in the range $0\% \leq \text{In} \leq 15\%$;
tin Sn in the range $0\% \leq \text{Sn} \leq 15\%$;
silicon Si in the range $0\% \leq \text{Si} \leq 15\%$;
chromium Cr in the range $0\% \leq \text{Cr} \leq 15\%$;
manganese Mn in the range $0\% \leq \text{Mn} \leq 15\%$;
germanium Ge in the range $0\% \leq \text{Ge} \leq 15\%$;
cobalt Co in the range $0\% \leq \text{Co} \leq 15\%$;
iridium Ir in the range $0\% \leq \text{Ir} \leq 2\%$;
ruthenium Ru in the range $0\% \leq \text{Ru} \leq 2\%$;
rhenium Re in the range $0\% \leq \text{Re} \leq 2\%$;
molybdenum Mo in the range $0\% \leq \text{Mo} \leq 2\%$.

29. Use of gallium Ga according to claim 28, for the production of master alloys which are free of palladium Pd.

30. Use of gallium Ga according to claim 28, for the production of master alloys also comprising palladium in a quantity, as a weight relative to the total weight of the master alloy, within the range $0\% < \text{Pd} \leq 30\%$.

31. Use of gallium Ga according to any of the claims from 19 to 26, for the production of master alloys which are free of palladium Pd.

32. Use of gallium Ga according to any of the claims from 19 to 26, for the production of master alloys also comprising palladium in a quantity, as a weight relative to the total weight of the master alloy, within the range $0\% < \text{Pd} \leq 30\%$.

Amended claims in accordance with Rule 137(2) EPC.

1. Use of gallium Ga as a whitening element for whitening gold alloys in the production of white gold alloys which are free of nickel Ni.

2. Use of gallium Ga according to claim 1, for white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $31\% \leq \text{Au} \leq 92\%$.

3. Use of gallium Ga according to claim 2, **characterised in that** the gallium Ga is used in a quantity, as a weight relative to the total weight of the white gold alloy, within one of the ranges $1.4\% \leq \text{Ga} \leq 30.0\%$ and $3\% \leq \text{Ga} \leq 30.0\%$.

4. Use of gallium Ga according to claim 3, for the production of white gold alloys having a gold Au content, as a weight relative to the total weight of the white gold alloy, within the range $73\% \leq \text{Au} \leq 77\%$, **characterised in that** the gallium Ga is used in a

quantity, as a weight relative to the

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EUROPEAN SEARCH REPORT

Application Number
EP 08 10 3100

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