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(54) **Title:** BLACK GOLD ALLOY, CORRESPONDING GALVANIC BATH, AND PROCESS FOR OBTAINING SAID ALLOY BY ELECTRODEPOSITION

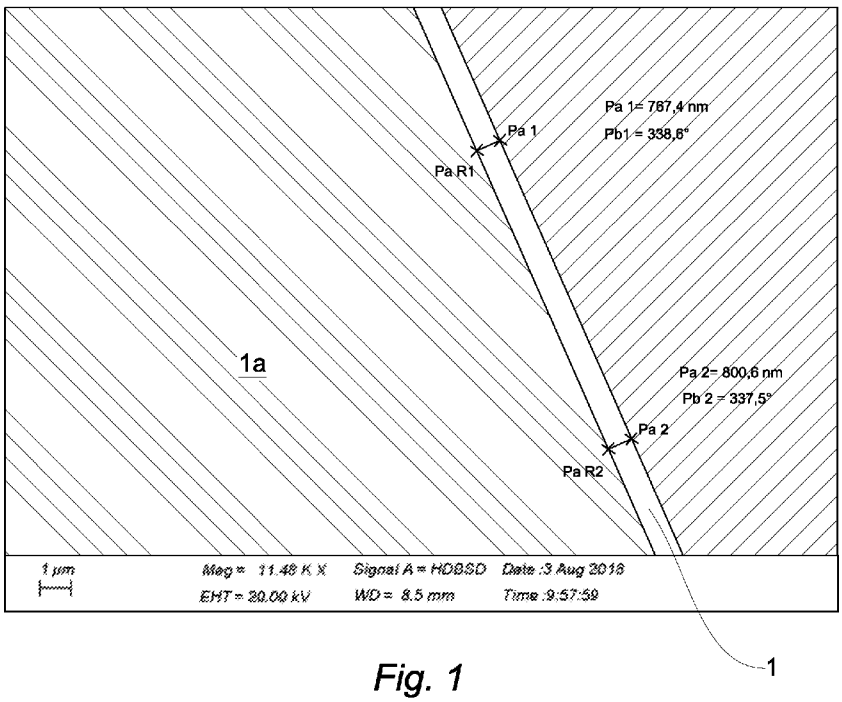

Fig. 1

(57) **Abstract:** A black gold alloy (1), galvanic bath and method for producing the black gold alloy comprising gold at from 30 to 60% by weight, palladium at from 35 to 65% by weight, iron as necessary to completely produce 100% by weight, and having a colour coordinate L* between 57 and 60.

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BLACK GOLD ALLOY, CORRESPONDING GALVANIC BATH, AND PROCESS FOR OBTAINING SAID ALLOY BY ELECTRODEPOSITION

Technological field

The present invention relates to a black gold alloy, a galvanic bath, a method for using the galvanic bath for producing the black gold alloy and use of the black gold alloy having the features present in the preamble of the independent claims.

Technological background

It is known to use ruthenium or rhodium as black finishing layers of objects having a final colouration of the "black gold" type (consistently with the commercial or industrial wording commonly used).

Typically, a deposit of black gold comprises a multi-layered system having a substrate (or base) of gold, copper or bronze on which there is deposited a layer of palladium and the system is completed with a finishing with a thin layer of black rhodium (or ruthenium).

These deposits may be produced by means of galvanic electrolytic deposition processes. Generally, the above-mentioned technologies comprise some significant limitations which are set out in greater detail below.

Firstly, the electrolytic deposits of ruthenium are difficult to produce so that it is defined as a "conformal coverage", that is to say, the capacity for covering the different portions of an object which has an overall form which it is desired to process in a uniform manner and with thicknesses which are substantially similar.

This limitation involves it being possible to produce covering portions having thicknesses less than those desired which thereby involve a zone with a

different hardness from others in accordance with the wear normally brought about by a user of the product covered in this manner.

Therefore, this implies a potential anticipated loss of the initial aesthetic characteristics of the product in some locations which can be reached only with difficulty by the ruthenium bath during deposition.

Alternatively, it is possible to select simpler forms to be coated which avoid having zones which have complex spatial criticalities to be achieved by the above-mentioned ruthenium bath. That is to say, however, this solution limits the artistic and decorative possibilities correlated with respect to the substrate, thereby reducing the attractive potential of the final product which can be obtained.

Furthermore, a covering of black gold alloy, that is to say, having a black colouration comprising ruthenium, has the limitation of having a maximum deposit thickness which can be produced equal to approximately one tenth of a micrometre. Clearly, this involves, following the normal wear of the product as a result of the standard use by a user, the black finishing layer comprising ruthenium being able to be reduced rapidly until it loses its own optical objective, thereby revealing the colouration of the layer underneath.

It may clearly be inferred that both in the case in which the original cause of the loss of the final layer comprising ruthenium is the lack of "conformal coverage" and in the case in which the cause is the excessively small thickness of the covering deposited, the removal of the black finishing is particularly evident given that the layer underneath is typically a palladium alloy which has a brightness and brilliance which are greatly superior to that of the black finishing.

For this reason, there immediately becomes perceptible to the client the loss of the functionality of the black finishing covering producing an understandable sense of critical compromise of the initial characteristics of the product as acquired.

Therefore, it is preferable to produce a multi-layered system for a black gold alloy which may have a capacity for maintaining longer than the solutions proposed by the prior art do a black colouration which is equal or similar to the initial finishing.

It is further preferable to have the possibility of producing electrolytical depositions which are less limiting in terms of the maximum thicknesses which can be produced and complex forms which can be covered in a uniform manner.

It is further appropriate to note that nickel is a material which is often used in metal alloys but which is toxic to humans and in recent years the use thereof beyond a given content, including in alloys which are intended for the application in the field of jewellery, has been greatly discouraged if not even forbidden.

Therefore, it is industrially advantageous to be able to produce an invention for a black gold alloy which may have brightness values equal or similar to those of the technical solutions present in the prior art together with an increased durability over time of those optical characteristics (because they are perceptible to the user) and which preferably does not contain nickel.

Statement of invention

An object of the present invention is to provide a black gold alloy, a galvanic bath, a method for use of the galvanic bath for producing the black gold alloy

and use of the black gold alloy which are structurally and functionally configured to overcome at least partially at least one of the disadvantages of the cited prior art.

Within this object, an objective is to provide a galvanic bath for deposition by means of galvanic electrodeposition of a black gold alloy which is capable of maintaining a black colouration which is equal or similar to the initial finishing for longer than the solutions proposed by the prior art do.

The invention produced according to the present invention is a black gold alloy having a colour coordinate value L* between 57 and 60, comprising from 30 to 60% gold by weight, from 35 to 65% palladium by weight, iron as necessary to completely produce 100% by weight.

The weight percentages set out for the above-mentioned different elements are in relation to the total weight of the black gold alloy to which the present invention relates.

In this manner, it is possible to produce a black gold layer having colourations which are equal or similar to those of the rhodium or ruthenium finishing. This technical solution involves the above-mentioned alloy being able to be used both as a black finishing layer and as an intermediate layer between a base and a black finishing layer.

It is in fact important to note that, by using this black gold alloy as an intermediate layer, the object which is covered will maintain a black colouration even following the total removal of the black finishing.

The Applicant has carried out numerous studies and dedicated substantial efforts and resources to be able to identify the range of percentages which are ideal for the respective elements contained in the black gold alloy to which the

present invention relates.

The technical solution identified by the Applicant thereby represents an ideal range of percentages of the various metal elements in an electrolytic solution as a result of which it is possible to obtain stable and well-bonded coatings of layers of black gold.

In this context, in a manner consistent with the use adopted in the prior art, the brightness or brilliance are identified and quantified with the parameter L* as defined by the Hunter coordinates L*a*b* or (L*a*b).

Furthermore, in this field, generally a black finishing is identified as a degree of black which is obtained by deposits of rhodium or ruthenium having a parameter L* which is between 57 and 60, more preferably between 58 and 60. As a result of the present invention, it is possible to obtain preferably black gold alloys having L* equal to approximately 58.6.

If the present invention is used as an intermediate layer having a black colouration, detailed results after abrasion and corrosion tests by synthetic sweat are set out below.

Preferably, the black gold alloy is an alloy in which gold is present at from 40% to 50% by weight, palladium at from 45% to 55% by weight and iron at from 5% to 15% by weight.

As a result of this technical solution, it is possible to further improve the brightness and chemical resistance of the black gold alloy produced according to the present invention with respect to the prior art, particularly when used as an intermediate layer.

According to an embodiment, the black gold alloy is an alloy in which gold is present at 39% by weight, palladium at 49% by weight, iron at 12% by

weight.

It is thereby possible to achieve ideal values of brightness and chemical resistance of the black gold alloy with respect to the prior art, particularly when used as an intermediate layer.

Preferably, the black gold alloy is a ternary alloy. This condition defines a uniform distribution of the iron inside the alloy with respect to the other two elements (gold and palladium), thereby identifying a technical solution which is ideal for obtaining a black brightness and optionally resistance behaviour with respect to chemical and mechanical attacks which are uniform in the black gold alloy to which the present invention relates.

According to an embodiment of the present invention, there is provision for a multi-layered system comprising the black gold alloy having at least one of the previously described features, and a layer of black rhodium or black ruthenium which is deposited above the above-mentioned black gold alloy as the final finishing layer.

According to an embodiment, the black gold layer has a thickness between 0.1 µm and 2 µm, preferably this thickness is 1 µm.

Preferably, the black gold alloy is obtained by an electrodeposition process which uses a galvanic bath having at least one of the features described below.

According to an embodiment of the present invention, there is provided a galvanic bath for deposition by galvanic electrodeposition of the black gold alloy having a colour coordinate value L* between 57 and 60 and preferably having at least one of the features described above, comprising aqueous solutions comprising chlorides or sulphates or sulphamates or phosphates or acetates or citrates or oxides or ammonium salts of palladium or cyanide-

containing salts of gold or ferrous or ferric sulphates or nitrates or chlorine-containing substances, in such a manner that the galvanic bath comprises gold at approximately from 0.5 to 5.0 g/l, palladium at approximately from 0.5 to 5.0 g/l, iron at approximately from 0.2 to 1.0 g/l.

Preferably, the galvanic bath comprises such aqueous solutions as to simultaneously comply with all the following concentration ratios (when in use):

- Au/Pd is between 1.2 and 3;
- Pd/Fe is between 2 and 3;
- Au/Fe is between 4 and 5.

After attentive and dedicated studies, the Applicant has found that it is sufficient for one of the three above-mentioned concentration ratios Au/Pd, Pd/Fe or Au/Fe to be outside the identified ranges to have an incorrect value of L* and therefore no longer to have a dark colouration in the deposit, that is to say, in the black gold alloy produced in this manner. Advantageously, this galvanic bath comprises aqueous solutions which allow the production, during the deposition, of a current density between 0.5 and 1.5 A/dm^2, a bath temperature between 25°C and 55°C.

Preferably, the galvanic bath for deposition by galvanic electrodeposition of a black gold alloy comprises such aqueous solutions as to allow a pH of the bath to be obtained between 8.0 and 12.0.

In this manner, the ideal conditions are obtained for being able to produce the deposition via galvanic electrodeposition.

The galvanic bath may further contain one or more complexing agents which confer stability on the entire electrolyte system, allowing greater control over the deposition of the alloyed metals. There may further advantageously be

present in the bath organic or inorganic brightenings, such as grain refiners, and one or more surfactants which act as wetting agents and which are very common in this type of electrolytes.

In this context, consistently with the adopted use in the prior art, the term "galvanic bath" is intended to be understood to be an aqueous solution which is suitable for being used in the electrogalvanic processes for the electrodeposition of the alloys.

As a result of this technical solution, it is possible to produce a black gold alloy having a colour coordinate value L* between 57 and 60 and having at least one of the above-described features. In particular, this galvanic bath allows the efficient deposition of a black gold alloy containing gold, palladium and iron having a brightness in which L* is between 57 and 60, more preferably between 58 and 60, even more preferably of 58.6 (see reasons set out below).

Preferably, the aqueous solutions for the respective metal elements of the galvanic bath are cyanide-containing salts and/or gold cyanurics, ammonium salts of palladium, palladium chloride salts or palladium sulphate salts, iron sulphate and/or iron nitrate and/or iron chloride.

It is thereby possible to electrolytically deposit the black gold alloy in an even more efficient and uniform manner.

Advantageously, the galvanic bath comprises gold at from 1 to 3 g/l, palladium at from 0.5 to 1.5 g/l, iron at from 0.5 to 0.7 g/l, and a pH of the bath between 8.5 and 10.0.

According to an embodiment, the above-mentioned galvanic bath is used with a current density between 0.7 and 1.2 A/dm^2, advantageously with a bath temperature between 27°C and 32°C.

This formulation of the galvanic bath allows the production of deposits of black gold alloy having further improved optical characteristics.

According to an embodiment, the above-mentioned galvanic bath is used with a current density of 1.0 A/dm^2 and advantageously with a temperature of 30°C.

Preferably, the bath comprises organic brightenings, such as derivatives of amines and/or halohydrin; inorganic brightenings such as grain refiners, such as bismuth salts, selenium, antimony, various sulphites and sulphonates, anionic and/or non-ionic surfactants intended as wetting agents, such as alkyl-ether phosphates, alkyl-ether sulphates, polyethylene glycols and/or quaternary ammonium salts of alkanes or aromatic compounds.

More advantageously, the galvanic bath comprises complexing agents, such as diethylenetriaminepentaacetic acid (DTPA),

nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), ethylenediamine tetra(methylene phosphonic) acid (EDTMPA), and the derivative salts thereof, aldonic acids and the derivatives thereof, such as gluconates and/or other complex carbohydrates.

Preferably, the above-mentioned galvanic bath comprises

- 2.5 g/l for Au,
- 1.5 g/l for Pd,
- 0.6 g/l for Fe,
- thereby defining such relationships for which the concentration ratios are:

– Au/Pd = 1.7,

– Pd/Fe = 2.5,

– Au/Fe = 4.2,

and advantageously the pH of the bath is 9.0.

This formulation of the galvanic bath allows the production of deposits of black gold alloy having a composition comprising gold at 39% by weight, palladium at 49% by weight and iron at 12% by weight approximately. Advantageously, this composition is in relation to alloys of black gold having a colour coordinate L* of approximately 58.6.

This condition represents an optimum technical solution as a balance of optical characteristics and resistance of the black gold alloy obtained in this manner.

Preferably, there are excluded from the composition of the above-mentioned galvanic bath

- compounds of Ni, Sn, Zn, Pb, Ir, Rh, V, Co or Ag.

These metals tend to lighten the alloy deposited and therefore to increase in an undesirable manner the value of the colour coordinate L* of the black gold alloy deposited.

The Applicant has found that the presence of the iron in the alloy is necessary in combination with the gold and palladium in order to be able to obtain the black colouration desired and in particular the value of the colour coordinate L* between 57 and 60.

The operating modes for carrying out the inventions according to the present invention will become clear from the process for depositing the black gold alloy having a colour coordinate value L* between 57 and 60 and having at least one of the features set out above in relation to this black gold alloy, comprising providing a galvanic electrodeposition device and anodes of mixed oxides, graphite or platinized titanium, providing a work tank with heating

elements and temperature control, providing a galvanic bath, in which there are dissolved aqueous solutions so as to comprise gold at from 0.5 to 5.0 g/l, palladium at from 0.5 to 5.0 g/l, iron at from 0.2 to 1.0 g/l.

Preferably, the galvanic bath comprises aqueous solutions so as to simultaneously comply with all the following concentration ratios (when prepared or in use):

- Au/Pd is between 1.2 and 3;
- Pd/Fe is between 2 and 3;
- Au/Fe is between 4 and 5.

Preferably, the aqueous solutions are such as to allow a pH of the galvanic bath to be obtained between 8.0 and 12.0.

The above-mentioned method continues with positioning of the galvanic bath inside the tank, heating the galvanic bath to a temperature between 25°C and 55°C, immersing one or more specimens to be coated in the tank containing the galvanic bath, applying a deposition current having a current density between 0.1 and 1.5 A/dm^2 for a time between 1 and 30 minutes, thereby coating the specimen with a deposit of the black gold alloy.

Preferably, the bath comprises organic brightenings, such as derivatives of amines and/or halohydrin; inorganic brightenings such as grain refiners, such as bismuth salts, selenium, antimony, anionic and/or non-ionic surfactants intended as wetting agents, such as alkyl-ether phosphates, alkyl-ether sulphates, polyethylene glycols and/or quaternary ammonium salts of alkanes or aromatic compounds.

More advantageously, the galvanic bath comprises complexing agents, such as diethylenetriaminepentaacetic acid (DTPA),

nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), ethylenediamine tetra(methylene phosphonic) acid (EDTMPA), and the derivative salts thereof, aldonic acids and the derivatives thereof, such as gluconates and/or other complex carbohydrates.

Preferably, the galvanic bath, that is to say, the electrolyte solution having the preceding composition, is placed in a tank of polypropylene and is heated to a temperature advantageously between 25°C and 55°C. By using a galvanic electrodeposition device (alternating to direct current rectifier), it is possible to deposit electrolytically the black gold alloy having at least one of the previously described features on one or more specimens which are placed inside the tank containing the galvanic bath.

Advantageously, the method continues by applying a direct deposition current so as to bring about a condition involving a surface current density between 0.5 and 1.5 A/dm^2 for a time preferably between 1 and 30 minutes.

The entire system for the electrodeposition of the black gold alloy is advantageously completed by using anodes which are made from mixed oxides or graphite and/or using anodes of mixed oxides, graphite and/or platinized titanium.

The specimen is thereby coated with a deposit of the black gold alloy having a colour coordinate value L* between 57 and 60.

According to an embodiment, the galvanic bath is heated to approximately 30°C and the deposition current preferably has a current density of approximately 1 A/dm^2 for a time of approximately 12 minutes and advantageously there are used anodes of mixed oxides.

According to an embodiment of the present invention, there is provision for

use of the galvanic bath having at least one of the above-described features for plating, with a coating of the black gold alloy, having a colour coordinate value (L*) between 57 and 60, accessories for clothing, jewellery, footwear and leather goods (for example, buckles, self-locking elements, chains, bangles, slides, drawing members, clips, shoe buckles, etc.) for high-end fashion, coating them with a black gold alloy having the features of the present invention.

Brief description of the drawings

The features and advantages of the present invention will be better appreciated from the detailed description of a preferred embodiment thereof which is illustrated by way of non-limiting example with reference to the appended drawings, in which:

- Figure 1 is a view through a scanning electron microscope (SEM) of a section of a deposit of an alloy produced according to the present invention,
- Figure 2 is another view via SEM of another point of the deposit of Figure 1,
- Figure 3 is another view by means of SEM of another point of the deposit of Figure 1,
- Figure 4 is a front view of a product coated with the deposit of the alloy of Figure 1 and a product coated with a deposit of a palladium alloy as an intermediate and black rhodium finishing placed in comparison after an abrasion test,
- Figure 5 is a front view of a product coated with the deposit of the alloy of Figure 1 and a product coated with a deposit of a palladium alloy as an intermediate and black rhodium finishing placed in comparison after immersion in synthetic sweat.

Preferred embodiment of the invention

In the Figures, there is designated 1 a black gold alloy which has a colour coordinate value L* between 57 and 60 comprising gold at from 30 to 60% by weight, palladium at from 35 to 65% by weight, iron as necessary to completely produce 100% by weight.

The Applicant has carried out scanning electron microscope (SEM) analysis with energy dispersive X-ray spectroscopy (EDS) on specimens of black gold alloy which are produced according to the present invention in order to determine the elemental composition and the thickness of the deposits of black gold alloy produced. In greater detail, the EDS sensor used is an OXFORD X-ACT with OXFORD AZ-TECH control software.

For completeness of the description, there will be set out below a table which describes a composition taken by EDS in a plurality of points (identified with Spectrum in the following Table 1) of an exemplary specimen.

	Fe	**Pd**	**Au**	Total
Spectrum 1	11.68	48.80	39.52	100
Spectrum 2	12.39	48.30	39.311	100
Spectrum 3	13.45	49.08	37.46	100
Spectrum 4	12.44	49.29	38.28	100
Spectrum 5	12.82	48.93	38.25	100
Mean	**12.56**	**48.88**	**38.56**	
St. Dev.	0.65	0.37	0.85	

Table 1: Values expressed in % by weight of the various metals present in the black gold alloy taken by EDS

With the same apparatus, the Applicant has also been able to establish the thicknesses of deposits of the black gold alloy produced according to the present invention.

More specifically, the Applicant has established the thickness of the deposit on sections of deposits of the black gold alloy according to the present invention produced on a plurality of rings of silver as a base on which there is produced an intermediate of black gold alloy (over a thickness of approximately 0.3 micrometres) and black rhodium finishing (see, for example, in Figure 4 with reference to the bottom row in relation to the test portion defined as "before the test"). These specimens have been cut in accordance with an automatic precision cutting machine (Struers Secotom 50), encased in conductive resin (Struers Polyfast) by means of a hot encasing press (Struers Citopress-10), polished by means of an automatic polisher (Struers Tegramin) with a final passage over cloth and diamond from 1 micrometre. The specimens polished in this manner have been observed with the SEM ZEISS EVO MA10 which is provided with an LaB6 filament. The control software of the instrument used is the SMARTSEM which allows precise thickness measurements to be carried out. Figures 1, 2 and 3 depict examples of galvanic deposits which have been carried out and which have the composition of the black gold alloy produced according to the present invention.

Table 2 below sets out the values of the thickness (expressed in micrometres (μm) of the deposit of the above-mentioned black gold alloy having a mean thickness of approximately 0.66 μm.

Investigation zone	Thickness (μm)

Point 1	0.77
Point 2	0.80
Point 3	0.72
Point 4	0.62
Point 5	0.69
Point 6	0.66
Point 7	0.52
Point 8	0.54
Point 9	0.65
Point 10	0.67
Mean	0.66
St. Dev.	0.09

Table 2: Values of the thicknesses at different points of the black gold alloy taken by SEM

The Applicant has further established the new and advantageous colouration values of the black gold alloy produced according to the present invention.

The colour coordinate system used by the Applicant is the CIELab system. The instrument used is a bench colorimeter of the Gretagmacbeth model Color i7. The measurements were carried out on planar specimens which have a surface of such a magnitude as to completely cover the opening of the instrument from 6 mm in diameter.

The illuminant used is the D65 as defined by ICI (International Commission on Illumination) and the measuring method is SCI (Specular Component Included). The reference standard is ISO 11664:2007. The values set out in

the table are the mean of 5 measurements carried out on the planar face of the specimens used and coated according to the present invention.

Three tables are set out below and referred to as Table 3, Table 4 and Table 5, respectively, in relation to the above-mentioned measurements of the colour coordinates of a deposit of black rhodium, black ruthenium and black gold alloy which is produced according to the teachings of the present invention, respectively.

L*	a*	b*	C	YI
58.5	0.4	1.1	1.2	3.5

Table 3. Colour coordinate of the deposit of black rhodium produced according to the teachings of the prior art.

L*	a*	b*	C	YI
59.0	0.3	1.4	1.5	4.4

Table 4. Colour coordinate of the deposit of black ruthenium produced according to the teachings of the prior art.

L*	a*	b*	C	YI
58.6	0.5	2.8	2.8	4.1

Table 5. Colour coordinate of the deposit obtained according to an embodiment of the present invention.

As can clearly be seen, the value L* (establishes the brightness of the galvanic deposit produced) of the black gold alloy produced according to the present

invention is equal to 58.6 and therefore practically equivalent to the value of L* of the deposit of black rhodium and even less than the value of L* of the black ruthenium alloy (which is clearly an improvement, the black gold alloy being an opaque alloy with values of L* which are preferably low).

Furthermore, it may be noted that the value of the Yellow Index YI is also less in the black gold alloy according to the present invention than the value of the black ruthenium deposit.

This involves a colour which is even more opaque than the black gold alloy according to the present invention with respect to the deposit of black ruthenium produced according to the teachings of the prior art.

It is immediately evident to the person skilled in the art that this value of L* and reduction of the YI involve an important advantage which is both technological and industrial. In fact, there should always be considered the fact that this black gold alloy may be used as a finishing agent (and it has been demonstrated that it can be even better than the known technical solutions) but also as an intermediate layer on which the finishing may be carried out, thereby solving the problem in relation to the appearance of the brilliant substrate once the black finishing is removed.

After attentive and dedicated studies, the Applicant has found that it is sufficient for one of the three ratios Au/Pd, Pd/Fe or Au/Fe to be outside the identified ranges to have an excessively high value of L* and therefore no longer to have a dark colouration.

The Applicant has measured the variation of colouration by carrying out a comparison between

- annular specimens which are produced from silver as a base on which there

has been deposited an intermediate coating of palladium alloy (thickness 0.3 micrometre) according to the teachings of the prior art and a finishing of black rhodium,

- annular specimens which are produced from silver as a base on which there has been deposited an intermediate coating of black gold alloy (thickness 0.3 micrometre) according to the teachings of the present invention and a finishing of black rhodium,

- laminar specimens which are produced from silver as a base on which there has been deposited an intermediate coating of black gold alloy (thickness approximately 0.6 micrometre) according to the teachings of the present invention and a finishing of black rhodium.

In order to make this property appreciable quantitatively and not only qualitatively, the Applicant has carried out colouration measurements before and after abrasion tests and chemical attack tests on the product coated with the palladium alloy 10, with black rhodium finishing (specimen A) and on the product coated with the black gold alloy 1 according to the present invention (specimen B).

In greater detail, there have been carried out two specific types of test on the above-mentioned specimens A and B which are described and discussed below.

A first type of test is the so-called "Turbula test" and is carried out by means of the Turbula model T2F instrument. The specimens to be tested are inserted inside the container with a volume of two litres together with the abrasive media and the lubricating solution. The abrasive media are ROSLER RS06/06S at a quantity of 2.5 kg; the lubricating solution is obtained by means of dilution of 50 ml of the soap "Tensioactif T77" of Wheelabrator plus in 500 ml

of demineralised water. The test lasted 30 minutes at a mean rotation speed of 62 rpm.

A Turbula test was thereby carried out on three specimens A and three specimens B. There are set out below in Tables 6 and 7 the respective values of the colour coordinates of the specimens A and the specimens B after the Turbula test.

L*	a*	b*	C	YI
62.50	1.15	2.5	2.75	4.27

Table 6. Colour coordinate of the specimen A after the Turbula test.

L*	a*	b*	C	YI
57.5	0.6	1.5	1.62	3.95

Table 7. Colour coordinate of the specimen B after the Turbula test.

The purpose of this test is to evaluate the variation in the colour coordinate following the probable and reasonable virtually total removal of the upper layer of black rhodium.

As can clearly be seen in the Tables set out above, the specimen B shows a variation of L* which is very small and which changes from the initial value of 58.6 to the final value of 57.5.

Conversely, the value of L* of the specimen A changes from 58.5 to 62.50, substantially leaving the ideal range of L* which is between 57 and 60.

In fact, as is reasonable to expect, the Turbula test simulates the condition of removal of the upper layer of black rhodium finishing, exposing the layer below. It is immediately evident that in the case of the specimen A, once the

finishing layer is removed and the lower layer of palladium alloy is exposed, the colouration appears much more bright and brilliant in respect of the palladium layer, producing an immediate sensation in the user of a modification of and/or damage to the initial characteristics of the specimen A.

Instead, the specimen B maintains a dark colouration as desired, even following the Turbula test and the reasonable removal of the upper layer of black rhodium. Clearly, therefore, a user would be more satisfied with a product which is produced according to the present invention, given that the specimen B maintains the black initial colouration in a substantially unchanged manner even following the Turbula test.

Furthermore, it is also important to note the variations of the yellow index (hereinafter, YI, Yellow Index) of the specimen A and specimen B following the Turbula test. The specimen A changes the value of YI from 3.50 to 4.27, thereby having a colouration which is more "warm and clear", absolutely counter and opposite to the effect which it is desired to produce with the black colouration.

Conversely, the specimen B changes the value of YI from 4.1 to 3.95, thereby having a variation less than YI with respect to the specimen A and an absolute value which is even less than the initial value (therefore, "darker").

A second type of test used is the so-called "synthetic sweat test" which is carried out according to the French standard NF S 80-772:2010-10. This standard provides for the specimens to be tested to be supported on a layer of cotton which is impregnated with synthetic sweat solution. The synthetic sweat is obtained by dissolving in water 100 grammes of NaCl and 50 grammes of lactic acid, bringing the whole to a final volume of one litre. The

crystalliser in which the cotton and the specimens are supported is closed with parafilm and placed in a temperature-controlled bath at 55°C for 24 hours.

With reference to Figures 4 and 5, there are shown test examples for abrasion and synthetic sweat attack, respectively.

In particular, and at a purely exemplary level, the product coated with a deposit of the black gold alloy 1 produced according to the present invention is placed in comparison, after the test involving an attack with synthetic sweat, with a product which is coated with a palladium alloy 10 with finishing with black rhodium. Figure 4 shows front views of the two products after an abrasion test, while Figure 5 shows front views of the two products after the test with synthetic sweat.

It is evident that the product comprising the palladium alloy 10 (set out in the upper row in Figures 4 and 5), once the black rhodium finishing coating is affected, has a colouration which is very different from the initial colouring, thereby exposing the silver substrate 1a underneath, therefore being much more brilliant and bright with respect to the pre-test condition.

By comparison, it may clearly be noted in Figures 4 and 5 that the product which is coated with the black gold alloy 1 according to the present invention (identifiable with the products set out in the lower portion in Figures 4 and 5) has a virtually unchanged colouration with respect to the initial colouration, including after being subjected to the abrasion test or test involving an attack with synthetic sweat. In particular, in Figure 4 there may be noted the comparison between a front surface 2 of the product which is coated with the black gold alloy 1 and black rhodium finishing and a front surface 12 of the product which is coated with the palladium alloy 10 and black rhodium

finishing.

A test involving an attack with synthetic sweat has thereby been carried out on a specimen A and on a specimen B (identified as set out in relation to the Turbula test). There are set out below in Tables 8 and 9 the respective values of the colour coordinate of the specimen A and the specimen B after the test involving an attack with synthetic sweat.

L*	a*	b*	C	YI
61.8	2.5	3.51	4.31	5.15

Table 8. Colour coordinate of the specimen A after the test involving an attack with synthetic sweat.

L*	a*	b*	C	YI
57.9	0.45	1.45	1.51	3.75

Table 9. Colour coordinate of the specimen B after the test involving an attack with synthetic sweat.

In this case, it may also immediately be appreciated how the value of L* is significantly increased in the specimen A following the attack with synthetic sweat.

In fact, the value of L* in the specimen A changes from 58.5 to 61.8, showing an evident movement of the colour coordinate towards a lighter, brighter and more brilliant colouration.

Conversely, the value of L* in the specimen B changes from 58.6 to 57.9, remaining completely within the desired ranges of L* for the "black gold" alloy

as defined above.

Similarly, the value of YI also shows a behaviour which is comparable with that shown after the Turbula test for the specimens A and B.

In greater detail and with further reference to Figures 7 and 8, the value of YI changes from 3.5 to 5.15, having a chromatic variation which is very significant and which produces a colouration which is more "warm and clear", absolutely counter and opposite to the effect which it is desired to produce with the black colouration.

Conversely, the specimen B changes the value of YI from 4.1 to 3.75, thereby having a variation less than YI with respect to the specimen A and even less than the initial value (therefore, "darker").

As may clearly be seen from the values set out in Tables 8 and 9, the deposit which is produced with the black gold alloy 1 according to the present invention (specimen B) has a variation, both following abrasion and following an attack with synthetic sweat, of all the values analysed which is substantially less than the variation which is undergone by the deposit which is produced with the palladium alloy 10 according to the teachings of the art (specimen A).

Preferably, the black gold alloy is an alloy in which the gold is present at from 40% to 50% by weight, the palladium at from 45% to 55% by weight and the iron at from 5% to 15% by weight.

Advantageously, the black gold alloy is an alloy in which the gold is present at 39% by weight, the palladium at 49% by weight and the iron at 12% by weight.

According to an embodiment, the black gold alloy 1 is a ternary alloy.

This means that the iron is distributed uniformly inside the structure of the

black gold alloy 1.

According to an embodiment of the present invention, there is provided a multi-layered system comprising the black gold alloy, at least one of the above-described characteristics and a black rhodium or black ruthenium layer which is deposited above the above-mentioned black gold alloy as the last finishing layer.

According to an embodiment, the black gold layer has a thickness between 0.1 micrometre and 2 micrometres, preferably this thickness is 1 micrometre.

For the person skilled in the art, the fact that the rhodium layer is deposited on or in the region of the black gold alloy 1 does not constitute a limitation to use this industrial technique but simply identifies a possible technological example, the alternatives to which may be, for example, lamination, etc.

According to an embodiment of the present invention, there is provided a galvanic bath for the deposition by means of galvanic electrodeposition of a black gold alloy having at least one of the above-described features, comprising aqueous solutions comprising chlorides or sulphates or sulphamates or phosphates or acetates or citrates or oxides or ammonium salts of palladium or palladium chloride or palladium sulphate or cyanide-containing salts of gold or ferrous or ferric sulphates or nitrates or chlorine-containing substances, in such a manner that the galvanic bath comprises gold at approximately from 0.5 to 5.0 g/l, palladium at approximately from 0.5 to 5.0 g/l, iron at approximately from 0.2 to 1.0 g/l.

Preferably, the galvanic bath comprises aqueous solutions so as to simultaneously comply with all the following concentration ratios (when in use):

- Au/Pd is between 1.2 and 3;

- Pd/Fe is between 2 and 3;
- Au/Fe is between 4 and 5.

There are set out below tests carried out by the Applicant which are advantageous to define even more clearly how the black colouration ($57<L^*<60$) desired is the result of a specific combination of predetermined restricted composition ranges of the alloy which is obtained by using a specific galvanic bath.

Example 1.

There is used a galvanic bath for the deposition by means of galvanic electrodeposition of a gold alloy having in solution the following concentrations:

- Au = 1.5 g/l,
- Pd = 1.5 g/l
- Fe = 0.6 g/l.

These values imply ratios Au/Pd = 1 (outside the reference range of the present invention), Pd/Fe = 2.5 (within the reference range of the present invention), Au/Fe = 2.5 (outside the reference range of the present invention). The colour coordinates measured on the deposits of alloy obtained in this manner are: L = 73.0; a = 1.1; b = 4.7; c = 4.8; YI = 12.0.

It is immediately apparent that a bath produced according to Example 1, though with respect to a concentration ratio of the three of the present invention, does not have a colour coordinate L* between 57 and 60 and therefore cannot be considered to be a black gold alloy.

Example 2.

There is used a galvanic bath for the deposition by means of galvanic

electrodeposition of a gold alloy having in solution the following concentrations:

- Au = 3.5 g/l,
- Pd = 1.5 g/l
- Fe = 0.1 g/l.

These values imply ratios Au/Pd = 2.3 (inside the reference range of the present invention), Pd/Fe = 15 (outside the reference range of the present invention), Au/Fe = 35 (outside the reference range of the present invention).

The colour coordinates measured on the deposits of alloy obtained in this manner are: L = 82.6; a = 6.0; b = 24.2; c = 24.96; YI = 38.5.

It is also immediately apparent in this case that a bath produced according to Example 2, though with respect to a concentration ratio of the three of the present invention, does not have a colour coordinate L* between 57 and 60 and therefore cannot be considered to be a black gold alloy. Particularly in this last case, the colour coordinates identify in an unequivocal manner a yellow tone (the coordinate b is high – the b is the parameter which changes from low values which identify bluer tonality to greater values which identify tonalities which become more and more yellow – this is also confirmed by a high value of the yellow index: the greater this parameter is, the greater is the degree of yellow colouration of the material measured).

Advantageously, this galvanic bath comprises aqueous solutions which allow the production, during the deposition, of a current density between 0.5 and 1.5 A/dm^2, a temperature of the bath between 25°C and 55°C.

Preferably, the galvanic bath for the deposition by means of galvanic electrodeposition of a black gold alloy comprises aqueous solutions so as to allow a pH of the bath to be obtained between 8.0 and 12.0.

The galvanic bath may further advantageously contain one or more complexing agents which confer stability on the entire electrolyte system in addition to allowing greater control over the deposition speed of the various metal elements to constitute the electrodeposited alloy. There may further also be present in the bath organic and inorganic brightenings, such as grain refiners, and also one or more surfactants which act as wetting agents, which are very common in this type of electrolytes.

Preferably, the aqueous solutions (that is to say, the dissolved saline species) for the respective metal elements included and advantageously dissolved in the galvanic bath are: copper cyanide and/or copper carbonate, sodium stannate and/or potassium stannate, zinc acetate or zinc cyanide or zinc oxide and rhodium phosphate and/or rhodium sulphate.

Preferably, the aqueous solutions for the respective metal elements of the galvanic bath are cyanide-containing salts and/or gold cyanurics, palladium ammonium salts, palladium chloride or palladium sulphate, iron sulphate and/or iron nitrate and/or iron chloride.

According to an embodiment, the aqueous solutions for the respective metal elements of the galvanic bath may also be palladium sulphate or palladium chloride or palladium nitrate or palladium nitrite or gold sulphite or potassium gold sulphite or ammonium gold sulphite or iron sulphate, iron nitrate or iron chloride.

Advantageously, the galvanic bath comprises gold at from 1 to 3 g/l, palladium at from 0.5 to 1.5 g/l, iron at from 0.5 to 0.7 g/l and a pH of the bath between 8.5 and 10.0.

According to an embodiment, the above-mentioned galvanic bath is used with

a current density between 0.7 and 1.2 A/dm^2, advantageously with a bath temperature between 27°C and 32°C.

Preferably, the bath comprises organic brightenings, such as derivatives of amines and/or halohydrin; inorganic brightenings such as grain refiners, such as bismuth salts, selenium, antimony, anionic and/or non-ionic surfactants intended as wetting agents, such as alkyl-ether phosphates, alkyl-ether sulphates, polyethylene glycols and/or quaternary ammonium salts of alkanes or aromatic compounds.

Further advantageously, the galvanic bath comprises complexing agents, such as diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), ethylenediamine tetra(methylene phosphonic) acid (EDTMPA), and the derivative salts thereof, aldonic acids and the derivatives thereof, such as gluconates and/or other complex carbohydrates.

Preferably, the galvanic bath comprises 2.5 g/l for Au, 1.5 g/l for Pd and 0.6 g/l for Fe, thereby defining such relationships for which: Au/Pd = 1.7, Pd/Fe = 2.5 and Au/Fe = 4.2, and advantageously the pH of the bath is 9.0.

According to an embodiment, the above-mentioned galvanic bath is used with a current density of 1.0 A/dm^2 and advantageously a temperature of 30°C.

Preferably, there are excluded from the composition of the above-mentioned galvanic bath

- compounds of Ni (nickel), Sn (tin), Zn (zinc), Pb (lead), Co (cobalt) and/or advantageously also other precious metals such as: Ir (iridium), Rh (rhodium), V (vanadium), Ag (silver).

In fact, those metals tend to further lighten the alloy which is deposited,

thereby increasing the colour coordinate value L* and moving away from the black colouration desired.

It is clear that traces or contaminations resulting from process imperfections or other causes are taken into consideration by the person skilled in the art in accordance with intrinsic characteristics of the process itself for producing the deposits.

The operating modes for producing the inventions according to the present invention will become clear from the process for depositing the black gold alloy, having a colour coordinate value L* between 57 and 60 and at least one of the previously described features, comprising providing a galvanic electrodeposition device and anodes of mixed oxides, graphite or platinized titanium, providing a work tank with heating elements and temperature control, providing a galvanic bath, in which there are dissolved aqueous solutions so as to comprise gold at from 0.5 to 5.0 g/l, palladium at from 0.5 to 5.0 g/l, iron at from 0.2 to 1.0 g/l.

Preferably, the aqueous solutions are such as to simultaneously comply with all the following concentration ratios:

- Au/Pd is between 1.2 and 3;
- Pd/Fe is between 2 and 3;
- Au/Fe is between 4 and 5,

and the aqueous solutions are preferably such as to allow a pH of the bath to be obtained between 8.0 and 12.0.

- The above-mentioned method continues with positioning the galvanic bath inside the tank, heating the galvanic bath to a temperature between 25°C and 55°C, immersing one or more specimens 1a to be

coated in the tank containing the galvanic bath, applying a deposition current having a current density between 0.1 and 1.5 A/dm^2 for a time between 1 and 30 minutes, thereby coating the specimen with a deposit of the black gold alloy having a colour coordinate value L* between 57 and 60, and being the black gold alloy 1 comprising

- from 30 to 60% gold by weight,
- from 35 to 65% palladium by weight,
- iron as necessary to completely produce 100% by weight.

The product obtained in this manner has a final outer layer of black gold 1 which may itself already be considered to be equivalent to a finishing and therefore already be ready for release on the market without additional coatings.

Alternatively, the method continues with deposition of a black rhodium layer as a finishing on the layer of black gold alloy 1.

Preferably, the galvanic bath is heated to approximately 30°C.

According to an embodiment, the method provides for a deposition speed of approximately 1 micrometre in from 12 to 15 minutes at a current density of approximately 1.0 A/dm^2.

According to an embodiment, some examples of galvanic baths constructed according to the teachings of the present invention are set out below and comprise:

Example 3

- 1.0-2.0 g/l of palladium as palladium tetraamine dichloride $[Pd(NH_3)_4]Cl_2$ or palladium tetraamine sulphate $[Pd(NH_3)_4]SO_4$
- 2.0-3.0 g/l of gold as gold (I) in the formulation $K[Au(CN)_2]$ or as gold

(III) in the formulation $K[Au(CN)_4]$

- 0.5-0.7 g/l of iron as iron sulphate or iron nitrate or iron chloride,
- pH 9.0-10.0,
- bath temperature 30°C,
- current density 1.0 A/dm^2.

The entire system for electrodeposition of the black gold alloy 1 is advantageously completed by using anodes which are made from mixed oxides or graphite and/or platinized titanium.

The specimen is thereby coated with a deposit of the black gold alloy.

According to an embodiment, the galvanic bath is heated to approximately 30°C and the deposition current preferably has a current density of approximately 1 A/dm^2 for a time of approximately 12 minutes and mixed oxide anodes are used.

The black gold alloy 1 according to the present invention having at least one of the above-described features can be used as a protective deposit and has greater brightness for a specimen 1a which acts as a substrate. Furthermore, this black gold alloy 1 having a colour coordinate value L* between 57 and 60 may be used as an intermediate layer, on which to deposit an additional layer of precious metal or non-precious metal and advantageously white, such as, for example, rhodium, in order to produce the so-called finishing of the specimen.

This black gold alloy 1 and/or this galvanic bath is/are an optimum solution including when used for plating, with coatings of black gold alloy, having a colour coordinate value (L*) between 57 and 60, accessories for clothing, jewellery, footwear and leather goods (for example, buckles, chains, bangles,

self-locking elements, slides, shoe buckles, etc.) for high-end fashion.

CLAIMS

1. A galvanic bath for deposition by galvanic electrodeposition of a black gold alloy (1) which has a colour coordinate value L* between 57 and 60, comprising

- aqueous solutions comprising chlorides or sulphates or sulphamates or phosphates or acetates or citrates or oxides or ammonium salts of palladium or cyanide-containing salts of gold or ferrous or ferric sulphates or nitrates or chlorine-containing substances, in such a manner that the galvanic bath comprises
  - gold at from 0.5 to 5.0 g/l,
  - palladium at from 0.5 to 5.0 g/l,
  - iron at from 0.2 to 1.0 g/l,
- the aqueous solutions being such as to simultaneously comply with all the following concentration ratios
  - Au/Pd is between 1.2 and 3;
  - Pd/Fe is between 2 and 3;
  - Au/Fe is between 4 and 5,
- the aqueous solutions being such as to allow a pH of the bath to be obtained from 8.0 to 12.0.

2. A galvanic bath according to the preceding claim, wherein the aqueous solutions for the respective metal elements are

- cyanide-containing salts and/or gold cyanurics,
- ammonium salts of palladium, and/or salts of palladium chloride or palladium sulphate,
- iron sulphate and/or iron nitrate and/or iron chloride.

3. A galvanic bath according to claim 1 or claim 2, comprising

- gold at from 1 to 3 g/l,
- palladium at from 0.5 to 1.5 g/l,
- iron at from 0.5 to 0.7 g/l,
- pH of the bath between 8.5 and 10.0.

4. A galvanic bath according to any one of claims 1 to 3, comprising

- organic brightenings, such as derivatives of amines and/or halohydrin; inorganic brightenings such as grain refiners, such as bismuth salts, selenium, antimony,
- anionic and/or non-ionic surfactants intended as wetting agents, such as alkyl-ether phosphates, alkyl-ether sulphates, polyethylene glycols and/or quaternary ammonium salts of alkanes or aromatic compounds.

5. A galvanic bath according to the preceding claim, comprising

- complexing agents, such as diethylenetriaminepentaacetic acid (DTPA),
- nitrilotriacetic acid (NTA),
- ethylenediaminetetraacetic acid (EDTA),
- ethylenediamine tetra(methylene phosphonic) acid (EDTMPA),
- and the derivative salts thereof, aldonic acids and the derivatives thereof, such as gluconates and/or other complex carbohydrates.

6. A galvanic bath according to one or more of claims 1 to 5, comprising

- gold at 2.5 g/l,
- palladium at 1.5 g/l,
- iron at 0.6 g/l,
- thereby defining ratios so that the concentration ratios are:

- Au/Pd = 1.7,

- Pd/Fe = 2.5,

- Au/Fe = 4.2,

- and the pH of the bath is 9.0.

7. A galvanic bath according to one or more of the preceding claims, wherein there are excluded from the composition of the above-mentioned galvanic bath

- compounds of Ni, Sn, Zn, Pb, Ir, Rh, V, Co or Ag.

8. A process for depositing a black gold alloy (1) having a colour coordinate value L* between 57 and 60, comprising:

- providing a galvanic electrodeposition device and anodes of mixed oxides, graphite or platinized titanium,
- providing a work tank with heating elements and temperature control,
- providing a galvanic bath, in which there are dissolved aqueous solutions so as to comprise
  - gold at from 0.5 to 5.0 g/l,
  - palladium at from 0.5 to 5.0 g/l,
  - iron at from 0.2 to 1.0 g/l,

  - the aqueous solutions being such as to simultaneously comply with all the following concentration ratios
  - Au/Pd is between 1.2 and 3,
  - Pd/Fe is between 2 and 3,
  - Au/Fe is between 4 and 5,
  - the aqueous solutions being such as to allow a pH of the bath to be obtained from 8.0 to 12.0,
- positioning the galvanic bath inside the tank;

- heating the galvanic bath to a temperature between 25°C and 55°C,
- immersing one or more specimens (1a) to be coated in the tank containing the galvanic bath,
- applying a deposition current having a current density between 0.1 and 1.5 A/dm^2 for a time between 1 and 30 minutes,
- thereby coating the specimen (1a) with a deposit of the black gold alloy (1) having a colour coordinate value L* between 57 and 60, and being the black gold alloy (1) comprising
  - from 30 to 60% gold by weight,
  - from 35 to 65% palladium by weight,
  - iron as necessary to completely produce 100% by weight.

9. A process according to the preceding claim, wherein

- the galvanic bath is heated to approximately 30°C,
- the deposition current has a current density of approximately 1 A/dm^2 for a time of approximately 12 minutes.

10. A black gold alloy (1) having a colour coordinate value L* between 57 and 60, comprising

- from 30 to 60% gold by weight,
- from 35 to 65% palladium by weight,
- iron as necessary to completely produce 100% by weight.

11. A black gold alloy (1) according to claim 10, wherein the black gold alloy (1) is obtained by means of an electrodeposition process which uses a galvanic bath according to any one of claims 1 to 8.

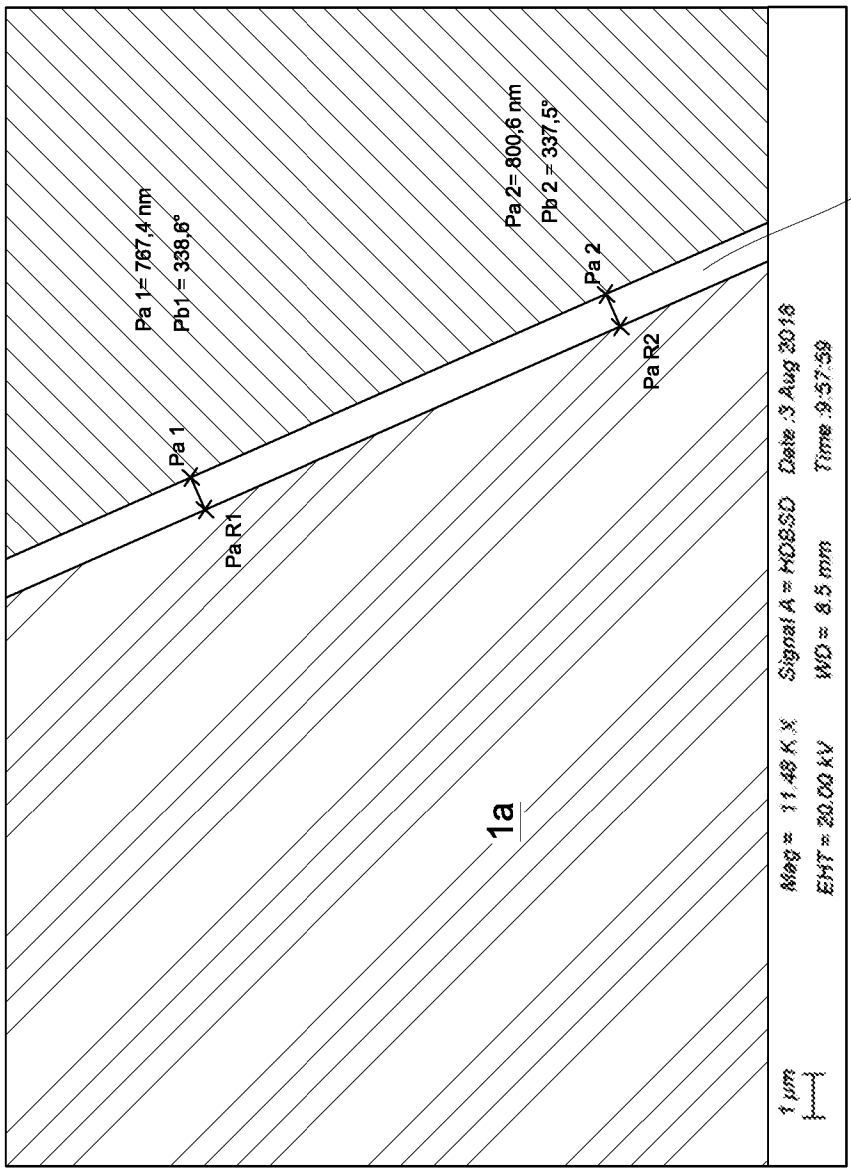
12. A black gold alloy (1) according to claim 10 or claim 11, wherein

- gold is contained at 39% by weight,

- palladium is contained at 49% by weight,
- iron is contained at 12% by weight.

13. A black gold alloy (1) according to any one of claims 10 to 12, wherein the black gold alloy (1) is a ternary alloy.

14. Use of a galvanic bath according to any one of claims 1 to 7 for plating, with a coating of black gold alloy having a colour coordinate value (L*) between 57 and 60, accessories for clothing, jewellery, footwear and leather goods for high-end fashion.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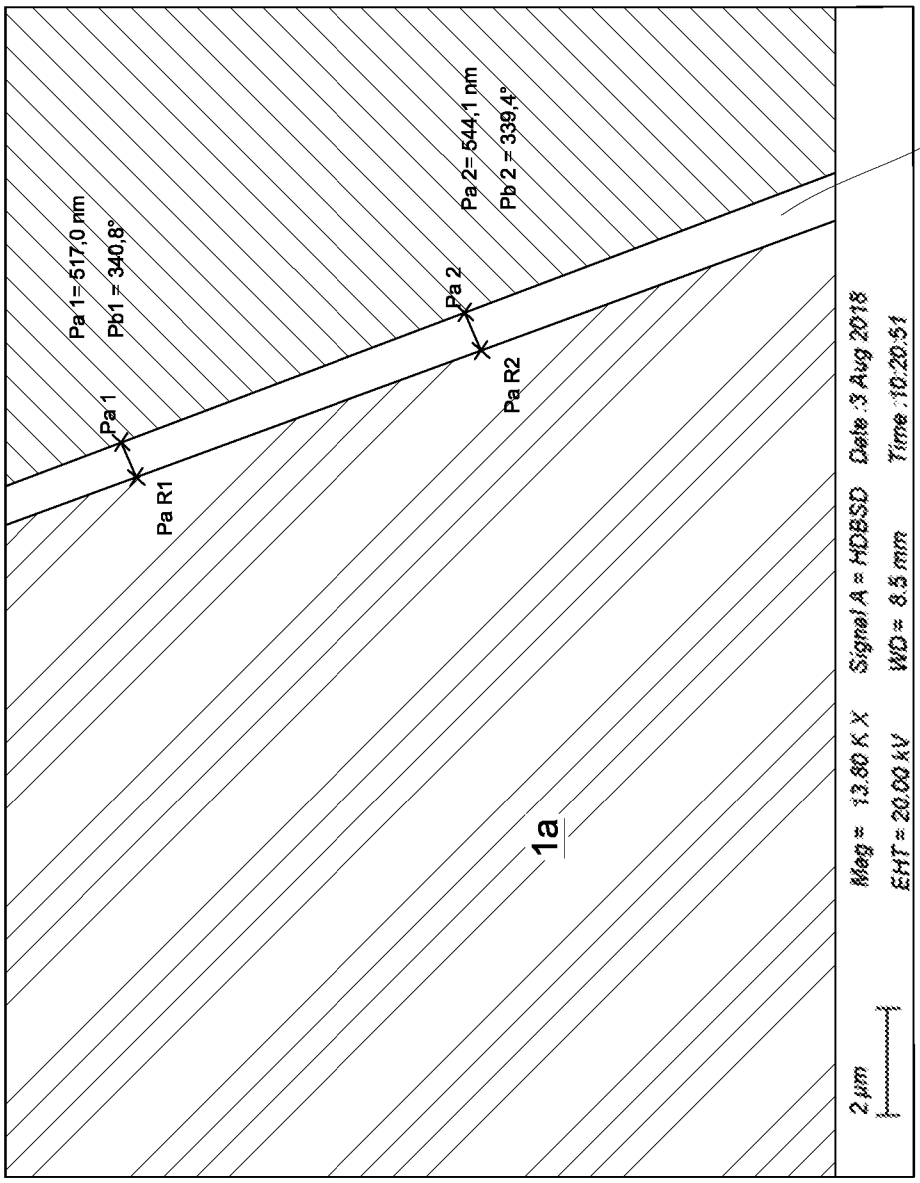
Pb1 = 338,6°
Pa 2= 800,6 nm
Pb 2 = 337,5°
Pa 2
Pa 1
Pa R2
Pa R1
1
1a
1 µm
Mag = 11.48 K X
EHT = 20.00 kV
Signal A = HDBSD
WD = 8.5 mm
Date :3 Aug 2016
Time :9:57:59

Fig. 1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Pb1 = 340,8°
Pa 1
Pa R1
Pa 2= 544,1 nm
Pb 2 = 339,4°
Pa 2
Pa R2
1a
1
2 µm
Mag = 13.80 K X
EHT = 20.00 kV
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WD = 8.5 mm
Date :3 Aug 2018
Time :10:20:51

Fig. 2

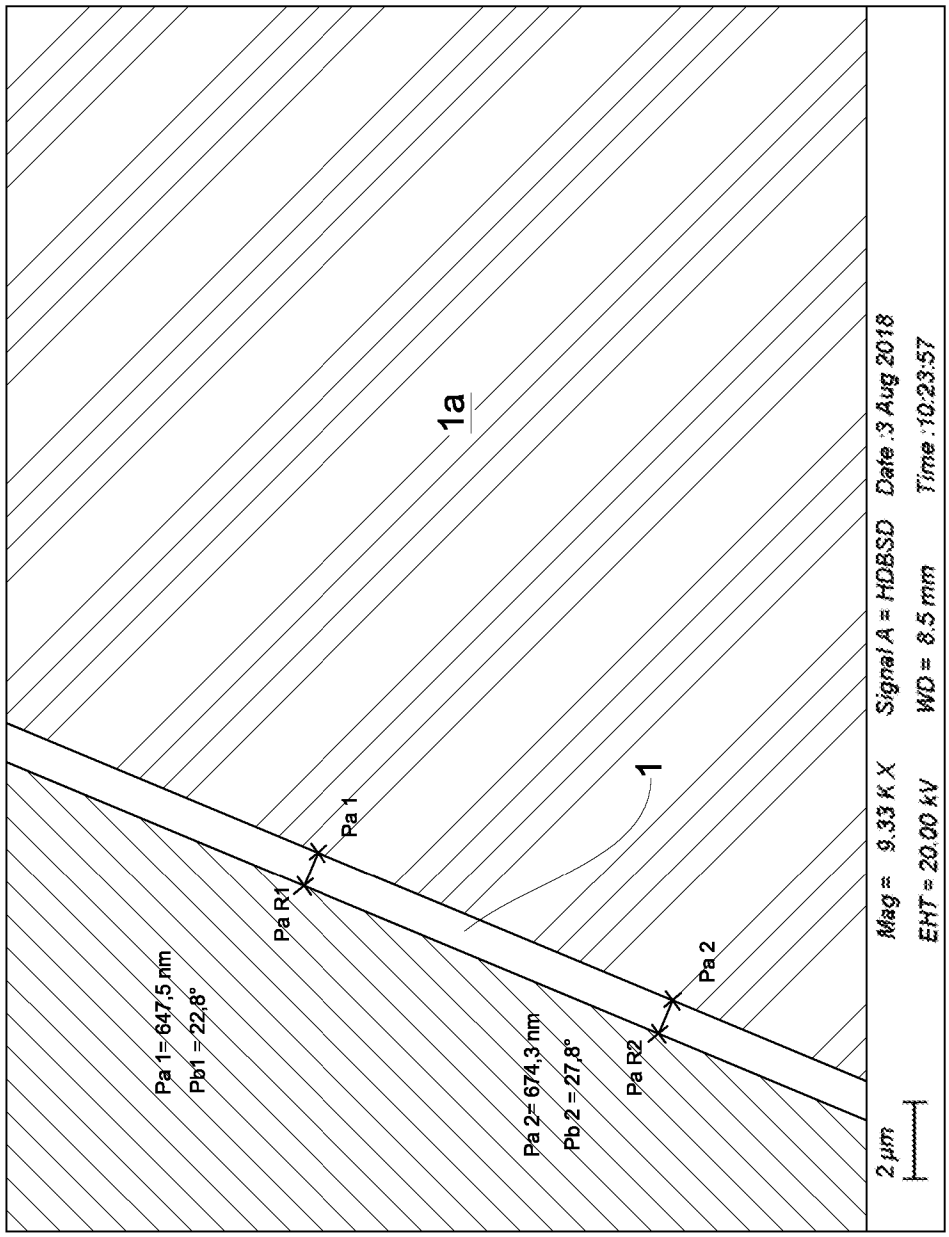
1a
1
Pa 1
Pa R1
Pa 2
Pa R2
Pa 1= 647,5 nm
Pb1 = 22,8°
Pa 2= 674,3 nm
Pb 2 = 27,8°
2 µm
Mag = 9.33 K X
EHT = 20.00 kV
Signal A = HDBSD
WD = 8.5 mm
Date :3 Aug 2018
Time :10:23:57

Fig. 3

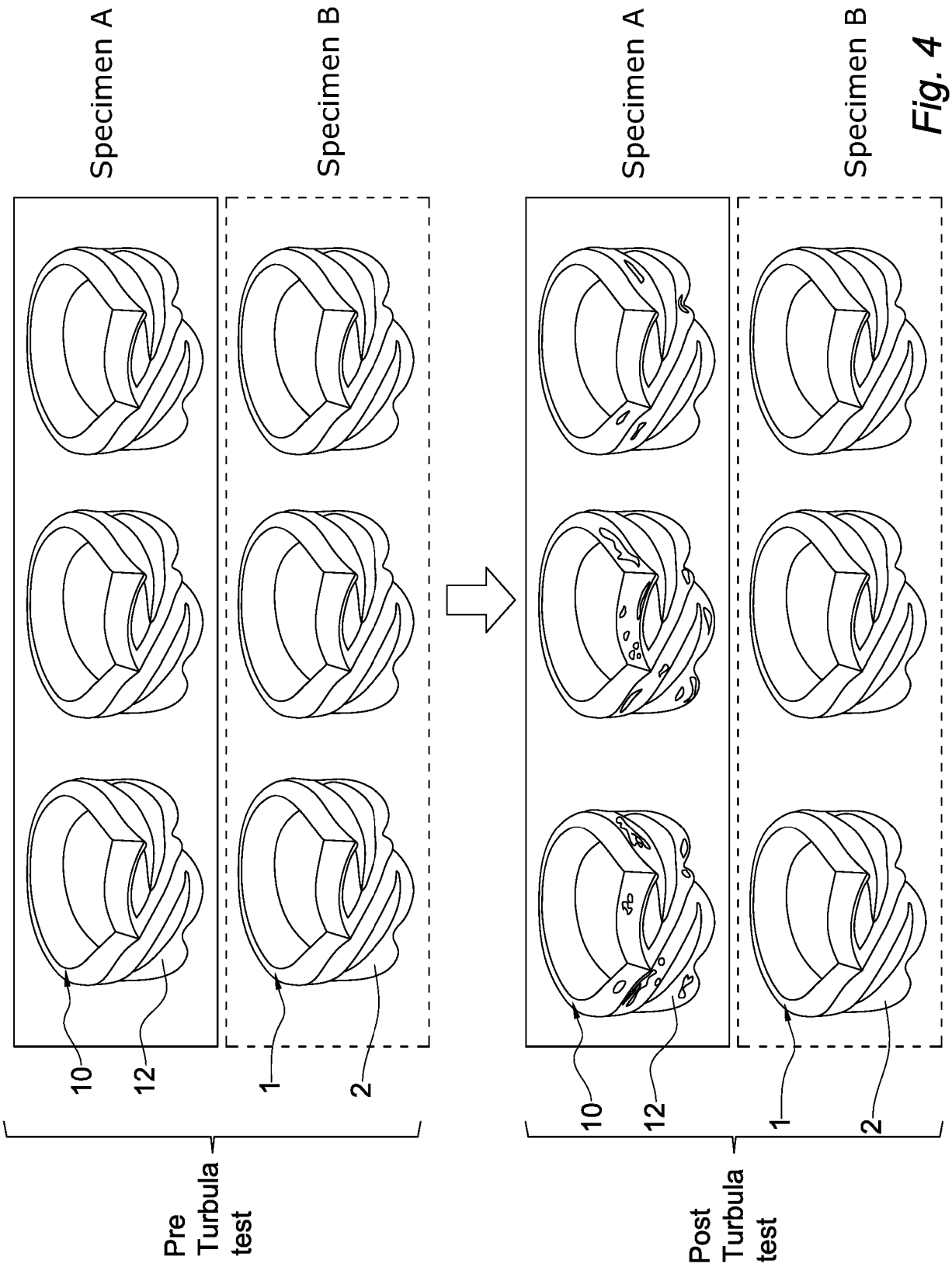
Specimen A
Specimen B
Specimen A
Specimen B
10
12
1
2
10
12
1
2
Pre Turbula test
Post Turbula test

Fig. 4

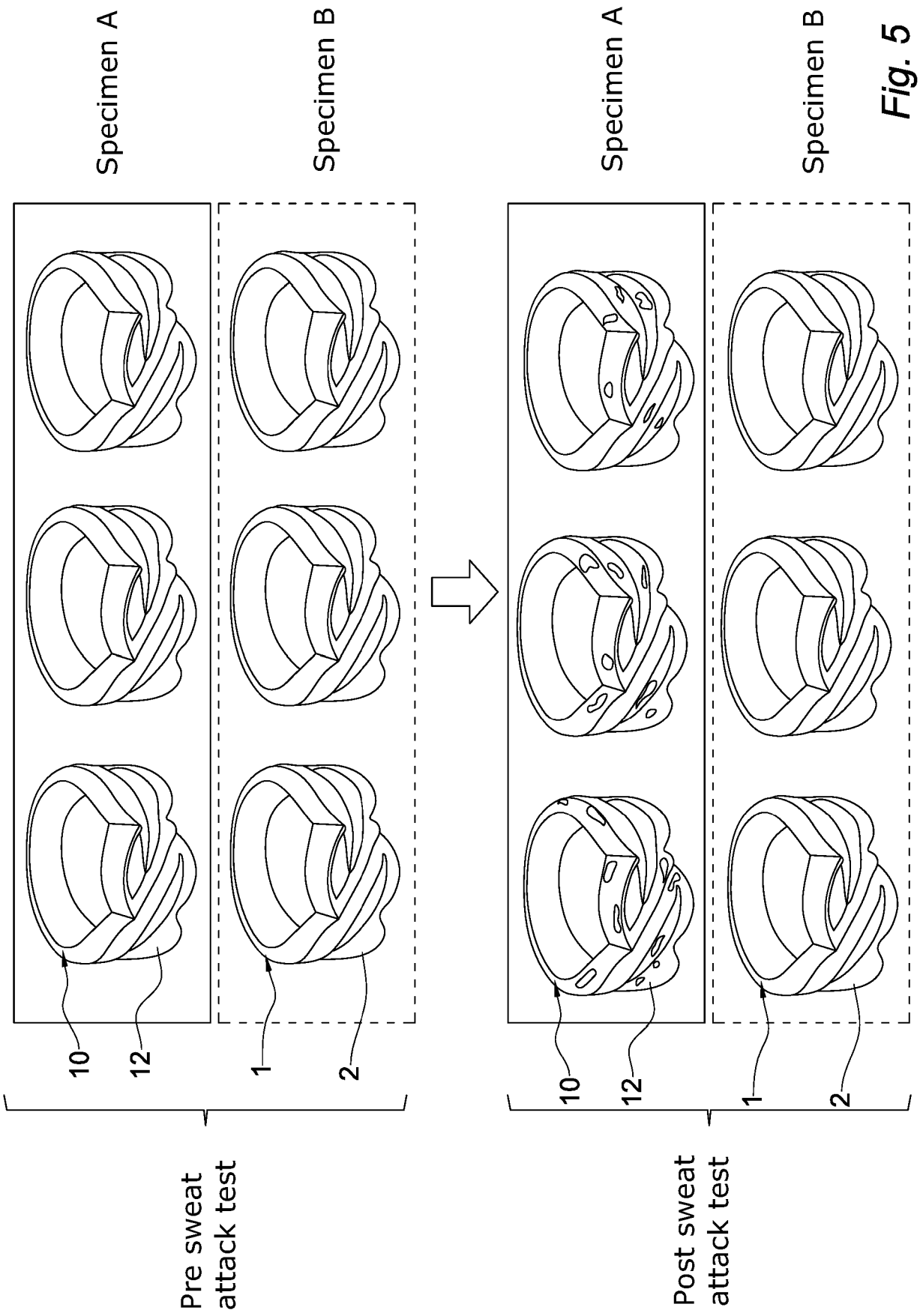
Specimen A
Specimen B
Specimen A
Specimen B
10
12
1
2
10
12
1
2
Pre sweat attack test
Post sweat attack test

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/057333

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25D7/00 C25D3/56 C25D3/62 C22C5/02 C22C5/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25D C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AT 201 867 B (ENGELHARD IND INC [US]) 26 January 1959 (1959-01-26) table 1 -----	10,11,13
Y	EP 2 781 629 A1 (BLUCLAD S R L [IT]) 24 September 2014 (2014-09-24) paragraph [0003]; claims 1-4, 6 paragraph [0012] paragraph [0014] paragraph [0016] paragraph [0019] paragraph [0024] paragraph [0026] paragraph [0028] - paragraph [0029] ----- -/--	1-9,14

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 December 2019	17/12/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Telias, Gabriela

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/057333

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No
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