

A DECORATIVE ARTICLE COATED WITH A SURFACE LAYER OF GOLD OR
A GOLD-CONTAINING MATERIAL AND A METHOD FOR ITS PRODUCTION

- 5 This invention relates to a decorative article coated with a surface layer of gold or gold-containing material having an underlayer of a high hardness material with a gold colour.
- 10 As decorative articles may be principally mentioned: writing implements, cigarette lighters, spectacle frames, watch cases and watch straps as well as ornaments of all types.
- 15 On the one hand it is desired with such articles to have a real gold surface with a "gold colour" typical of gold and gold plate in conjunction with the "brilliance" also typical of gold, but on the other hand it is desired to keep the amount of gold required per
- 20 unit area as small as possible on cost grounds. On this basis, methods have long since been developed for producing surface layers of gold or gold-containing material. As here also the thickness of the surface layers and/or other gold parts are to be kept as low as
- 25 possible on cost grounds, there was an increased risk of a premature wearing away of the surface layer from the articles, especially at their projecting parts.
- Depending upon the type of demands placed on the

article, a mechanical and/or chemical wear can be involved, as for example by perspiration, detergents etc.

5 It is known from DE-OS 2825513 to provide an underlayer of titanium nitride beneath the surface layer, which because of its gold colour disguises wearing away of the surface layer with the passage of time. It is also known from the same publication that the gold colour of the underlayer on the one hand and
10 the surface layer on the other hand can be influenced or adapted to one another by admixing or alloying other materials.

15 It has in any event been shown that titanium nitride can not on its own produce a realistic gold colour, which is also apparent from the diagram of the publication referred to. It has, however, been shown further that titanium nitride even with admixture of further metals, does not exhibit the "brilliance" that
20 belongs to gold, and thus has a more matt effect. Matt surfaces, however, generally look darker, so that with the known articles the parts that show through appear darker on account of lacking brilliance even though they have the same colour. So for example by measurements
25 with a colour measuring apparatus of the type "MacBeth 1500" using a light source of type C the so-called CIELAB-units are determined for a whole series of coating materials. The results of the measurements are

summarised in the table at the end of the description;
so far as the diagrams of the spectral dependance on the
reflection values are shown, they are to be found in the
annexed figures as well as in the table. Details of the
measuring process are given in the detailed description.

Of particular significance under the CIELAB-units is in
this instance the L*-value, which characterises the
brilliance of the coating material. It is to be noted
that the L*-value for different gold alloys as well as
copper and silver lies above 85. This value represent a
high brilliance.

In practice, therefore, coatings with a
brilliance value above 80, preferably 85, are chosen
preferentially for use as decorative coatings. The known
underlayers of TiN, however, have an L*-value of only
73, which represents a much reduced brilliance. Here it
is to be noted that a deep matt coating does not have a
zero L*-value, but a value between about 40 and 50.

The present invention provides improved coated
decrative articles and a method for producing them.

The invention comprises a decorative article
coated with a surface layer of gold or gold-containing
material having an underlayer of a high hardness
material with a gold colour comprising at least one high
hardness material selected from the carbonitrides of
titanium, zirconium, hafnium, and vanadium and hafnium
nitride.

An element selected from Al, Cr, Fe, Co, Ni, Cu,
Zn, Nb, Mo, Rh, Pd, Ag, In, Sn, W, Ir, Pt may be added
to the high hardness material layer.

The article supporting the underlayer may comprise at least one material selected from steel, brass, a nickel, copper, manganese and iron alloy, German silver, aluminium, Al_2O_3 or zinc die casting.

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The above named high hardness materials have an outstanding mechanical and chemical durability against all types of attack experienced by decorative articles. They have also, however - as seen from the table - a
10 markedly increased brilliance as compared to titanium nitride, which means that evidence of wear on the articles in question much less obvious than with the known titanium nitride.

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Experiments have also been carried out to increase the L^* -value of titanium nitride by altering the stoichiometry of the compound. Thus for example in the compound TiN_x , x is selected to be less than 1, which gives a brighter gold colour as compared to
20 stoichiometric titanium nitride. The relatively trivial increase in the L^* -value to 77 is bought with the disadvantage that the gold colour exhibits a green tint. Such a method is, however, undesirable from the point of view of colour compatibility of the hard material layer
25 on bright gold coloured surface layers with a red component, as after eroding the surface layer there is an obvious colour difference to the underlying hard material layer.



The use of the high hardness materials of the invention lead in all cases to L^* -values of 80 and above, so that there is no marked loss of brilliance in the appearance of the abraded places and as a result - colour compatibility being assumed - no dark patches are apparent. Nevertheless it is possible, by suitable selection from among the high hardness materials of the invention, to get a match to a certain extent to the gold colour of the surface layer.

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This matching is, however, not possible with only the TiN layer, and - as already explained - the brilliance does not have the desired value. By varying the carbon and nitrogen components of the carbonitrates in the coating material as well as by influencing the coating growth by different conditions, the palette of colour matching possibilities can be broadened still further, the shades of gold being determined by simple trials.

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In the production of gold coloured coatings on articles, galvanic (electroplating) and physical deposition methods (PVD) have proved effective. Whereas electroplating does not effect deposition of the gold coloured, high hardness compounds mentioned, these coatings can be deposited with no problem by the PVD process. In particularly advantageous manner the method of cathode vaporisation can be used. It is to be

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observed that by virtue of the high melting points of the named high hardness materials, which lie between 2000 and 3000°C, only a columnar growth of coating can be produced according to the model described by Thornton (J. Vac. Sci., Technol. 11, p666, 1974) at the temperatures of up to 300°C at which such decorative substrates are usually coated. This has very poor mechanical properties and corrosion resistance as a result. A thick coating structure can, however, be produced by using ion bombardment of the substrate as in cathode vaporisation.

Particularly favourable coating conditions are achieved using the cathode vaporisation process in association with a double arrangement of high performance cathodes (magnetron-cathodes) as described in DE - OS 31 07 914 and US 4426267.

By the method of cathode vaporisation it is possible to vaporise a metal target directly without melting it. The same method also makes it possible to apply securely the surface layer of gold or gold-containing material, which is not immediately possible by the electroplating process. The disadvantage of electroplating is that the indicated high hardness materials on the coating surface cannot be activated directly for a subsequent bonding deposition of the surface layer.

It is here particularly advantageous if the gold coloured high hardness material layer has a thickness of 0.2 to 0.3 μ m. With regard to the thickness of the gold or gold-containing material layer, one of 0.05 to 1.0 μ m is especially suitable. The gold-containing surface layer may have a colour value similar to a Swiss Gold-Standard 1N14, 2N18 or 3N18.

The invention also relates to a method for producing articles of the aforementioned type by coating correspondingly shaped bodies as substrates with an underlayer of a high hardness material having a gold colour and with a surface layer of gold or gold-containing material.

This method is, for solving the same problem according to the invention, characterised in that one first vaporises a material selected from Ti, Zr, Hf and V from a metallic target by a cathode vaporisation process in a reactive atmosphere in the presence of an inert gas and a gas, N_2 and a hydro carbon which is gaseous at room temperature, and deposits on the substrate the reaction product of the metal and at least one component from the gases, and then one deposits the surface layer of gold or gold-containing material in a neutral or reactive atmosphere.

Further advantageous features of the subject of the invention will appear below.

The invention will now be further described with respect to Figures 1 to 7.

These show:

- Figure 1 the spectral dependence of the
10 reflection value for pure gold.
- Figure 2 the spectral dependence of the
 reflection value for pure copper.
- 15 Figure 3 the spectral dependence of the
 reflection value for pure silver.
- Figure 4 the spectral dependence of the
 reflection value for titanium nitride.
- 20 Figure 5 the spectral dependence of the
 reflection values for hafnium nitride.
- Figure 6 a schematic representation of one
25 possible layer structure of
 underlayer and surface layer.

From the graphs it can be seen that with a gold alloy, which contains copper and silver a high brilliance is as a rule to be expected. Thus, for example, an 18 carat gold alloy with a 9% silver content, the remainder copper can be expected to have the high brilliance of $L^* = 86$ shown in the table.

As in particular is to be seen from the graph of Figure 4, titanium nitride has a substantially lower brilliance in the visible region of the spectrum, compared to a layer of gold or gold alloy.

From Figure 5, which show the spectral reflection relationships of hafnium nitride, it can be seen that the reflection values, from a wavelength of about 400nm, first increase sharply and then approach a limiting value asymptotically from about 500nm. For the comparatively measured titanium nitride, Figure 4 shows a relatively slow increase of the reflection relationship starting at about 450nm, followed by the asymptotic approach to a limiting value which occurs only above about 650nm.

In Figure 6 is shown a substrate (1) which is formed by the shaped body of the article. To this substrate is first applied an underlayer (2) of the high hardness material according to the invention and on this a surface layer (3) of gold or gold-containing material. A bonding layer of the pure metal of the high hardness material between the substrate (1) and the underlayer (2) is not specifically shown.

The CIELAB Measuring Method

The CIELAB units set out in the Table were determined by means of a measuring method which was laid down some time ago by manufacturers of surface coatings, especially decorative coatings. It is a colorimetric measuring method, in which a measuring light beam from a standard light source with quite specific spectral properties is directed at the object to be measured and the reflected part of the measuring light is evaluated in the visible wavelength region of the spectrum. By calculated evaluation the degree of brilliance can be determined as well as for example the colour proportions of red and yellow which determine the gold colour.

The bases of the method are for example described by R.M.German, M.M.Guzarsky and D.C.Wright in "Journal of Metals" March 1980, pages 113 ff. Manufacturers of instruments for colour measurement are given in the "Handbook of Optics" of Walter G.Driscoll

and W.Vaughan, MacGraw-Hill Book Company, Edition 1978 in Chapter 9. Instruments with indications specially according to CIELAB units are supplied by the following companies:

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|---|---------------------------|--------------------------------|
| 5 | MacBeth | (Newbury, N.Y./USA) |
| | Hunterlab | (Reston, Virginia/USA) |
| | Instrument Colour Systems | (Newbury, Berkshire/GB) |
| | Diano Corp. | (USA - TypMatch Scan DTM 1045) |

10 Example 1:.

A cleaned watch case of stainless steel is placed in a cathode vaporisation device with two double cathode arrangements according to DE - 05 31 07 914.

- 15 The targets of the two pairs of cathodes are oppositely arranged, so that the watch case arranged in the middle between the cathodes is equally coated from both targets.

- 20 One of the double cathode arrangements is loaded with targets of zirconium, the other cathode pair has targets of a 14 carat gold alloy with 30% silver, remainder copper.

- 25 The watch case is first positioned in the middle between two erosive treatment screens and the cathode vaporisation device is then evacuated to 3×10^{-5} mbar. For the erosive treatment a negative d.c. potential of about 1800 volts is applied to the screens and argon is

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admitted into the apparatus up to a total pressure of about 1.8×10^{-2} mbar. An argon arc is struck through a brief impulse, and a substrate current of about 50mA instituted by controlling the d.c. potential. The erosive treatment is maintained for long enough to render the surface of the watch case metallically clean.

For the purpose of cleaning the targets a grid is placed between the double arrangement of zirconium cathodes. The argon pressure is reduced to about 8×10^{-3} mbar and the substrate potential reduced to the value 0V. The current of the cathodes is regulated to give a mean current density of 10 Wcm^{-2} . Once stable conditions have been established at the cathodes, the screens are removed from the cathode arrangement and the watch case put at a substrate potential of -150V and positioned between the zirconium cathodes. A metallic binding layer of zirconium of $0.05 \mu\text{m}$ layer thickness is now deposited on the substrate.

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Subsequently measured flows of nitrogen and acetylene are introduced through a gas inlet, of which the input is predetermined as follows: The nitrogen flow into the apparatus is so dimensioned for carrying out the experiment that without introduction of argon into the apparatus there is a nitrogen pressure of 2×10^{-3} mbar. By feeding nitrogen and acetylene into the discharge is effected the formation of

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zirconium carbonitride on the surface of the watch case by the reaction of zirconium with the reactive gases activated by the plasma.

5 By means of the proposed negative potential on the watch case during the deposition there is set up a current density of 4mA/m^2 on the substrate. As a result of this, the dense deposition of the zirconium carbonitride layer is achieved, which makes possible a
10 good corrosion protection of the substrate. The coating thickness of the zirconium carbonitride is set at $0.7\mu\text{m}$. After ceasing the coating with zirconium carbonitride, a screen is introduced between the double cathode arrangement, loaded with targets of gold alloy.
15 More argon is now introduced into the equipment up to a total of 8×10^{-3} mbar. Then an externally controlled negative d.c. potential is applied to the targets such that their mean current density is 3Wcm^{-2} . The cathodes are cleaned by a vaporisation process against a
20 screen. Then the watch case is set at a substrate potential of 0V and positioned between the alloy cathodes.

 The coating duration for the gold alloy is
25 selected so that a 0.4 μm thick layer of gold alloy is deposited on to the watch case. The measurement of the CIELAB value gives the values shown in the table.

Example 2:

A cleaned watch case of brass, in which additionally tarnish film and other surface deposits have been removed by special brass cleaning means, is put into a comparable cathode vaporisation apparatus which is equipped with three cathode pairs. As target materials for the three cathode pairs are used:

1. Cathode pair NiCr (50/50)
2. Cathode pair Titanium
3. Cathode pair Gold alloy of 50% Au, 42% Cu,
3% Ni and 5% Al

(Note: all percentages are by weight)

The cathode vaporisation apparatus is evacuated to a pressure of 3×10^{-5} mbar, and the watch case subjected to erosive treatment as in Example 1. For this there is a screen between the first cathode pair.

After conclusion of the etching process, the argon pressure in the apparatus is reduced to

8x10⁻³ mbar, and the NiCr targets are cleaned by vaporisation against a zero potential screen. Finally, a substrate potential of -150V is established and the watch case positioned between the NiCr cathodes. The vaporisation process is carried out with a mean current density of 10Wcm⁻² at the targets until a nickel/chrome layer is produced with a thickness of 1.5μm. Then the screens are inserted between the titanium cathodes, the substrate potential set to zero, and the titanium cathodes are cleaned by evaporation against the screens.

Subsequently, a substrate potential of -160V is established and the watch case introduced between the titanium cathodes. The vaporisation process is carried out with a mean current density of 10Wcm⁻² at the cathodes, until the (metallic) titanium layer has reached a thickness of 0.05μm.

For the coating with TiC_xN_y (with x smaller than 1 and y smaller than 1) calibrations for the gas flows of C₂H₂ and N₂ are determined. Pressures of 2.0x10⁻⁴ mbar for C₂H₂ and 1.3x10⁻³ mbar for N₂ are set up without the supply of argon. The appropriate gas flows are to be fixed for the process. The watch case coated with NiCr and Ti is now coated with admission of argon up to a pressure of 8x10⁻³ mbar as well as N₂ and C₂H₂ for such a

time that a layer of titanium carbonitride of $0.8\mu\text{m}$ thickness has been produced. Finally the supply of C_2H_2 and N_2 is adjusted and the substrate set at zero potential. A screen is introduced between the gold alloy targets and the targets cleaned at a mean current density of 3Wcm^{-2} . Then the screen is taken away and the watch case arranged between the gold and alloy targets, and the coating process carried out until a $0.5\mu\text{m}$ thick alloy coating is deposited. The CIELAB units for this coating are likewise given in the table. Comparison with the CIELAB values for the titanium carbonitride coating show that these also approximate to the colour of the surface layer i.e. with respect to the values a^* and b^* , very well and, with respect to the brilliance, L^* , well.

Example 3:

In the already described cathode vaporisation device the first cathode pair is fitted with targets of hafnium and the second cathode pair with targets of a gold alloy of composition 58.5% Au, 34% Cu, remainder Ag. As substrate is used a stainless steel watch case. The cleaning, pumping operations and the cleaning of the substrate are carried out as in Example 1.

Then a screen is introduced between the hafnium targets and zero volts selected as substrate and screen

potential. Argon is introduced up to a pressure of 5×10^{-3} mbar, and the hafnium targets cleaned by vaporisation at a mean current density of 10 Wcm^{-2} . Subsequently a substrate potential of -170 V is applied, and the substrate is positioned between the hafnium cathodes and coated with a mean current density of 10 Wcm^{-2} up to a coating thickness of $0.1 \mu\text{m}$ of (metallic) hafnium. After the conclusion of the metallic coating a nitrogen flow corresponding to a predetermined calibration is introduced at 2.5×10^{-3} mbar. The coating process is carried on at a mean current density of 9 Wcm^{-2} until a hafnium nitride layer with a thickness of $0.8 \mu\text{m}$ is produced. Finally the substrate and the screens are set to zero potential and the screens inserted between the gold alloy cathodes. The nitrogen input is stopped and the gold alloy targets vaporised with a mean current density of 2 Wcm^{-2} . The coating is carried out up to a layer thickness of $0.2 \mu\text{m}$. CIELAB values were determined as in the table. Comparison with the hafnium nitride CIELAB values found in the table shows that with respect to the colour values a good to very good agreement, and with respect to the brilliance values a quite good agreement is obtained.

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Table

Material	CIELAB -units			Figure
	L*	a*	b*	
	Brilliance	Red value	Yellow value	
24-K-Gold	89.3	3.2	40.0	1
Copper	85.6	11.2	20.3	2
Silver 99.2	-0.3	1.0	3	
18-K-Gold				
(9% Ag, rest Cu)	86.0	5.5	22.0	
Titanium Nitride				
(TiN)	76.0	3.6	36.0	4
TiN _x (x<1)	73.0	-0.4	17.0	
Titanium				
Carbonitride	80.0	0.2	14.0	
Hafnium				
Nitride	80.0	-4.7	30.9	6
<u>Examples</u>				
1. 58.5% Au, 30%Ag rest Cu	90.7	-2.2	23.0	
2. 50% Au, 42% Cu 3% Ni, 5% Al	88.0	0.1	15.5	
3. 58.5% Au, 39% Ag rest Cu	91.9	-3.8	21.8	

CLAIMS

1. A decorative article coated with a surface layer of gold or gold-containing material having an underlayer of a high hardness material with a gold colour comprising at least one high hardness material selected from the carbonitrides of titanium, zirconium, hafnium, and vanadium and hafnium nitride.
- 10 2. An article according to claim 1, comprising a metallic addition to the high hardness material layer of at least one element selected from Al, Cr, Fe, Co, Ni, Cu, Zn, Nb, Mo, Rh, Pd, Ag, In, Sn, W, Ir, Pt.
- 15 3. An article according to claim 1 or claim 2, in which the article supporting the underlayer comprises at least one material selected from steel, brass, a nickel, copper, manganese and iron alloy, German silver, aluminium, Al_2O_3 or zinc die casting.
- 20 4. An article according to claim 1, in which the gold coloured high hardness material layer has a thickness of 0.2 - 0.3 m.



5. An article according to claim 1, in which the gold-containing surface layer contains at least one of the elements Al, Pd, Zn, Sn, Ag, Co, Ni, Cu, Ti, Ga, Cd.
- 5 6. An article according to claim 1, in which the gold-containing surface layer has a layer thickness of 0.05 - $1\mu\text{m}$.
7. An article according to claim 1, in which the
10 gold-containing surface layer has a colour value similar to a Swiss Gold-Standard 1N14, 2N18 or 3N18.
8. An article according to claim 1, in which the
15 shaped body is a part of a wristlet watch or writing implement or spectacles frame.
9. A method for producing decorative articles by coating suitably shaped bodies as substrates with an underlayer of a high hardness material having a gold
20 colour and with a surface layer of gold or a gold-containing material, comprising first vaporising a material selected from Ti, Zr, Hf and V from a metallic target by the known cathode vaporisation process in a reactive atmosphere in the presence of an inert gas, N_2
25 and a hydrocarbon which is gaseous at room temperature, and depositing on the substrate the reaction product of the metal and at least



one component from the gases, and then depositing the surface layer of gold or a gold-containing material in a neutral or reactive atmosphere.



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