

METHOD FOR THE PREPARATION OF A TWO-TONE COLOUREDMETAL-MADE PERSONAL ORNAMENT

The present invention relates to a method for the preparation of a two-tone coloured metal-made personal ornament, such as frames and temples of spectacles, watch cases, tiepins and the like.

Two-tone coloured metal-made personal ornaments are conventionally prepared by first providing a metal-made base body of the ornament with an undercoating layer of a hard material formed by the method of ion plating and an intermediate coating layer of an alloy of gold and palladium exhibiting a pinkish-tinted golden colour, then forming a masking film covering patternwise or a part of the gold-palladium coating layer, colouring the unmasked areas of the surface, for example in black using a titanium compound, and removing the masking film, for example by dissolving away with a remover or stripper solution, to expose the underlying surface of the gold-palladium layer.

One of the problems in the above-described two-tone colouring method lies in the step of removal of the masking film. Namely, the removing work sometimes takes an unduly long time or the masking film sometimes cannot be removed completely unless the

dipping time in a remover solution is significantly extended or the concentration of the effective ingredients in the remover solution is greatly increased; as a result, the coloured layer of the titanium compound on the unmasked areas may be subject
5 to attack by the remover solution, with the consequence that the aesthetic value of the article is greatly decreased.

The present invention accordingly has an object to provide a method for the preparation of a two-tone coloured metal-made personal ornament without the above-described problems and
10 disadvantages of the prior art method and capable of giving a two-tone coloured surface pattern composed of the areas of golden colour and areas of a different colour, to give a very beautiful appearance, without the problem in the stripping of the masking film.

15 As is mentioned above, the masking film in the conventional method is formed on the surface plated with a gold-palladium alloy exhibiting a pinkish golden colour. The inventors have begun investigating the reasons for the great difficulties encountered in removing the masking film and arrived at the following
20 presumption of the factors responsible for the difficulties.

Namely, (1) palladium absorbs hydrogen gas in a dissociated atomic form so that the surface of the gold-palladium alloy is always in an active state and enhances the adhesive bonding of the masking film to the alloy surface and (2) due to the
25 relatively low vapour pressure of palladium, for example in the decreasing order of $Cu > Au > Ni > Pd$, palladium is sputtered in

a condition of a large particle diameter and is therefore deposited on the surface of the substrate in the form of a rough surface having an increased surface area acting to increase the adhesive bonding strength of the masking film to the gold-palladium alloy surface.

The present invention has been completed on the basis of the above-given presumption of the reasons for the difficulties in the removal of the masking films. The method of the invention for the preparation of a two-tone coloured metal-made personal ornament comprises the steps of:

(a) providing a metal-made substrate body of a personal ornament with a hard undercoating layer of a carbide, nitride or carbonitride of a metal or metals selected from titanium, zirconium, hafnium, vanadium, tantalum and chromium;

(b) forming an intermediate coating layer of an alloy of gold, nickel and copper on the undercoating layer;

(c) forming a masking layer of an organic coating material patternwise on or on a part of the intermediate coating layer;

(d) forming a coloured top coating layer on the surface areas of the intermediate coating layer unmasked with the masking layer; and

(e) removing the masking layer.

The metal-made substrate body of the personal ornament to which the method according to the invention is applied is usually made from a metal or alloy such as titanium, titanium-based alloy, nickel, nickel-based alloy or stainless steel. When the metal-made substrate body is made of a copper-based alloy, it is usual to plate the surface of the copper-based alloy with a monolayer

of nickel or with a bilayer composed of a layer of nickel and a layer of chromium or palladium thereon.

The above-mentioned metal-made substrate body is first provided with a hard undercoating layer which is formed from
5 a carbide, nitride or carbonitride of a metal or metals selected from titanium, zirconium, hafnium, vanadium, tantalum and chromium.

The intermediate coating layer on the above-mentioned hard undercoating layer is formed of a ternary alloy of gold, nickel
10 and copper. Preferably, the ternary alloy is composed of from 70 to 88% by weight of gold, from 10 to 20% by weight of nickel and from 2 to 10% by weight of copper with trace amounts of other unavoidable impurities. The alloy exhibits a pinkish golden colour. When the proportion of nickel in the ternary
15 alloy exceeds 20% by weight, the colour tone of the alloy has an increased yellowish tint. Similarly, an excessively large proportion of copper renders the colour tone of the alloy reddish. The corrosion resistance of the alloy is decreased by increasing the proportions of nickel and/or copper. When
20 the proportions of nickel and copper are too small, the alloy would lose the pinkish tint to be purely golden. The above-specified composition of the ternary alloy is important to ensure good removability of the organic masking layer thereon by using a remover solution, giving almost the same aesthetically
25 preferred pinkish golden colour as the conventional gold-palladium alloy.

The method according to the invention will now be described

in more detail with reference to the accompanying drawing, of which each figure illustrates a partial cross-sectional view of a metal-made personal ornament coated according to that method. Figure 1 illustrates a partial cross-sectional view in an
5 intermediate step of the coating process and Figure 2 illustrates the same cross-section after completion of the coating process to give a two-tone coloured surface pattern. Figure 3 illustrates a partial cross-sectional view of another two-tone coloured personal ornament of which the substrate body is made of a
10 copper alloy.

A metal-made substrate body 1 for a personal ornament, such as a spectacle frame, made of titanium metal is mounted on the base holder in the vacuum chamber of an apparatus for ion plating. Evacuation of the vacuum chamber is followed by introduction of
15 argon gas to give a reduced pressure of about 5×10^{-3} torr inside the vacuum chamber by balancing the continuous evacuation and introduction of the argon gas and a negative voltage of about 50 volts is applied to the substrate body so as to clean the substrate surface by the bombardment with argon ions. Thereafter,
20 nitrogen gas as a reactive gas is introduced into the chamber as mixed with the argon gas. The pressure inside the chamber is kept at about 5×10^{-4} torr and the evaporation source of titanium metal is bombarded with electron beams accelerated at an appropriate voltage to effect vaporization of the titanium
25 metal. The vapour of titanium metal is ionized by means of the ionization electrodes installed at an intermediate position in

the vacuum chamber along with ionization of the nitrogen molecules to react with each other forming titanium nitride, which is deposited on the substrate surface to form a hard undercoating layer 2 on the surface of the substrate 1.

5 The next step is to form an intermediate coating layer of the ternary alloy of gold, nickel and copper. This plating treatment is performed in the same vacuum chamber as above by the bombardment of an evaporation source of the alloy composed of, for example, 82% by weight of gold, 14% by weight of nickel and
10 4% by weight of copper, so that the alloy is vaporized and deposited on the surface of the hard undercoating layer 2 to form an intermediate coating layer 3 of the alloy. A negative voltage of 10 to 200 volts is applied to the substrate body 1 to facilitate deposition of the alloy vapour thereon. The
15 intermediate coating layer preferably has a thickness in the range from 0.1 to 5 μm .

 The substrate body 1 coated in the above-described manner with the layers 2 and 3 is taken out of the vacuum chamber and provided with an organic masking layer 5 patternwise or partly
20 by a suitable method, such as screen printing, tacho printing, hand brushing and the like, excepting the areas where the surface of the ternary gold-nickel-copper alloy should be coloured. Examples of suitable masking inks include those based on a modified acrylic resin and epoxy resin. The masking
25 layer 5 is then dried as completely as possible by heating at a temperature of 120 to 150°C for 30 to 60 minutes in order to

avoid any possible adverse influences by the vaporized matter in the next step, which is also performed in a vacuum chamber of an ion-plating apparatus.

The substrate body 1 provided with the patternwise or partial masking layer 5 is then again mounted on a base holder in the vacuum chamber and cleaning of the surface is performed by the bombardment with argon ions in a similar manner to before. Thereafter, the atmosphere inside the chamber is kept at a pressure of about 5×10^{-4} to 1×10^{-2} torr by introducing a mixed gas of nitrogen and argon containing small volumes of oxygen and carbon dioxide. While a negative voltage is applied to the substrate body 1, an evaporation source of titanium metal is bombarded with electron beams at an appropriate accelerating voltage to vaporize the metal and the vapour of titanium metal is ionized by means of the ionization electrodes, to be reacted with ionized species of the oxygen and carbon dioxide gases in the atmosphere and deposited on the surface of the intermediate coating layer of the gold-nickel-copper alloy 3 to form a black-coloured top coating layer 4.

The thus top-coated body 1 is taken out of the vacuum chamber and immersed in a remover solution to dissolve away the organic masking layer 5 together with the coloured top coating layer 4 deposited thereon, to exhibit a two-tone coloured pattern 6 shown in Figure 2, in which the pattern is formed of the areas 3 exhibiting the pinkish golden colour of the gold-nickel-copper alloy and the areas 4 of the black-coloured top

coating layer.

The above-described process for practising the method of the present invention is given only by way of example and various modifications can be effected. For example, the material of the substrate body is not limited to the titanium metal used above but can be a titanium-based alloy, nickel, nickel-based alloy, stainless steel or the like conventionally used for making personal ornaments such as spectacle frames and temples, watch cases, tiepins and the like. The material of the hard undercoating layer is also not limited to titanium nitride but can be any of the carbides, nitrides or carbonitrides of a metal including titanium, zirconium, hafnium, vanadium, tantalum and chromium. In the above-described example, the patternwise top coating layer 4 is formed by the method of ion plating to exhibit a black colour but of course any aesthetically acceptable colour can be obtained by undertaking an appropriate coating method therefor, such as the conventional wet-process plating method and the like.

When the substrate body 10 illustrated in Figure 3 is made of a copper alloy, such as brass, as is conventional in watch cases, it is preferable that the surface of the substrate body 10 is first provided with a bilayered plating layer composed of a layer of nickel plating 7 having a thickness of 3 to 5 μm and a layer of chromium 8 having a thickness of 0.1 to 0.3 μm , each formed by the electrolytic method. The subsequent procedure is substantially the same as in the above-described first

example using a titanium-made substrate body, including the steps for successively forming the hard undercoating layer 2, intermediate coating layer 3 of the ternary alloy of gold, nickel and copper, patternwise organic masking layer 5 and coloured top coating layer 4, followed by removal of the organic masking layer 5 to form the two-tone coloured surface in a desired pattern 11. The removal of the organic masking layer 5 with a remover solution is as easy as in the first example using a titanium-made substrate body. A watch case provided with a two-tone coloured surface pattern according to the method of the present invention displays top quality, with a very beautiful appearance.

The plating layers of nickel and chromium formed on the surface of a brass-made watch case have an effect to improve the corrosion resistance and the adhesion of the hard undercoating layer of titanium nitride to the substrate surface. Similar effects can be obtained by replacing the chromium plating layer 8 with a palladium plating layer. Though somewhat inferior in corrosion resistance, the aesthetic value in the appearance of the finished watch case is about the same even with a monolayer plating of nickel alone by omitting the chromium or palladium plating. The above-mentioned thickness of each of the plating layers is selected by balancing the advantageous effects obtained thereby increasing with the plating thickness and the costs for the plating treatment also increasing with the plating thickness.

The results of the evaluation tests undertaken with the spectacle frames and watch cases provided with a two-tone coloured surface pattern according to the method of the present invention were all quite satisfactory, including the 180° bending test for the adhesive bonding strength of the coating layer to the substrate surface and the spraying test of an aqueous 5% sodium chloride solution for 140 hours as well as 96 hours of artificial perspiration test for the corrosion resistance.

Following are comparative results showing the great improvement in the efficiency of the removal of the organic masking layer by using a remover solution, on the coating layer of the ternary alloy of gold, nickel and copper according to the method of the present invention and on the coating layer of a binary alloy of gold and palladium according to the conventional method. Thus, 50 pieces each of the test bodies coated patternwise with an acrylic resin-based organic masking layer were immersed at room temperature in a remover solution prepared from a chlorinated hydrocarbon solvent, an alcoholic solvent, formic acid and other additives and the number of the test pieces from which the organic masking layer had been spontaneously and completely removed was counted after 15, 30, 45, 60 and 120 minutes of immersion. In the test pieces according to the invention, 35 pieces were already free from the masking layer after 15 minutes of immersion and all of the test pieces were free from the masking layer after 30 minutes

of immersion. In the test pieces according to the conventional method on the contrary, no test pieces were freed from the masking layer by the immersion for 30 minutes and the cumulative numbers of the test pieces free from the masking layer were

5 2, 5 and 7 after 45 minutes, 60 minutes and 120 minutes, respectively, of immersion, leaving 43 test pieces left with the unremoved masking layer which must be removed by brushing.

The advantages attributable to the improved efficiency in the stripping of masking layers described above are so
10 great in respect of the overall working efficiency of the process for the formation of the two-tone coloured pattern on the surface of metal-made personal ornaments, not only in the productivity of the products but also in the increase of the yield of acceptable products and improvement in the high quality appearance of the
15 ornaments.



CLAIMS

1. A method for the preparation of a two-tone coloured metal-made personal ornament which comprises the steps of:
 - (a) providing a metal-made substrate body of a personal ornament with a hard undercoating layer of a carbide, nitride or carbonitride of a metal or metals selected from titanium, zirconium, hafnium, vanadium, tantalum and chromium;
 - (b) forming an intermediate coating layer of a ternary alloy of gold, nickel and copper on the undercoating layer;
 - 10 (c) forming a masking layer of an organic coating material patternwise on or on a part of the intermediate coating layer;
 - (d) forming a coloured top coating layer on the surface areas of the intermediate coating layer unmasked with the masking layer; and
 - 15 (e) removing the masking layer.
2. The method for the preparation of a two-tone coloured metal-made personal ornament as claimed in claim 1, wherein the ternary alloy is composed of from 70 to 88% by weight of gold, from 10 to 20% by weight of nickel and from 2 to 10% by weight of copper with unavoidable impurities.
- 20 3. The method for the preparation of a two-tone coloured metal-made personal ornament as claimed in either of claims 1 and 2, wherein the intermediate coating layer of the ternary alloy has a thickness of the range from 0.1 to 5 μm .



4. The method for the preparation of a two-tone coloured metal-made personal ornament as claimed in any of claims 1 to 3, wherein the organic coating material for the masking layer is a masking ink containing a modified acrylic resin or an epoxy resin as the vehicle.

5. The method for the preparation of a two-tone coloured metal-made personal ornament as claimed in any of claims 1 to 4, wherein the coloured top coating layer is formed by the vapour deposition of ionized titanium metal reacted with ionized molecules of oxygen and carbon dioxide.

6. A method for the preparation of a two-tone coloured metal-made personal ornament, substantially as hereinbefore described with reference to the accompanying drawings.
