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A METHOD FOR THE PREPARATION OF A BLACK-COLOURED
ORNAMENTAL ARTICLE

The present invention relates to a method for the preparation of a personal ornamental article, including cases and straps of watches, frames of spectacles and the like, coloured in grey to black of an aesthetically attractive colour tone. More particularly, the invention relates to a method for imparting an aesthetically attractive blackish colour to the surface of an article for personal ornamental use by utilizing the method of ion plating.

It is well known in the prior art that the surface of an article for personal ornamental use, such as cases of wrist watches, watch straps, frames of spectacles and the like, can be provided with a surface film having a beautiful blackish colour by the techniques of so-called ion plating. For example, Japanese Patent Publication 58-53716 discloses a process of such an ion plating method in which a high electric voltage of 500 to 4000 volts is established between the article to be surface-treated and a titanium metal, under heating in an atmosphere of nitrogen at a reduced pressure, so that a black-coloured surface film composed mainly of titanium nitride is deposited on the surface of the article. Japanese Patent Kokai 60-208472 also discloses an ion plating method in which the atmosphere for ion plating contains argon, nitrogen and a hydrocarbon compound.

Although the above-described prior art methods are effective to form a lustrous black-coloured surface film on the surface of the article, the methods are not free from several problems and disadvantages. In the first method, for example, the surface of the article is rarely completely free of remaining abrasive particles of glass beads, alumina powder and the like used in the pretreatment of the surface by honing prior to the ion plating, so that abnormal electric discharge or sputtering may sometimes take place when a high voltage is established between the article and the titanium source. Further, the process of deposition of titanium nitride cannot be stable or controllable as desired, so that the uniformity of the black-coloured surface film is not so high and the surface film cannot have a delicately controlled black colour tone; the film may sometimes display a yellowish tint, which reduces the chance of the thus surface-treated ornamental article meeting the users' aesthetic requirements. In the second method, the deposited surface film necessarily contains more or less of a carbon constituent, which may cause increased stress in the deposited surface film leading to eventual loss of the surface film. Moreover, it is a rather troublesome matter to exactly control the proportion of the three components of the gaseous atmosphere so that the reproducibility of the colour tone of the deposited surface film is sometimes poor.

It is therefore an object of the present invention to provide an improved method for the preparation of a black-coloured ornamental article by ion plating, by which method an article may be obtained having a beautiful colour tone, with a lustre in some cases resembling that of a precious stone.

Accordingly, the method of the present invention for the preparation of a black-coloured ornamental article comprises the steps of:

- 5 (a) holding a substrate article having an electro-conductive surface in an atmosphere of a gaseous mixture essentially composed of nitrogen or a mixture of nitrogen and argon with admixture of from 0.1 to 5.0% by volume of oxygen and from 0.1 to 3.0% by volume of carbon dioxide under a pressure in the range from 5×10^{-4} to 1×10^{-2} Torr facing an evaporation source of titanium metal;
- 10 (b) heating the evaporation source of titanium metal to a temperature in the range from 1500° to 1700°C , to effect vaporization of the metal; and
- 15 (c) establishing an electric voltage in the range from 1 to 450 volts or, preferably, from 10 to 100 volts between the substrate article and the evaporation source of titanium metal.

In the following, the method of the present invention is described in more detail with reference to the accompanying drawing, which schematically illustrates an apparatus useful in practising the method of the present invention.

In the figure, a small piece of titanium metal 2 to serve as the evaporation source is placed on a table 8 installed in a vessel 1, which is in communication with a source of vacuum. A substrate article 4 having an electroconductive surface, eg a watch case after a surface finishing by pretreatment such as honing and chemical treatment, is supported above and facing the titanium metal source 2 by a substrate holder 3. The type of the substrate article 4 is not particularly critical provided that the surface thereof is electrically conductive. Thereafter, the vessel 1 is first evacuated through a pumping duct 6 to exclude the air inside it and then a gaseous mixture

of nitrogen or a mixture of nitrogen and argon is introduced via the gas inlet port 5 at such a rate that the pressure inside the vessel 1 is controlled and maintained in the range from 5×10^{-4} to 1×10^{-2} Torr or, preferably, from 8×10^{-4} to 5×10^{-3} Torr by balance with continued evacuation. When the gaseous feed is a mixture of nitrogen and argon, the volume proportion of them is not particularly critical provided that the major constituent, eg 50% by volume or larger, is nitrogen. Characteristically, the gas introduced into the vessel 1 should contain from 0.1 to 5.0% by volume of oxygen and from 0.1 to 3.0% by volume of carbon dioxide, in contrast to the prior art method of ion plating in which the atmospheric gas of nitrogen or a mixture of nitrogen and argon should be as completely free from impurities such as oxygen and carbon dioxide as possible.

While keeping this atmospheric condition, a DC voltage in the range from 1 to 450 volts or, preferably, from 10 to 100 volts is established between the titanium metal source 2 as the anode and the substrate article 4 as the cathode, by means of a DC power source 9. Such a relatively low voltage is also a very characteristic feature of the method according to the invention since it is usual in the conventional method for the voltage between the substrate article and the evaporation source to be 500 volts or higher. Although the electric current therebetween is not particularly critical depending on the size of the substrate article under treatment, the electric current is usually kept in the range from 0.1 to 5 amperes or, preferably, from 0.5 to 2 amperes assuming that a relatively small article, such as a watch case or strap, a spectacle frame or the like, is treated. Simultaneously, the titanium metal evaporation source 2 is heated to cause vaporization of the metal,

by a suitable means, the choice of which is not particularly critical. In order to cause efficient vaporization of the titanium metal, the temperature of the metal evaporation source 2 should be kept at about 1600° C or in the range from 1500 to 1700° C. A convenient method for heating the titanium metal source 2 is to bombard the titanium metal with electron beams emitted from an electron gun 7 at an appropriate accelerating voltage relative to the titanium metal evaporation source 2. It should be noted that this electron bombardment has an effect to cause the ionization of the gaseous impurities, such as oxygen, carbon dioxide and the like having a relatively low ionization potential, contained in the gaseous feed introduced from the port 5 exhibiting some influences on the colour tone of the deposited surface film. It is a very surprising discovery that the presence of such impurities in the gaseous atmosphere significantly influences the colour tone of the surface film of titanium nitride deposited on the surface of the substrate article to form a beautifully coloured black surface film with high reliability and reproducibility. It is also a surprising discovery that this surface film of beautiful black colour, which is principally titanium nitride, deposited on the substrate article contains unexpectedly large amounts of oxygen and carbon, each, in some cases, in excess of 20% by weight. In one example, the surface film deposited according to the inventive method was composed of 35% by weight of titanium, 20% by weight of nitrogen, 25% by weight of oxygen and 20% by weight of carbon. This analytical result is clearly distinguished from the ordinary golden-coloured titanium nitride film composed of, for example, 45% by weight of titanium, 45% by weight of nitrogen, 5% by weight of oxygen and 5% by weight of carbon deposited according to the conventional method

in an atmosphere containing only unavoidable amounts of oxygen and carbon compound as the impurities.

The above-described limitation in the pressure of the gaseous atmosphere in the vessel 1 is important since, when the pressure is lower than the above-mentioned lower limit, the potential difference between the titanium metal source 2 and the substrate article 4 cannot be high enough to ensure efficient deposition of titanium nitride by ion plating while, when the pressure is too high, glow discharge may take place and cause roughening of the surface of the titanium nitride film deposited on the substrate article 4. When the electric current between the titanium metal evaporation source 2 and the substrate article 4 is too large relative to the substrate article under treatment, the colour of the surface film deposited on the substrate article 4 may be yellowish and lose the desired aesthetic value as a black-coloured ornamental article due to the preferentially proceeding reaction for the formation of TiN with smaller contents of oxygen and carbon therein.

In the following, the method of the present invention is described in more detail by means of illustrative examples. These examples may be carried out in apparatus such as that described above and illustrated in the accompanying drawing.

Example 1.

A spectacle frame made of titanium metal as the substrate article to be surface-treated was mounted on the holder above an evaporation source of titanium metal in a chamber for ion plating treatment and the pressure inside the chamber after evacuation was controlled and maintained at 5×10^{-3} Torr by the balance of continued evacuation and introduction of nitrogen gas containing oxygen and carbon dioxide each in a varied volume proportion as indicated in

Table 1 below in % by volume. A DC voltage of 10, 50, 100, 200 or 400 volts as the cathode voltage was impressed between the evaporation source of titanium metal as the anode and the substrate article as the cathode to give an ion current of 1, 10, 15, 20 or 30 amperes, respectively. Simultaneously, the titanium metal was heated at a temperature of 1600° C by bombardment with an electron beam of 0.3 ampere at an accelerating voltage of 10 kilovolts to cause vaporization of the metal, whereby a surface film was deposited on the surface of the frame. This procedure of ion plating was continued for 30 minutes. The thus-formed surface film was visually examined to evaluate its aesthetic qualities in terms of lustre and colour tone. It was noted that lustrous surfaces could be obtained only when the cathode voltage was 50 volts or higher. The colour tone for each combination of the cathode voltage and the contents of oxygen and carbon dioxide in the atmospheric gas of nitrogen was as tabulated in Table 1 below. The reference to "scorched" colours obtained when the cathode voltage was 400 volts means a dark colour giving an impression of intermingled red, blue and green.

Table 1

Concentrations of O ₂ / CO ₂ , %	Cathode voltage, volts				
	10	50	100	200	400
0.1 / 0.1	Light grey	Light grey	Light grey	Reddish light grey	Scorched grey
2 / 1	Dark grey	Dark grey	Dark grey	Reddish dark grey	Scorched grey
3 / 2	Black	Black	Black	Black	Scorched grey

Example 2

The experimental procedure was substantially the same as in Example 1 except that the pressure inside the ion plating chamber was decreased to 8×10^{-4} Torr and the concentrations of oxygen and carbon dioxide were as shown in Table 2. The temperature of the evaporation source of titanium metal was 1500° C. The ion current between the substrate article and the evaporation source of titanium metal was 0.5, 5, 10, 15 or 20 amperes for the cathode voltage of 10, 50, 100, 200 and 400 volts, respectively. After surface treatment for 30 minutes, no blackish colouration could be obtained when the concentrations of oxygen and carbon dioxide were lower than the values given in Table 2. The surface film obtained when the cathode voltage was 10 volts was less lustrous and somewhat matted. Table 2 below shows the colour tone of the thus surface-treated frames for each combination of

the concentrations of oxygen and carbon dioxide in the nitrogen gas and the cathode voltage.

Table 2

Concentrations of O ₂ / CO ₂ , %	Cathode voltage, volts				
	10	50	100	200	400
0.5 / 1	Light grey	Light grey	Light grey	Reddish light grey	Reddish light grey
3 / 3	Dark grey	Dark grey	Dark grey	Dark grey	Dark grey
5 / 3	Black	Black	Black	Black	Black

Example 3

The substrate article was a brass-made watch case plated first with nickel in a thickness of 3 μm and then with an alloy of palladium and nickel in a thickness of 3 μm . The procedure of ion plating treatment of this watch case was substantially the same as in Example 1 except that the pressure of the nitrogen atmosphere was 8×10^{-4} Torr, concentrations of oxygen and carbon dioxide were 4% by volume and 3% by volume respectively, the cathode voltage was 50 volts to give an ion current of 5 amperes and the current of the electron beam for bombardment was 0.3 ampere at an accelerating voltage of 10 kilovolts to heat the titanium metal at 1500°C . The thus-obtained surface film of lustrous and beautiful black colour had a thickness of 1 μm .

Example 4

The experimental procedure was substantially the same as in the preceeding example except that the

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substrate article to be treated was a stainless steel watch strap, the pressure of the nitrogen atmosphere was 5×10^{-3} Torr, the concentrations of oxygen and carbon dioxide in nitrogen were each 0.1% by volume, the cathode voltage was 100 volts to give an ion current of 5 amperes and the electric current of the electron beam for bombardment was 0.3 ampere at an accelerating voltage of 10 kilovolts to heat the titanium metal evaporation source at 1600° C. The resultant surface film deposited on the substrate article had a thickness of $0.8 \mu\text{m}$ and the colour thereof was a beautiful dark grey.

Example 5

15 The experimental procedure was substantially the same as in Example 4 except that the concentrations of oxygen and carbon dioxide in the nitrogen atmosphere were each 2% by volume. The resultant surface film had a colour of beautiful black.

CLAIMS

1. A method for the preparation of a black-coloured ornamental article which comprises the steps of:
- 5 (a) holding a substrate article having an electro-conductive surface in an atmosphere of a gaseous mixture essentially composed of nitrogen or a mixture of nitrogen and argon with admixture of from 0.1 to 5.0% by volume of oxygen and from 0.1 to 3.0% by volume of carbon dioxide under a pressure in the range from 5×10^{-4} to 1×10^{-2} Torr facing
- 10 an evaporation source of titanium metal;
- (b) heating the evaporation source of titanium metal to a temperature in the range from 1500° to 1700°C , to effect vaporization of the metal; and
- (c) establishing an electric voltage in the range from
- 15 1 to 450 volts between the substrate article as the cathode and the evaporation source of titanium metal as the anode.
2. A method as claimed in claim 1, wherein said electric voltage is in the range from 10 to 100 volts.
- 20 3. A method as claimed in either of the preceding claims, wherein said pressure is in the range from 8×10^{-4} to 5×10^{-3} Torr.
4. A method for the preparation of a black-coloured ornamental article, said method being substantially as
- 25 hereinbefore described in any of the foregoing Examples.

