METHOD OF FORMING ANODIC TITANIUM OXIDE LAYERS HAVING DUAL-COLOR APPEARANCE AND ARTICLE HAVING THE SAME

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Abstract

A method of forming anodic titanium oxide layers having dual-color appearance includes the following steps: providing a cleaned substrate; depositing a titanium film on the substrate; forming a mask of a desired pattern covering a portion of the substrate; carrying out a first anodization by immersing the substrate in an electrolytic solution as anode; applying a first direct-current voltage to produce a first titanium oxide layer; removing the mask; carrying out a second anodization by immersing the substrate in the electrolytic solution as anode; applying a second direct-current voltage having a value smaller than that of the first voltage to produce a second titanium oxide layer; and cleaning the coated substrate. The instant disclosure also includes an article made by the above method.
FIG. 2

B1

immersing the substrate in an electrolytic solution and serving as an anode

applying a first direct-current voltage through the electrolytic solution to oxidize the surface of the titanium film

producing a first titanium oxide layer

FIG. 3
B2

immersing the substrate in the electrolytic solution and serving as an anode

B21

applying a second direct-current voltage having a lower value than that of the first direct-current voltage through the electrolytic solution to oxidize the surface of the titanium film

B22

producing a second titanium oxide layer on the substrate

B23

FIG. 4

FIG. 5
METHOD OF FORMING ANODIC TITANIUM OXIDE LAYERS HAVING DUAL-COLOR APPEARANCE AND ARTICLE HAVING THE SAME

BACKGROUND OF THE INVENTION

[0001] Field of the Invention

[0002] The instant disclosure relates to a method of forming anodic titanium oxide layers having dual-color appearance and an article having the same; more particularly, to a method of forming titanium oxide layers on a substrate, such that the substrate would have at least two different color finishes, and an article having the same.

[0003] Description of Related Art

[0004] Portable electronic devices are very popular today, such as mobile phones, personal digital assistants (PDAs), laptops, etc. As the consumers begin to put more focus on the aesthetic appearances of these portable electronics, the housings of most portable electronics have shiny finishes for attractiveness. Especially for metal surfaces, which typically are specially processed to attain smoothness and shininess for visual attractiveness.

[0005] To apply color on surfaces of a housing, the existing technique involves anodizing to form a thin layer of titanium oxide on the metal surface for coloring. However, coloration done by such technique restricts the metal surfaces to a monocolored state, unable to generate multi-color variations. Furthermore, the titanium oxide layer of different thicknesses formed by anodizing generates different colors, while its thickness depends on factors such as applied voltage. However, in practice, the process of forming multiple titanium oxide layers on a same housing to create different coloration thereon is quite challenging.

[0006] To form a different color on the housing, an alternative solution is to apply a plastic adhesive film to its metal surface. However, since the adhesive film covers the metal housing, the user is unable to sense the actual metallic color and touch feel.

[0007] Therefore, the challenge of producing at least two different colors on a metallic housing while maintaining the metallic touch feel is a main issue the manufacturers intend to resolve.

SUMMARY OF THE INVENTION

[0008] To address the aforementioned issues, the instant disclosure provides a method of forming anodic titanium oxide layers having dual-color appearance and an article having the same. The main objective is to resolve the issue of forming at least two metallic colors on a substrate, especially by anodizing, while maintaining metallic luster and its touch feel.

[0009] The method comprises the following steps: providing a substrate; cleaning the substrate; depositing a titanium film on the substrate; forming a mask of desired pattern over a portion of the substrate; taking the substrate having titanium film formed thereon as an anode and immersing it in electrolytic solution; applying a first direct-current voltage through the electrolytic solution to oxidize the surface of the titanium film and produce a first titanium oxide layer on the substrate; removing the mask; taking the substrate as an anode and immersing it again in the electrolytic solution; applying a second direct-current voltage having a smaller value than that of the first-direct voltage through the electrolytic solution, to oxidize the surface of the titanium film and produce a second titanium oxide layer on the substrate; and cleaning the substrate.

[0010] The instant disclosure also provides an article having anodic titanium oxide layers with dual-color appearance obtained by the above method. The article comprises a substrate and a titanium film formed thereon. The surface of the titanium film is oxidized in forming a first titanium oxide layer and a second titanium oxide layer thereon in a non-overlapping manner. The first titanium oxide layer shows a first color, while the second titanium oxide layer shows a second color.

[0011] For advantages, by first passing a high-voltage direct current for anodizing in forming the first titanium oxide layer having the first color, followed by passing a low-voltage direct current for anodizing in forming the second titanium oxide layer having the second color, the metal housing can be easily color-coated and maintain its metallic luster. The method does not produce dust contaminants and surface damages as would with sand blasting, nor requires adhesive film. For the above method, the processing time is short, which is suitable for mass production. For example, each oxidation process only takes approximately one minute, while a particular color is being introduced on the surface of the housing. The color-forming oxidation process can be repeated with great accuracy by controlling the factors such as electroplating time, electrolytic solution, and voltage.

[0012] In order to further appreciate the characteristics and technical contents of the instant disclosure, references are hereunder made to the detailed descriptions and appended drawings in connection with the instant disclosure. However, the appended drawings are merely shown for exemplary purposes, rather than being used to restrict the scope of the instant disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a step-by-step illustration of forming anodic titanium oxide layers having dual-color appearance of the instant disclosure.

[0014] FIG. 2 is a flowchart showing the steps of a preparation process A of the instant disclosure.

[0015] FIG. 3 is a flowchart showing the steps of a first anodizing B1 of the instant disclosure.

[0016] FIG. 4 is a flowchart showing the steps of a second anodizing B2 of the instant disclosure.

[0017] FIG. 5 is a perspective view showing the use of instant disclosure for a housing of the electronic device.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

[0018] Please refer to FIG. 1, which shows a step-by-step illustration of the method in forming anodic titanium oxide layers having dual-color appearance of the instant disclosure. The present method can be broken into a preparation process A, a first anodizing B1, removal of the mask A2, and a second anodizing B2. Each different stage is explained in details hereinbelow.

[0019] [Preparation Process A]

[0020] Please refer to FIGS. 1 and 2, with FIG. 2 showing a flowchart listing the steps of the preparation process A of the instant disclosure. In step A11, a substrate 102 is provided. The substrate 102 is mainly made of metallic material and can be a metal housing, such as aluminum, aluminum alloy, stain-
less steel, or magnesium alloy housing. The substrate 102 may also be a non-metallic housing as well.

[0021] Then, for step A12 regarding the metal housing, the substrate 102 may first be cleaned prior to anodic treatment. Generally speaking, the cleaning process includes degreasing, acid washing (pickling), rinsing (water), and drying. Degreasing is performed to remove oil and grease off the surface of the substrate 102, which can be done by immersing the substrate 102 in a solvent bath. Acid washing, or pickling, is used to remove rust or oxidation layer from metal surfaces. Different pickle liquors, which contain strong acids, are used for different metals. For example, common steel can be treated with hydrochloric acid or sulfuric acid. If necessary, a corrosion inhibitor can be added to decrease the corrosion rate of the metal. For stainless steel, mixed acid of nitric acid and hydrofluoric acid is used. Low concentrations of nitric acid can be used to treat aluminum and its alloy. Rinsing is then performed to remove any debris left on the surface of the substrate 102 after acid washing, followed by drying the substrate 102 itself.

[0022] Next, in step A13, a titanium film 104 is deposited on the substrate 102. The deposition technique may be physical vapor deposition (PVD), such as vacuum sputtering or evaporative deposition. The thickness of the titanium film may be 0.5 to 1.5 micrometers. The aforementioned coating technique can be used for substrate made of different metallic material or even for non-metallic substrate.

[0023] Then, in step A14, a mask 106 of desired pattern is formed on the substrate 102. The masked portion of the substrate 102 is reserved for second anodizing, while the first anodizing B1 is being conducted. The preparation process A has thus been completed up to this point, before advancing to the process of applying first coloration through anodizing.

[0024] The aforementioned mask 106 can be a tape, preferably a peelable mask. The peelable mask has a low cost, is easy to use, and does not leave any mark behind. Using the peelable mask, the mask 106 can be formed on the substrate 102 by the screen printing technique in a particular pattern. Often used to protect certain parts of a printed circuit board, the peelable mask is a stripable coating formed by a dried liquid-based protective ink after being transferred onto the substrate 102.

[0025] [First Anodizing B1]

[0026] Please refer to FIGS. 1 and 3, with FIG. 3 being a flowchart showing the steps of the first anodizing B1. For a first step B11, the substrate 102 having the titanium film 104 thereon is immersed in an electrolytic solution and serves as an anode. For the instant disclosure, the electrolytic solution must be acidic, such as sulfuric acid, sodium phosphate, chromic acid, etc. For example, a sample electrolytic solution can include sulfuric acid in an amount between approximately 0.1% and 10% by volume. The preceding example is only for explaining purpose. Since different electrolytic solutions differ chemically, the oxide coatings to be grown would have different characteristics as well. For example, the oxide coating obtained through the sulfuric acid solution has excellent corrosion and wear resistances.

[0027] Next, for step B12, a first direct-current voltage is applied through the solution to oxidize the surface of the titanium film 104. The value of the first direct-current voltage is greater than a second direct-current voltage to be applied later in the second anodizing B2. Preferably, the first direct-current voltage is above 30 volts to oxidize the surface of the titanium film 104, where the first direct current may be a constant current. After a short period, approximately one minute, as shown in step B13, a first titanium oxide layer 104′ is formed on the substrate 102. If the voltage is high enough, the thickness of the first titanium oxide layer 104′ can be increased to top 300 nanometers. Thereby, the surface hardness of the titanium coating can be increased against wear, such as for a housing of the electronic device. Through the formation of the first titanium oxide layer 104′, a first color is applied on the substrate 102. The color is produced by the reflection of light at and through the formed oxide layer, which is transparent and electrically insulated. More specifically, the color is produced by the interference of first reflected light wave from the upper surface of the titanium oxide layer with the second reflected light wave from the lower surface of the titanium oxide layer, where the interaction of light waves produces the phenomenon called interference coloring. Oxide layers having different thicknesses can produce different light interferences of various colors. Notably, the nanopores formed on the titanium oxide due to the acid in the electrolytic solution do not require sealing.

[0028] Next, the substrate 102 is removed from the electrolytic solution. If necessary, the substrate 102 can be cleaned with water and dried. The drying process is conducive in removing the peelable mask. Then, the mask removal process A2 is proceeded to remove the mask 106 for exposing portion of the substrate 102 not oxidized. The substrate 102 is now ready to undergo the second anodizing B2 in forming a second color.

[0029] [Second Anodizing B2]

[0030] Please refer to FIG. 4, which is a flowchart showing the steps of second anodizing of the instant disclosure, in conjunction with FIG. 1. In step B21, the substrate 102 having a first color is again immersed in the electrolytic solution and serves as an anode. The electrolytic solution used during the first anodizing B1 may be used again for the present step. Next, for step B22, the second direct-current voltage having a smaller value than that of the first direct-current voltage is applied through the electrolytic solution to oxidize the surface of the titanium film 104. For example, the first direct-current voltage may be 35 volts, and the second direct-current voltage can be 15 volts. The recommended minimum difference is in the 2- to 5-volt range. After a period of time, approximately one minute, as indicated by step B23, a second titanium oxide layer 104′ is formed on the substrate 102. Visually, the formation of the second titanium oxide layer 104′ by the second direct-current voltage does not cause any significant negative impact on the cosmetic effect of the earlier formed first titanium oxide layer 104′. In other words, the first color formed by the first titanium oxide layer 104′ is not affected by the second color formed by the second titanium oxide layer 104″.

[0031] During anodizing, if the composition and concentration of the electrolytic solution changes within a tolerated range, only the sizes of the nanopores would be affected, while the thicknesses and colors of the oxide layers remain basically unaffected. The overriding factor in determining the thicknesses of the oxide layers is current density, which is typically voltage-controlled. As voltage increases, a thicker coating is produced. Combines with the light interference effect as previously mentioned, the change in coating thickness produces different coloration on the substrate 102.

[0032] The instant disclosure also discovered that if lower voltage is applied before higher voltage for anodizing, the produced oxide layers and colorations are unstable. Con-
versely, if the surface of the substrate first undergoes high voltage process in the first anodizing and followed by low voltage process in the second anodizing, the earlier formed oxide layer by the high voltage process can remain stable with minimal color change over time.

[0033] To illustrate the above argument, an example is given hereinbelow. The first direct-current voltage is 35 volts, and the second direct-current voltage is 15 volts, with sulfuric acid being the electrolytic solution. The measured lab values based on the CIE (Int'l Commission on Illumination) are as follows:

[0034] [After the First Anodizing]

[0035] The lab values of the first color are: 75.25, -9.72, -7.03

[0036] [After the Second Anodizing]

[0037] The lab values of the first color are: 72.01, -9.43, -4.34

[0038] The lab values of the second color are: 26.23, 26.75, 12.98

[0039] The above lab results show the first color is not significantly affected after the second anodizing. However, if the setting is reversed, such that the first direct-current voltage for the first anodizing is 15 volts and the second direct-current voltage for the second anodizing is 35 volts, the corresponding lab results show the first color is significantly affected by the second anodizing where the first color suffers significant change.

[0040] Lastly, the substrate 102 is thoroughly cleaned. The cleaning step can include water rinsing and drying, where the drying temperature may be approximately in the 120-150°C range.

[0041] Based on the above method of the instant disclosure, an article having anodic titanium oxide layers with dual-color appearance can be fabricated. Moreover, by using the peelable mask and the screen printing technique, different cosmetic designs can be formed on the metal substrate, such as letters, decorative patterns, etc. As shown in FIG. 5, a housing 100 of an electronic device is illustrated. The first color of the first titanium oxide layer 104 on the substrate 102 serves as the background color. A decorative pattern made up by the letters “A,” “B,” and “C,” which is created by the peelable mask, is shown by the second color of the second titanium oxide layer 104 without affecting the first color.

[0042] Based on the method of forming anodic titanium oxide layers having dual-color appearance and the article having the same of the instant disclosure, the associated advantages and attributes are as follows. By using the deposition technique to deposit the titanium film, such as vacuum sputtering for the housing of the electronic device, up to thousands of housings can be processed simultaneously, with titanium coating being more cost-effective than using pure titanium substrate. Furthermore, by first forming the first titanium oxide layer having the first color through high-voltage anodizing, followed by forming the second titanium oxide layer having the second color through low-voltage anodizing, the metal housing can be easily processed to display its colorations with metallic touch feel. Moreover, the second titanium oxide layer formed by the low-voltage anodizing would not induce any negative impact on the color of the first titanium oxide layer formed earlier in the process.

[0043] Other attributes of the instant disclosure include short fabrication time, which is suitable for mass production. Special colorations can be formed on the surfaces of the housing. By adjusting the electroplating time, the electrolytic solution, and voltage, the colorization of the substrate can be accurately controlled with excellent repeatability. The yield rate can be improved significantly.

[0044] The descriptions illustrated supra set forth simply the preferred embodiment of the instant disclosure; however, the characteristics of the instant disclosure are by no means restricted thereto. All changes, alternations, or modifications conveniently considered by those skilled in the art are deemed to be encompassed within the scope of the instant disclosure delineated by the following claims.

What is claimed is:

1. A method of forming anodic titanium oxide layers having dual-color appearance, comprising the steps of:
   a. providing a substrate;
   b. cleaning the substrate;
   c. depositing a titanium film on the substrate;
   d. forming a mask of desired pattern over a portion of the substrate;
   e. carrying out a first anodization process by immersing the substrate in an electrolytic solution as an anode;
   f. applying a first direct-current voltage through the electrolytic solution to produce a first titanium oxide layer on the substrate;
   g. removing the mask;
   h. carrying out a second anodization process by immersing the substrate in the electrolytic solution as an anode;
   i. applying a second direct-current voltage having a value smaller than that of the first voltage to produce a second titanium oxide layer on the substrate; and
   j. cleaning the substrate.

2. The method of forming anodic titanium oxide layers having dual-color appearance of claim 1, wherein the substrate is a metallic housing.

3. The method of forming anodic titanium oxide layers having dual-color appearance of claim 1, wherein the thickness of the titanium film is in the range of 0.5 to 1.5 micrometers.

4. The method of forming anodic titanium oxide layers having dual-color appearance of claim 1, wherein the cleaning step before depositing the titanium film includes degreasing, acid washing (pickling), rinsing (water), and drying in sequence.

5. The method of forming anodic titanium oxide layers having dual-color appearance of claim 1, wherein the difference between the voltages of the first direct current is at least 30 volts.

6. The method of forming anodic titanium oxide layers having dual-color appearance of claim 1, wherein the difference between the voltages of the first direct current and the second direct current is at least 2 volts.

7. The method of forming anodic titanium oxide layers having dual-color appearance of claim 1, wherein the mask may be a peelable mask formed on the substrate by the screen printing technique.

8. An article having titanium oxide layers with dual-color appearance, fabricated by the method of forming anodic titanium oxide layers having dual-color appearance of claim 1, comprising:
   a. a substrate; and
   b. a titanium film formed on the surface of the substrate, wherein the surface of the titanium film includes a first titanium oxide layer region showing a first color and a second titanium oxide layer region showing a second color, the second titanium oxide layer region being formed on a masked area.
9. The article having titanium oxide layers with dual-color appearance of claim 8, wherein the substrate is a metallic housing.

10. The article having titanium oxide layers with dual-color appearance of claim 8, wherein the thickness of the titanium film is in the range of 0.5 to 1.5 micrometers.

11. The article having titanium oxide layers with dual-color appearance of claim 8, wherein the thickness of the first titanium oxide layer is greater than 300 nanometers.

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