Method of coloring titanium and its alloys through anodic oxidation

The following is a method of coloring titanium and titanium alloys through anodic oxidation in an electrolytic bath. This method is characterized by the fact that titanium and its alloys undergo a preliminary anodic treatment at a constant potential in an electrolytic bath consisting of hydrohalogen acids or salts, fluoboric, fluosilic, acetic, oxalic, tartaric, nitric, phosphoric acids and their mixtures, possibly in the presence of oxidizing agents.
Description

[0001] This invention concerns a method of coloring titanium and titanium alloys through anodic oxidation. The invention also deals with the use of this method to color articles made of titanium and or titanium alloys, providing them with particular chromatic properties and resistance to corrosion.

[0002] When titanium is electrochemically oxidized in any one of a number of aqueous solutions, the film of titanium oxide produced on its surface takes on a variety of interference colours which change according to the potential applied—and thus to the thickness of the film—in a chromatic scale which goes from yellow to purple to blue, and back to yellow, then to pink, cobalt and green. This behaviour has been recognized for decades, and anodically colored titanium has been used in a wide variety of fields, with applications in, for example: decorative panels for interior and exterior use, furnishings, architecture, painting, monuments, costume jewellery, ornaments, precious jewellery, eyeglasses, the biomedical area, etc. In the traditional technique for coloring titanium through anodic oxidation, introduced at the end of sixties, a titanium sample is immersed in an electrolytic solution and connected to the positive plug of a direct current power supply whose negative plug is connected to a metallic counter-electrode made, for example, of stainless steel. When the circuit is closed, the titanium plate behaves as anode and the oxide film formed has a thickness, and thus a tint, which depends on the potential applied. A variety of electrolytic solutions may be used: for example diluted phosphoric or sulphuric acids (1-5% by weight), sulphamic acid (1-15% by weight) or ammonium sulphate or sodium bicarbonate solutions (1-15% by weight).

[0003] The extension of colours can be controlled by limiting the area to be oxidised with screens or lacquers or through the use of special electrochemical brushes adapted with a cathodic ring to carry the current. A current density in the range of 1-100 A/m² is normally used and the potential applied is higher than that used in galvanics: depending on the color desired, potential varying from a few Volt to more than 100 Volt are applied.

[0004] It has been noted that the intensity and beauty of the various colors produced, as well as other properties such as resistance to corrosion and abrasion, will vary according to environmental and electrochemical conditions and to the procedures used to obtain them.

[0005] For example, US Patent No 5160599 describes a method of coloring titanium, including two separate stages of anodization at constant current density, by which many shades of color are obtained.

[0006] Other methods are known and have been described in numerous patent requests, but they do not provide completely satisfactory results from the point of view of chromatics nor of corrosion resistance.

[0007] A new, improved technique has now been found for anodic coloring, that produces more intense colors which display greater resistance than those traditionally obtained.

[0008] The procedure in this invention is characterized by the fact that the titanium or its alloy undergoes a preliminary anodic treatment at constant potential in a first electrolytic solution consisting of hydrohalogen acids or salts, fluoboric, fluorosilic, acetic, oxalic, tartaric, nitric, phosphoric acids and their mixtures, possibly in the presence of oxidizing agents.

[0009] When titanium acts anodically in certain baths, even for very brief periods (from a few thousandths of a second and up), the potential remaining constant and contained within a well-defined interval, its surface is modified so that when it is subsequently oxidized with the usual solutions and techniques, it takes on colors which are particularly intense and more resistant than those traditionally obtained.

[0010] Coloration carried out on such pre-treated titanium not only differs in appearance and in its corrosion resistance in solutions (such as sulphuric-hydrchloric and phosphoric nitric-hydrofluoric, or organic acids) but can also be distinguished from traditional coloring at a microscopic level: observations made under a metallographic microscope show that all the crystalline grains of the metal are colored equally and uniformly, while this does not happen in traditional coloring.

[0011] During the pre-treatment stage, the potential to be applied depends on the type of bath used, and runs from 2 to 15 Volt. Hydrochloric acid or nitric acid / hydrofluoric acid are the solutions of choice.

[0012] When the electrolytic bath consists of an aqueous solution of hydrochloric acid, at a concentration of, for example, 10%, the potential is normally between 3.0 and 5.0 V, and preferably between 3.5 and 4.0 V.

[0013] When the bath consists of a mixture of hydrofluoric and nitric acids, the potential may run from 4.0 to 8.0 V. The treatment time may vary widely, for example from 1/1000 sec. to 60 seconds or more.

[0014] Pre-treatment is carried out by immersing the pickled titanium in one of baths mentioned, at a potential within the critical interval cited, then rinsing it in water and drying it. If, at some time during immersion, the potential rises or falls outside the critical interval, for example if a pulsating potential is applied, the treatment will be valid only for those portions of the surface that come into contact with the bath at the moment the potential applied lies within the critical interval. Thus a subsequent oxidation will allow intense colours to be obtained only in those regions.

[0015] The second oxidation instead, is carried out in any of the electrolytic baths utilized for traditional anodic oxidation of titanium—and, that is, for example, diluted phosphoric or sulphuric acids (1-5% by weight), solutions of sulphamic acid (1-15% by weight) or solutions of ammonium sulphate or sodium bicarbonate (1-15% by weight), etc., with a current density, in general, between 1 and 100 A/m².

[0016] The following examples illustrate the invention
in greater detail.

EXAMPLES

Example 1

[0017] A titanium plate is pickled in a bath of nitric and hydrofluoric acid (35%-5% by weight). After being rinsed in water, the plate is dried and then dipped in a bath of hydrochloric acid (10%) under an anodic potential of 4 Volt until it is completely immersed. The treatment is continued for 5-15 seconds, after which it is interrupted. After being rinsed in water, the plate is then oxidized according to the traditional techniques.

Example 2

[0018] The same procedure of Example 1 is used, applying a pulsating anodic potential as follows: 4 Volt for 1 second, 0 Volt the following second, 4 Volt the third second, and so on, for a variable number of cycles.

Claims

1. A method of coloring titanium and its alloys through anodic oxidation in an electrolytic bath characterized in that titanium or its alloys undergoes an anodic pre-treatment at constant potential in a first electrolytic bath consisting of hydrohalogen acids or salts, fluoboric acid, fluosilic acid, acetic acid, oxalic acid, tartaric acid, nitric acid, phosphoric acid and their mixtures, optionally in the presence of oxidizing agents.

2. A method according to claim 1, in which titanium or its alloys, pickled and dried, are connected to the electrode before immersion in the first electrolytic bath.

3. A method, according to claim 1 or 2, in which the constant anodic potential is between 2.0 and 15.0 Volts.

4. A method, according to claim 3, in which the first electrolytic bath consists of an aqueous solution of hydrochloric acid, and the constant anodic potential is between 3.0 and 5.0 Volts.

5. A method, according to claim 4, in which the constant anodic potential is between 3.0 and 4.0 Volts.

6. A method, according to claim 3, in which the first electrolytic bath consists of an aqueous solution of fluohydric and nitric acid and the constant anodic potential between 4.0 and 8.0 Volts.

7. A method, according to any of claims 1 to 6, in which the pre-treatment is carried out for periods of time ranging from 1/1000 second to 30 seconds.

8. Articles of titanium or its alloys colored using the methods according to any one of claims 1 to 6.