

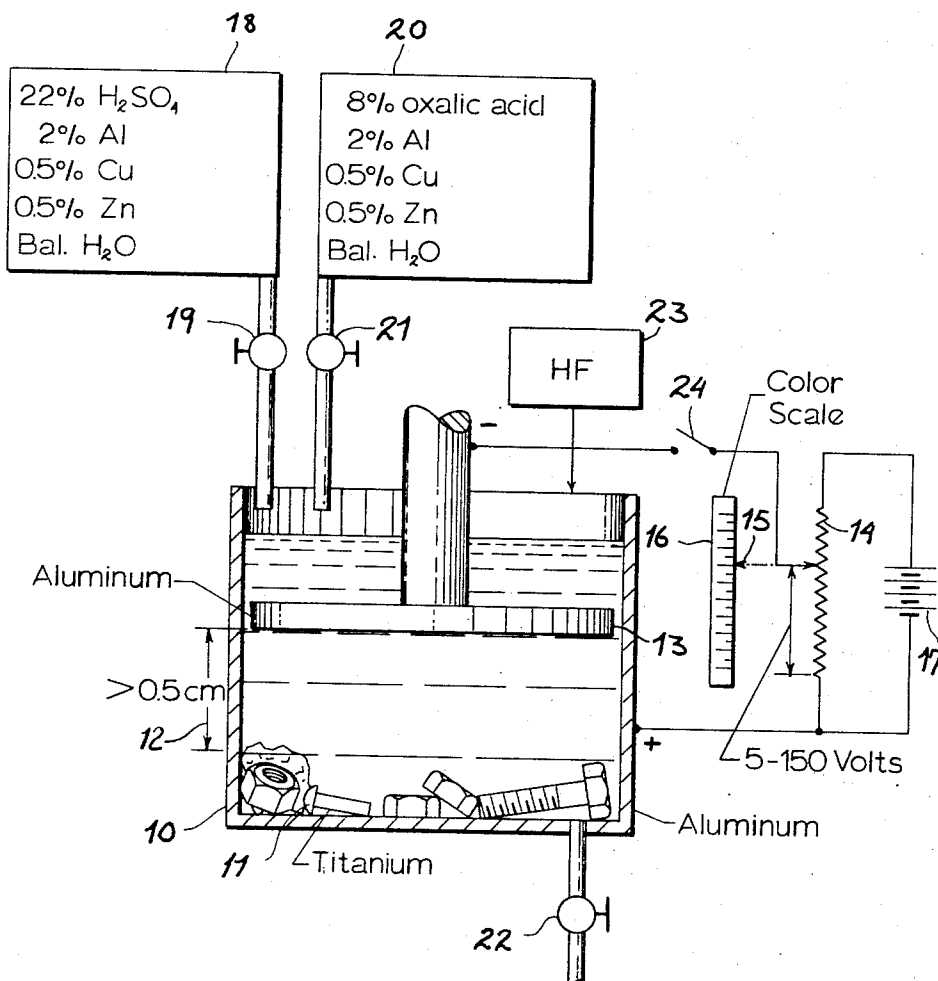
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METHOD OF SELECTIVELY COLORING TITANIUM BODIES

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**METHOD OF SELECTIVELY COLORING
TITANIUM BODIES**

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ABSTRACT OF THE DISCLOSURE

Method of anodically coloring titanium bodies wherein the body is juxtaposed with a counterelectrode of aluminum in an electrolyte consisting essentially of 22% by weight sulfuric acid, 2% by weight dissolved aluminum, 0.5% by weight dissolved copper, 0.5% by weight dissolved zinc and the balance water; or 8% by weight oxalic acid, 2% by weight dissolved aluminum, 0.5% by weight dissolved copper, 0.5% by weight dissolved zinc and the balance water; or mixtures of these electrolytes and the anodization is carried out at a direct-current potential between 5 and 150 volts at a temperature of 0° C. to 60° C. to color the surface of the metal in dependence upon the electric potential used within a relatively wide range of coloration.

My present invention relates to a method of coloring the surface of a body of an anodizable metal and, more particularly, to the selective coloring of bodies or parts thereof composed of titanium or titanium alloys.

While it has been proposed heretofore to color metals by anodization, it is common knowledge that conventional anodizing methods are generally restricted to imparting a single characteristic color to the surface of the metallic body. Moreover, it is a conventional practice in the treatment of titanium and titanium-alloy bodies, to subject these bodies to anodization in an electrolyte containing phosphoric acid or phosphorated sulphuric acid prior to heat treating the bodies. This anodization process serves merely to provide the titanium bodies with a durable oxide film adapted to protect the exposed surfaces of the bodies against adverse influences during the subsequent heat treatment. It may be further noted that it is also common practice to deposit metal oxides or elemental metals from their ionic solutions onto bodies which have been rendered cathodic in an electrolyte to color the surface of these bodies; the latter process amounts to a conventional electroplating operation and results in a film of low durability and low adhesion to the substrate. The anodizing techniques mentioned above were not, in general, used effectively for the coloring of titanium or titanium-alloy bodies because of the fact that it was impossible to modify the color produced by this technique.

It is a principal object of the present invention to provide an improved method of coloring titanium bodies wherein the aforementioned disadvantages can be eliminated and a durable coloration of the surface of the body can be produced effectively, rapidly and inexpensively.

It is a further object of this invention to provide a method of selectively coloring the surface of a body composed at least in part of titanium metal whereby any desired single color within a wide range of coloration may be imparted to the body.

Still another object of this invention is to provide an improved method of selectively and concurrently marking a multiplicity of titanium-containing objects distinctively.

These objects are attained, in accordance with the present invention, by providing a method of coloring bodies composed of titanium and titanium-alloys in a durable

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manner and with any selected color from a complete color scale or range. The invention is based upon my discovery that, when an anodizable metal and particularly titanium or titanium alloy is immersed in an aqueous electrolyte, which contains an ionizable substance such as an acid or a base, and is then juxtaposed with a counterelectrode and anodized, the particular coloration imparted to the body is determined by the magnitude of the direct-current electrical potential applied to the body. More specifically, it may be noted that any given range of coloration within the color scale mentioned above has associated therewith a range of voltage magnitude with low voltage amplitude corresponding to colors of the range of low wave length (e.g. toward the violet end of the spectrum) while larger voltage amplitudes correspond to colorations at the high-wave length end of the particular spectrum or range. It should be noted, however, that the "range" or "spectrum" of colors referred to herein need not be considered as a conventional white-light spectrum, but is more aptly described as a range of hues of varying intensity and predominantly characterized by violets, blues, greys, browns, gold and other mixtures of the usual spectrum colors as will be apparent hereinafter. In summary, therefore, it can be stated that lower applied voltages result in color hues of predominantly low-wave length while higher voltages yield color hues of predominantly higher wave lengths.

It is a more specific feature of the present invention that the aqueous electrolyte mentioned above contains between substantially 0.1 and 25% by weight of ionizable substance, i.e. an acid or base, and, preferably, one or more dissolved metals, these metals being present in toto in an amount ranging between substantially 0.1 and 8% by weight. Best results are obtained when the metals, which are aluminum, copper and zinc, are present in combination.

Apparently, the present method involves the surface oxidation of the titanium or titanium-alloy body to a titanium oxide. The particular coloration resulting is determined to a certain extent by the reagents provided, but more characteristically by the applied voltage. The color layer is produced in less than a second and it is not altered by subsequent modification of the applied potential; it is, therefore, preferred to immerse the body to be colored in the electrolyte together with the counterelectrode and only then to apply the desired electrical potential. The process of the present invention can thus serve for the inexpensive, simple, rapid and durable marking by coloring of titanium objects; the color layer has, moreover, been found to increase the corrosion resistance of the body whose color layer is found to have a high degree of adhesion to the remainder of the body and cannot be easily removed therefrom. Plastic deformation of the body, as for example in the deep drawing, forging or stamping thereof, does not injure the layer. Furthermore, this method of coloring and improving the corrosion resistance is especially suitable for precision parts, since the protective and coloring layer has a thickness less than 0.0001 mm., a measurement within the range of the usual finishing accuracy. A further advantage of the present method is that the coloring layer is very difficult to attack chemically.

I have found that acids and bases suitable for the practice of the present invention, alone or in combination in the aqueous electrolyte should best be selected from the group consisting of sulphuric acid, oxalic acid, acetic acid, nitric acid, hydrochloric acid, phosphoric acid, boric acid, ammonium hydroxide, sodium hydroxide, potassium hydroxide and sodium bicarbonate. With each of these acids, bases and combinations thereof, the dissolved metal content should range between 0.1 and 8% by weight of the solution.

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I have found that particularly effective results can be obtained by using applied voltages ranging between substantially 5 and 150 volts, this voltage range corresponding to an especially broad scale of coloration when the following electrolyte solutions are employed:

Solution A

	Percent by weight
Sulphuric acid	22
Dissolved aluminum	2
Dissolved copper	0.5
Dissolved zinc	0.5
Balance: water.	

Solution B

	Percent by weight
Oxalic acid	8
Dissolved aluminum	2
Dissolved copper	0.5
Dissolved zinc	0.5
Balance: water.	

A combination of solutions A and B using the voltage range given above is capable of yielding a color scale with 40 to 50 color tones, from dark brown through violet, blue, light blue, grey, gold, light brown, black, colorless, green to lilac.

In practice, the method of the present invention can be carried out by connecting the titanium-containing body and the positive pole of a direct-current source after immersion of the body and the counterelectrode in the electrolyte. The counterelectrode or cathode is provided with a corrosion-resistant material which cannot be significantly attacked by either of the electrolytes given above. Of particularly suitability, when solutions A and B are employed, is aluminum. Substantially simultaneously with the closing of the circuit, the desired coloration of the surface of the titanium body results. As soon as the color layer develops, the current flow is reduced to a value close to zero.

A rapid coloring of a multiplicity of titanium bodies, e.g. bolts, rivets and the like, can, according to another feature of this invention, be carried out in such manner that the titanium bodies are received within an anodically connected drum composed of an electrolyte-resistant metal, preferably aluminum. In this case, a substance should be added to the electrolyte capable of dissolving any oxide layer formed on the interior of the drum. A suitable acid for this purpose is a hydrofluoric acid solution, the hydrofluoric acid being added to the electrolyte. It has been found that the coloring process is independent of the temperature of the electrolyte although the reaction takes place more rapidly at elevated temperatures. A temperature range between 0 and 60° C. gives repeatedly satisfactory results. The titanium body may be relatively pure titanium or a titanium alloy, but should contain at least 20% by weight titanium. In the case of alloys, it may be noted that the magnitude of the titanium content controls the color tone produced.

The invention will be more readily apparent from the following description, reference being made to the accompanying drawing, the sole figure of which is a perspective view of an apparatus for carrying out the present invention.

In the drawing, I show a drum 10 composed of aluminum and adapted to receive the titanium bodies 11 with the spacing 12 from the aluminum counterelectrode 13 as indicated. The drum 10 and the counterelectrode 13 are connected across a voltage-dividing potentiometer 14, whose slider can be provided with an indicator 15 co-operating with a color scale 16 along which the desired color can be set. Each color corresponds to a particular voltage as is indicated above. The potentiometer 14 is connected across a direct-current source 17. A first reservoir 18 is provided for supplying an electrolyte corresponding to solution A as described above to the

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drum 10 via a valve 19 while a second reservoir 20 holds the solution B which can be introduced via valve 21 and interchanged with solution A when the latter is discharged via outlet valve 22. A source 23 of hydrogen fluoride can also be provided for adding this acid to the electrolyte to remove oxide films from the interior of the drum. When the titanium objects 11 are in position and are immersed together with the electrode 13 in the electrolyte, switch 24 is closed to effect the anodization. When the current falls, switch 24 is opened to permit removal of the colored bodies, the electrolyte can then be changed or the potentiometer setting altered to the proper parameters for application of a different color to the next group of titanium bodies.

Example

Using solutions A and B at a temperature of about 30° C. and a spacing between the counterelectrode and the titanium body greater than about 0.5 cm., a body of substantially pure titanium was anodized at voltages between 5 and 150 volts to give the color hues indicated in the following table:

TABLE

Colors	Voltage	Solution
Dark brown.....	10-12	A or B.
Violet.....	14-17	A or B.
Blue.....	20-23	20% by volume A and 80% B.
Light blue.....	25-29	Do.
Grey.....	30-40	B.
Gold.....	50-55	B.
Light brown.....	5-9	A.
Do.....	56-60	B.
Black.....	130-150	B.
Colorless.....	60-70	B.
Green.....	90-110	B.
Lilac.....	60-65	B.

I claim:

1. A method of selectively coloring a surface of a titanium or titanium alloy body containing at least 20% by weight titanium metal with any one color within a range of coloration, comprising the steps of:

juxtaposing said body with a counterelectrode with said surface and said counterelectrode immersed in at least one aqueous electrolyte from the group of electrolytes A and B, wherein:

electrolyte A consists essentially of 22% by weight sulfuric acid, 2% by weight dissolved aluminum, 0.5% by weight dissolved copper, 0.5% by weight dissolved zinc, and the balance water, and

electrolyte B consists essentially of 8% by weight oxalic acid, 2% by weight dissolved aluminum, 0.5% by weight dissolved copper, 0.5% by weight dissolved zinc, and the balance water; and applying a direct-current electrical potential across said body and said counterelectrode while rendering said body anodic with respect to said counterelectrode for a period sufficient to anodically oxidize said surface.

2. The method defined in claim 1 wherein said counterelectrode consists essentially of aluminum.

3. The method defined in claim 1 wherein said body is retained in a drum of an electrolyte-resistant metal and said drum is rendered anodic, further comprising passing a hydrofluoric acid solution through the interior of said drum to dissolve oxide layers formed thereon during coloring of said body.

4. The method defined in claim 3 wherein said drum is composed of aluminum.

5. The method defined in claim 1 wherein the anodization of the body is carried out at a temperature between 0° C. and 60° C. at an anodization potential between substantially 5 and 150 volts whereby the potential employed determines the coloration of said surface.

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