

SPECIFICATION

Method for manufacturing a bicolored polyhedral body of aluminum

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The present invention concerns a method for manufacturing a bicolored polyhedral body of aluminum, more particularly a method for providing decorative coloring on the surface of a polyhedral body made of aluminum or an alloy mainly composed of aluminum, in two different colors, in which the faces colored in dark and in light tones are precisely and attractively demarcated by the ridgeline of the polyhedral body.

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A diversity of articles made of aluminum or an aluminum alloy (hereinafter referred to simply as aluminum) and anodized and colored on the surface are widely used because of their lightness in weight and attractiveness as well as their high anti-corrosion resistance. For example, aluminum watch cases with anodization and coloring on their surface have acquired a substantial commercial success. These conventional aluminum watch cases are, however, colored with a single tone and ways have therefore been sought of overcoming the monotonousness of these unicolored cases and of further enhancing their aesthetic value by providing bicolored surfaces in dark and light colors.

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Such a bicolored polyhedral body, in particular a watch case, of aluminum can be obtained in principle by subjecting an anodized and colored article with a partly removed surface layer to a second anodization and coloring treatment using a different color. This method is not always satisfactory because the anodized and colored surface film of the article formed in the first step is readily degraded in the second anodization and coloring treatment resulting in poor surface properties. Various attempts have been made to overcome the above mentioned problems but without noticeable success.

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Thus the present invention seeks to solve the problem of providing a novel and improved method for manufacturing a bicolored polyhedral body of aluminum using a two-step anodization and coloring treatment, according to which the faces of the polyhedral body colored in dark and in light tones are precisely and attractively demarcated by a ridgeline of the body between the faces and the surface film of the oxide on the dark-colored face formed in the first anodization and coloring treatment is free from deterioration in the second anodization and coloring treatment.

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The method of the invention for manufacturing a bicolored polyhedral body of aluminum comprises (a) anodically oxidizing the surface of the aluminum body to form an oxide film on the surface.

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(b) coloring the oxide film on the surface of the body in a dark tone color,

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(c) subjecting the thus anodized and colored surface to a sealing treatment,

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(d) mechanically removing the oxide film on the surface from a part of the polyhedral faces of the body to expose a bare aluminum surface,

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(e) activating the thus exposed bare aluminum sur-

face,

(f) anodically oxidizing the thus activated bare aluminum surface in an electrolyte bath containing at least one organic acid by the application of a voltage in the range from 50 to 80 volts to form an oxide film on the surface,

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(g) coloring the oxide film on the surface of the body formed in the second anodization in a light tone color, and

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(h) subjecting the thus anodized and colored surface to a second sealing treatment.

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The invention also provides a bicolored polyhedral body made of aluminum and having at least two faces with an anodically oxidized layer on the surface of the aluminum base and colored in different colors on a first face and a second face demarcated by a ridgeline, wherein the peripheral margin of the anodically oxidized layer on the second face extends and intrudes interstitially between the anodically oxidized layer on the first face and the surface of the aluminum base.

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Preferred embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which:-

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Figure 1 is a perspective view of a blank for a watch case as an example of a polyhedral body before coloring.

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Figures 2a, 2b and 2c each illustrates a step in the method of the invention and shows a partial enlarged cross section of the polyhedral body.

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Figure 3 is a perspective view of a bicolored watch case finished by the method of the invention.

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The term 'polyhedral body' as used herein means, though it may be not in strict compliance with a geometrical definition, a body having at least two faces, which may be flat or curved, intersecting to form one or more ridgelines and desired to be colored in different colors for aesthetic reasons. Typical examples of the polyhedral body are watch cases, bracelets and other ring-like articles and bands but the invention is applicable to other bodies having a ridgeline.

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The polyhedral body of aluminum is colored in a combination of two different colors on respective faces. The two different colors have desirably a definite difference in luminosity (dark and light). Examples of the dark color are black, dark blue, dark brown, dark green, deep red and the like and the light color is exemplified by golden yellow, silver white, yellow, light green, light blue and the like. The combination of the dark and light colors is not important and may be selected from the aesthetic viewpoint. For example, combination of black and gold, brown and gold, black and silver white and the like may be preferred.

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The polyhedral body is made of aluminum or an aluminum alloy provided that the alloy is susceptible to anodic oxidation.

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For better comprehensibility, the following description is given with reference to an aluminum watch case but it should be understood that the applicability of the method is not limited to watch cases but extends to other polyhedral aluminum bodies.

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FIGURE 1 is a perspective view of a blank for a

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watch case obtained by machining operations such as punching and cutting. Prior to the first anodization, the blank is degreased and washed in a conventional manner. The thus cleaned blank is then anodically oxidized in an electrolyte bath containing, for example, sulfuric acid to form an anodically oxidized oxide film on the surface. Typical electrolytic conditions for the first anodization are: temperature from -10 to +10°C; voltage from 30 to 40 volts; current density from 3 to 6 amperes/dm²; and time of electrolysis from 30 to 60 minutes. By this anodic oxidation, an oxide film 2 is formed on the surface of the aluminum base 1 on both sides of the ridgeline 3 as is shown in FIGURE 2a in a partial enlarged cross section. The thickness of the thus formed oxide film is usually in the range from 40 to 60 μm.

After completion of the first anodization treatment as described above followed by rinsing with water, the blank is dipped in a dye solution so that it is dyed a dark tone color, for example, black. The dyeing conditions may widely differ depending on the type of dye and the concentration of the dyeing solution but usually dipping of the blank in a dye solution at 50°C or higher for 10 to 30 minutes is sufficient. The thus dyed blank is then rinsed with water and subjected to a sealing treatment in hot pure water, for example, at 90°C for 10 to 60 minutes to provide a unicolored blank colored in black all over the surface.

One or more particular faces of the blank thus colored in a dark color are then mechanically worked, e.g. ground, to remove the colored oxide layer and to expose the bare surface of the aluminum base, and polished by buffing. Care should be taken that the neatness of the ridgeline 3 or rather the demarcating line between the remaining oxide layer 2 and the exposed bare face of aluminum is not unduly impaired, as is shown in FIGURE 2b in cross section.

The next step is the activation of the thus exposed and polished bare surface of the aluminum base. This activation treatment is carried out by dipping the blank in an aqueous acid solution. Suitable acid solutions are sulfuric acid in a concentration of 20 to 50% by weight and nitric acid in a concentration of 5 to 40% by weight at a temperature from 15 to 40°C and the dipping time is usually from 1 to 5 minutes. The conditions for this activation treatment should be determined so as not to deteriorate the colored oxide film 2 obtained in the first anodization and coloring treatment and so as not to reduce the metallic lustre on the mirror-polished bare aluminum surface.

The blank thus activated on the bare aluminum surface is then subjected to a second anodization in an electrolyte bath containing at least one organic acid. Suitable organic acids are exemplified by oxalic acid, tartaric acid, malic acid, sulfophthalic acid and the like and they may be used either alone or as a combination of two or more. The concentration of the organic acid in the electrolyte bath is usually in the range from 3 to 200 g/liter.

Characteristically different from the first anodization, the second anodization is carried out by applying a voltage in the range from 50 to 80 volts, considerably higher than in the first anodization. Other

electrolytic conditions are: temperature from 20 to 40°C; current density from 3 to 6 amperes/dm²; and time of electrolysis from 15 to 40 minutes. The oxide film formed by this second anodization should have a thickness of at least 20 μm or, preferably, at least 30 μm in order that the finished watch case has a sufficient anti-corrosion resistance and anti-scratch resistance as well as full decorativeness as is required for an ornamental article such as a watch.

It has been generally understood that in repeating the anodization treatment of the aluminum surface the voltage in the second anodization should be lower than in the first anodization because otherwise the oxide film formed in the first anodization is deteriorated and readily exfoliated during the second anodization treatment. A disadvantage inherent in such a low-voltage anodization is that the rate of oxide film formation in the second anodization is necessarily low and an excessively long time is taken to obtain a desired thickness of the oxide film, which again causes deterioration of the oxide film obtained in the first anodization treatment.

Notwithstanding the above described problems in the conventional second anodization treatment, the second anodization treatment in the method of the invention can be performed with a higher voltage of 50 to 80 volts without causing deterioration of the oxide film formed in the first anodization treatment. This unexpected advantage is obtained presumably by virtue of the preceding activation treatment of the bar surface of the aluminum base resulting in a thick barrier layer between the aluminum surface and the oxide film without decreasing the metallic lustre of the activated surface which in turn leads to the improvement of the adhesion of the oxide film to the aluminum surface and the anti-corrosion resistance of the surface. In other words, the second anodization treatment should be carried out with the composition and concentration of the electrolyte bath and the electrolytic conditions arranged to satisfy these requirements within the limitations above described.

After completion of the second anodization treatment followed by rinsing with water, the blank is colored by dipping in a second dyeing solution containing a dye of a light tone color, for example, golden yellow. The dyeing conditions may be the same as in the first dyeing. The final step of the method is the second sealing treatment which may be carried out under conventional conditions to give a bicolored blank for a watch case as is shown in FIGURE 2c in cross section in which the dark-colored face 2 and the light-colored face 4 are precisely and attractively demarcated by the ridgeline 3.

As is shown in the enlarged cross section in FIGURE 2c, interstitial intrusion of the peripheral margin of the oxide film 4 formed in the second anodization is found between the oxide film 2 formed in the first anodization and the aluminum surface along the ridgeline 3. This interstitial intrusion of the oxide film 4 is very effective in emphasizing the color contrast between the dark- and light-colored faces at the demarcating line 3 and gives good anti-corrosion resistance and adhesion of both the oxide films 2 and 4.

The bicolored polyhedral bodies obtained have precise and attractive demarcation of two faces colored in dark and light on respective sides of the ridgeline, with good adhesion and anti-corrosion resistance of the oxide films formed in both of the first and the second anodization treatments.

Example.

(i) A blank for a watch case as shown in FIGURE 1 was prepared from an aluminum slab by punching under pressure, cutting and grinding. The blank was degreased and cleaned by dipping first in a 7% aqueous solution of sodium hydroxide at 70°C for 2 minutes and then in a 35% nitric acid solution at 50°C for 1 minute followed by rinsing with water.

(ii) The blank was anodized in an electrolyte bath at 0°C containing 150 g/liter of sulfuric acid and 15 g/liter of glycerin for 40 minutes with a current density of 4 amperes/dm² by applying a voltage of 35 volts, followed by rinsing with water. The oxide film formed in this first anodization had a thickness of about 50 µm.

The thus anodized blank was dipped in a dyeing solution containing 10 g/liter of a black dye (Alumisol Black MLB, a tradename) at 50°C or higher for 30 minutes so that it was dyed black and then subjected to a sealing treatment in pure water at 90°C for 30 minutes followed by drying.

(iii) Several faces of the blank, i.e. the faces 4 shown in white in FIGURE 3, were mechanically ground to remove the black-colored oxide film and to expose the bare surface of the aluminum base which was mirror-polished by buffing.

(iv) The blank was dipped in a 400 g/liter solution of sulfuric acid at 30°C for 2 minutes to activate the polished bare surface of the aluminum base. After rinsing with water, the thus activated surface was anodized in an electrolyte bath at 30°C containing 100 g/liter of sulfophthalic acid, 50 g/liter of oxalic acid, 10 g/liter of tartaric acid and 5 g/liter of malic acid for 20 minutes with a current density of 4 amperes/dm² by applying a voltage of 60 volts. The oxide film formed in this second anodization treatment had a thickness of about 30 µm.

The thus anodized blank was dipped in a dyeing solution containing 10 g/liter of a golden yellow dye (Alumisol Gold ZL, a tradename) at 50°C or higher for 30 minutes so that it was dyed an attractive golden color on the surface of the oxide film formed in the second anodization, followed by a second sealing treatment in water at 90°C for 30 minutes.

The thus finished blank for a watch case has an appearance as illustrated in FIGURE 3 in a perspective view and was colored pure black on the faces 2 shown in black in the figure and golden yellow on the faces 4 shown in white in the figure, with very sharp demarcating lines 3.

CLAIMS

1. A method for making a bicolored polyhedral body of aluminum which comprises
 (a) anodically oxidizing the surface of the aluminum body to form an oxide film on the surface,
 (b) coloring the oxide film on the surface of the aluminum body in a dark tone color,
 (c) subjecting the thus anodized and colored surface of the aluminum body to a first sealing treatment,

(d) mechanically removing the oxide film on the surface of the aluminum body from a part of the polyhedral faces of the body to expose the bare surface of aluminum,

(e) activating the thus exposed bare surface of aluminum,

(f) anodically oxidizing the thus exposed and activated bare surface of aluminum in an electrolyte bath containing at least one organic acid by the

application of an electric voltage in the range from 50 to 80 volts to form an oxide film on the bare surface of aluminum,

(g) coloring the oxide film on the surface of the aluminum body formed in step (f) above of the second anodization in a light tone color,

and

(h) subjecting the surface thus anodized and colored in a light tone color to a second sealing treatment.

2. The method as claimed in claim 1 wherein the activation in step (e) is carried out by bringing the exposed bare surface of aluminum into contact with an aqueous acid solution.

3. The method as claimed in claim 2 wherein the aqueous acid solution is a sulfuric acid solution in a concentration from 20 to 50% by weight or a nitric acid solution in a concentration from 5 to 40% by weight.

4. The method as claimed in any preceding claim wherein the organic acid in step (f) is selected from sulfophthalic acid, oxalic acid, tartaric acid and malic acid.

5. The method as claimed in any preceding claim wherein the concentration of the organic acid in the electrolyte bath is in the range from 3 to 200 g/liter.

6. A bicolored polyhedral body made of aluminum and having at least two faces with an anodically oxidized layer on the surface of the aluminum base and colored in different colors on a first face and a second face demarcated by a ridgeline, wherein the peripheral margin of the anodically oxidized layer on the second face extends and intrudes interstitially between the anodically oxidized layer on the first face and the surface of the aluminum base.

7. The bicolored polyhedral body made of aluminum as claimed in claim 6 wherein the color on the second face is lighter in luminosity than the color on the first face.

8. The method as claimed in Claim 1, substantially as hereinbefore described with reference to the drawings.

9. The method as claimed in Claim 1, substantially as hereinbefore described in the Example.

10. A polyhedral body of aluminum when made by the method as claimed in any one of Claims 1-5, 8 and 9.

11. The bicolored polyhedral body made of aluminum as claimed in Claim 6, substantially as hereinbefore described with reference to the drawings.

12. The bicolored polyhedral body made of aluminum as claimed in Claim 6, substantially as hereinbefore described in the Example.



The bicolored polyhedral bodies obtained have precise and attractive demarcation of two faces colored in dark and light on respective sides of the ridgeline, with good adhesion and anti-corrosion resistance of the oxide films formed in both of the first and the second anodization treatments.

Example.

(i) A blank for a watch case as shown in FIGURE 1 was prepared from an aluminum slab by punching under pressure, cutting and grinding. The blank was degreased and cleaned by dipping first in a 7% aqueous solution of sodium hydroxide at 70°C for 2 minutes and then in a 35% nitric acid solution at 50°C for 1 minute followed by rinsing with water.

(ii) The blank was anodized in an electrolyte bath at 0°C containing 150 g/liter of sulfuric acid and 15 g/liter of glycerin for 40 minutes with a current density of 4 amperes/dm² by applying a voltage of 35 volts, followed by rinsing with water. The oxide film formed in this first anodization had a thickness of about 50 μm.

The thus anodized blank was dipped in a dyeing solution containing 10 g/liter of a black dye (Alumisol Black MLB, a tradename) at 50°C or higher for 30 minutes so that it was dyed black and then subjected to a sealing treatment in pure water at 90°C for 30 minutes followed by drying.

(iii) Several faces of the blank, i.e. the faces 4 shown in white in FIGURE 3, were mechanically ground to remove the black-colored oxide film and to expose the bare surface of the aluminum base which was mirror-polished by buffing.

(iv) The blank was dipped in a 400 g/liter solution of sulfuric acid at 30°C for 2 minutes to activate the polished bare surface of the aluminum base. After rinsing with water, the thus activated surface was anodized in an electrolyte bath at 30°C containing 100 g/liter of sulfophthalic acid, 50 g/liter of oxalic acid, 10 g/liter of tartaric acid and 5 g/liter of malic acid for 20 minutes with a current density of 4 amperes/dm² by applying a voltage of 60 volts. The oxide film formed in this second anodization treatment had a thickness of about 30 μm.

The thus anodized blank was dipped in a dyeing solution containing 10 g/liter of a golden yellow dye (Alumisol Gold ZL, a tradename) at 50°C or higher for 30 minutes so that it was dyed an attractive golden color on the surface of the oxide film formed in the second anodization, followed by a second sealing treatment in water at 90°C for 30 minutes.

The thus finished blank for a watch case has an appearance as illustrated in FIGURE 3 in a perspective view and was colored pure black on the faces 2 shown in black in the figure and golden yellow on the faces 4 shown in white in the figure, with very sharp demarcating lines 3.

CLAIMS

1. A method for making a bicolored polyhedral body of aluminum which comprises

- (a) anodically oxidizing the surface of the aluminum body to form an oxide film on the surface,
- (b) coloring the oxide film on the surface of the aluminum body in a dark tone color,
- (c) subjecting the thus anodized and colored surface of the aluminum body to a first sealing treatment,

(d) mechanically removing the oxide film on the surface of the aluminum body from a part of the polyhedral faces of the body to expose the bare surface of aluminum,

(e) activating the thus exposed bare surface of aluminum,

(f) anodically oxidizing the thus exposed and activated bare surface of aluminum in an electrolyte bath containing at least one organic acid by the

application of an electric voltage in the range from 50 to 80 volts to form an oxide film on the bare surface of aluminum,

(g) coloring the oxide film on the surface of the aluminum body formed in step (f) above of the second anodization in a light tone color,

and

(h) subjecting the surface thus anodized and colored in a light tone color to a second sealing treatment.

2. The method as claimed in claim 1 wherein the activation in step (e) is carried out by bringing the exposed bare surface of aluminum into contact with an aqueous acid solution.

3. The method as claimed in claim 2 wherein the aqueous acid solution is a sulfuric acid solution in a concentration from 20 to 50% by weight or a nitric acid solution in a concentration from 5 to 40% by weight.

4. The method as claimed in any preceding claim wherein the organic acid in step (f) is selected from sulfophthalic acid, oxalic acid, tartaric acid and malic acid.

5. The method as claimed in any preceding claim wherein the concentration of the organic acid in the electrolyte bath is in the range from 3 to 200 g/liter.

6. A bicolored polyhedral body made of aluminum and having at least two faces with an anodically oxidized layer on the surface of the aluminum base and colored in different colors on a first face and a second face demarcated by a ridgeline, wherein the peripheral margin of the anodically oxidized layer on the second face extends and intrudes interstitially between the anodically oxidized layer on the first face and the surface of the aluminum base.

7. The bicolored polyhedral body made of aluminum as claimed in claim 6 wherein the color on the second face is lighter in luminosity than the color on the first face.

8. The method as claimed in Claim 1, substantially as hereinbefore described with reference to the drawings.

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