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(54) COLORED SHAPED ALUMINUM ARTICLE AND METHOD FOR MANUFACTURING

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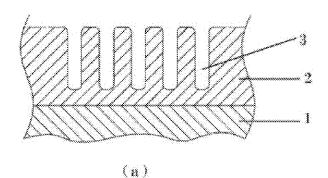
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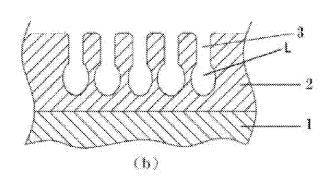
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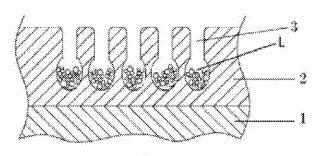
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(57)**ABSTRACT**

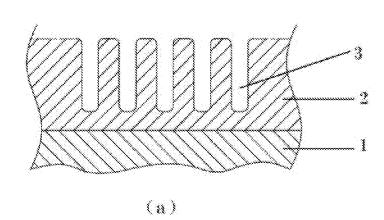
A shaped aluminum article has an anodized film formed on a surface, where a coloring pigment is filled in fine pores formed on the anodized film, achieving sufficient coloring.

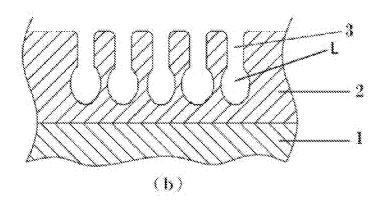


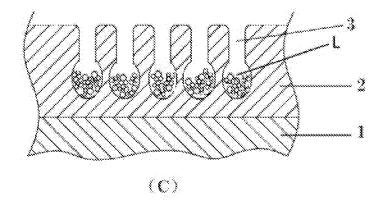




[FIG. 1]







COLORED SHAPED ALUMINUM ARTICLE AND METHOD FOR MANUFACTURING SAME

TECHNICAL FIELD

[0001] The present invention relates to a shaped aluminum article to which color has been added, as well as a method of manufacturing such shaped aluminum article.

BACKGROUND ART

[0002] A shaped aluminum article naturally has the characteristic metallic gloss of metal aluminum, and when such shaped article is used in applications where coloring is required, a conventional way has been to give a known surface treatment to the shaped article, as necessary, and then paint it using a pigmented paint of black, red, white, or other desired color.

[0003] Besides painting as mentioned above, a method whereby the surface of a shaped aluminum article is anodized according to the sulfuric acid method or oxalic acid method, for example, and then a desired dye is impregnated or pigment is filled in the micro-fine pores formed on the surface, as well as a method whereby nickel, etc., is electrolytically deposited to add color electrolytically, are also known. However, these methods, especially the electrolytic coloring method, can add only limited colors.

[0004] In addition, the method using electrophoretic migration whereby a pigment is introduced into fine pores formed on the surface of a shaped aluminum article to add color, requires that the fine pore diameter is large enough to accommodate the pigment and that the pigment diameter is also small. With this method, however, it is difficult to add color in a stable and uniform manner, and also because the amount of pigment that can be introduced into the fine pores is limited, it is also difficult to add a deep color.

[0005] Also, as described in Patent Literature 1, a method, which is not a coloring method, is known which comprises: a titanyl electrolytic treatment step to anodize the surface of a shaped aluminum article beforehand and then electrolytically treat the shaped aluminum article in a mixed solution containing titanyl sulfate, etc., and complexing agent forming anions, in order to cause titanium dioxide to deposit onto the surface of the anodized film and interior surface of the fine pores, thereby forming a film containing titanium dioxide; and a sintering step to sinter the film of titanium dioxide to change it to a photocatalytic film constituted by titanium dioxide having photocatalytic action; so that a photocatalytic film constituted by titanium dioxide is formed on the surface of the anodized film and interior surface of the fine pores. [0006] In addition, Patent Literature 2 describes an aluminum or aluminum alloy material characterized in that it is constituted by a base material being aluminum or aluminum alloy on the surface of which an anodized film is formed in areas that are not fine pores, and this film is coated with a photocatalytic film produced by aggregated and deposited fine semiconductor grains of titanium oxide, etc., having photocatalytic action and an average grain size of 1 nm to

[0007] Patent Literature 3 describes applying AC voltage, in a metallic salt solution, to an aluminum material that has been anodized at high voltage to achieve electrolytic coloring, while Patent Literature 4 describes using a diluted

1000 nm, where titanium oxide, etc., is not adsorbed into the

fine pores formed on the anodized film.

alkaline aqueous solution to etch an aluminum material on which an anodized film has been formed and thereby chemically dissolve the exposed surface of the barrier layer at the bottom of the fine pores in the anodized film, which is followed by electrolytic coloring, or coloring by means of electrophoretic migration, in an electrolytic coloring bath containing pigment grains or metallic salt.

BACKGROUND ART LITERATURE

Patent Literature

[0008] Patent Literature 1: Japanese Patent No. 4905659
[0009] Patent Literature 2: Japanese Patent No. 3326071
[0010] Patent Literature 3: Japanese Patent Laid-open No. Hei 11-335893

[0011] Patent Literature 4: Japanese Patent Laid-open No. Hei 11-236697

SUMMARY OF THE INVENTION

Problems to Be Solved by the Invention

[0012] According to the prior art, where paint is applied to add color to the surface of a shaped aluminum article, the white coating film may peel or otherwise the aesthetic appearance may be reduced as the shaped aluminum article is used continuously.

[0013] Also, according to the method whereby a pigment is filled in the fine pores in the anodized film by means of electrophoretic migration, the fine pores must have a large diameter so that the pigment can be filled in them by an amount sufficient for it to demonstrate coloring strength. This can make the surface of the shaped aluminum article rough and reduce the aesthetic appearance as a result.

[0014] Furthermore, the colored film thus obtained is not a dense film; instead, the shaped aluminum article has a transparent white color because it already has some optical interference property, before titanium oxide is filled in the fine pores, due to the large diameter of the fine pores. Consequently, an opaque, white film cannot be obtained.

[0015] In addition, an attempt to achieve stable, deep coloring by means of electrophoretic migration tends to cause the pigment to deposit excessively on the surface outside the fine pores, instead of inside the fine pores, because the bath current is low during the electrophoretic migration.

[0016] Moreover, according to the method described in Patent Literature 1 above, which comprises a titanyl electrolytic treatment step to cause titanium dioxide to deposit onto the surface of the anodized film and interior surface of the fine pores and thereby form a titanium dioxide film, and a step to sinter this titanium dioxide film, it is difficult to cause a sufficient amount of photocatalytic titanium dioxide to deposit, and because the shaped aluminum article whose heat resistance is relatively poor is heated to high temperature, the shaped article may deform or its physical properties may change.

[0017] The method described in Patent Literature 2 is one whereby an anodized aluminum sheet is soaked in a titanium oxide sol to cause electrophoretic migration, so that titanium oxide grains are deposited not inside the fine pores formed on the surface of the aluminum sheet, but onto the surface, and the photocatalyst is supported as a result; however, the supported titanium oxide is used as photocatalyst; it is not

supported inside the fine pores, and any amount supported inside the fine pores is minimal.

[0018] The method described in Patent Literature 3 is one whereby AC voltage is applied, in a metallic salt solution, to the surface of an aluminum material on which an anodized film has been formed, to achieve coloring; however, anodization treatment is given only once and the depositing of a metallic compound inside the fine pores is not suggested.

[0019] Also regarding the method described in Patent Literature 4 whereby a pigment is filled in fine pores formed by an anodized film, there is a step to etch the anodized film to dissolve the barrier layer before the pigment is filled, and, needless to say, this etching step is incapable of dissolving only the barrier layer inside the fine pores and clearly the entire anodized film is etched. As a result, an irregular surface is formed over the entire anodized film, and even if color is added, the formed aluminum sheet will have an irregular, non-uniform surface at best.

[0020] In addition, etching the formed anodized film means that the anodized film is lost. Therefore, although there are fine pores, the interior of the fine pores is not protected by the anodized film and, as the aluminum material is used over time, the interior of the fine pores and surface of the aluminum material will corrode.

[0021] Accordingly, an object of the present invention is to obtain a shaped aluminum article which has an opaque and sufficient colored film produced by filling grains of titanium dioxide or other pigment into fine pores formed by means of anodization, maintains its original shape, and provides the inherent physical properties of the anodized film.

Means for Solving the Problems

[0022] The inventors of the present invention studied in earnest to achieve the aforementioned object and invented the shaped aluminum article and method of manufacturing such shaped aluminum article as described below:

[0023] 1. A shaped aluminum article having an anodized film formed on its surface, where a pigment is filled in fine pores formed on the anodized film at a density of 2 mg to 30 mg per 1 square decimeter.

[0024] 2. A shaped aluminum article according to 1, wherein the diameters of the openings of the fine pores are 5 to 300 nm.

[0025] 3. A shaped aluminum article according to 1 or 2, wherein the lengths of the fine pores in the depth direction of the shaped article are 5 to 50 µm.

[0026] 4. A shaped aluminum article according to any one of 1 to 3, wherein the fine pores have a portion having an enlarged diameter at the bottom.

[0027] 5. A shaped aluminum article according to any one of 1 to 4, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.

[0028] 6. An anodization treatment that includes an anodization treatment implemented under a condition of constant current, and a subsequent anodization treatment implemented at a constant voltage, are given to a shaped aluminum article to form an anodized film having fine pores on the surface of the shaped aluminum article. A method of coloring the surface of shaped aluminum article, comprising: soaking the obtained shaped aluminum

num article in an aqueous solution of metallic salt and then applying alternating current to it in this aqueous solution to cause a pigment to deposit in, and fill, the fine pores formed.

Effects of the Invention

[0029] Compared to the conventional painting method, according to the present invention prevents, the colored film is not removed unless the anodized film peels. In addition, the shaped aluminum article that has been colored by a pigment or dye introduced into the fine pores of the anodized film exhibits an especially deep color in a stable manner because more pigment can be fixed. Moreover, sufficient coloring can be achieved even when a pigment whose primary grain size is too small for the pigment color to be exhibited is used, because secondary aggregation can be achieved inside the fine pores.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] FIG. 1 A schematic view of the step in which titanium oxide grains are introduced under the present invention.

MODE FOR CARRYING OUT THE INVENTION

[0031] The present invention can be implemented by consequently filling pigment grains in fine pores formed on an anodized film. In addition, even when grains of titanium oxide, etc., are used whose grain size is smaller to a point where the primary grains are too small to normally exhibit a white color, for example, use of a solution of the applicable compound allows the pigment to deposit from this solution into the fine pores so that the light entering from the outside reflects diffusely between the titanium oxide grains constituting these aggregated grains to increase the opacity, which in turn causes the aggregated titanium oxide grains to exhibit a white color and consequently the anodized film exhibits a white color. The same can be said with other pigments, not just titanium oxide.

[0032] In particular, the fine pores formed on the surface of the shaped aluminum article as proposed by the present invention assume what looks like an urn shape because their diameter increases from the opening at the surface toward the interior of the shaped aluminum article. As a result, more pigment can be deposited into the fine pores, which in turn improves the coloring strength.

[0033] Such shaped aluminum article proposed by the present invention is manufactured through a fine pore formation step, which is a two-stage anodization treatment step, and a subsequent pigment filling step.

[0034] The anodization method used under the present invention is one which is applied to shaped articles made of the aluminum materials described below.

(Aluminum Material for Shaped Aluminum Article)

[0035] The aluminum material constituting the shaped aluminum article proposed by the present invention may be made only of aluminum, but it can also be made of any so-called aluminum alloy (such as Al—Mn alloy, Al—Mg alloy, Al—Mg—Si alloy, etc.), so long as fine pores will be formed through anodization treatment. In addition, any material which is made by alloying aluminum material with other metal and thus is already colored, can also be used.

[0036] Which aluminum material should be used is determined according to the application of the shaped aluminum article proposed by the present invention.

[0037] The pigment filled in the shaped aluminum article under the present invention only needs to be a pigment that can be deposited, under electrodeposition conditions, from a solution of a compound such as those listed below, for example, and specifically titanium oxide, iron oxide or zinc oxide, etc., can be used.

[Anodization Treatment Step]

[0038] The fine pore formation step based on a method of two-stage anodization is described.

(Two-stage Anodization Method)

(First Anodization Treatment)

[0039] The first stage of anodization treatment to obtain the shaped aluminum article proposed by the present invention is the same as a treatment to form an anodized film on the surface of a shaped aluminum article to add corrosion resistance and decorativeness to the surface, and it must be able to form fine pores on the anodized film.

[0040] A shaped aluminum article is soaked in an electrolytic solution together with the anode and cathode of an anodization treatment apparatus in such a way that it is electrically contacting the anode, and by supplying power between the anode and cathode, an anodized film is formed on the shaped aluminum article.

[0041] The electrolytic solution used here is preferably an electrolytic solution constituted by sulfuric acid, phosphoric acid, maleic acid, malonic acid, oxalic acid, or chromic acid, but it is not limited to the foregoing in any way.

[0042] In the first stage of anodization, the treatment is performed under a condition of maintaining the current density at a constant level. Here, the current density is preferably 0.5 to $3.0~\text{A/dm}^2$.

[0043] The fine pores that generate are formed as fine pores 3 that are long columnar voids extending in the depth direction of the anodized film 2 formed on the surface of the shaped aluminum article 1, as shown in FIG. 1 (a), for example. However, they are not necessarily formed at right angles to the surface of the shaped aluminum article as illustrated; instead, they actually assume a bent, branched, or other irregular shape. The diameters of their openings can be adjusted as desired according to the anodization conditions, but under the present invention, the fine pores of the anodized film generated in this step have an opening diameter of 5 to 300 nm, or preferably 5 nm or more but less than 50 nm, or more preferably 8 to 50 nm. If the opening diameter is larger than 300 nm, obtaining a uniform anodized film becomes difficult; on the other hand, it is difficult to obtain a porous film of less than 5 nm in opening diameter. [0044] Also, the lengths of fine pores are not limited in any way; to deposit the amount of pigment needed to ensure sufficient coloring by the pigment, however, the fine pores

(Second Anodization Treatment)

[0045] The second anodization treatment is performed primarily for the purpose of increasing the fine pore diameter inside the fine pores that have been formed by the first

are 5 to 50 µm long, or preferably 10 to 40 µm long, from

the aluminum surface in the thickness direction.

anodization treatment on the surface of the shaped aluminum article, not around the openings of the fine pores.

[0046] For this reason, the second anodization treatment, for which a phosphoric acid solution is selected as the solution to be used, is performed by soaking the target which is the shaped aluminum article that has completed the first anodization treatment, in the phosphoric acid solution and applying direct current to it.

[0047] As a result of this, the diameters of the generated fine pores increase near the bottom L, as shown in FIG. 1 (b). The fine pores assume such shape probably because the aluminum and anodized film are highly soluble in phosphoric acid.

[Electrodeposition Step]

[0048] (Step to Deposit Pigment into Fine Pores)

[0049] Under the present invention, the step to deposit the pigment into the fine pores of the anodized film is an electrodeposition step wherein the shaped aluminum article completing the aforementioned anodization treatment is soaked in an aqueous solution of a compound that will be electrodeposited as pigment, and alternating current is applied to this shaped article.

[0050] As a result of this, the electrodeposited pigment is filled primarily in the locations L of increased diameter in the fine pores formed in the previous steps, as shown in FIG. 1 (c).

[0051] The compound used here is preferably an anionic complex salt of titanium, iron, copper, zinc, or other metal. In particular, ammonium bis (oxalato) oxotitanate (IV), titanium lactate or ammonium salt thereof, titanium triethanol aminate, tris (salicylato) titanium acid complex, titanium peroxo citrate complex or titanium peroxo glycolate complex having citric acid or glycolic acid as a ligand, or other metallic complex, such as titanium or other metallic complex of malic acid or tartaric acid, is preferable as the compound to deposit the pigment, among others.

[0052] Additionally, instead of using a metallic complex itself, the aqueous solution used in the pigment filling step may be an aqueous solution prepared by adding oxalic acid and ammonia, or ammonium oxalate or other substance that can become a ligand, to a titanium source such as titanium oxide sulfate (IV), for example.

[0053] The compound solution used here may contain, in addition to any of the aforementioned compounds, an acid, ammonia or other alkali, ammonium oxalate or other salts, etc., for adjusting the pH. Furthermore, any known additive can be combined, as necessary.

[0054] In this step, the concentration of the aforementioned compound in the aqueous solution is in a range of 0.1 to 10.0 percent by weight, and if it deviates from this range, the pigment may not be filled sufficiently or the efficiency of deposition work may drop.

[0055] Also, when an aqueous solution of ammonium bis (oxalato) oxotitanate (IV) is used, for example, preferably the equivalent concentration of titanium oxide is adjusted to a range of 0.5 and 2.0 percent by weight, with the pH adjusted to a range of 4.0 to 6.0 or preferably 4.5 to 5.0.

[0056] The principle behind the deposition of pigment through application of alternating current is as follows: when the shaped aluminum article to which alternating current is applied is the anode, the ions of the compound which will be deposited as pigment migrate and are introduced into the fine pores; when the shaped aluminum article

is the cathode, on the other hand, the hydroxy ions generated from electrolysis of water hydrolyze the compound that has been introduced and cause it to deposit as a pigment compound.

[0057] Titanium oxide grains are thus deposited into the fine pores, and consequently the titanium oxide grains 4 are deposited primarily at the bottom of the fine pores 3, as shown in FIG. 1 (c), when an aqueous solution of ammonium bis (oxalato) oxotitanate (IV) is used. Needless to say, a different pigment can be deposited when other metallic salts are used.

[0058] In addition to using alternating current, the electrodeposition step can also be implemented using a method that uses pulsed current or other known conventional methods.

[0059] In addition, soaking in a diluted alkali solution of triethanol amine, etc., for example, can be added after the pigment has been deposited from the complex by applying alternating current, in order to fully hydrolyze the deposited compound.

[0060] The shaped aluminum article formed in accordance with the present invention has titanium oxide filled by 2 to 30 mg of titanium per 1 dm² inside the fine pores on its surface. As titanium oxide is filled at a density such as 2 to 30 mg/dm², the coloring strength can be improved further compared to when any conventional coloring method is used

[0061] When titanium oxide pigment is filled, for example, the surface color corresponds to an L* value of 73 or more, and a* and b* values in a range of 0±5, which represents a color whiter than the color achieved by anodization treatment alone (L*=58.22, a*=-0.83, b*=-0.01).

[0062] Furthermore, the shaped aluminum article proposed by the present invention need not be deglossed.

[0063] The shaped aluminum article proposed by the present invention can be used in many fields and applications where shaped aluminum articles have been used. For example, it can be adopted in all applications relating to enclosures of information home appliances, furniture, table-

ware, containers, home appliances, articles of daily use, etc., where a shaped aluminum article with a white surface is required.

Examples

(Aluminum Sheet Anodization Treatment Step)

[0064] The anodization treatment step was implemented as a standard anodization treatment plus a subsequent reanodization treatment.

(Standard Anodization Treatment)

[0065] A 20° C. $\rm H_2SO_4$ solution of 15 percent by weight was prepared and the aluminum sheet was soaked in it. Direct current was applied for 45 minutes to this aluminum sheet at 1.5 $\rm A \cdot dm^{-2}$, to form a porous film of 22 μm in thickness.

(Re-Anodization Treatment)

[0066] Next, the shaped aluminum article was soaked in a $20^{\rm o}$ C. 10% aqueous solution of phosphoric acid, and direct-current voltage of 16 V was applied for 5 to 15 minutes. The internal diameters of the fine pores were increased by means of this re-anodization treatment.

(Electrodeposition)

[0067] Electrodeposition was performed on the aluminum sheet, in which fine pores of increased internal diameters have been provided by means of anodization treatment, for 5 minutes at alternating current and specified constant voltage in an electrodeposition bath (temperature: 20° C.) containing ammonium bis (oxalato) oxotitanate (IV) of 1 percent by weight in equivalent titanium oxide concentration that has been adjusted to pH 5.0 with ammonium.

(After-Treatment)

[0068] The aluminum sheet was soaked for 3 minutes in a 50° C. solution containing triethanol amine by 0.5 percent by weight, and then washed with hot water.

TABLE 1

Second anodization time	Electro- deposition conditions	After-treatment	L *	a *	b *	Color difference from aluminum sheet surface before first anodization treatment (ΔE)	Amount of titanium per square decimeter of surface (mg)	
			58.22	-0.83	-0.01	19.89		
		Yes	58.93	-0.92	0.52	20.66		
	9 V, 5 min.	Only washed with hot water.	62.86	-0.88	-0.93	24.45		
	9 V, 5 min.	Yes	68.74	-1.09	-1.29	30.32	1.87	
	10 V, 5 min.	Yes	Yes Spalling occurred.					
10 min.			64.81	-0.93	0.07	26.46		
10 min.		Only washed with hot water.	65.81	-0.88	-0.51	27.42		
10 min.		Yes	63.73	-0.96	-0.48	25.34		
5 min.	8 V, 5 min.	Yes	73.46	-1.31	-3.89	35.07		
5 min.	9 V, 5 min.	Yes	75.11	-1.05	0.12	36.74		
5 min.	10 V, 5 min.	Yes	77.86	-0.83	0.03	39.48	2.90	
10 min.	10 V, 5 min.	Only washed with hot water.	78.78	-0.91	-0.41	40.37	4.90	
10 min.	10 V, 5 min.	Yes	79.55	-0.87	0.09	41.17	5.10	
10 min.	10 V, 5 min.	Yes	81.55	-1.11	1.88	43.30	5.90	

[0069] The method used to measure the amount of titanium per square decimeter of surface, shown in Table 1 above, is as follows.

[0070] A solution was prepared by mixing and dissolving 35 ml of 85% phosphoric acid and 20 g of chromic acid anhydride in 1 L of ion exchanged water, from which 50 ml was taken, and the aluminum sheet of 20 mm×30 mm in size that had completed the electrodeposition was soaked in this solution to let its film part dissolve at 50 to 100° C. At that point, the dissolved film component, and some titanium oxide grains that had been present in the film component, were present in the solution. Accordingly, the solution was heated after adding an appropriate amount of concentrated sulfuric acid (approx. 10 ml) to dissolve the titanium oxide. This solution was adjusted to a total volume of 100 ml, and the amount of titanium in the solution was quantified using an ICP-AES (inductively coupled plasma atomic emission spectroscope).

[0071] L*, a* and b* shown in Table 1 above were measured using the spectrophotometer SE2000 manufactured by Nippon Denshoku Industries.

[0072] According to the results in Table 1, the examples in which re-anodization and electrodeposition were both performed resulted in formation of a bright film whose L* exceeded 73.00. This is due to the deposition of a lot of titanium oxide pigment at the location of increased diameter inside the fine pores.

[0073] When all that is shown in Table 1 is put into perspective, it is clear that the treated aluminum sheets conforming to the present invention have many fine pores at their surface which are extending in the thickness direction, and that the titanium oxide pigment is filled in these fine pores, especially in deep areas.

[0074] As a result, the surfaces of these aluminum sheets have a color that strongly reflects the color of the titanium oxide pigment, or specifically a white color.

DESCRIPTION OF THE SYMBOLS

[0075] 1 - - - Shaped aluminum article

[0076] 2 - - - Anodized film

[0077] 3 - - - Fine pore [0078] 4 - - - Titanium oxide grain

- 1. A shaped aluminum article having an anodized film formed on a surface, where a pigment is filled in fine pores formed on the anodized film at a density of 2 mg to 30 mg per 1 square decimeter.
- 2. A shaped aluminum article according to claim 1, wherein a diameter of an opening of the fine pore is 5 to 300
- 3. A shaped aluminum article according to claim 1, wherein a length of the fine pore in a depth direction of the shaped article is 5 to 50 μm.
- 4. A shaped aluminum article according to claim 1, wherein the fine pores have a portion having an enlarged diameter at a bottom.
- 5. An shaped aluminum article according to claim 1, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- **6**. A method of coloring a surface of a shaped aluminum article, comprising:
 - giving to a shaped aluminum article an anodization treatment that includes an anodization treatment implemented under a condition of constant current, and a

- subsequent anodization treatment implemented at a constant voltage, to form an anodized film having fine pores on a surface of the shaped aluminum article; and
- soaking the obtained shaped aluminum article in an aqueous solution of metallic salts and then applying alternating current thereto in the aqueous solution to cause a pigment to deposit in, and fill, the fine pores formed.
- 7. A shaped aluminum article according to claim 2, wherein a length of the fine pore in a depth direction of the shaped article is 5 to 50 µm.
- 8. A shaped aluminum article according to claim 2, wherein the fine pores have a portion having an enlarged diameter at a bottom.
- 9. An shaped aluminum article according to claim 2, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- 10. A shaped aluminum article according to claim 3, wherein the fine pores have a portion having an enlarged diameter at a bottom.
- 11. A shaped aluminum article according to claim 7, wherein the fine pores have a portion having an enlarged diameter at a bottom.
- 12. An shaped aluminum article according to claim 3. wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- 13. An shaped aluminum article according to claim 4, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- 14. An shaped aluminum article according to claim 7, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- 15. An shaped aluminum article according to claim 8, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- 16. An shaped aluminum article according to claim 10, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.
- 17. An shaped aluminum article according to claim 11, wherein the anodized film on the surface of the shaped aluminum article has been formed using a method that includes an anodization treatment stage implemented under a condition of constant current, and a subsequent anodization treatment implemented in a phosphoric acid solution.