Method for Producing White Anodized Aluminum Oxide

A method for forming substantially white anodized aluminum oxide on an aluminum or aluminum alloy substrate is provided. A porous aluminum oxide layer is formed on the aluminum or aluminum alloy substrate by anodization in an acid electrolyte. Following formation of the anodized porous layer of aluminum oxide, the aluminum/aluminum alloy substrate is sequentially immersed in at least two reaction material solutions. The two or more reaction materials react to deposit a substantially white pigment material in the pores of the anodized aluminum oxide.
Method for Producing White Anodized Aluminum Oxide

Field of the Invention

[001] The present invention relates to methods for anodizing aluminum to produce aluminum oxide and, more particularly, methods for producing white anodized aluminum oxide.

Background of the invention

[002] Anodized aluminum oxide (AAO) on aluminum/aluminum alloys is widely used as a decorative finished surface due to its excellent hardness, corrosion resistance and abrasion resistance. Because anodized aluminum oxide layer can be colored by dyes or pigments, it has been employed in products such as automotive hardware and accessories, home furnishings, building and architectural materials, electronics, and ornaments.

[003] AAO is formed by the anodization of aluminum or aluminum alloys in inorganic or organic acids. Sulfuric, oxalic, phosphoric and chromic acids are generally used as electrolytes in the anodization process. By adjusting anodization parameters such as acid concentration, voltage, current density, temperature and time, pore size of the resulting oxide layer can be controlled within the range of a few nanometers to several hundred nanometers.
Colorization of AAO can be achieved by dyeing methods such as dipping (or immersion) and electro-deposition. Electro-deposition, also known as electro-coloring, is a process used to deposit metals/metallic compounds into the pores of AAO by electrolysis. Colors are generated by light scattering of the deposits in the AAO and from the interface between AAO and the unanodized aluminum substrate. U.S. Patent No. 4,251,330 describes a method for producing colored AAO through a process of pore enlargement using alternating current (AC) followed by electro-coloring. U.S. Patent No. 5,472,788 produces a colored anodic film made from three electrolytically-formed superposed AAO layers. Current and time are varied during deposition and metal pigments are embedded within the pores of the three combined layers. A broad range of colors within the visible spectrum was displayed by the deposited film as a result of light interference and multiple refractions.

Another common industrial method for producing colored AAO is by dipping (or immersing) the anodic aluminum film in dyes or pigments. Organic dyes are widely used, owing to the range of colors available and ease of fabrication. Colorization by inorganic pigments is uneven since inorganic pigment particles are large in size. The pore size of AAO can influence the resulting color by affecting the adsorption of dye or pigment particles on the inner walls of AAO channels.

However, despite the variety of colored AAO products that have been produced, white anodized aluminum oxide is not commercially available. To date, only a few methods for manufacturing white AAO have been reported. JP 1-205,094 describes a method of producing white AAO by depositing magnesium oxide into the pores of AAO. Aluminum was electrolytically treated with an aqueous solution containing a pH stabilizer and magnesium salt such as magnesium sulfate. To achieve a high degree of whiteness, AAO pore enlargement was conducted.

In JP 63-247,396 an opaque white AAO film was generated by a one- or two-step treatment using an aqueous solution of F⁻ ions (such as hydrofluoric acid, ammonium fluoride or metallic fluoride salts). However, F⁻ ions destroy the inner structure of AAO and hence substantially decrease the resulting hardness.

In JP 57-092,194 an opaque white AAO film was formed by subjecting an anodized Al or Al alloy material to AC or DC cathodic electrolysis in a weak alkaline solution of Ti complex ions in the absence of K⁺ and Na⁺ ions. However, this method involves complicated Ti complex preparation, neutralization, and AC or DC cathodic electrolysis.
Thus there remains a need in the art for cost-effective and efficient methods to produce white anodized aluminum oxide. Such techniques could be used to form hard, scratch-resistant, decorative surfaces in a variety of products such as construction materials, automotive body surfaces, and electronic device surfaces.

Summary of the Invention

The present invention provides a simple, effective and low cost process for producing substantially white AAO with high color intensity and uniformity utilizing a multi-step anodization technique and deposition of inorganic/organic salts. Unstable and complicated steps such as pore enlargement and electrolytic deposition of metals/metal compounds are eliminated in this method. Hardness and other desirable surface properties of the AAO are retained. Post-treatments such as sealing and polishing can be carried out with ease.

According to the present invention, a method for forming white anodized aluminum oxide on an aluminum or aluminum alloy substrate is provided. A porous aluminum oxide layer is formed on the aluminum or aluminum alloy substrate by anodization in an acid electrolyte. The AAO on the aluminum/aluminum alloy is sequentially immersed in two or more solutions. The two or more solutions will each flow into the AAO pores, react and form a
substantially white metal compound pigment reaction product in the pores of the aluminum oxide layer.

[0013] Selected solutions include aqueous solutions or organic solvents-based solutions containing compounds which react with each other to form a substantially white precipitate. Such solution combinations vary upon the choice of the final white pigment, which includes, but is not limited to, aluminum hydroxide, aluminum phosphate, aluminum silicate, antimony hydroxide, barium carbonate, barium oxalate, barium sulfate, barium titanate, barium tungstate, bismuth subnitrate, boron nitride, calcium carbonate, calcium oxalate, calcium sulfate, calcium silicate, magnesium silicate, magnesium carbonate, magnesium hydroxide, silver chloride, silver oxalate, tin (II) oxide, zinc oxide, zinc phosphate, zinc sulfide.

[0014] Other white pigments include lead compounds such as lead sulfate, lead chloride, lead carbonate, lead hydroxide and lead phosphate. However, this group of pigments is toxic. This will limit their usage.

[0015] In an optional modification to enhance product quality, the first porous aluminum oxide layer is removed, typically by etching with an acidic or alkaline solution, followed by formation of a second porous aluminum oxide layer on the aluminum or aluminum alloy substrate by anodization.
Following formation of the white pigment, the aluminum/aluminum alloy substrate is subjected to a further anodization process in a dilute acid with organic additives. In this process, branched anodized aluminum oxide channels are formed which increases the opacity of the anodized aluminum oxide layer. The final degree of opacity depends on the anodization temperature and time. At high temperatures, the dissolution rate of AAO is faster than the formation rate during anodization. If the anodization time is too long, the AAO layer will become thinner and more transparent. Conversely, if the anodization time is too short, an insufficient number of branched channels will be formed to make the AAO layer opaque. After anodization, the AAO - aluminum/aluminum alloy with white pigment materials deposited in the channels of the AAO is sealed to reduce pore size and increase corrosion resistance, followed by optional polishing.

Through the present method, a white anodized aluminum oxide layer is formed in an inexpensive, reproducible process suitable for commercialization.

Detailed Description

The process of the present invention creates white anodized aluminum oxide through commercial grade process steps that permit industrial-scale production of white AAO. The present invention will be described with respect to various exemplary embodiments for carrying out the invention.
The present invention is carried out on aluminum or aluminum alloy substrate surfaces; these aluminum/aluminum alloy substrates can be formed in a variety of shapes depending upon the final use. Prior to anodization, the aluminum/aluminum alloy substrate is cleaned, typically through degreasing using an acidic or alkaline solution and detergent, followed by thorough rinsing with distilled water and organic solvents such as ethanol and acetone, and drying. In an exemplary process, the Al/Al alloy substrate is washed with a mixture of acetone and ethanol (1:1 v:v). The substrate is then etched by a sodium hydroxide solution. After being washed by DI water, the substrate is pickled and desmutted in nitric acid. In desmutting, non-aluminum metals are removed from the aluminum alloy surface, resulting in a more pure starting material for anodization. The substrate is then thoroughly washed in distilled water, sonicated in distilled water and then air-dried.

Following cleaning, the aluminum/aluminum alloy substrate is anodized. In anodization, the aluminum/aluminum alloy substrate forms the anode of an electrolytic cell. The cathode may be selected from suitable electrically-conductive materials such as carbon, lead, stainless steel, aluminum, titanium or platinum. The electrolyte includes an acid; exemplary acids are sulfuric acid, oxalic acid, phosphoric acid, or chromic acid. Typically anodization is carried out using direct current (DC anodization) although AC anodization is also possible. In an exemplary embodiment, DC-powered
anodization is carried out at 2 - 20°C in sulfuric acid of 10 - 20 wt%. Voltage of 10 - 25 V or current density of 1.0 - 2.0 A/cm² is maintained throughout the anodization. The time of anodization depends on the application of the AAO layer. If the first layer of AAO will be the only layer of AAO formed, the duration will be on the order of one to two hours to produce an AAO film of 10 - 30 μm in thickness with an average pore diameter of 6 - 20 nm. If the first layer of AAO is removed during an optional process, as described below, a duration of less than 60 minutes is sufficient.

[0021] During anodization, oxygen is generated on the surface of the aluminum/aluminum alloy substrate anode which reacts with the aluminum to form aluminum oxide. Because the aluminum oxide formed during the anodization is porous, oxygen generated at the anode can reach the aluminum/aluminum alloy substrate to further maintain the growth of the oxide layer to a desired thickness (the desired thickness depends on the application of the final product with thicker aluminum oxide layers used in structural/outdoor applications and thinner aluminum oxide layers used in interior decorative applications).

[0022] Optionally, to produce a higher quality AAO-based product, a second AAO layer is produced. In this optional process, the first AAO layer on the aluminum/aluminum alloy substrate is removed using an acidic or alkaline
solution. Exemplary solutions include phosphoric acid, chromic acid or sodium hydroxide. In an exemplary embodiment, a mixed solution of phosphoric acid (6 wt%) and chromic acid (3 wt%) generates a uniform and polished Al or Al alloy substrate surface. Heating at 60°C can increase the rate of the AAO removal. Following removal of the aluminum oxide, the aluminum/aluminum alloy is washed with distilled water, preferably at least three times.

[0023] The optional second anodized aluminum oxide layer is formed on the aluminum/aluminum alloy substrate using substantially similar conditions to those described above with respect to the formation of the first AAO layer. The duration of the treatment is approximately one to two hour(s) to form an AAO film of 10 - 30 µm in thickness with an average pore diameter of 6 - 20 nm. Longer anodization times can be used to produce thicker films while shorter times can be used to produce thinner films, depending on the final application, as discussed above.

[0024] Using either the first or the second anodized aluminum oxide film, the aluminum/aluminum alloy substrate with the AAO film is sequentially immersed in two or more reaction material solutions such that the two or more reaction materials react to form a metal compound reaction product that fills the pores/channels of the anodized aluminum oxide layer as a substantially white pigment/colorant. During the first immersion process, the first reaction material
solution flows into the pores/channels of the AAO layer. During immersion in the second/subsequent reaction solutions, the second/subsequent reaction solution reacts with the material from the first solution to form a deposit in the pores/channels of the AAO that is a metal compound pigment reaction product.

[0025] The reaction materials may be dissolved in organic or inorganic solvent(s) depending upon the selected reaction material(s). Prior to immersion, it is preferable to ultrasonicate the AAO/A1 or AAO/A1 alloy substrate in distilled water for 5 - 10 minutes to remove gas bubbles in the AAO channels.

[0026] Selected solutions include aqueous solutions or organic solvents-based solutions containing compounds which react with each other to form a substantially white precipitate. Such solution combinations vary upon the choice of the final substantially white pigment, which includes, but is not limited to, metal compounds such as aluminum hydroxide, aluminum phosphate, aluminum silicate, antimony hydroxide, barium carbonate, barium oxalate, barium sulfate, barium titanate, barium tungstate, bismuth subnitrate, boron nitride, calcium carbonate, calcium oxalate, calcium sulfate, calcium silicate, magnesium silicate, magnesium carbonate, magnesium hydroxide, silver chloride, silver oxalate, tin (II) oxide, zinc oxide, zinc phosphate, zinc sulfide.
[0027] Other white pigments include lead compounds such as lead sulfate, lead chloride, lead carbonate, lead hydroxide and lead phosphate. However, this group of pigments is toxic. This will limit their usage.

[0028] Suitable reaction material solutions can include a chloride, nitrate, or sulfate of a pigment reaction product metal component (e.g., of aluminum, barium, zinc, etc.), and a second reaction material solution can includes a hydroxide, phosphate, carbonate, silicate, or oxalate component (such as ammonium carbonate, or potassium oxalate).

[0029] Particular sequential solution combinations that are used to form the above-recited pigment materials are set forth below. However, this list is not exhaustive and any sequential combination of solutions that form the above pigments may be used in the present invention. Selected aqueous or organic solvent-based solutions include, but are not limited to aluminum chloride/aluminum nitrate with sodium hydroxide/potassium hydroxide/ammonium hydroxide in water, aluminum chloride/aluminum nitrate with sodium phosphate/potassium phosphate/ammonium phosphate in water, aluminum chloride/aluminum nitrate with sodium silicate/potassium silicate/ammonium silicate in water, antimony chloride/antimony nitrate with sodium hydroxide/potassium hydroxide/ammonium hydroxide in water, barium chloride/barium nitrate with sodium carbonate/potassium carbonate/ammonium
carbonate in water, barium chloride/barium nitrate with sodium oxalate/potassium oxalate/ammonium oxalate in water, barium chloride/barium nitrate/barium sulfide with sodium sulfate/potassium sulfate/ammonium sulfate/dilute sulfuric acid in water, barium chloride/barium nitrate with titanium tetrachloride and diethyl oxalate in water, barium chloride/barium nitrate with sodium tungstate/potassium tungstate/ammonium tungstate in water, bismuth chloride and/or bismuth nitrate with ammonium hydroxide in water, bismuth chloride/bismuth nitrate with sodium/potassium/ammonium hydroxide and sodium/potassium/ammonium nitrate in alcohol or organic solvents, boric acid with ammonia/urea (nitrogen atmosphere) in water, calcium chloride/calcium nitrate with sodium carbonate/potassium carbonate/ammonium carbonate in water, calcium chloride/calcium nitrate with sodium oxalate/potassium oxalate/ammonium oxalate in water, calcium chloride/calcium nitrate with sodium sulfate/potassium sulfate/ammonium sulfate in water, calcium chloride/calcium nitrate with sodium silicate/potassium silicate/ammonium silicate, magnesium chloride/magnesium nitrate with sodium silicate/potassium silicate/ammonium silicate in water, magnesium chloride/magnesium nitrate with sodium carbonate/potassium carbonate/ammonium carbonate in water, magnesium chloride/magnesium nitrate with sodium hydroxide/potassium hydroxide/ammonium hydroxide in water, silver nitrate with sodium chloride/potassium chloride/ammonium chloride in water, silver nitrate with

[0030] Other reaction systems can also be used such as lead nitrate with sodium sulfate/potassium sulfate/ammonium sulfate in water, lead nitrate with sodium chloride/potassium chloride/ammonium chloride in water, lead nitrate with sodium carbonate/potassium carbonate/ammonium carbonate in water, lead nitrate with sodium hydroxide/potassium hydroxide/ammonium hydroxide in water, lead nitrate with sodium phosphate/potassium phosphate/ammonium phosphate in water. However, the reactants and products are toxic which can limit their application.

[0031] In an exemplary embodiment, an aluminum/aluminum alloy substrate with a first/second AAO layer formed thereon is immersed in a solution of barium chloride with or without ultrasonication for 5 min. The immersed substrate is heated at approximately 60°C for 30 - 60 min. Following immersion, thorough rinsing with distilled water followed optionally by wiping the surface with a clean, soft cloth or tissue paper removes any surface residue. The
substrate is then immersed in a solution of sodium sulfate with or without ultrasonication for 5 min. The immersed substrate is again heated at approximately 60°C for 30 - 60 min, followed by rinsing and cleaning as above. As a result, a deposit of barium sulfate (BaSO₄) is formed in the porous channels of the AAO layer. A concentration of 0.05-0.5 mol/L is preferred for each solution. In general, the temperature should not exceed 70°C to prevent sealing of the anodized aluminum oxide pores in aqueous solutions. In an exemplary embodiment, the substrate remains undisturbed in the solution following ultrasonication. A small amount of surfactant, particularly anionic or amphiprotic surfactant, can optionally be added to improve the immersion efficiency.

[0032] Depending upon the degree of whiteness desired in the final product and the thickness of the anodized aluminum oxide, the immersion and rinsing process is repeated approximately 3-5 times.

[0033] Following immersion in the two or more reactant solution(s), the aluminum/aluminum alloy substrate with the first/second AAO layer infiltrated with the white precipitate/product is anodized in dilute acid solution with organic additives, to produce a branched nano-channel structure of AAO. The anodization occurs in a dilute solution of weak or strong acid and organic additives under DC power. In an exemplary embodiment, a dilute solution of
sulfuric acid (1 - 2 g/L) is mixed with a weak organic acid (8 - 12 g/L), such as boric acid, lactic acid, or citric acid, and organic additives such as ethanol, ethylene glycol, or glycerin. Anodization is operated at 15 - 25 V and at 20 - 60°C. The duration of anodization is carefully controlled since it influences the degree of whiteness in the final product. A period of 10 - 30 min is selected. During this process, branched AAO channels are formed, which will make enhance the opacity of the AAO layer. In general, during anodization, AAO is both formed and dissolved simultaneously but at different rates. At elevated temperatures, the dissolution rate of AAO is greater than the rate of formation. Thus the time and temperature are carefully controlled to ensure creation of branched AAO channels without thinning the AAO layer.

[0034] Following anodization, the anodized aluminum/aluminum alloy is thoroughly washed with distilled water and organic solvents and air-dried.

[0035] Optionally, a process of pore-sealing follows anodization. In pore sealing, treatment with steam or boiling water is used to convert at least a portion of the oxide to the hydrated form. The larger hydrated oxide molecule results in pore closings of the AAO channels. Alternatively, inorganic sealing reagents such as potassium bi-chromate, nickel sulfate, cobalt sulfate, cobalt acetate, can be used for pore sealing. However, it is noted that the colors of nickel and cobalt salts can affect the degree of whiteness of the final product.
Alternatively, sealing is performed by organic sealing reagents like grease, wax, resins, and polymers. In an exemplary embodiment, a polymer liquid is used as a sealant. A polymer sealant is formed by the following processes:

Mix 20 mL of iso-propanol, 40 mL of tetraethyl orthosilicate, 50 mL of DI-water and 5 mL of acetic acid;

Stir the mixture vigorously until a uniform tacky liquid is formed;

Add 0.4 g of sodium acetate until it is dissolved;

Optionally add 1 - 20 g of aluminum oxide, silicon oxide, titanium oxide, and/or zinc oxide into above liquid. Stir vigorously for uniform dispersion. This step or amount of the materials above depends upon the degree of whiteness desired.

The anodized aluminum/aluminum alloy substrate is immersed in the polymer liquid for 1-3 minutes. Following immersion, the substrate is dried at approximately 60°C for approximately 10 min and subsequently at approximately 120°C for approximately 1 hour.

Following pore sealing, the sealed anodized aluminum/aluminum alloy substrate is mechanically polished to reach a desired degree of gloss.
Typical polishing materials include textiles such as wool. This polishing step is not necessary when a polymer sealant has been used.

Industrial Applicability

[0043] The resultant substantially white anodized aluminum oxide on aluminum/aluminum alloy substrates form hard, scratch-resistant, decorative surfaces in a variety of products such as construction materials, automotive body surfaces, and electronic device surfaces. The surfaces resist weathering and thus can be used for either structural or ornamental applications.

[0044] Further advantages and modifications of the present invention will be apparent to those of ordinary skill in the art. Modifications such as those suggested above, but not limited thereto, are considered to be within the scope of the following claims.
WHAT IS CLAIMED IS:

1. A method for forming a substantially white anodized aluminum oxide layer on an aluminum or aluminum alloy substrate comprising:

   forming a porous aluminum oxide layer on the aluminum or aluminum alloy substrate by anodization in an acidic electrolyte;

   sequentially immersing the aluminum or aluminum alloy substrate with the porous aluminum oxide layer formed thereon in at least first and second reaction material solutions such that the first reaction material solution infiltrates pores of the porous aluminum oxide layer and the second reaction material solution infiltrates the pores of the porous aluminum oxide layer to react at least portions of the first and second reaction material solutions with each other to form one or more substantially white metal compound pigment reaction product deposited in the pores to create an anodized aluminum oxide layer having a substantially white appearance.

2. The method according to claim 1 further comprising anodizing the aluminum or aluminum alloy substrate having the porous aluminum oxide layer formed thereon and the one or more substantially white metal compound pigment reaction product deposited in the pores of the porous aluminum oxide layer to form branched channels in the porous aluminum oxide layer.

3. The method according to claim 1 wherein the one or more substantially white metal compound pigment reaction product includes one or more of
aluminum hydroxide, aluminum phosphate, aluminum silicate, antimony hydroxide, barium carbonate, barium oxalate, barium sulfate, barium titanate, barium tungstate, bismuth subnitrate, boron nitride, calcium carbonate, calcium oxalate, calcium sulfate, calcium silicate, magnesium silicate, magnesium carbonate, magnesium hydroxide, silver chloride, silver oxalate, tin (II) oxide, zinc oxide, zinc phosphate, zinc sulfide, lead sulfate, lead chloride, lead carbonate, lead hydroxide or lead phosphate.

4. The method according to claim 3 wherein the first reaction material solution is a chloride, nitrate, or sulfate of a metal component of the metal compound pigment reaction product, and the second reaction material solution includes a hydroxide, phosphate, carbonate, silicate, or oxalate component.

5. The method according to claim 1 further comprising pore sealing the porous aluminum oxide layer following deposition of the one or more substantially white pigment reaction products.

6. The method according to claim 5 wherein the pore sealing is performed using steam or boiling water.

7. The method according to claim 5 wherein the pore sealing is performed using a polymer material.
8. The method according to claim 7 wherein the pore sealing is performed by immersion in a polymer liquid followed by drying.

9. The method according to claim 1 wherein the thickness of the anodized aluminum oxide layer is approximately 10 - 30 µm.

10. The method according to claim 1 wherein the average pore diameter is approximately 6 - 20 nm.

11. The method according to claim 1 wherein the first reaction material solution comprises barium chloride and the second reaction material solution comprises sodium sulfate and the substantially white metal compound pigment reaction product is barium sulfate.

12. A substantially white anodized aluminum oxide layer on an aluminum or aluminum alloy substrate formed according to the process of claim 1.

13. A substantially white anodized aluminum oxide layer on an aluminum or aluminum alloy substrate formed according to the process of claim 11.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN201 1/071616

A. CLASSIFICATION OF SUBJECT MATTER

see extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C25D11/

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

VEN, CNABS, CNKI, alumin?um, anodization, anodic oxidation, anodizing, anodic oxidation, colour, color, white, precipitate, barium, calcium, magnesium, silver

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

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| "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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| "Y" | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
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Date of mailing of the international search report
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Name and mailing address of the ISA/CN
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Facsimile No. 86-10-62019451

Authorized officer
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Telephone No. (86-10)62084392

Form PCT/ISA 210 (second sheet) (July 2009)
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A. CLASSIFICATION OF SUBJECT MATTER

C25D 11/14 (2006.01) i
C25D 11/04 (2006.01) i
C25D 11/02 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC