⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 065 421**
A1

⑫
EUROPEAN PATENT APPLICATION

㉑ Application number: **82302504.4**

㉒ Date of filing: **17.05.82**

(51) Int. Cl.³: **C 25 D 11/22**, C 25 D 11/12

㉚ Priority: **19.05.81 JP 75408/81**
20.05.81 JP 76313/81

㊸ Date of publication of application: **24.11.82**
Bulletin 82/47

(84) Designated Contracting States: **CH DE FR GB LI**

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(54) **Method of treating a surface of an aluminum to form a pattern thereon.**

(57) A method of treating a surface of aluminum to form a pattern thereon is disclosed, which comprises electrolyzing the aluminum, after anodic oxidation in usual manner, in a bath containing at least one substance selected from organic acids having OH or COOH group, orthophosphoric acid, pyrophosphoric acid, chromic acid, phosphorous acid, sulfuric amide, highly concentrated sulfuric acid and salts thereof, subjecting to a hot-water rinsing treatment, adhering at its dried surface a substance contributing to the formation of the pattern at a subsequent electrolytic pigmentation and then subjecting to an electrolytic pigmentation, whereby a colored pattern based on a difference of color tone between adhered portion and nonadhered portion is formed on the aluminum surface.

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Method of treating a surface of an aluminum to form a pattern thereon

The present invention relates to a method of treating a surface of an aluminum to freely form various patterns thereon.

Throughout the specification, the term "aluminum" used herein means to include aluminum and aluminum alloys.

As a method of forming a pattern on a surface of an aluminum for buildings having a complicated sectional shape, there have hitherto been proposed various methods wherein the aluminum before an anodic oxidation treatment is dipped into a predetermined electrolytic liquid while applying an electric current thereto.

In these methods, hydrogen gas produced on the surface of the aluminum by the application of electric current rises upward on the aluminum surface to form a bubble-traced pattern. However, the generation of hydrogen gas is not always constant and is very irregular, so that a fixed regular pattern can not be formed on the aluminum surface and also the same pattern can not be reproduced repeatedly.

Moreover, the patterns formed by these methods exclusively rely on the rising trace of hydrogen gas, so that there are obtained only monotonous line and grain-like patterns.

Therefore, the above methods have also a drawback that patterns having appearance and design suitable for various applications can not optionally be obtained.

On the other hand, if it is intended to form a freely designed pattern, usual printing methods are most preferable, but they can not be applied to the aluminum for buildings having a complicated sectional shape.

It is, therefore, an object of the present invention to provide a method of treating a surface of an aluminum to form pattern, which can produce not only a monotonous line pattern but also the same freely designed pattern as in the printing method even on the surface of the aluminum for buildings having a complicated sectional shape.

According to the present invention, there is the provision of a method of treating a surface of an aluminum to form a pattern thereon, characterized in that the aluminum after anodic oxidation treatment in usual manner is electrolyzed in a bath containing at least one substance selected from organic acids having a hydroxyl or carboxyl group, orthophosphoric acid, pyrophosphoric acid, chromic acid, phosphorous acid, sulfuric amide, highly concentrated sulfuric acid of not less than 40 V/V % and salts thereof, subjected to a hot-water rinsing treatment, adhered at its dried surface with a substance contributing to the formation of proper pattern at a subsequent electrolytic pigmentation and then subjected to an electrolytic pigmentation, whereby a pattern based on the difference of color tone between the adhered portion and the nonadhered portion is formed on the surface of the aluminum.

According to the present invention, the aluminum surface after the electrolysis may be subjected to a primary coloration treatment to form a colored anodic oxide film thereon prior to the hot-water rinsing. As the substance contributing to the formation of proper pattern at the subsequent electrolytic pigmentation, there are used substances capable of inhibiting the electrolytic pigmentation (hereinafter referred to as inhibitation substance) and substances capable of promoting the electrolytic pigmentation (hereinafter referred to as promotion substance).

The present invention will now be described in greater detail below.

According to the present invention, the aluminum is first subjected to a pretreatment of degreasing, rinsing, etching and desmutting in a usual manner. The thus treated aluminum is electrolyzed in an electrolytic bath containing sulfuric acid, oxalic acid or a mixture therof for the production of porous anodic oxide film by a direct current porcess, an alternating current process, a process of superimposed alternating current to direct current or the other process of using a current wave capable of developing the same effect to form an anodic oxide film on the aluminum surface. Moreover, this anodic oxidation may be accompanied with a color development without interference.

Next, the resulting anodic oxide film of the aluminum is further subjected to an electrolytic treatment, whereby the properties of the anodic oxide film such as structure of micropores and the like are changed.

To this end is used a bath containing at least one of inorganic acids and salts thereof selected from chromic acid, orthophosphoric acid, pyrophosphoric acid, phosphorous acid, sulfuric amide and highly concentrated sulfuric acid of not less than 40 V/V %, or a bath containing at least one of organic acids having a hydroxyl or carboxyl group and salts thereof selected from malic acid, gluconic acid, maleic acid, citric acid, malonic acid, tartaric acid, cresol sulfonic acid, sulfophthalic acid, sulfosalicylic acid, gallic acid, benzoic acid, phthalic acid, carbolic acid and the like. Furthermore, a proper mixture of the above inorganic acid and organic acid may be used as an electrolytic bath.

As a current wave, there are used an alternating current wave, a wave of alternately changing positive and negative polarities, a direct current wave and a superimposed alternating-direct current wave. In the electrolytic treatment, the treating voltage is preferably 5 - 50 volts and the treating time is 1 - 10 minutes in order to obtain a sufficient effect. When using the alternating current, the properties of the previously formed anodic oxide film can be largely changed as compared with the case of using the direct current. On the other hand, the use of direct current is small in the range changing the properties the anodic oxide film as compared with the use of alternating current, but has an effect of controlling a current density during the treatment, so that the properties of the resulting colored film become good as compared with the case of using the alternating current.

If necessary, the aluminum may be subjected to a primary coloration treatment after the electrolytic treatment. In this case, any conventional well-known methods can properly be adopted as the primary coloration treatment. For instance, there are mentioned various methods wherein the aluminum is electrolyzed in a coloring bath containing an acid or a salt of a colorable metal selected from nickel, cobalt, copper, tin, manganese, zinc, chromium, iron, lead, molybdenum and the like or further containing hydrogen peroxide by using a proper wave of electric current such as alternating current, direct current, superimposed alternating-direct currents or the like. Alternatively, the aluminum may be colored by a dyeing treatment.

By such a primary coloration treatment, the anodic oxide film is colored into various color tones of bronze, amber, black and the like as well as green, blue, red, yellow, brown and the like.

According to the present invention, the subsequent hot-water washing treatment is closely related to the above mentioned electrolytic treatment or primary coloration treatment as apparent from the following reason. That is, according to the present invention, it is an essential feature that an inhibition substance or promotion substance for subsequent electrolytic pigmentation is adhered to the surface of the anodic oxide film or the colored anodic oxide film according to a desired pattern. Therefore, it is necessary to make the surface of the aluminum into dried state for adhering, the inhibition or promotion substance thereto.

In general, the aluminum is subjected to a rinsing treatment with water after the electrolytic treatment, but it is very difficult to dry the aluminum surface after the rinsing with water. Therefore, a hot-water rinsing treatment is practically preferable in order to increase the production efficiency. However, when the anodic oxide film or the colored anodic oxide film as described above is merely subjected to a hot-water rinsing treatment, the surface of this film is sealed to lose its activity, which prevents the deposition of colorable metal at the subsequent electrolytic pigmentation step.

According to the present invention, therefore, it is necessary to perform the electrolytic treatment for changing the properties of the anodic oxide film as described above in order to ensure the hot-water rinsing treatment without sealing. On the other hand, if the anodic oxide film is subjected to the electrolytic treatment and further to the electrolytic pigmentation without hot-water rinsing, it is certainly colored, but the adhesion of colorable metal is insufficient, so that uniform and beautiful colored anodic oxide film can not be obtained. Therefore, the hot-water rinsing treatment is required for obtaining practically satisfactory films. By the hot-water rinsing treatment, the activity of the anodic oxide film after the electrolytic treatment is made uniform all over the surface of the aluminum, whereby the scattering of metal deposition is prevented at the subsequent electrolytic pigmentation step.

Moreover, when the primary coloration treatment is carried out between the electrolytic treatment and the hot-water rinsing treatment, the properties of the anodic oxide film are never further changed because metal is merely deposited in the micropores or the film is dyed. Therefore, the primary coloration treatment does not adversely affect the subsequent hot-water treatment.

In the hot-water rinsing treatment, pure water is preferably used as a rule, but water containing a surfactant of approximately neutrality or other chemicals may be used. In order to ensure the hot-water rinsing without sealing, the treating time is preferably 1 - 30 minutes when the treating temperature is 50 - 90°C and 1 - 15 minutes when the treating temperature is 90 - 100°C.

When the anodic oxide film or the colored anodic oxide film is subjected to the hot-water rinsing treatment as described above, the surface of the film is made uniform without sealing, so that when the aluminum is taken out from the treating tank, the surface thereof is rapidly made into a dried state. After the hot-water rinsing treatment, the aluminum can be moved to a subsequent treatment of adhering the inhibition or promotion substance for the formation of desired pattern at an electrolytic pigmentation step.

The inhibition substance includes substances flowing no electric current at electrolytic pigmentaion step, substances inhibiting the coloring action itself to hardly deposit metal into micropores of the anodic oxide film and the like. As the former substance, mention may be made of kaolin, dibutyl phthalate, acetate, glycerin, ethylene glycol, higher fatty acid esters, insulating substances such as resist ink, synthetic resins and the like. As the latter substance, use may be made of substances producing sodium ion, potassium ion, ammonium ion or nitric acid ion by hydrolysis, an example of which includes aqueous solutions or pastes of sodium hydroxide, potassium hydroxide, ammonia water, nitric acid, sodium nitrate, sodium sulfate, ammonium sulfate, potassium sulfate and the like.

As the promotion substance, use may be made of aqueous solutions or pastes of concentrated sulfuric acid, phosphoric acid, phosphorous acid, sulfuric amide, carboxylic acid, oxycarboxylic acid and the like.

Moreover, the electrolytic pigmentation can be obstructed by using a masking tape.

As a means for adhering the above inhibition or promotion substance to the aluminum surface, there are used direct application of adhesion of these substance as well as various printing processes such as screen printing, off-set printing and the like.

Particullarly, it is advantageous to apply the following process to the aluminum having a complicated and irregular surface.

That is, the inhibition or promotion substance is first printed on a thin film according to a predetermined design pattern, which is floated on a liquid upward its printed surface. Then, the aluminum is submerged into the liquid while pushing on the printed surface, whereby the thin film is adhered closely to the overall surface of the aluminum under a liquid pressure to adhere and fasten the inhibition or promotion substance from the printed surface to the aluminum surface. In this case, it is necessry to remove the thin film after the inhibition or promotion substance is adhered to the aluminum surface. Such a removal of the thin film is carried out by various processes such as hot-water rinsing and the like.

After the adhesion of the inhibition or promotion substance at a patterned state, the aluminum surface is subjected to an electrolytic pigmentation treatment. As the electrolytic pigmentation treatment, the conventionally well-known processes can properly be adopted without particlular limitation.

For instance, there may be mentioned various electrolytic pigmentation processes wherein the aluminum is electrolyzed in a coloring bath containing an acid or a salt of a colorable metal selected from nickel, cobalt, copper, tin, manganese, zinc, chromium, iron, lead, molybdenum and the like or further containing hydrogen peroxide by using a proper wave of electric current such as alternating current, direct current, superimposed alternating-direct currents or the like. This treatment may be the same as the aforementioned primary coloration treatment. In the latter case, the treating conditons are optionally selected in accordance with desirable colored patterns.

By the electrolytic pigmentation treatment, the anodic oxide film is colored in various color tones such as bronze, amber, black, green, red, blue, yellow, brown and the like irrespective of the previous hot-water rinsing treatment because the properties of the film are previously changed by the electrolytic treatment before the hot-water rinsing.

In the electrolytic pigmentation, when the insulating substance is used as the inhibition substance, the adhered portions are not colored by the electrolytic pigmentation treatment. Therefore, a pattern based on the difference of color tone between the colored portion and the noncolored portion is formed on the aluminum surface.

Moreover, when the primary coloration treatment is previously performed before the electrolytic pigmentation treatment, a colored pattern based on the difference between the color tone in the primary coloration and the color tone in the electrolytic pigmentation is depicted on the aluminum surface.

When the substance inhibiting the coloring action is used as the inhibition substance, the electrolytic pigmentation is not advanced too in the adhered portions, so that there is caused a difference in the coloring degree between the adhered portion and the nonadhered portion. As a result, a colored pattern based on such a difference of the coloring degree is depicted on the aluminum surface.

In case of using the promotion substance, the coloring degree of the adhered portion becomes higher than that of the nonadhered portion, so that the color tone of the adhered portion becomes deeper than that of the nonadhered portion or changes into a different color, whereby a colored pattern is depicted on the aluminum surface.

According to the present invention, the activity of the anodic oxide film is uniformized by the hot-water rinsing treatment after the electrolytic treatment, so that the adhesion property of the colorable metal during the electrolytic pigmentation is good and also the coloring degree is uniform all over the irregular surface of the aluminum. Further, there is no limitation for the application of the inhibition or promotion substance to the aluminum surface, so that design patterns can freely be selected and also the same pattern can surely and easily be reproduced.

After the electrolytic pigmentation, the inhibition or promotion substance adhered to the aluminum surface may be left as it is or may be removed in accordance with its nature. In the removal of this substance, the aluminum is subjected to a hot-water rinsing treatment or an immersion treatment in an organic solvent.

The present invention will be described in detail with reference to the following examples.

Example 1

Aluminum alloy A 6063 S was degreased by immersing in a 10 wt % solution of nitric acid for 5 minutes, etched by immersing in a 5 wt % solution of sodium hydroxide at 50°C for 8 minutes, and desmutted by immersing in a 10 wt % solution of nitric acid. Then, the alluminum alloy was anodically oxidized in a 15 wt % solution of sulfuric acid at a bath temperature of 20°C under a current density of $1.0A/dm^2$ for 30 minutes and thereafter electrolyzed in a bath containing 100g/l of phosphorous acid at a bath temperature of 20°C by applying a direct current at 10 volts for 4 minutes. Next, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 80°C for 10 minutes, dried and closely adhered with a water-soluble thin film previously printed by grease according to a desired pattern under a water pressure, whereby grease was adhered to the aluminum alloy surface. The thus treated aluminum alloy was immersed in pure water of 60°C for 15 minutes to remove the water-soluble thin film and then electrolyzed in a bath containing 10g/l of stannous sulfate and 10g/l of sulfuric acid at a bath temperature of 20°C by applying an alternating current at 25 volts for 40 seconds, whereby non-adhered portions were colored green. After the aluminum alloy was immersed in a boiling water for 5 minutes to remove grease, a silver grey-green pattern colored film was formed on the aluminum alloy.

Example 2

Aluminum plate A 1200 P was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 1 and then electrolyzed in a bath containing 55 V/V % sulfuric acid at a bath temperature of 20°C by using it as an anode and applying a direct current at a voltage of 20 volts for 7 minutes. Next, the aluminum plate was subjected to a hot-water rinsing treatment by immersing in pure water of 85°C for 5 minutes, dried, locally covered with a masking tape and electrolyzed in a bath containing 30g/l of nickel sulfate and 40g/l of boric acid at a bath temperature of 20°C by using it as a cathode at a voltage of 15 volts for 30 seconds, whereby the noncovered portions were colored lemon gold. After the removal of the masking tape, a beautiful silver grey-lemon gold pattern colored film was formed on the aluminum plate.

Example 3

Aluminum alloy A 6063 S was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 1 and electrolyzed in a bath containing 150g/l of sulfuric amide and 50g/l of pyrophosphoric acid at a bath temperature of 25°C by appling a direct current at 15 volts for 5 minutes. Then, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 70°C for 3 minutes, dried, adhered with a mixed solution of dibutyl acetate and vaseline according to a desired pattern and electrolyzed in a bath containing 10g/l of manganese sulfate and 10 ml/l of hydrogen peroxide at a bath temperature of 20°C by using it as a cathode at a voltage of 40 volts for 90 seconds, whereby the nonadhered portions were colored brick red. After the adhered substance was removed by immersing in pure water of 100°C for 5 minutes, a silver grey- brick red pattern colored film was formed on the aluminum alloy.

Example 4

Aluminum plate A 1100 P was subjected pretreatment and anodic oxidation treatment in the same manner as described in Example 1 and electrolyzed in a bath containing 150g/l of phosphorous acid and 30g/l of tartaric acid at a bath temperature of 20°C by using it as an anode and applying a direct current at 15 volts for 2 minutes. Then, the aluminum plate was subjected to a hot-water rinsing treatment by immersing in pure water of 80°C for 4 minutes, dried, adhered with a resist ink by a screen printing process according to a desired pattern and anodically electrolyzed in a bath containing 100g/l of sulfosalicylic acid and 5g/l of sulfuric acid at a bath temperature of 20°C at a current density of 2.0 A/dm^2 for 20 minutes, whereby the nonadhered portions were colored greenish amber. After the resist ink was removed with an organic solvent, a silver grey-greenish amber pattern colored film was formed on the aluminum plate.

Example 5

Aluminum alloy A 6063 S was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 1 and electrolyzed in bath containing 50g/l of ammonium phosphate and 50g/l of chromic acid at a bath temperature of 15°C by applying an alternating current at 25 volts for 3 minutes. Then, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 90°C for 3 minutes, dried and coated with a clear lacquer according to a desired pattern. Thereafter, the aluminum alloy was electrolyzed in a bath containing 30g/l of copper sulfate and 5g/l of sulfuric acid at a bath temperature of 25°C by applying an alternating current at 20 volts for 2 minutes, whereby the non-adhered portions were colored copper red. After the aluminum alloy was coated with a clear lacquer over a whole surface, a beautiful silver grey-copper red pattern colored film was formed on the aluminum alloy.

Example 6

Alluminum alloy A 6063 S was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 1 and electrolyzed in a bath containing 150g/l of phosphorous acid at a bath temperature of 20°C by applying a direct current at 30 volts for 3 minutes. Then, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 80°C for 4 minutes, dried and printed with a paste of tartaric acid by a screen printing process according to a desired pattern. Thereafter, the aluminum alloy was electrolyzed in a bath containing 10g/l of stannous sulfate, 30g/l of nickel sulfate and 20g/l of cresol sulfonic acid at a bath temperature of 20°C by applying an alternating current at 13 volts for 3 minutes, whereby the paste adhered portions were colored greenish amber and the nonadhered portions were colored gold to form a beautiful pattern colored film on the aluminum alloy.

Example 7

Alluminum alloy A 6063 S was degreased by immersing in a 10 wt % solution of nitric acid, etched by immersing in a 5 wt % solution of sodium hydroxide at 50°C for 10 minutes, and desmutted by immersing in a 10 wt % solution of nitric acid. Then, the aluminum alloy was anodically oxidized in a 15 wt % solution of sulfuric acid at a bath temperature of 20°C under a current density of 1.0 A/dm^2 for 30 minutes and electrolyzed in a bath containing 100g/l of phosphorus acid at a bath temperature of 20°C by applying a direct current at 20 volts for 3 minutes. Thereafter, the aluminum alloy was electrolyzed in a bath containing 30g/l of nickel sulfate and 30g/l of boric acid at a bath temperature of 20°C by applying an alternating current at 10 volts for 1 minute, whereby the anodic oxide film was colored greyish blue. Next, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 80°C for 10 minutes, dried and adhered with glycerin according to a desired pattern. Then, the aluminum alloy was electrolyzed in a bath containing 30g/l of nickel sulfate and 30g/l of boric acid at a bath temperature of 20°C by applying an alternating current at 15 volts for 5 minutes, wherby the nonadhered portions were colored dark bronze. After glycerin was removed by rinsing with pure water of 90°C for 15 minutes, a greyish blue-dark bronze pattern colored film was formed on the aluminum alloy.

Example 8

Aluminum alloy A 6063 S was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 1 and electrolyzed in a bath containing 200g/l of orthophosphoric acid and 5g/l of oxalic acid at a bath temperature of 25°C by applying an alternating current at 15 volts for 5 minutes. Then, the aluminum alloy was electrolyzed in a bath containing 20g/l of manganese sulfate and 20 ml/l of hydrogen peroxide at a bath temperature of 20°C by using it as a cathode and applying a direct current at 30 volts for 1 minute, whereby the anodic oxide film was colored yellow. Thereafter, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 80°C for 10 minutes, dried and closely adhered with a water-soluble thin film previously printed by dimethyl phthalate according to a desired pattern under a water pressure, whereby dimethyl phthalate was adhered to the aluminum alloy surface. Next, the aluminum alloy was immersed in pure water of 80°C for 20 minutes to remove the water-soluble thin film, dried and electrolyzed in a bath containing 20g/l of manganese sulfate and 20ml/l of hydrogen peroxide at a bath temperature of 20°C using it as a cathode and by applying a direct current at 50 volts for 2 minutes, whereby the nonadhered portions were colored dark brown. After the aluminum alloy was immersed in pure water of 80°C for 10 minutes to remove dimethyl phthalate and coated with a clear lacquer, a beautiful yellow-dark brown pattern colored film was formed on the aluminum alloy.

Example 9

Aluminum plate A 1200 P was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 7, electrolyzed in a bath containing 50 V/V % sulfuric acid at a bath temperature of 15°C by applying a direct current at 10 volts for 7 minutes and further electrolyzed in a bath containing 40g/l of nickel sulfate and 40g/l of boric acid at a bath temperature of 20°C by using it as a cathode and applying a direct curent at 20 volts for 1 minute, whereby, the anodic oxide film was colored gold. Then, the aluminum plate was subjected to a hot-water rinsing treatment by immersing in pure water of 100°C for 5 minutes, dried and coated with a clear lacquer by screen printing process according to a desired pattern.

Next, the aluminum plate was electrolyzed in a bath containing 10g/l of stannous sulfate and 10g/l of sulfuric acid at a bath temperature of 20°C by applying an alternating current at 20 volts for 5 minutes, whereby the nonadhered portions were colored black. After the aluminum plate was immersed in pure water of 80°C for 10 minutes and coated with a clear lacquer over a whole surface, a beautiful gold-black pattern colored film was formed on the aluminum plate.

Example 10

Aluminum alloy A 6063 S was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 7, electrolyzed in a bath containing 100g/l of chronic acid and 5g/l of sulfuric acid at a bath temperature of 25°C by using it as an anode and applying a direct current at 35 volts, and further electrolyzed in a bath containing 40g/l of cobalt sulfate and 30g/l of boric acid at a bath temperature of 20°C by using it as a cathode and applying a direct current at 18 volts for 3 minutes, whereby the anodic oxide film was colored yellowish bronze. Thereafter, the aluminum alloy was subjected to a hot-water rinsing treatment by immersing in pure water of 70°C for 8 minutes, dried and locally adhered with a resist ink. Then, the aluminum alloy was electrolyzed in a bath containing 30g/l of cobalt sulfate and 20ml/l of hydrogen peroxide at a bath tempeature by using it as a cathode and applying a direct current at 40 volts for 5 minutes, whereby the nonadhered portions were colored brick red. After the resist ink was removed with an organic solvent, a yellowish bronze-brick red pattern colored film was formed on the aluminum alloy.

Example 11

Aluminum plate A 1100 P was subjected to pretreatment and anodic oxidation treatment in the same manner as described in Example 7, electrolyzed in a bath containing 80g/l of sulfuric amide and 50g/l of pyrophosphoric acid at a bath temperature of 20°C by applying an alternating current at 20 volts for 3 minutes and immersed in an aqueous solution of 10g/l of ammonium ferric oxalate at 50°C for 1 minute, whereby the anodic oxide film was dyed gold. Thereafter the aluminum plate was subjected to a hot-water rinsing treatment by immersing in pure water of 90°C for 5 minutes, dried and locally adhered with a masking tape. Then, the aluminum plate was electrolyzed in a bath containing 30g/l of nickel sulfate, 1g/l of stannous sulfate and 3g/l of tartaric acid at a bath temperature of 20°C by applying an alternating current at 10 volts for 3 minutes, whereby the nonadhered portions were colored purple. After the removal of the masking tape, a beautiful gold-purple pattern colored film was formed on the aluminum plate.

Claims:

1. A method of treating a surface of aluminum to form a pattern thereon, characterized in that the aluminum after anodic oxidation treatment is electrolyzed in a bath containing at least one substance selected from organic acids having a hydroxyl or carboxyl group, orthophosphoric acid, pyrophosphoric acid, chromic acid, phosphorous acid, sulfuric amide, highly concentrated sulfuric acid of not less than 40 V/V % and salts thereof, subjected to a hot-water rinsing treatment, has adhered to its dried surface a substance which contributes to the formation of the pattern at a subsequent electrolytic pigmentation and is then subjected to an electrolytic pigmentation, whereby a pattern based on the difference of color tone between the adhered portion and the nonadhered portion is formed on the surface of the aluminum.

2. The method according to claim 1, wherein said aluminum is subjected to a primary coloration treatment between said electrolytic treatment and hot-water rinsing treatment.

3. The method according to claim 1 or 2, wherein said substance contributing to the formation of proper pattern is a substance capable of inhibiting said subsequent electrolytic pigmentation.

4. The method according to claim 3, wherein said substance is a substance flowing no electric current at electrolytic pigmentation step selected from kaolin, dibutyl, phthalate, acetate, glycerin, ethylene glycol higher fatty acid ester, resist ink and synthetic resin.

5. The method according to claim 3, wherein said substance is a substance inhibiting a coloring action selected from aqueous solution and pastes of sodium hydroxide, potassium hydroxide, ammonia water, nitric acid, sodium nitrate, sodium sulfate, ammonium sulfate and potassium sulfate.

6. The method according to claim 3, wherein said substance is a masking tape.

7. The method according to claim 1, wherein said substance contributing to the formation of proper pattern is a substance capable of promoting said subsequent electrolytic pigmentation.

8. The method according to claim 7, wherein said substance is selected from aqueous solution and pastes of concentrated sulfuric acid, phosphoric acid, phosphorous acid, sulfuric amide, carboxylic acid and oxycarboxylic acid.

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EUROPEAN SEARCH REPORT

Application number
EP 82302504.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	<u>US - A - 4 066 516</u> (T. SATO) * Totality; especially columns 2-4; claims * --	1,4,5,6,8	C 25 D 11/22 C 25 D 11/12
Y	<u>US - A - 4 221 640</u> (K. SHIBATA et al.) * Totality; especially column 2, lines 37-62; column 3, lines 52-63; column 4, lines 16-26; claims * ----	1,4,5,8	

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 25 D

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	07-07-1982	SLAMA

EPO Form 1503.1 06.78