

SPECIFICATION

Method of Forming Coloured Patterns on Aluminum or its Alloys

This invention relates to a method of forming
5 coloured patterns on the surface of aluminum or its alloys without using any dies or pigments and to an aluminum article having a coloured pattern of wood grain.

Hitherto, there have been known many
10 methods of forming coloured patterns of the surface of aluminum or its alloys. In prior methods, as disclosed in Japanese Patent Publication No. 3895/77 and 4616/75 and Japanese Patent Application No. 41735/75 as laid
15 open to public inspection, a resist film is applied to or printed on an aluminum workpiece to form protected areas in conformity with a desired pattern the workpiece is then subjected to an anodic oxidation to form a barrier-type oxide film
20 or to a chemical conversion to form a chemically oxidized film and, after removal of the resist film, to a second anodic oxidation or chemical conversion to form a pattern of a coloured film. Thus, the prior methods includes the steps of
25 resist pattern printing, primary anodic oxidation, (stopping-up of pores), removal of resist film, and secondary anodic oxidation (electrolytic colouring); or, resist pattern printing, chemical oxide film formation, removal of resist film, and
30 chemical conversion (chemical formation of coloured oxide film). Another method which also includes a printing process for patterning is disclosed in Japanese Patent Publication No. 21022/76 which comprises applying a TFS
35 coating to the surface of an aluminum workpiece, applying a pattern coating thereon by means of screen or offset printing and drying and baking together the TFS coating and the patterning ink. These methods which include a printing process
40 for patterning, however, have the shortcoming that the printing process is expensive and takes much time and, consequently, results in decrease in the mass productivity or productivity of these methods and, in addition, the printing process
45 makes it difficult to produce a variety of patterns each in relatively small quantities. Japanese Patent Application No. 60244/77 as laid open to public inspection discloses a method which includes no printing process. This method of
50 electrolytically coloring aluminum to form a pattern of wood grain comprises subjecting an aluminum workpiece to electrolysis in an alkaline electrolytic bath to which there is added a barrier-type oxide film forming electrolyte by means of an
55 alternating current or a current exhibiting the same effect with an alternating current. Japanese Patent Application Nos. 3535/77, 61139/77 and 70951/77 as laid open to public inspection disclose methods of forming patterns on
60 aluminum surfaces by electrolytic colouring through control of electrolytic formation of a barrier layer after anodic oxidation. However, these methods in which coloured patterns are formed by electrolytic colouring after modification

65 of the thickness of the barrier layer are unsuitable for workpieces having complicated shapes and poor in productivity because of difficulty in modification of the thickness of the barrier layer. On the other hand, the method disclosed in
70 Japanese Patent Application No. 60244/77 as laid open to public inspection is applicable to workpieces having complicated shapes, though the patterns formed in this method are lengthwise extending short etching figures which are
75 somewhat similar to but far apart from the straight grain of natural wood and it is impossible to form patterns imitating the cross or flat grain of wood.

Accordingly, it is an object of the present invention to provide a method of forming a
80 coloured pattern with a close resemblance to a straight or cross grain of natural wood without using any dyes or pigments on the surface of aluminum or its alloy.

85 According to one aspect of this invention there is provided a method of forming a coloured pattern on the surface of an article made of aluminum or its alloys comprising the steps of dipping said article in a coating bath including a
90 coating material in a multilinear or multiannular pattern floating therein to form thereon a mask coating in a wood grain pattern, subjecting said article to a surface modification to form an oxide film in unmasked areas of the surface of said
95 article, removing the mask coating, and subjecting said article to an electrolytic colouring.

According to another aspect of this invention there is provided a method of forming a coloured pattern on the surface of an article made of
100 aluminum or its alloys comprising the steps of dipping said article in a coating bath including a coating material in a multilinear or multiannular pattern floating therein to form thereon a mask coating in a wood grain pattern, subjecting said
105 article to a surface modification by etching using an alkaline solution, removing the mask coating, and subjecting said article to an electrolytic colouring.

The present invention can provide a method of
110 forming wood grain patterns having a stereographic effect on the surface of aluminum or its alloy without using a printing process.

Further the present invention can provide an aluminum article having a coloured pattern which
115 resembles closely to a straight or cross grain of natural wood.

Further, the present invention can provide an aluminum article having a coloured pattern of wood grain with a stereographic effect.

120 In an exemplary method in accordance with the present invention, an aluminum or its alloy article, hereinafter referred to as a "workpiece", is subjected to degreasing, washing, drying and other conventional pretreatments and, optionally,
125 to etching, desmutting and like special treatments and then dipped in a coating bath in which there floats a coating material in a multilinear or multiannular pattern to deposit thereon a wood grain pattern. If the coating material floats in the

multilinear pattern, there is formed a pattern of a straight wood grain, and if it floats in the multiannular pattern or pattern of water rings, there is formed a pattern of a cross grain of wood.

- 5 The workpiece is then drawn out from the coating bath and dries in air or in an appropriate heating chamber to form a coating film in the pattern of a wood grain. The residue of the coating material floating in the surface of the coating bath deposits on the surface of the workpiece as it is drawn up from the bath, but the deposits can easily be removed by treating in a washing bath equipped with, e.g., an air agitator because of the loose adhesion of the deposits to the wetted surface of the workpiece. If washing with water is omitted, it is desirable to draw out the workpiece after removal of the residual coating layer by overflow of the coating bath.

- 20 The workpiece thus masked with a coating film in the pattern of a wood grain is, after washing and other optional processes, subjected to a surface modifying process. The proposed surface modifying is to create a difference in surface property between the masked areas and the unmasked areas in the course of the following anodic oxidation where there is formed an oxidized film such as, e.g., a chemically oxidized film, an anodic oxide film or a coloured anodic oxide film and a barrier-type oxide film by the known methods. The chemically oxidized film may be formed by dipping the workpiece into a solution containing chromate, phosphate, acetate, sulfate, nitrate or fluoride. The anodic oxide film may be formed by electrolytically oxidizing the workpiece in an acid electrolyte, such as sulfuric acid, oxalic acid or chromic acid, and the coloured anodic oxide film may be formed by using an electrolyte containing at least one of the following organic acids viz.:— oxalic acid, malonic acid, 40 sulfo-salicylic acid, sulfo-phthalic acid, citric acid, maleic acid and tartaric acid, or a mixture solution of inorganic acid with said organic acid. The barrier-type oxide film may be formed by an electrolysis in an inorganic or organic acid 45 electrolyte such as boric acid, citric acid, tartaric acid, maleic acid, glycolic acid or a salt thereof, wherein the electrolysis is carried out by applying a higher voltage than that applied to a conventional anodic oxidation.

- 50 The workpiece is then, after removal of the masking film by means of, e.g., a solvent, sulfuric acid or an organic remover, subjected to an electrolytic colouring by a known method. The electrolytic colouring processes may be carried out by anodic oxidation in an ordinary electrolytic bath containing an organic acid, such as oxalic acid, malonic acid, citric acid, maleic acid, tartaric acid or sulfo-salicylic acid. Further the electrolytic colouring process may be carried out by anodic 60 oxidation using an acid electrolyte, such as sulfuric acid, oxalic acid, or chromic acid, and following electrolysis using an acid electrolyte containing a metallic salt, such as nitrate, sulfate, phosphate, oxalate, acetate, or tartrate, of nickel, 65 chrome, cobalt, copper, magnesium, iron,

manganese, molybdenum, lead, or zinc. The workpiece may be subjected, if necessary, to washing with water, drying and other pretreatments before electrolytic colouring.

- 70 In another embodiment of the present invention, a workpiece is, after masking with a coating film in the pattern of a wood grain in the way mentioned above, subjected to etching as a surface modifying process. This etching process 75 results in a finished product having a touch substantially same with that of natural wood and a rough surface appearance. The subsequent treatments are carried out in the same way as mentioned above.

- 80 The aforesaid mask coating may be carried out in the procedure as follows. A coating material is poured onto the surface of a coating bath filled up with slowly flowing water from the up-stream end of the bath as to form a number of streaks floating on the surface of water. Flow of the bath and feed 85 of the coating material are stopped just before the front ends of the extending streaks of the coating material arrive at the overflow end of the bath, and a workpiece which is hung down lengthwise is 90 dipped in the bath to deposit on its surface the floating coating material in a pattern of wood grain. For this process, it is preferred that the workpiece has previously been well dried and is hung down lengthwise and that the width of the coating bath is $1/2$ to $2/3$ times the length of the 95 workpiece. When the width of the coating bath is not enough, the coating material should be continuously poured in the coating bath at a feed rate so controlled as to form the continuous thin streaks like a wood pattern of the surface of the 100 workpiece in accordance with the dipping speed of the workpiece. The floating streaks of the coating material may also be formed by feeding the coating material to the end opposite to the 105 overflow end of the coating bath to accumulate therein the coating material and spreading it towards the overflow end by means of a blade having notches at intervals in its bottom edge. When the mask coating is carried out with this 110 procedure, there is formed a mask coating in a pattern of straight grain of wood.

- In order to form a pattern of cross grain of wood, the coating material is dropped to the surface of coating bath to form thereon a multiannular pattern or pattern of water rings and the dropping of the coating material is continued at a rate suitable to the dipping speed of the 115 workpiece.

- Water is usually used for floating the coating material, though the workability of the coating bath is improved by adding thereto a surface-active agent.

- Coating materials suitable for patterning are acrylic resin coatings such as, e.g. modified acrylic lacquers (acrylic resin/nitrocellulose), alkyd resin coatings such as, e.g. high solid lacquers (benzoic acid modified alkyd resin/nitrocellulose), but others are also suitable.

- Since it is necessary for obtaining a finely 125 finished pattern to prevent break-up of the streaks 130

of the coating material, it is occasionally preferred to reinforce the coating layer by incorporating therein a small amount of microfilm.

As illustrated above, in accordance with the present invention a fine wood grain pattern can be applied to the whole surface of a workpiece by processing it in lengthwise hung-down state even if it is of a complicated shape, because the patterned mask coating is carried out in a dip coating process. The method of the present invention can be carried out as a step in an alumite line in which workpieces are processed in lengthwise hung-down state. The workpieces may be coloured by a subsequent modifying process and an electrolytic colouring process into bronze, amber, silver, gold and various other tones. The coloured pattern prepared by the method of the present invention exhibits excellent durability, i.e. excellent weathering resistance and corrosion resistance when used as an exterior material of buildings.

Since a mask coating is deposited on the workpiece from a floating layer of a coating material over liquid surface, there are obtained coloured patterns which closely resemble but are not identical.

The coloured pattern produced by a method in accordance with the present invention may be made more corrosion and weathering resistant by applying thereto a clear lacquer in a spray, dip or electrodeposition coating process.

The present invention will now be illustrated in more detail by the following examples.

Example 1

An aluminum extruded sheet A-6063s 20 cm length and 7 cm in width which had previously been degreased, etched and desmutted was dried. A black modified acrylic lacquer (acrylic resin/nitrocellulose) enamel diluted with a thinner to an IHS cup consistency of 11 seconds was poured at five points into the surface of water slowly flowing in one direction to form five thin streaks of the enamel extending in the direction of the flow of water. The flow of water and pouring of the enamel were both terminated immediately before the front ends of the streaks of the enamel arrived at the overflow end. The dried aluminum sheet was slowly dipped therein to deposit the enamel in a wood grain pattern on its surfaces. The sheet was drawn out and dried at 100°C for 10 minutes. The sheet was soaked in an electrolytic bath containing boric acid in a strength of 20 g/l and caustic soda in a concentration of 1 g/l and maintained at 20°C and electric current was supplied for 40 seconds at a current density of 2 A/dm² between the sheet and a stainless steel (SUS 304) counter electrode to form a barrier film. After this surface modification, the sheet was treated with an organic paint remover, Saprotite P-19 supplied by Chugai Kasei K.K. to remove the patterned mask coating, washed with water and then soaked in a 17.5 w/v % sulfuric acid electrolytic bath in which direct electric current was supplied at a current

density of 1.2 A/dm² for 35 minutes between the sheet and an aluminum cathode to form an anodic oxide film in the surfaces of the sheet. The sheet was then, after washing with water, subjected to electrolysis by alternating current of a voltage of 18 volts for 3 minutes in a bath of the following composition.

Electrolytic bath:

Nickel sulfate (hexahydrate)	30 g/l
Magnesium sulfate (heptahydrate)	15 g/l
Boric acid	20 g/l
Ammonium sulfate	30 g/l
Sodium dithionite	0.5 g/l
pH	5.6
Temperature	20°C

Thus there was formed a pattern of the grain of wood comprising dark areas corresponding to the areas marked by the surface modification and light bronze areas corresponding to the unmasked areas.

Example 2

The aluminum sheet used in Example 1 was subjected, in place of the surface modification by barrier film forming electrolysis in boric acid-caustic soda bath in Example 1, to a surface modification by electrolysis for 1 minute in a 15 g/l sulfuric acid bath at 20°C by means of 23 V direct current imposed between the sheet and an aluminum cathode. The sheet was then treated with an organic paint remover, Saprotite p-19 supplied by Chugai Kasei K.K. to remove the patterned mask coating, washed with water and soaked in a 17.5 w/v % sulfuric acid electrolytic bath in which electric current was supplied first at 21V for 20 seconds and then at a direct current density of 1.2 A/dm² for 35 minutes between the sheet as anode and an aluminum counter electrode as cathode to perform anodic oxidation. The sheet was then treated in the same manner as in Example 1 to obtain a wood grain pattern comprising dark masked areas and light bronze unmasked areas.

Example 3

An aluminum sheet to which there had been applied a mask coating in a wood grain pattern in the manner of Example 1 was subjected to etching at 60°C for 3 minutes in a 70 g/l caustic soda bath to etch unmasked areas thereby to form difference in metallic luster between the masked and unmasked areas. The sheet was then processed with the same procedure as in Example 1 to obtain a finished sheet having a wood grain pattern exhibiting a stereographic effect in addition to a similar appearance as obtained in Example 1.

Example 4

An aluminum sheet was processed in the manner of Example 1 until removal of mask coating and then subjected to anodic oxidation in

an electrolyte containing 5 g/l of sulfuric acid and 100 g/l of sulfo-salicylic acid at 20°C, at a current density of 2 A/dm², for 35 minutes using an aluminum counter electrode as cathode to obtain a finished sheet having a wood grain pattern comprising dark masked areas and light amber unmasked areas.

Example 5

Through surface modification to removal of mask coating there was repeated the same process as in Example 3, and then the so treated sheet was processed in the same manner as in Example 4 to obtain a wood grain pattern exhibiting, in addition to an appearance as obtained in Example 4, a stereographic effect.

Example 6

The procedure of Example 2 was repeated except that there was used for surface modification a 20 g/l oxalic acid bath at a liquid temperature of 20°C in place of a 15 g/l sulfuric acid bath to obtain a wood grain pattern wherein masked areas are dark and unmasked areas are light bronze.

Claims

1. A method of forming a coloured pattern on the surface of an article made of aluminum or its alloys comprising the steps of dipping said article in a coating bath including a coating material in a multilinear or multiannular pattern floating therein to form thereon a mask coating in a wood grain pattern, subjecting said article to a surface modification to form an oxide film in unmasked areas of the surface of said article, removing the mask coating, and subjecting said article to an electrolytic colouring.

2. A method as claimed in claim 1, wherein the coating material is floating on water.

3. A method as claimed in claim 2, wherein a surface-active agent is incorporated into the water.

4. A method as claimed in any of claims 1 to 3, wherein the surface modification is performed by either a chemical conversion to form a chemically oxidized film, or anodic oxidation in an acid electrolyte to form an anodic oxide film or a coloured anodic oxide film, or electrolysis in an acid electrolyte to form a barrier-type oxide film.

5. A method as claimed in claim 1, wherein the electrolytic colouring is performed by subjecting the masked and surface-modified article to an anodic oxidation in an acid electrolyte and then to an electrolysis in an acid electrolyte containing a metallic salt to form a coloured oxide film.

6. A method as claimed in claim 1, wherein the electrolytic colouring is performed by an anodic oxidation in an organic acid electrolyte to form a coloured oxide film.

7. A method of forming a coloured pattern on the surface of an article made of aluminum or its alloys comprising the steps of dipping said article in a coating bath including a coating material in a multilinear or multiannular pattern floating therein to form thereon a mask coating in a wood grain pattern, subjecting said article to a surface modification by etching using an alkaline solution, removing the mask coating, and subjecting said article to an electrolytic colouring.

8. A method as claimed in claim 7, wherein the coating material is floating on water.

9. A method as claimed in claim 8, wherein a surface-active agent is incorporated into the water.

10. A method as claimed in claim 7, wherein the electrolytic colouring is performed by subjecting the masked and surface-modified article to an anodic oxidation in an acid electrolyte and then to an electrolysis in an acid electrolyte containing a metallic salt to form a coloured oxide film.

11. A method as claimed in claim 7, wherein the electrolytic colouring is performed by an anodic oxidation in an organic acid electrolyte to form a coloured oxide film.

12. A method of forming a coloured pattern on the surface of an article made of aluminum or its alloys substantially as hereinbefore described with reference to the Examples.

13. An aluminum produced by a method as claimed in any of claims 1 to 12.

14. An aluminum article as claimed in claim 13 as appendant to claim 1, which has a close resemblance to a straight or cross grain of natural wood.

15. An aluminum article as claimed in claim 13 as appendant to claim 7, which has a close resemblance to a straight or cross grain of natural wood with a stereographic effect.

an electrolyte containing 5 g/l of sulfuric acid and 100 g/l of sulfo-salicylic acid at 20°C, at a current density of 2 A/dm², for 35 minutes using an aluminum counter electrode as cathode to obtain a finished sheet having a wood grain pattern comprising dark masked areas and light amber unmasked areas.

Example 5

Through surface modification to removal of mask coating there was repeated the same process as in Example 3, and then the so treated sheet was processed in the same manner as in Example 4 to obtain a wood grain pattern exhibiting, in addition to an appearance as obtained in Example 4, a stereographic effect.

Example 6

The procedure of Example 2 was repeated except that there was used for surface modification a 20 g/l oxalic acid bath at a liquid temperature of 20°C in place of a 15 g/l sulfuric acid bath to obtain a wood grain pattern wherein masked areas are dark and unmasked areas are light bronze.

Claims

1. A method of forming a coloured pattern on the surface of an article made of aluminum or its alloys comprising the steps of dipping said article in a coating bath including a coating material in a multilinear or multiannular pattern floating therein to form thereon a mask coating in a wood grain pattern, subjecting said article to a surface modification to form an oxide film in unmasked areas of the surface of said article, removing the mask coating, and subjecting said article to an electrolytic colouring.
2. A method as claimed in claim 1, wherein the coating material is floating on water.
3. A method as claimed in claim 2, wherein a surface-active agent is incorporated into the water.
4. A method as claimed in any of claims 1 to 3, wherein the surface modification is performed by either a chemical conversion to form a chemically oxidized film, or anodic oxidation in an acid electrolyte to form an anodic oxide film or a coloured anodic oxide film, or electrolysis in an acid electrolyte to form a barrier-type oxide film.

5. A method as claimed in claim 1, wherein the electrolytic colouring is performed by subjecting the masked and surface-modified article to an anodic oxidation in an acid electrolyte and then to an electrolysis in an acid electrolyte containing a metallic salt to form a coloured oxide film.

6. A method as claimed in claim 1, wherein the electrolytic colouring is performed by an anodic oxidation in an organic acid electrolyte to form a coloured oxide film.

7. A method of forming a coloured pattern on the surface of an article made of aluminum or its alloys comprising the steps of dipping said article in a coating bath including a coating material in a multilinear or multiannular pattern floating therein to form thereon a mask coating in a wood grain pattern, subjecting said article to a surface modification by etching using an alkaline solution, removing the mask coating, and subjecting said article to an electrolytic colouring.

8. A method as claimed in claim 7, wherein the coating material is floating on water.

9. A method as claimed in claim 8, wherein a surface-active agent is incorporated into the water.

10. A method as claimed in claim 7, wherein the electrolytic colouring is performed by subjecting the masked and surface-modified article to an anodic oxidation in an acid electrolyte and then to an electrolysis in an acid electrolyte containing a metallic salt to form a coloured oxide film.

11. A method as claimed in claim 7, wherein the electrolytic colouring is performed by an anodic oxidation in an organic acid electrolyte to form a coloured oxide film.

12. A method of forming a coloured pattern on the surface of an article made of aluminum or its alloys substantially as hereinbefore described with reference to the Examples.

13. An aluminum produced by a method as claimed in any of claims 1 to 12.

14. An aluminum article as claimed in claim 13 as appendant to claim 1, which has a close resemblance to a straight or cross grain of natural wood.

15. An aluminum article as claimed in claim 13 as appendant to claim 7, which has a close resemblance to a straight or cross grain of natural wood with a stereographic effect.