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NO DRAWINGS.

Inventors:—TOSHIYUKI OHTA and HISASHI TAKAO.

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Int. Cl.:—C 23 b 13/00.

COMPLETE SPECIFICATION.

Improvements in or relating to Aluminium Articles having an Electro-Deposited Resin Surface Coating of High Durability.

We, HONNY KASEI KABUSHIKI KAISHA (HONNY CHEMICALS Co., LIMITED), a Japanese body corporate, of No. 8—6, 3 chome, Hiyoshi-cho, Nagata-ku, Kobe-shi, Hyogo-Ken, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of treating aluminium to provide aluminium articles having a surface coating of high durability.

Henceinafter, the term "alumite" is used to denote aluminium having an oxidised film on its surface.

Processes are known for oxidising aluminium anodically in an electrolyte, such as oxalic acid, sulphuric acid or chromic acid, in order to produce a corrosion inhibiting film thereon. These films comprise film thereon. These films comprise γ - Al_2O_3 and have a porous surface immediately after the electrolytic oxidation and are normally treated with steam at 4 to 5 atmospheres pressure for between a half and one hour to close the pores therein and turn the film into γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Boehmite).

However, it is generally not possible to close every pore of the porous film of γ - Al_2O_3 in such processes, and on inspection open pores are found still to remain. Therefore, if acids, alkalis or other corrosive chemicals come into contact with the surface of articles made of such alumite the chemicals may penetrate through the

film and corrode the aluminium. Thus, the alumite, which has a surface coating never completely free from defects, exhibits poor resistance to corrosion.

According to the present invention there is provided a method of treating an aluminium article, which comprises oxidising the surface of the aluminium article to form a porous oxide film thereon, contacting the porous film with an aqueous dispersion, emulsion or solution of a resin, electrodepositing the resin on the porous film, and curing the resin adsorbed on the porous film.

Thus, a continuous resin film is formed, either by adsorbing a thermosetting resin with excellent chemical resistance into the pores, which usually number approximately 60 to 800 per square micron, of the oxide film, preferably immediately after the production of said film by electrolytic oxidation, or by covering the film surface with a thin resin layer and heating the coated material, for instance in a furnace to carry out the cross-linking reaction of the adsorbed or adhering thermosetting resin.

Thus, this invention has succeeded in remarkably advancing the operational efficiency as compared with the conventional process of closing pores by the use of a steam or boiling water treatment, and provides alumite having excellent corrosion resistance and electrical insulating qualities without loss of the good appearance, the smoothness and the other valuable qualities

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possessed by alumite produced by the conventional processes.

The film produced on aluminium in the process of this invention is fundamentally different from one produced by simply coating an aluminium oxide film with a solution of a water-soluble resin or an aqueous solution of an emulsive resin immediately after electrolytic oxidation by a conventional coating process, such as spray-coating or dipping, in that the resin grains are moved electrically and adsorbed on the oxidised film.

With this invention, such even resin films can be provided as were not readily possible to manufacture using a conventional coating process and products can be obtained which have a peculiar feel not usually possible to obtain by using a conventional coating process. In addition, if a water soluble resin having a small molecular diameter is used, it is possible to permeate the resin grains electrically into pores of the oxidised aluminium to obtain a resin film in contact with substantially the whole of the area of the oxidised film. Thereafter, when the resin is set thermally, in the presence of water and ammonia or amines contained in the aqueous dispersion, emulsion or solution of the thermosetting resin, the structure of the porous oxidised film is changed from $\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Boehmite). Thus, the pores of the oxidised film are closed entirely.

When water-soluble resin particles of small diameter are adsorbed electrically into the pores of the oxidised film, the pores will be filled with the resin grains. Therefore, the film will exhibit better corrosion resistance and will be smoother than can be provided in a similar process in which a thermosetting film is baked on the surface and unfilled pores still remain.

The thermosetting resin used in the present invention may, for example, be an acrylic resin, such as acrylic acid resin, an acrylate resin or acrylamide resin, or a reaction product or a mechanical mixture of an alkyd resin and water-soluble melamine resin or of a vinyl-modified unsaturated alkyd resin and a water-soluble melamine resin, the water-soluble melamine resin being obtained from hexamethylol melamine hexaalkylether. The vinyl modified unsaturated alkyd resins are made by the polymerization of a vinyl monomer with an alkyd resin composed of an unsaturated oil or fatty acid. Herein, by the term "vinyl monomer" is meant a monomer having a vinyl group ($-\text{CH}=\text{CH}_2$) in the molecule, such as an acrylic ester, for example methyl acrylate and ethyl acrylate, a methacrylic ester, for example methyl methacrylate and hydroxyethyl methacrylate, an unsaturated

organic acid, for example acrylic acid and methacrylic acid, and styrene.

The above-mentioned thermosetting acrylic resins may be made by heating and stirring a mixture consisting of organic solvents such as methanol, ethylene glycol monobutyl ether and/or cyclohexanone, unsaturated organic acids such as acrylic acid, methacrylic acid and/or maleic anhydride, a cross-linking vinyl monomer (as defined above) such as methylol-acrylamide and/or methylol methacrylamide, a polymerizable vinyl monomer (as hereinabove defined) such as styrene and/or acrylic acid ester, polymerization catalysts such as benzoyl peroxides and/or lauroyl peroxides, and polymerization regulators such as dodecyl mercaptan and/or carbon tetrachloride, to carry out polymerization, thereafter neutralizing the product with, for example, an aqueous solution of ammonia and/or triethylamine to make the resin soluble in water.

Thermosetting resins composed of alkyd resins and water-soluble melamine resin obtained from hexamethylol melamine hexaalkyl ether, may be obtained by mixing a water-soluble melamine resin at a temperature of from room temperature to 100°C with an alkyd resin modified with a fatty acid, the alkyd resin having an acid value of from 10 to 80 and an oil length of from zero to 80%, and being obtained by heating a mixture consisting of (1) a saturated or unsaturated aliphatic acid, (2) ethylene glycol, glycerol, polyethylene glycol, other polyhydric alcohol or an epoxide, (3) adipic acid, sebacic acid, maleic anhydride or other polybasic acid or anhydride, and (4) a small quantity of cyclohexanone, toluene or other organic solvent.

Alternatively the thermosetting resin may be obtained by mixing a water-soluble melamine resin and an alkyd resin from the ester exchange process, the resin being obtained by esterifying a mixture of dehydrated castor oil, an above-mentioned polyhydric alcohol and a small amount of an ester exchanging catalyst such as caustic potash, and thereafter esterifying also an above-mentioned polybasic acid or anhydride.

Thermosetting resins consisting of a modified acrylic resin and a water-soluble melamine resin, obtained from hexamethylol melamine hexaalkyl ether, may be obtained by polymerising by heating and stirring a mixture consisting of organic solvents such as methanol, ethylene glycol monobutyl ether and/or cyclohexanone, unsaturated acids such as acrylic acid and/or methacrylic acid, a vinyl monomer (as hereinabove defined), such as styrene and/or acrylic acid ester, a cross-linking vinyl monomer, if necessary, such as methylol

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65 acrylic amide or glycidyl methacrylate and polymerization catalysts and/or polymerization regulators, thereby obtaining a modified acrylic polymer; mixing said modified acrylic polymer with a water-soluble melamine resin, which is obtained from hexamethylol melamine hexaalkyl ether and heating at a temperature under 100°C; making it soluble in water by neutralizing with, for example, an aqueous solution of ammonia and/or triethylamine or by treating the acrylic polymer with, for example, ammonia and thereafter mixing with water-soluble melamine at ambient temperature.

10 A thermosetting vinyl modified unsaturated alkyd resin may be obtained by dissolving an unsaturated alkyd resin in methanol, ethylene glycol-monobutyl ether or other suitable organic solvent and performing a graft copolymerization with a mixture consisting of unsaturated organic acid(s) such as acrylic acid and/or methacrylic acid, vinyl monomer(s) such as styrene, methacrylic acid ester and/or acrylic acid ester, cross-linking monomer(s) such as methylol acrylic amide if necessary, and peroxide polymerization catalyst(s) and/or polymerization regulator(s), and thereafter neutralizing the thus obtained vinyl modified unsaturated alkyd resin with an aqueous solution of ammonia, for example, to make it soluble in water.

Further, with regard to the resins composed of vinyl modified unsaturated resin(s) and water-soluble melamine resin(s), obtained from hexamethylol melamine hexaalkyl ether, the thermosetting resins may be obtained by heating and mixing the foregoing vinyl modified unsaturated alkyd resin(s) with said-water-soluble melamine resin(s) at a temperature below 100°C, and making it soluble in water by neutralizing it with, for example, an aqueous solution of ammonia; or they may be obtained by rendering the said vinyl modified unsaturated alkyd resin(s) soluble in water by neutralizing with, for example, an aqueous solution of ammonia, and thereafter mixing it with the water-soluble melamine resin(s) at ambient temperature.

In the foregoing operations, it is necessary to select the optimum content of unsaturated organic acids in the vinyl resins or the optimum acid value of the alkyd resins accurately.

Resins for electrodeposition normally have a muddy white emulsive appearance and are useful to regulate the thickness of the resin film and the surface condition of the obtained alumite products.

In preparing a dispersion, emulsion or solution of the thermosetting resin, the concentration of the resin is selected depending on the conditions to be employed, but a concentration of resin of from 3 to 40%

by weight is normally used. The best results are obtained when using a concentration of resin of from 5 to 20% by weight and by regulating the voltage and the initial current density within a safe and economical range.

In the process of the present invention, it is preferred to wash the porous film of aluminium oxide with cool or hot water immediately after electrolytic oxidation of the aluminium, to dip it in a bath of the above-mentioned resin solution together with another electrode, to apply direct current between the aluminium article and the electrode to adsorb the resin on the porous film electrolytically and to thereafter cure the adsorbed resin.

If it is desired to colour the porous film of aluminium oxide, a dye stuff may be adsorbed into the porous film of aluminium oxide prior to the adsorption of resin thereon, or there may be added a water paint to the resin dispersion, emulsion or solution in an amount large enough to colour the said resin dispersion, emulsion or solution. Thus, products coloured as desired and smooth to touch can be provided. In addition, if heat resistant dyes or pigments are used as colorants, the colour of the product will be thermally stable.

Furthermore, there are cases where it is desirable to heat the resin dispersion, emulsion or solution to a temperature of from 30°C to 50°C., which heating of the resin dispersion, emulsion or solution makes the resin grains therein move more freely and makes them more readily electrically adsorbable. In some cases, if the resin dispersion, emulsion or solution is not heated it is impossible to adsorb the resin electrically because the pH value of the solution rises owing to the accumulation of ammonia, amines or other additives which are necessary to render the resin soluble in water or to stabilize dispersion or emulsion while the resin bath is used continuously. Therefore, it is advantageous to heat the dispersion, emulsion or solution, whilst not disturbing its stability, to maintain its pH value by evaporating off excess ammonia and amines.

The resin electrodeposited on and in the oxide film in the manner mentioned above are baked at a temperature sufficient to cause cross-linking of the thermosetting resin(s). Usually, a suitable temperature is from 100° to 250°C, but a temperature of from 120° to 160°C is preferred, for a period of from 10 to 60 minutes.

The invention as further illustrated in the following Examples, in which all parts are by weight unless otherwise specified.

EXAMPLE 1

After de-greasing and washing, an aluminium plate was anodically oxidized at 20°C

for one hour by using an electrolyte containing 15% of sulphuric acid and a direct current of 1.5 A/dm².

Thereafter, adhering electrolyte was washed off the aluminium plate. Products with an oxide film produced as in this Example were employed in the following Examples.

EXAMPLE 2

Into a reactor equipped with an agitator, a thermometer and a reflux condenser, 42.5 parts of ethylene glycol monobutyl ether and 44.5 parts of methanol were fed and heated at 70°C. Whilst maintaining a reflux temperature of 70°C, 5.5 parts of methacrylic acid, 25 parts of ethyl acrylate, 44.5 parts of methyl methacrylate, 5 parts of styrene, 1.5 parts of benzoyl peroxide and one part of dodecyl mercaptan were mixed together and then added to the ethylene glycol monobutyl ether and methanol in the reactor together with 20 parts of methylol acrylamide, in five portions at half-hourly intervals. The reactants were then heated and agitated for four hours under reflux at the same temperature. After the conclusion of the reaction, the contents were cooled to 60°C. The acid component was neutralized with 28% aqueous solution of ammonia, and the reaction product was diluted with water until the solid matter content was 30% by weight.

Thus obtained was a water-soluble resin solution which is dilutable with water freely. This resin solution was diluted with water until the solid matter content was 10% by weight and a resin solution for the electrodeposition was made therefrom.

The electrolytically oxidised aluminium obtained in Example 1 was dipped in the above-mentioned resin solution maintained at 25°C and was made an anode for a source of direct current. A stainless steel plate was utilised as a cathode. The electrolytic treatment was performed for one and a half minutes by passing a direct current with a voltage of 100V and an initial current density of 500 mA/dm². The product was then taken from the bath, washed lightly to remove the adhering excess resin and baked at 150°C for 30 minutes. Thus, an aluminium article with excellent durability was obtained.

EXAMPLE 3

Into a reactor equipped with an agitator, a thermometer and a reflux condenser attached with a blowing inlet for nitrogen gas and a separating tube, 332 parts of soybean oil, 120 parts of glycerol and 0.2 part of sodium methoxide (NaOCH₃) were fed. Under nitrogen, the ester-exchanging reaction was carried out at a temperature of between 230 and 240°C for two hours. After

cooling, 222 parts of phthalic anhydride and 50 parts of cyclohexanone were added and esterified at a temperature of between 180 and 210°C to produce an alkyd resin with an acid value of 50. To 100 parts of alkyd resin, 40 parts of ethylene glycol monobutyl ether were added. Then, it was neutralized with 28% aqueous solution of ammonia and diluted with water until solid matter content became 30% by weight. In this way, a resin solution entirely soluble in water was obtained. The solution was mixed with a water-soluble melamine resin obtained from hexamethylol melamine hexaalkyl ether (made by the Nippon Carbide Company) at a ratio of solid matter content of 1:1. The mixture was diluted with water up to 15% of the gross solid matter content to make a resin solution for electrodeposition. Thereafter, electrolytically oxidised aluminium obtained as in Example 1 was treated with a direct current at a voltage of 80V and an initial current density of 400 mA/dm² for one minute in the above resin solution in the manner similar to that used in Example 2. After being taken out from the resin solution and washed lightly to remove adhering excess resin, it was baked at 130°C for half an hour. The cross-linking reaction of the resin adsorbed on the surface of the oxide film was carried out during the heating. Thus a continuous resin film was formed.

EXAMPLE 4

Into a reactor equipped with an agitator, a thermometer and a reflux condenser, 50 parts of ethylene glycol monobutyl ether and 37 parts of methanol were fed and heated under reflux. To the reactor, a mixture of 5 parts of acrylic acid, 5 parts of hydroxyethyl acrylate, 20 parts of ethyl acrylate, 45 parts of methyl methacrylate, 5 parts of butyl acrylate, 1.5 parts of benzoyl peroxide and 0.5 part of dodecyl mercaptan was added in five portions at half-hourly intervals. After conclusion of the feeding, the contents of the reactor were heated and stirred for five hours under reflux, and after conclusion of the reaction, the reactor and its contents was cooled. Acid components were rendered neutral with triethylamine, and thereafter the mixture was diluted with water until the solid matter content was 30% by weight.

In this manner, a resin solution entirely soluble in water was produced. This solution and the water-soluble melamine resin used in Example 3 were mixed at a ratio of solid matter content of 1:1 and were reacted together at 80°C for one hour. The product was diluted with water until the gross solid matter content was 15% by weight to give a resin solution for electrodeposition. Electrolytically oxidised aluminium, produced as in Example 1, was

treated in a manner using 2 initial moved from water to and bake

(1) A using 33% glycerol in the example 3, value of parts of (2) in Example resin produced by ethylene glycol monobutyl ether, 5 parts of hydroxyethyl acrylate, 5 parts of benzoyl peroxide added to hourly contents of Thereafter, four hours reaction were cooled acid and with water until the by water there matter thereby was made dis at 25°C 100V 100 mA/dm manner After the remove 130°C

(1) in Example 3, 13 safflower hexanone produce, with the (2) Example obtained

65 treated in the said resin solution at 20°C
in a manner similar to that used in Example
2 using direct current of voltage 80V and an
70 initial current density of 200 mA/dm², re-
moved from the resin solution, washed with
water to remove the adhering excess resin
and baked at 120°C for one hour.

EXAMPLE 5

10 (1) An ester exchange was carried out
using 330 parts of safflower oil, 100 parts of
75 glycerol and 0.2 part of sodium methoxide
in the manner similar to that used in Ex-
ample 3. An alkyd resin having an acid
15 value of 30 was produced by adding 220
parts of phthalic anhydride.

80 (2) Into a reactor similar to that used
in Example 2 and 4, 20 parts of the alkyd
resin produced in (1) above, 55 parts of
20 ethylene glycol monoethyl ether and 32
parts of methanol were fed. A mixture of
85 5 parts of methacrylic acid, 5 parts of 2-
hydroxyethyl methacrylate, 40 parts of
ethyl acrylate, 5 parts of methyl methacry-
late, 5 parts of styrene, 1.5 parts of benzoyl
25 peroxide, and 20 parts of methylol acryl-
amide was divided into five portions and
added to the contents of the reactor at half-
hourly intervals, whilst maintaining the con-
30 tents of the reactor at their boiling point.
Thereafter, it was heated and stirred for
four hours under the reflux. After the re-
action finished, the contents of the reaction
35 were cooled. The acid values of methacrylic
acid and alkyd resin were rendered neutral
with diethylamine. By diluting with water
until the content of solid matter was 30%
100 by weight, a resin solution freely soluble in
water was obtained. The solution was fur-
ther diluted with water until the solid
40 matter content was 15% by weight, and
thereby a resin solution for electrodeposition
was made. Thereafter, electrolytically ox-
idised aluminium produced as in Example 1
105 was treated in the resin solution maintained
at 25°C, with a direct current of voltage
45 100V and an initial current density of 300
mA/dm² for one and a half minutes in the
manner similar to that used in Example 2.
110 After being taken out of the resin solution
the aluminium was washed with water to
50 remove adhering excess resin and baked at
130°C for a half hour.

EXAMPLE 6

55 (1) Into a reactor similar to that used
in Example 3, 192 parts of trimethylpro-
pane, 132 parts of sebacic acid, 67 parts of
safflower aliphatic acid and 8 parts of cyclo-
hexanone were fed and heated to 200°C to
60 produce, by esterification, an alkyd resin
with the acid value of 50.

125 (2) Into a reactor similar to that used in
Example 2 and 4, 20 parts of the alkyd resin
obtained in (1), 35 parts of cyclohexanone,

13 parts of isopropylalcohol and 10 parts of
methanol were fed. Whilst maintaining the
65 contents of the reactor at their boiling point,
a mixture of 3 parts of methacrylic acid, 40
parts of methyl methacrylate, 42 parts of
ethyl acrylate and 1.5 parts of benzoyl per-
oxide was added thereto in five portions at
70 half hourly intervals. After the conclusion
of the addition, polymerization was con-
tinued for six hours under reflux. The con-
tents were cooled and triethylamine was
added to render the acid value of the alkyd
75 resin and methacrylic acid neutral. By di-
luting it with water until the content of solid
matter was 30%, by weight a resin solution
freely soluble in water was produced. This
resin solution and the water-soluble mel-
80 amine resin hereinabove described were
mixed at the ratio of solid matter content
of 1:1 and then diluted with water until
the content of solid matter was 15% by
weight. This solution was used as the resin
85 solution for electrodeposition. Subsequently,
electrolytically oxidised aluminium pro-
duced as in Example 1 was treated in the
said resin solution, maintained at 30°C, with
direct current of voltage 100V and an initial
90 current density of 600 mA/dm² for one and
a half minutes in the manner similar to that
of Example 2. The product was taken out
of the resin solution, washed with water to
95 remove adhering excess resin and baked at
150°C for a half hour.

EXAMPLE 7

A milk-white emulsion was prepared by
polymerizing 20 parts of an alkyd resin
100 with an acid value of 10 (said alkyd resin
having been prepared by mixing 100 parts
of soybean oil, 100 parts of glycerol and 0.5
parts of sodium methoxide and reacting
them at a temperature of from 230°C to
105 240°C. Then 200 parts of anhydrous
phthalic acid in 50 parts of cyclohexane was
reacted therewith at a temperature of from
180°C to 210°C), 35 parts of cyclohexanone,
13 parts of isopropylalcohol, 10 parts of
110 methanol, 1.5 parts of methacrylic acid, 42
parts of methyl methacrylate, 42 parts of
ethyl acrylate and 1.5 parts of benzoyl per-
oxide in the above-mentioned manner, and
was neutralised with triethylamine and di-
luted with water to a solids content of 30%
115 by weight.

This emulsion and the water-soluble mel-
amine resin hereinabove described were
mixed in the ratio of solid matter content
of 1:1 and diluted with water until the total
120 content of the solid matter was 20% by
weight. This emulsion was excellent in
stability over a long term and was employ-
able as a resin solution for electrodeposition.

125 Electrolytically oxidised aluminium ob-
tained as in Example 1 was treated in the
said resin solution with a direct current

6 voltage of 50V and an initial current density of 200 mA/dm² for one minute in the manner similar to that of Example 2. The product was removed from the resin solution, washed with water to remove adhering excess resin and baked at 130°C for a half hour.

10 The aluminium treated in the above-mentioned manner was extremely excellent in durability, appearance and the sense of touch.

EXAMPLE 8

15 Examples 2 to 7 were repeated with 5% by weight of a red water-soluble dye in the resin solution or emulsion. Red coloured products were produced which were soft to the touch and possessed the advantageous properties of the products of Examples 2 to 7.

20 WHAT WE CLAIM IS:—

1. A method of treating an aluminium article, which comprises oxidising the surface of the aluminium article to form a porous oxide film thereon, contacting the porous film with an aqueous dispersion, emulsion or solution of a resin, electrodepositing the resin on the porous film, and curing the resin adsorbed on the porous film.

30 2. A method according to Claim 1, wherein the aluminium article is oxidised electrolytically.

35 3. A method according to Claim 1 or 2, wherein the aluminium article is dipped into a bath of said aqueous dispersion, emulsion or solution of the resin.

4. A method according to Claim 1, 2 or 3 wherein the resin is cured by heating at a temperature of from 100 to 250°C.

5. A method according to Claim 4, 40 wherein the resin is cured by heating at a temperature of from 120 to 160°C.

6. A method according to Claim 4 or 5, wherein the resin is cured by heating for a period of from 10 to 60 minutes.

7. A method according to any preceding claim, wherein the resin is an acrylic resin; or a reaction product or mechanical mixture of an alkyd resin or a vinyl modified alkyd resin having an acid value of from 10 to 80 and an oil length of from zero to 80% and a water-soluble melamine resin.

8. A method according to any preceding claim, wherein electro-deposition of the resin is effected using direct current at a voltage of from 50 to 100 V and an initial current density of from 200 to 600 mA/dm², for a period of from 1 to 1½ minutes.

9. A method according to any preceding claim, wherein the porous oxide film is coloured with a dye prior to electro-deposition of the resin or a water-soluble dye is present in the resin dispersion, emulsion or solution.

10. A method of treating an aluminium article, substantially as described with reference to any of the foregoing Examples 2 to 8.

11. An aluminium article whenever produced by the method claimed in any preceding claim.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28 Southampton Buildings,
Chancery Lane,
London, W.C.2.
Agents for the Applicants.

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- 4 voltage of 50V and an initial current density of 200 mA/dm² for one minute in the manner similar to that of Example 2. The product was removed from the resin solution, washed with water to remove adhering excess resin and baked at 130°C for a half hour.

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