

PATENT SPECIFICATION

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(54) COATING ANODICALLY-OXIDIZED ALUMINIUM ARTICLES

(71) We, YOSHIDA KOGYO KABUSHIKI KAISHA, of No. 1 Kanda Izumi-cho, Chiyoda-ku, Tokyo, Japan, a Corporation duly organized under the laws of 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:-

The present invention relates to a method for providing a coating film on an anodically-oxidized layer of aluminium oxide on the surface of an aluminium article of aluminium or an aluminium-based alloy.

Several methods are known for sealing the micropores or pinholes in the anodically-oxidized surface layer of an aluminium article and include the use of pressurized steam or boiling water and chemical sealing methods which employ certain salts for example nickel acetate or cobalt acetate. After the anodically-oxidized surface layer has been subjected to sealing by one of the above described prior art methods it can be provided with a coating film using a coating composition, but the anodically-oxidized surface layer is liable to formation of cracks if drying by heating of the coating composition is undertaken at the usual temperature of 140°C or higher. Such cracks result in inferior adhesion of the coating film to the underlying surface, inferior appearance and mechanical properties of the coating film as well as poor corrosion resistance of the thus coated articles. Therefore it is a generally accepted practice that an aluminium article which has been subjected to sealing is coated with a low-temperature-drying coating composition which is curable at a temperature of lower than 140°C. However, such low temperature-drying coating compositions are not as effective as those drying at 140°C or above, and disadvantageous properties are obtained with the resultant films in comparison with those from the high temperature-drying coating compositions. In consideration of these problems, the selection of a coating composition is critical and the properties of the coating films e.g. adhesion to the underlying surface and corrosion resistance, are never usually satisfactory.

Certain techniques are well known which permit coating with a high temperature-drying coating composition. Coating is usually preceded by sealing of the micropores in the anodically-oxidized surface layer with a synthetic resin by means of electrodeposition or immersion. The sealing treatment is a semi-sealing to such a halfway extent that no crack formation will take place upon coating. Completion of sealing occurs by hydration simultaneously with high temperature curing and drying of the coating composition by utilizing moisture contained in the coating composition. However, small amounts of the sealing liquid, e.g. sulphuric acid, often remain absorbed in the micropores in the anodically oxidized surface layer and the resultant coated article is often defective with poor corrosion resistance as well as low wear resistance, durability and adhesion of the coating film.

In addition, electrolytic colouring of an anodically oxidized surface layer can bring problems. For example in the method proposed by Asada (see Japanese Patent Publication No. 38 - 1715) a coloured metal oxide of a low oxidation state is deposited electrolytically into the micropores of the anodically-oxidized surface layer before the article is coated with an organic coating composition. This procedure can lead to degradation of the coating film due to migration of the coloured metal oxide out of the micropores in to the overlying coating film.

Aluminium articles of aluminium or aluminium-based alloys coated with either high or low temperature-drying coating compositions on an anodically-oxidized surface layer thus often have defective coating films which lack adhesion to the underlying surface, resistance to wear,

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resistance against alkali solution, hydrochloric acid, saline solution, sulfurous acid solution and cement mortar, and resistance to weathering during outdoor exposure. Such defects and deficiencies arise because of the presence of unsealed or semi-sealed micropores when the coating is with a high temperature-drying coating composition or because one has had to use a low temperature-drying coating composition with inferior properties.

According to the present invention we provide a method of coating a film on the surface oxide layer of an anodically-oxidized aluminium article which comprises the steps of

(a) sealing micropores in the oxide layer by dipping the aluminium article in an aqueous sealing liquid at 80°C or higher and containing from 0.005 to 60 g/litre of a silicic acid or a silicate dissolved or dispersed therein,

(b) coating the thus treated aluminium article with a coating composition, and

(c) drying or curing the coating at a temperature of 140°C or higher.

The method of the present invention can be used with aluminium articles of aluminium or of an aluminium-based alloy comprising aluminium with one or more alloying elements, for example silicon, magnesium, copper, nickel, zinc, chromium, lead, bismuth, iron, titanium or manganese. The shape of the aluminium articles is not critical and suitable articles include plates, pipes, rods, extruded bars with regular or irregular cross section and shaped articles obtained by deep drawing, pressing or other means. The aluminium articles employed have an oxide layer from surface anodic oxidation. Typically such oxidation is performed, desirably after degreasing and washing of the article, in a conventional manner by passing DC electric current through an acidic electrolyte solution of sulfuric, oxalic or sulfamic acid using the aluminium article as the anode and a cathode as the counterelectrode and then washing the article in water.

The aluminium article with the anodically-oxidized surface layer is subjected to sealing treatment of the micropores in the oxide layer. In accordance with the invention, an aqueous sealing liquid containing a silicic acid or silicate dissolved or dispersed therein is employed for a primary sealing treatment. Among the silicic acids and silicates soluble or dispersible in water and thus suitable for the present purpose, the silicates expressed by the general formula $xM_2O \cdot ySiO_2$, where M is an alkali metal, x is an integer from 1 to 10, and y is an integer from 10 to 100, are especially preferred. Other inorganic silicates can be used, as also can silicates containing organic moieties. Examples of suitable silicic acids and silicate compounds thus include orthosilicic acid, metasilicic acid, sodium silicates, potassium silicates, borosilicates, potassium aluminium silicates, sodium aluminium silicates, sodium methylsilicates, potassium methylsilicates, sodium butylsilicates, sodium propylsilicates, lithium propylsilicates, triethanolammonium silicates, tetramethanolamine silicates, hexafluorosilicic acid, zinc hexafluorosilicate, ammonium hexafluorosilicate, cobalt hexafluorosilicate, iron hexafluorosilicate, sodium hexafluorosilicate, nickel hexafluorosilicate, barium hexafluorosilicate and hydroxyammonium hexafluorosilicate.

The concentration of the silicic acid or silicate dissolved or dispersed in the aqueous sealing liquid is in the range from 0.005 to 60 g/liter or, more preferably, from 0.03 to 30 g/liter. Recognizable effects can be obtained even with an extremely low concentration of as low as a few ppm though when the concentration of the silicic acid or silicate in the sealing liquid is outside the range as specified undesirable drawbacks may arise in the performance and appearance of the finished aluminium articles as well as in the stability of the aqueous sealing liquid. The sealing treatment is performed by dipping the aluminium article in the aqueous sealing liquid at an elevated temperature of 80°C or higher. Dipping will usually be for a time less than 30 minutes or, preferably, from 2 to 20 minutes and in this way can give excellent sealing results with respect to corrosion resistance in comparison with conventional sealing methods with chemicals or boiling water. A temperature lower than 80°C for the sealing liquid is undesirable because of the less satisfactory appearance of the finished aluminium articles as well as the lower electric conductivity of the sealing liquid which is disadvantageous when the sealing treatment is conducted electrolytically as discussed below. Improvements in the sealing can be obtained by adding to the aqueous sealing liquid a small amount of a polyol, e.g. glycerin, ethyleneglycol, propyleneglycol or diethyleneglycol, a surface active agent be it a cationic, anionic, nonionic or amphoteric surface active agent, a defoaming composition, and/or a chelating agent.

Instead of the simple dipping of the aluminium article in the aqueous sealing liquid as described above, further improvement in the sealing effect and corrosion resistance of the finished aluminium article can be obtained by an electrolytic sealing treatment for example in which an AC, DC or DC-biased AC voltage of 200 volts or below, preferably from 5 to 110 volts, is applied between the aluminium article and a counterelectrode such as stainless steel electrode, the aluminium article being the cathode and the stainless steel electrode being the anode when using a DC voltage. The frequency of the AC voltage is not critical but conveniently is the conventional frequency of 50 or 60 Hz. The duration of dipping and the temperature of the sealing liquid in this electrolytic sealing treatment can be the same as for

simple dipping.

It has been unexpectedly discovered that still better results in the properties of the coating film and in the appearance of the finished aluminium article, as well as in the stability of the aqueous sealing liquid containing the silicic acid or silicate can be obtained by subjecting the aqueous sealing liquid prior to use to a pretreatment in which an AC, DC or DC-biased AC voltage of usually 110 volts or below or, preferably, from 5 to 15 volts is applied between electrodes of, for example, stainless steel for 2 to 20 minutes and passed through the liquid. The mechanism by which an improvement is obtained in the above pretreatment of the sealing liquid is not well understood at present but presumably the application of the voltage leads to better colloidal dispersion of the silicic acid or silicate in the aqueous sealing liquid.

The effect of the sealing treatment described above employing an aqueous sealing liquid containing a silicic acid or a silicate is a primary sealing treatment, and may be supplemented by a secondary sealing treatment such as in a sealing manner which is conventional in the prior art. The conditions for the secondary sealing treatment are not critical but the following procedure is recommended:

Secondary sealing treatment is best effected with pressurized steam at a steam of 3 to 6 kg/cm²G for 10 minutes or longer or with boiling water for 10 minutes or longer in hot water at a temperature higher than 95°C, the water optionally containing sodium carbonate, ammonia or triethanolamine as an auxiliary additive in a concentration of 0.005 to 1g/liter.

The secondary sealing treatment following the primary sealing treatment can also be effectively carried out chemically with a sealing liquid containing a salt which is a nickel salt such as nickel acetate, a molybdate such as ammonium molybdate, a phosphate such as sodium dihydrogenphosphate or a bichromate such as sodium bichromate. Examples of formulations of sealing liquids for chemical secondary sealing treatment are as follows:

Sealing with a nickel salt solution: nickel acetate 2 to 5 g/liter; cobalt acetate 1g/liter, boric acid 2 to 5g/liter pH 5 to 6; temperature of the solution 70°C or higher; and treatment time 2 to 30 minutes.

Sealing with a phosphate solution: sodium or ammonium dihydrogenphosphate 0.03 g/liter; pH 5 to 6; temperature of the solution 95°C or higher; and treatment time 2 to 30 minutes.

Sealing with a bichromate solution: sodium bichromate 50 to 100 g/liter; sodium carbonate 18g/liter (optional); pH 6.5 to 7.5; temperature of the solution 95°C or higher; and treatment time 2 to 20 minutes.

Sealing with a molybdate solution: ammonium or sodium molybdate 1 to 2 g/liter; pH 5.5 to 8.0; temperature of the solution 90°C or higher, and treatment time about 30 minutes.

If desired the primary sealing treatment can be preceded by colouring of the anodically-oxidized surface film of the aluminium article. The colouring can be performed by any conventional electrolytic or chemical method.

In the electrolytic colouring, electrolysis is carried out with an electrolyte solution prepared in accordance with known methods by adding a small amount of a metal salt of an inorganic acid to an aqueous solution of an inorganic acid or an ammonium, amino or imino salt thereof. Suitable metal salts include nitrates, sulfates, chlorides, phosphates, borates, chromates, oxalates, acetates and tartrates of nickel, cobalt, copper, chromium, tin, selenium, molybdenum and gold. The concentration of these metal salts in the electrolyte solution is typically in the range 5 to 500 g/liter. The electrolysis is performed at 5 to 75 volts AC but it is also possible to perform the electrolysis with a DC voltage or DC-biased AC voltage. A voltage higher than 75 volts normally destroys the oxidized surface film and no colouring is obtained.

Chemical colouring is performed by dipping the aluminium article with anodically-oxidized surface layer in a solution of iron (III) sodium oxalate or iron (III) ammonium oxalate at a concentration of 1 to 10 g/liter and at 40 to 70°C for 1 to 10 minutes.

After having been subjected to the primary and optional secondary sealing treatments described above and, if necessary, after having been washed with water, the aluminium article is dried and coated with a coating composition. The coating composition may be conventional and can be an aqueous solution, aqueous dispersion or an organic solution. The principal advantage of the sealing treatment in accordance with the present method is that a coating composition with a drying or curing temperature of 140°C or higher, which was not used in the prior art due to the problems of crack formation and insufficient adhesion, can be used for the finishing coating. With respect to the coating with a high temperature-drying coating composition, a method is disclosed in Japanese Patent Publication 47-51092, which is a combination of a primary sealing treatment with electrodeposition of a thermosetting resin followed by curing in a drying kiln. With the method of the present invention excellent sealing effects are possible with only the primary sealing treatment. In addition, the present method is not greatly restricted in the selection of the coating process and coating can be by electrodeposition, by dipping and by electrostatic coating.

In summarizing the above description of the inventive method, the potential advantages which are obtainable with the present method are not limited to improvement of the corrosion resistance of the anodically-oxidized surface layer of an aluminium article by the sealing treatment. Difficulty in quality control and the inferior appearance of a coating film electrodeposited on an unsealed or semi-sealed oxide layer arising from residual impurities such as sulfate ions in the micropores can be completely eliminated by the use of an aqueous sealing liquid containing a silicic acid or silicate. The corrosion resistance of the aluminium articles obtained by the above primary sealing treatment can be further strengthened by the secondary sealing treatment with pressurized steam, boiling water or chemicals to give resistance against alkali, acid and saline solution leading, as a consequence, to excellent finished aluminium articles having coating films superior in corrosion resistance against hydrochloric acid and sulphurous acid solution, in wear resistance and in adhesion to the underlying surface as well as in appearance.

The following Examples of the present invention and Comparative Examples serve to illustrate and to compare the method of the invention.

In the following Examples, the anodically-oxidized aluminium articles were subjected to the primary sealing treatment with a silicic acid or silicate-containing sealing liquid and, optionally, to the secondary sealing treatment and then finished by coating with a coating composition in one of three different ways as given below. The thus finished aluminium articles were subjected to examination of the sealing effect after the coating film had been removed with a paint remover and to examination of the properties of the complex coating film itself. The coating procedures (A), (B) and (C), the testing procedures for the sealing effect and the testing procedures for the properties of the complex coating film are summarized in the following.

Coating procedure (A): Electrodeposition with a water-soluble electrodeposition coating composition was carried out using coating composition at a solids content of 12% by weight at 22°C with aluminium article as the anode and a stainless steel rod as the cathode by applying 140 to 180 volts DC voltage for 2 minutes followed by washing with water and drying by heating at 180°C for 40 minutes to give a finished coating film of about 8μm thickness.

Coating procedure (B): The aluminium article was dipped in a water-soluble coating composition of a thermosetting acrylic resin with a solids content of 26% by weight by weight at 40°C, gradually extracted at a speed of about 1 meter/minute and kept at 35°C for 10 minutes followed by drying at 180°C for 40 minutes to give a finished coating film of about 8μm thickness.

Coating procedure (C): The aluminium article was spray-coated with a thermosetting acrylic resin coating composition diluted with an equal amount of a thinner solvent by use of a spray gun driven with compressed air of 4 kg/cm²G and dried with heat at 180°C for 20 minutes to give a finished coating film of about 8μm thickness.

Testing procedures for testing the sealing effect.

(1) Alkali solution dropping test: by the procedure specified in JIS H 8681.
(2) Cass test: by the procedure using saline solution which is specified in JIS H 8681 with the testing time of 8 hours.

(3) Cape test: visual examination of the appearance and determination of the change in the thickness of the surface film after immersion of the aluminium article in an aqueous solution prepared by dissolving 10g/liter of sodium sulfite followed by a step adjustment of the pH first to 3.75 with glacial acetic acid and then to 2.5 with 5-normal sulphuric acid at 92°C for 30 minutes.

Testing procedures for testing the properties of the coating film.

(1) Adhesion of the coating film by the procedure specified in JIS A 4706.
(2) Impact test with Du Pont impact tester: the impact test was carried out by dropping a weight of 1000 g from a height of 50 cm to the surface to be tested, and the damage caused in the coating film was examined visually. The tip of the weight was spherical with a radius of 1/4 inch.

(3) Alkali corrosion test: by the procedure specified in JIS A 4706 after immersion for 72 hours in 1% NaOH solution.

(4) Sulphuric acid corrosion test: by the procedure specified in JIS A 4706 after immersion for 72 hours in 5% H₂SO₄ solution.

(5) Hydrochloric acid corrosion test: the same procedure as specified in JIS A 4706 but with 5% HCl solution as the test solution and after 72 hours of immersion.

(6) Cass test: by the procedure specified in JIS K 5400 with 72 hours spraying of saline solution.

(7) Corrosion test with sulfurous acid solution: 30 hours of immersion in a 1% aqueous solution of sulfurous acid at 25°C.

(8) Corrosion test with boiling water: 5 hours of immersion in water at 98°C or higher.

The results of the above testing were rated in 5 grades (I) to (V) with the following scale.

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- (I) Excellent
- (II) Good
- (III) Reasonable
- (IV) Poor
- (V) Bad

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Examples 1 to 6

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An extruded bar of A-6063S aluminium of H cross section after degassing, etching and removal of smuts was anodically oxidized in a 17.5% sulphuric acid solution at 20°C by passing DC electric current 16 volts DC for 30 minutes between the aluminium bar as anode and an aluminium rod as the cathode with a current density of 1.3 A/dm² to give an anodically oxidized surface layer of about 12μm thickness and washed with water. 18 aluminium bars thus anodically oxidized on the surface were subjected to sealing treatment by being immersed in various aqueous sealing liquids containing a silicic acid or a silicate, the nature, concentration, pH and temperature of the liquid and the treating time being indicated in Table 1, and dried at room temperature. Each bar was further coated with a coating composition in one of the three different ways as mentioned above.

The conditions of the sealing treatment and coating as well as the results of the testing undertaken on these coated aluminium bars are summarized in the Table 1.

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Table I

Example No.	1	2	3	4	5	6
Sealing treat-ment	Silicic acid or silicate (g/liter)	Sodium silicate (0.03)	Sodium silicate (0.05) + trietha-molam-monium silicate (0.05)	Sodium silicate (10)	Sodium silicate (0.1)	Trietha-molam-monium silicate (0.1)
	pH	10	10	10	10	10
	Temperature, °C	98	98	98	80	98
	Time, minutes	20	20	10	20	20
Coating procedure with voltage for A	A(180 V)	A(180 V) B C	A(180 V)	A(180 V)	A(150 V)	A(180 V)
Coating film	Appearance	A (I) B (I) C (II)	(I)	(I)	(I)	(I)
	Cracks	Each none	None	None	None	None
	Adhesion	Each 100/100	100/100	100/100	100/100	100/100
Sealing effect after removal of coating film	Alkali dropping (seconds)	Each 65	65	60	50	65
	Cass Test (RN)	Each 10	10	9.8-10	9.8	10
	Cape test	Each (III)	(III)	(III)	(III)	(III)

Table I cont.

Example No.	1	2	3	4	5	6
	Silicic acid (0.03)	Sodium silicate (0.03)	Sodium silicate (0.05) + triethanolmonium silicate (0.05)	Sodium silicate (10)	Sodium silicate (0.1)	Triethanolmonium silicate (0.1)
Corrosion test of coating film	1% NaOH	A (I) B (I) C (II)	(I)	(I)	(II)	(I)
	5% H ₂ SO ₄	Each (I)	(I)	(I)	(I)	(I)
	5% HCl	A (II) B (II) C (III)	(II)	(II)	(III)	(II)
	1% SO ₂	A (II) B (II) C (III)	(II)	(II)	(III)	(II)
	Cass test	A (I) B (II) C (III)	(I)	(I)	(I)	(I)
	Boiling water	A (I) B (II) C (III)	(I)	(I)	(I)	(I)

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Comparative Examples 1 to 5.

5 Excepting for the sealing treatment, the same procedure was repeated as in Examples 1 to 6. Instead of the aqueous sealing liquid containing a silicic acid or a silicate, the sealing treatment was performed with deionized water at 80°C (Comparative Example 1) water at near boiling, 98°C (Comparative Example 2) pressurized steam of 5kg/cm² pressure (Comparative Example 3) an aqueous salt solution containing 5 g/liter of nickel acetate, 1 g/liter of cobalt acetate, and acetate, and 4 g/liter of boric acid (Comparative Example 5). In Comparative Example 5 the aluminium bar anodically oxidized on the surface was subjected to electrolytic colouring before the sealing treatment while no colouring was undertaken in the other Comparative Examples.

10 The conditions of the treatment and the results of the testing undertaken for these aluminium bars are summarized in Table II below.

Table II

Comparative Example No.		1	2	3	4	5
Electrolytic colouring		No	No	No	No	Yes
Sealing or semi-sealing	Method	Hot	Boiling water	Pressurized steam	Chemicals	Hot water
	pH	7	7	-	5.5	7
	Temperature, °C	80	98	-	98	80
	Time, minutes	10	20	30	20	10
Coating procedure		A (130 V) B C	A (160 V)	A (180 V)	A (160 V)	A (130 V) B C
Coating film	Appearance	A (III) B (III) C (IV)	(III)	(III)	(III)	A (III) B (III) C (IV)
	Cracks	Each none	Yes	Yes	Yes	Each none
	Adhesion	A 98/100 B 98/100 C 80/100	80/100	80/100	70/100	A 98/100 B 98/100 C 98/100
	Alkali dropping, sec.	Each 30	60	160	65	Each 30
Sealing effect after removal of coating film	Cass test (RN)	Each 9.0	9.5	9.8-10	9.8	Each 9.5
	Cape test	Each (IV)	(III)	(II)	(III)	Each (IV)

Table II

Comparative Example No.	1	2	3	4	5
Electrolytic colouring	No	No	No	No	Yes
Method	Hot	Boiling water	Pressurized steam	Chemicals	Hot water
1% NaOH	A (III) B (IV) C (V)	-	-	-	A (II) B (III) C (V)
5% H ₂ SO ₄	A (I) B (I) C (II)	-	-	-	A (I) B (I) C (II)
5% HCl	A (IV) B (IV) C (V)	-	-	-	A (III) B (IV) C (V)
1% SO ₂	A (IV) B (IV-V) C (V)	-	-	-	A (III) B (IV) C (V)
Cass test	A (II) B (IV) C (V)	-	-	-	A (II) B (IV) C (V)
Boiling water	A (II) B (IV) C (V)	-	-	-	A (II) B (IV) C (V)

Corrosion
test of
coating
film

Examples 7 to 9.

After a primary sealing treatment with aqueous sealing liquid containing a silicic acid or a silicate as in Example 1, secondary sealing treatment was undertaken with pressurized steam (Example 7) boiling water (Example 8) or an aqueous solution of pH 5.5 containing 0.03 g/liter sodium dihydrogenphosphate (Example 9).

The conditions of the treatment and the results of the testing undertaken for the thus treated and coated aluminium bars are summarized in Table III below.

Table III

Example No.		7	8	9
Primary sealing treatment	Silicic acid or silicate (g/liter)	Sodium silicate (0.05)	Sodium silicate (0.05)	Silicic acid (0.05)
	pH	10	10	5.5
	Temperature, °C	98	98	98
	Time, minutes	10	10	10
Secondary sealing treatment	Pressurized steam	5 kg/cm ² G, 30 minutes	-	-
	Boiling water	-	98°C, 10 mins.	-
	Phosphate solution	-	-	95°C, 10 mins.
Coating procedure		A (200 V)	A (190 V)	A (180 V)
Coating film	Appearance	(II)	(II)	(I)
	Cracks	None	None	None
	Adhesion	100/100	100/100	100/100

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Table III cont.

	Example No.	7	8	9
Sealing effect after removal of coating film	Alkali dropping, sec.	170	70	80
	Cass test (RN)	10	10	10
	Cape test	(II)	(III)	(III)
Corrosion test of coating film	1% NaOH	(I)	(II)	(I)
	5% H ₂ SO ₄	(I)	(I)	(I)
	5% HCl	(I)	(II)	(II)
	1% SO ₂	(II)	(II)	(II)
	Cass test	(I)	(II)	(I)
	Boiling water	(I)	(I)	(I)

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Examples 10 to 15.

5 The same experimental procedure as in Example 1 was repeated except that certain additives were added to the aqueous sealing liquids as indicated in Table IV below (Examples 10 to 12 and 19) or, along with the addition of an additive to the sealing liquid, a secondary sealing treatment with pressurized steam of 5 kg/cm² G pressure for 30 minutes (Example 13) or with the same salt solution as in Comparative Example 4 (Example 15) was undertaken.

The conditions of the treatment and the results of testing undertaken for the thus treated and coated aluminium bars are summarized in Table IV.

10 Examples 16 to 20.

The same experimental procedure as in Example 1 was repeated except that each of the aqueous sealing liquids was subjected before use to a pretreatment by applying 5 volts AC between stainless steel electrodes immersed in it, the other conditions of the procedure being the same as in Example 1.

15 The conditions of treatment and the results of the testing undertaken for the treated and coated aluminium bars are summarized in Table V below.

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Table IV

Example No.	10	11	12	13	14	15
Primary sealing treat- ment	Silic acid silicate (g/liter)	Sodium silicate (0.05)	Silicic acid (0.05)	Sodium silicate (0.05)	Sodium silicate (0.03) + trietha- nolam- monium silicate (0.03)	Silicic acid (0.05)
	Additive (g/liter)	Di- ethylene glycol (0.01)	EDTA (0.1) + NaH ₂ PO ₄ (0.03)	Di- ethylene glycol (0.01)	NaH ₂ PO ₄ (0.03)	EDTA (0.03) + NaH ₂ PO ₄ (0.03)
	pH	10	5.5	9	10	5.5
	Temperature, °C	98	98	98	98	98
	Time, minutes	10	10	10	20	20
Secondary sealing treatment	Electrolysis (volts)	-	-	AC (15)	AC/DC (15)	AC (15)
		No	No	Yes	No	Yes
	Coating procedure	A(180 V)	A(180 V)	A(200 V)	A(190 V)	A(180 V)

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Table IV cont.

Example No.		10	11	12	13	14	15
Coating film	Appearance	(I)	(I)	(I)	(I)	(I)	(I)
	Cracks	None	None	None	None	None	None
	Adhesion	100/100	100/100	100/100	100/100	100/100	100/100
Sealing effect after removal of coating film	Alkali dropping (seconds)	65	65	70	180	70	85
	Cass test (RN)	10	9.8-10	10	10	10	10
	Cape test	(III)	(III)	(III)	(III)	(III)	(III)
Corrosion test of coating film	1% NaOH	(I)	(I)	(I)	(I)	(I)	(I)
	5% H ₂ SO ₄	(I)	(I)	(I)	(I)	(I)	(I)
	5% HCl	(II)	(II)	(II)	(II)	(II)	(II)
	1% SO ₂	(II)	(II)	(II)	(II)	(II)	(II)
	Cass test	(I)	(II)	(I)	(I)	(I)	(I)
	Boiling water	(I)	(I)	(I)	(I)	(I)	(I)

Table V

Example No.		16	17	18	19	20
Sealing treatment	Silicic acid or silicate (g/liter)	Silicic acid (0.03)	Sodium silicate (0.03)	Sodium silicate (0.05) + triethanolammonium silicate (0.05)	Sodium silicate (0.05)	Triethanolammonium silicate (0.1)
	pH	5.5	10	10	10	10
	Temperature, °C	98	98	98	98	98
	Time, minutes	20	20	20	20	20
Coating procedure		A (180 V)	A (180 V) B C	A (180 V)	A (180 V)	A (180 V)
Coating film	Appearance	(I)	Each (I)	(I)	(I)	(I)
	Cracks	None	Each none	None	None	None
	Adhesion	100/100	Each 100/100	100/100	100/100	100/100

Table V cont.

	Example No.	16	17	18	19	20
Sealing effect after removal of coating film	Alkali dropping (seconds)	65	Each 65	65	65	65
	Cass test (RN)	10	Each 10	10	10	10
	Cape test	(III)	Each (III)	(III)	(III)	(III)
	1% NaOH	(I)	Each (I)	(I)	(I)	(I)
Corrosion test of coating film	5% H ₂ SO ₄	(I)	Each (I)	(I)	(I)	(I)
	5% HCl	(II)	Each (II)	(II)	(II)	(II)
	1% SO ₂	(II)	Each (II)	(II)	(II)	(II)
	Cass test	(I)	A (I) B (II) C (II)	(I)	(I)	(I)
	Boiling water	(I)	A (I) B (II) C (III)	(I)	(I)	(I)

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Examples 21 to 26.

The experimental procedure in each example was much the same as in Example 16 except that a secondary sealing treatment was undertaken in each of the Examples with pressurized steam of 5 kg/cm²G pressure for 30 minutes (Examples 21 and 25), with boiling water at 98°C for 10 minutes (Example 22) or with an aqueous solution of 0.03 g/liter of sodium dihydrogenphosphate with a pH of 5.5 for 10 minutes (Examples 23, 24 and 26). The aqueous sealing liquids in the primary sealing treatment in Examples 24 to 26 were each admixed with 0.01 g/liter of diethylene glycol as an additive and the primary sealing in Example 25 was performed electrolytically by applying 15 volts of AC voltage between the aluminium bar under treatment and a stainless steel counterelectrode. The aluminium bar used in Example 26 has been electrolytically coloured on its surface.

The conditions of the treatment and the results of the testing undertaken for the thus treated and coated aluminium bars are summarized in the Table VI below.

Table VI

	Example No.	21	22	23	24	25	26
Primary sealing treatment	Silicic acid or silicate (g/liter)	Sodium silicate (0.05)	Sodium silicate (0.05)	Silicic acid (0.05)	Sodium silicate (0.05)	Sodium silicate (0.05)	Sodium silicate (0.05)
	Additive (g/liter)	None	None	None	Di- ethylene glycol (0.01)	Di- ethylene glycol (0.01)	Di- ethylene glycol (0.01)
	pH	10	10	5.5	10	10	10
	Temperature, °C	98	98	98	98	98	98
	Time, minutes	10	10	10	20	20	20
Secondary sealing	Electrolysis (volts)	No	No	No	No	AC (15)	No
	Pressurized steam	Yes	-	-	-	Yes	-
	Boiling water	-	Yes	-	-	-	-
	Phosphate solution	-	-	Yes	Yes	-	Yes
Coating procedure		A(200 V)	A(190 V)	A(180 V)	A(180 V)	A(200 V)	A(180 V)
Coating film	Appearance	(I)	(I)	(I)	(I)	(I)	(I)
	Cracks	None	None	None	None	None	None
	Adhesion	100/100	100/100	100/100	100/100	100/100	100/100

Table VI cont.

Example No.	21	22	23	24	25	26
Sealing effect after removal of coating film	170	70	80	75	180	85
Cass test (RN)	10	10	10	10	10	10
Cape test	(II)	(III)	(III)	(III)	(III)	(III)
Corrosion test of coating film	(I)	(I)	(I)	(I)	(I)	(I)
1% NaOH	(I)	(I)	(I)	(I)	(I)	(I)
5% H ₂ SO ₄	(I)	(I)	(I)	(I)	(I)	(I)
5% HCl	(I)	(II)	(II)	(II)	(I)	(II)
1% SO ₂	(II)	(II)	(II)	(II)	(II)	(II)
Cass test	(I)	(I)	(I)	(I)	(I)	(I)
Boiling water	(I)	(I)	(I)	(I)	(I)	(I)

Examples 27 to 34.

Extruded bars of aluminium were anodically oxidized on the surface as in Example 1 and, prior to the sealing treatment, subjected to colouring either (1) electrolytically by dipping the aluminium bar in an electrolyte solution prepared by dissolving 30 g/liter of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 25 g/liter of H_3BO_3 and 15 g/liter of $(\text{NH}_4)_2\text{SO}_4$ in water and adjusting to a pH of 5.6 at 25°C and electrolyzing for 5 minutes with the application of 15 volts DC or (2) chemically by dipping the aluminium bar in an aqueous solution containing 5 g/liter of sodium iron (III) oxalate and having a pH of 5.2 at 45°C for 3 minutes and 40 seconds. The sealing treatments and coating were carried out in much the same manner as in the preceding examples with the formulations of the sealing liquids and the conditions of treatment as set out in Table VII below.

The conditions of the treatment and the results of the testing undertaken for the thus treated and coated aluminium bars are summarized in the Table.

Table VII

Example No.	27	28	29	30	31	32	33	34
Colouring	Electrolytic	Yes	-	Yes	Yes	Yes	Yes	Yes
	Chemical	-	Yes	-	-	-	-	-
Primary sealing treatment	Silicic acid or silicate (g/liter)	Sodium silicate (0.03)	Sodium silicate (0.05)	Sodium acid (0.05)	Sodium silicate (0.05)	Sodium silicate (0.05)	Sodium silicate (0.05)	Sodium silicate (0.03) + triethanolammonium silicate (0.03)
	Additive (g/liter)	None	None	None	Di-ethylene glycol (0.01)	NaH ₂ PO ₄ (0.03)	Di-ethylene glycol (0.01)	NaH ₂ PO ₄ (0.03)
	pH	10	10	5.5	10	9	10	10
	Temperature, C°	98	98	98	98	98	98	98
	Electrolysis (volts)	-	-	-	-	-	AC (15)	AC/DC (15)
Secondary sealing	Pressurized steam	-	-	-	-	-	Yes	-
	Phosphate solution	-	-	Yes	-	-	-	-
	Coating procedure	A(180 V) B C	A(180 V)	A(200 V)	A(180 V)	A(200 V)	A(190 V)	
Coating film	Appearance	Each (1)	(1)	(1)	(1)	(1)	(1)	(1)
	Cracks	Each none	none	none	none	none	none	none
	Adhesion	Each 100/100	100/100	100/100	100/100	100/100	100/100	100/100

Table VII cont.

Example No.	27	28	29	30	31	32	33	34
Sealing effect after removal of coating film	Alkali dropping (seconds)	65	180	90	75	80	190	80
	Cass Test (RN)	Each 10	10	10	10	10	10	10
Corrosion test of coating film	Cass Test	Each (III)	(II)	(III)	(III)	(III)	(II)	(III)
	1% NaOH	A (I) B (I) C (II)	(I)	(I)	(I)	(I)	(I)	(I)
	5% H ₂ SO ₄	Each (I)	(I)	(I)	(I)	(I)	(I)	(I)
	5% HCl	Each (II)	(II)	(II)	(II)	(II)	(II)	(II)
	1% SO ₂	A (III) B (II) C (III)	(II)	(II)	(II)	(II)	(II)	(II)
	Cass test	A (I) B (II) C (III)	(I)	(I)	(I)	(I)	(I)	(I)
Boiling water		A (I) B (I) C (III)	(I)	(I)	(I)	(I)	(I)	(I)

As will be apparent from the foregoing Examples and Comparative Examples treatment of an anodically-oxidized aluminium article prior to coating when carried out in a hot aqueous liquid containing a silicic acid or a silicate which is soluble or dispersible in water can readily result in several advantages:

(1) no cracks are formed in the anodically-oxidized surface layer after the sealing treatment even when it is coated with a high temperature drying coating composition, e.g. aqueous solution, organic solution or aqueous dispersion, by means of electrodeposition, dipping or electrostatic coating followed by heating for drying at 140°C or higher;

(2) the high temperature-drying coating composition can be freely selected in accordance with the intended use of the coated articles;

(3) no difficulty is encountered in electrophoresis when coating by electrodeposition due to the extreme increase of the electric resistance of the anodically oxidized surface layer having micropores; and

(4) excellent coating films can be obtained irrespective of the coating means which give good adhesion and wear resistance of the coating film as well as strong corrosion resistance against alkali solution, acids and saline solution in a Cass test.

In particular, it has been also unexpectedly discovered that a pretreatment of the aqueous sealing liquid can give still better results of coating in which electric voltage is applied to the sealing liquid prior to its use. The method of the present invention is also applicable to the surfaces of aluminium articles coloured by any conventional means following the anodic oxidation.

WHAT WE CLAIM IS:-

1. A method of coating a film on the surface oxide layer of an anodically-oxidized aluminium article which comprises the steps of

(a) sealing micropores in the oxide layer by dipping the aluminium article in an aqueous sealing liquid at 80°C or higher and containing from 0.005 to 60 g/litre of a silicic acid or a silicate dissolved or dispersed therein;

(b) coating the thus treated aluminium article with a coating composition, and

(c) drying or curing the coating at a temperature of 140°C or higher.

2. A method as claimed in claim 1 wherein the silicate is represented by the general formula $xM_2O.ySiO_2$, where M is an alkali metal, x is an integer of 1 to 10 and y is an integer of 1 to 10.

3. A method as claimed in claim 1 wherein the silicic acid or silicate is orthosilicic acid, metasilicic acid, sodium silicate; potassium silicate; potassium aluminium silicate; sodium aluminium silicate; sodium methylsilicate; potassium methylsilicate; sodium butylsilicate; sodium propylsilicate; lithium propylsilicate; triethanolammonium silicate; tetramethanolamine silicate; hexafluorosilicic acid; zinc hexafluorosilicate; ammonium hexafluorosilicate; cobalt hexafluorosilicate; iron hexafluorosilicate; sodium hexafluorosilicate; nickel hexafluorosilicate; barium hexafluorosilicate; or hydroxyammonium hexafluorosilicate.

4. A method as claimed in any of claims 1 to 3 wherein the concentration of silicic acid or silicate is from 0.3 to 30 g/litre.

5. A method as claimed in any preceding claim wherein the article is dipped in the aqueous sealing liquid in step (a) for from 2 to 20 minutes.

6. A method as claimed in any one preceding claim wherein the aqueous sealing liquid additionally contains a polyol.

7. A method as claimed in any one preceding claim wherein step (a) is performed electrolytically by applying an electric voltage between the aluminium article and a counter-electrode dipped in the aqueous sealing liquid.

8. A method as claimed in claim 7 wherein the voltage is in the range 5 to 110 volts.

9. A method as claimed in any one preceding claim wherein before step (a) the aqueous sealing liquid is subjected to a pretreatment of applying an electric voltage between electrodes dipped therein.

10. A method as claimed in claim 9 wherein the voltage is in the range from 5 to 15 volts.

11. A method as claimed in claim 9 or 10 wherein the pretreatment voltage is applied for 2 to 20 minutes.

12. A method as claimed in any one preceding claim wherein a secondary sealing treatment is carried out between step (a) and step (b).

13. A method as claimed in claim 12 wherein the secondary sealing treatment is carried out with pressurized steam.

14. A method as claimed in claim 12 wherein the secondary sealing treatment is carried out with boiling water.

15. A method as claimed in claim 12 wherein the secondary sealing treatment is carried out with a salt solution.

16. A method as claimed in any one preceding claim wherein the aluminium article is one

As will be apparent from the foregoing Examples and Comparative Examples treatment of an anodically-oxidized aluminium article prior to coating when carried out in a hot aqueous liquid containing a silicic acid or a silicate which is soluble or dispersible in water can readily result in several advantages:

- 5 (1) no cracks are formed in the anodically-oxidized surface layer after the sealing treatment even when it is coated with a high temperature drying coating composition, e.g. aqueous solution, organic solution or aqueous dispersion, by means of electrodeposition, dipping or electrostatic coating followed by heating for drying at 140°C or higher;
- 10 (2) the high temperature-drying coating composition can be freely selected in accordance with the intended use of the coated articles;
- (3) no difficulty is encountered in electrophoresis when coating by electrodeposition due to the extreme increase of the electric resistance of the anodically oxidized surface layer having micropores; and
- 15 (4) excellent coating films can be obtained irrespective of the coating means which give good adhesion and wear resistance of the coating film as well as strong corrosion resistance against alkali solution, acids and saline solution in a Cass test.

In particular, it has been also unexpectedly discovered that a pretreatment of the aqueous sealing liquid can give still better results of coating in which electric voltage is applied to the sealing liquid prior to its use. The method of the present invention is also applicable to the surfaces of aluminium articles coloured by any conventional means following the anodic oxidation.

WHAT WE CLAIM IS:-

1. A method of coating a film on the surface oxide layer of an anodically-oxidized aluminium article which comprises the steps of
- 25 (a) sealing micropores in the oxide layer by dipping the aluminium article in an aqueous sealing liquid at 80°C or higher and containing from 0.005 to 60 g/litre of a silicic acid or a silicate dissolved or dispersed therein,
- (b) coating the thus treated aluminium article with a coating composition, and
- (c) drying or curing the coating at a temperature of 140°C or higher.
- 30 2. A method as claimed in claim 1 wherein the silicate is represented by the general formula $xM_2O.ySiO_2$, where M is an alkali metal, x is an integer of 1 to 10 and y is an integer of 1 to 10.
3. A method as claimed in claim 1 wherein the silicic acid or silicate is orthosilicic acid, metasilicic acid, sodium silicate; potassium silicate; potassium aluminium silicate; sodium aluminium silicate; sodium methylsilicate; potassium methylsilicate; sodium butylsilicate; sodium propylsilicate; lithium propylsilicate; triethanolammonium silicate; tetramethanolamine silicate; hexafluorosilicic acid; zinc hexafluorosilicate; ammonium hexafluorosilicate; cobalt hexafluorosilicate; iron hexafluorosilicate; sodium hexafluorosilicate; nickel hexafluorosilicate; barium hexafluorosilicate; or hydroxyammonium hexafluorosilicate.
- 40 4. A method as claimed in any of claims 1 to 3 wherein the concentration of silicic acid or silicate is from 0.3 to 30 g/litre.
5. A method as claimed in any preceding claim wherein the article is dipped in the aqueous sealing liquid in step (a) for from 2 to 20 minutes.
- 45 6. A method as claimed in any one preceding claim wherein the aqueous sealing liquid additionally contains a polyol.
7. A method as claimed in any one preceding claim wherein step (a) is performed electrolytically by applying an electric voltage between the aluminium article and a counterelectrode dipped in the aqueous sealing liquid.
- 50 8. A method as claimed in claim 7 wherein the voltage is in the range 5 to 110 volts.
9. A method as claimed in any one preceding claim wherein before step (a) the aqueous sealing liquid is subjected to a pretreatment of applying an electric voltage between electrodes dipped therein.
10. A method as claimed in claim 9 wherein the voltage is in the range from 5 to 15 volts.
- 55 11. A method as claimed in claim 9 or 10 wherein the pretreatment voltage is applied for 2 to 20 minutes.
12. A method as claimed in any one preceding claim wherein a secondary sealing treatment is carried out between step (a) and step (b).
13. A method as claimed in claim 12 wherein the secondary sealing treatment is carried out with pressurized steam.
- 60 14. A method as claimed in claim 12 wherein the secondary sealing treatment is carried out with boiling water.
15. A method as claimed in claim 12 wherein the secondary sealing treatment is carried out with a salt solution.
- 65 16. A method as claimed in any one preceding claim wherein the aluminium article is one



whose surface layer has been coloured before the dipping of step (a).

17. A method as claimed in any one preceding claim wherein the aluminium article is of aluminium.

5 18. A method as claimed in any one of claims 1 to 17 wherein the aluminium article is of an aluminium alloy.

19. A method of coating a film on the surface oxide layer of an anodically-oxidized aluminium article, the method being substantially as described in any one of the Examples herein.

10 20. An aluminium article when coated by a method as claimed in any one preceding claim.

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Chartered Patent Agents
57-60 Lincolns Inn Fields
London WC2A 3LS
Agents for the Applicant(s)

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