

PATENT SPECIFICATION

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(54) PROCESS FOR COATING ALUMINUM AND ALUMINUM ALLOYS

(71) We, YOSHIDA KOGYO KK, a Corporation duly organised under the laws of Japan and existing at No. 1, Kanda Izumicho, Chiyoda-ku, Tokyo, 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 generally to the coating of aluminum and aluminum alloys, and more specifically to a process including the production of sealed anodic oxide films on such metal for subsequent coating or painting.

For coating or painting articles of aluminum or aluminum alloy, there has been known and practiced a process wherein the articles are first anodized to form oxide films thereon and wherein coatings are applied to these oxide films after sealing the pores therein as by live steam, by boiling water, or by boiling water containing typical chemicals such as nickel acetate and cobalt acetate. The oxide films subjected to such conventional methods of sealing treatment, however, have the critical defect of cracking or crazing when coatings applied subsequently thereon are dried at desired temperatures of 140° C or more.

Heretofore this defect has usually been circumvented by applying to the sealed oxide films coating material which dries at less than 140° C, although the coatings produced by such material are of generally inferior quality. For the use of coating material which dries at higher temperatures, it has been necessary either: (1) to coat unsealed oxide films electrophoretically as with a resin paint, thereby sealing the pores in the oxide films by the resin; (2) to coat oxide films which have been semisealed, that is, sealed only to such an extent that the films will not develop cracks during the subsequent high temperature drying of the coatings formed thereon; or (3) to coat unsealed oxide films with a resin paint containing water so that the pores in the oxide films may be sealed by hydration as the coatings thereon are dried at high temperatures.

The present invention seeks to provide a novel, simplified process for production of sealed anodic oxide films on aluminium and aluminium alloys, such that they can be coated subsequently without the above-noted difficulties of the prior art.

The invention also seeks to provide a process such that the sealed anodic films can be coated with material which dries at relatively high temperatures, there being practically no possibility of the films developing cracks during the drying of the coatings thereon.

The invention further seeks to provide a process such that the sealed oxide films can be coated by any such desired method as electrophoretic, electrostatic or dip coating, with equally favourable results.

According to the invention, there is provided a process for coating aluminium and aluminium alloys comprising the steps of:—

(a) anodising a workpiece of aluminium or an aluminium alloy to form an oxide film thereon;

(b) sealing pores in the oxide film formed by immersing the workpiece in an aqueous solution of a phosphorus compound or compounds only at a temperature of at least 80° C for at least 10 minutes;

(c) applying a coating material to the sealed anodised surface of said workpiece to form a coating thereon.

With anodised aluminium or aluminium alloy subjected to the sealing treatment according to the invention, the oxide film develops no cracks when a coating produced subsequently thereon is dried at temperatures exceeding 140° C. Furthermore, the invention process gives rise to no such drawbacks as poor adhesion of coatings to the sealed oxide films and the increase in the electrical resistance of the sealed oxide films with consequent difficulty in, for example, electrophoretic coating.

The above and other objects, features and advantages of this invention will become more apparent and understandable from the following detailed description, Examples and claims.

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It is understood that aluminum and aluminum alloys to be processed in accordance with this invention comprise pure aluminum and the alloys of pure aluminum and at least one of such elements as silicon, magnesium, copper, nickel, zinc, chromium, lead, bismuth, iron, titanium, and manganese.

For anodizing aluminum or any of such aluminum alloys, the basis metal may first be degreased, rinsed and otherwise suitably pretreated in the conventional manner. The pretreated basis metal is then made anodic in the usual acid electrolytic solution containing sulfuric acid, oxalic acid, sulfamic acid or the like, and a suitable voltage is impressed between the anodic basis metal and a cathode such as lead or aluminum also immersed in the solution as the counter electrode.

In accordance with the process of this invention, the pores in the anodic oxide film which has been formed on the basis metal in the above described manner are sealed by immersing the basis metal in an aqueous solution containing a phosphorus compound, which solution is heated to temperatures at least 80° C. for at least 10 minutes.

As the phosphorus compound there may be used any of the following substances: phosphoric acid (including both ortho-, pyro-, and meta-phosphoric acid), potassium phosphate, sodium dihydrogen phosphate, sodium ammonium hydrogen phosphate, diammonium hydrogen phosphate, disodium hydrogen phosphate, tetracalcium phosphate, potassium dihydrogen phosphate, phosphotungstic acid, sodium phosphotungstate, phosphomolybdic acid, sodium phosphomolybdate, phosphorous acid, sodium phosphite, potassium phosphite, sodium hydrogen phosphite, ammonium hydrogen phosphite, triethyl phosphate, and aniline phosphate. An aqueous solution containing only several parts per million of any such phosphorus compound has been found to be effective to some extent. In practice, however, the concentration of any selected phosphorus compound in the aqueous solution is preferably in the range of from about 0.005 to 100 grams per liter and, for the best results, from about 0.01 to 30 grams per liter. It has been confirmed by experiment that anodic oxide films when sealed by the aqueous solution containing any selected phosphorus compound, particularly when used in the range of concentration specified above, have better corrosion resistance and less porosity than when sealed, for example, by boiling water containing commercially available chemicals such as nickel acetate and cobalt acetate or by boiling water.

For sealing treatment, anodized aluminum or aluminum alloy is immersed in the above described aqueous solution for at least 10 and preferably for 10 to 60 minutes. Thereafter the anodized basis metal may be rinsed and dried where necessary, and then a desired

coating is applied to the sealed oxide film thereon. Coating material for use should preferably be of the class that must be baked at temperatures at least about 140° C to develop desired final properties of strength and hardness. Any known or suitable coating method can be employed, such as electrophoretic coating, electrostatic coating, or dip coating. The coating produced on the sealed oxide film is then dried by baking at about 140° C or more.

The sealing of anodic oxide films by use of a heated aqueous solution of a phosphorus compound in accordance with this invention is effective not simply to improve their corrosion resistance. The inventive process totally eliminates the conventional deficiency of fluctuations in the quality and appearance of coatings produced electrophoretically on unsealed or semisealed anodic oxide films, such fluctuations having been caused heretofore by residual sulfuric acid or like impurity material within the pores of the oxide films.

Another advantage of the inventive process is that it permits the use of coating material which dries at relatively high temperatures. Japanese Patent Publication No. 47-51092 discloses a process comprising initial sealing treatment of anodic oxide films with a metallic salt and, after electrophoretically coating the films with a thermosetting resin, secondary sealing treatment wherein the pores in the films are further sealed as the coatings thereon are dried at high temperatures within a drying furnace. By contrast, in accordance with the inventive process, a single step of sealing treatment suffices to give desired effects, and further it permits the use of the electrophoretic, electrostatic, dipping or any other suitable method for coating the sealed oxide films.

If desired, oxide films which have been subjected to sealing treatment with a heated aqueous solution of a phosphorus compound according to the invention may be further treated with live steam or like conventional sealing means. In this manner the merits of the secondary sealing treatment will be added to the oxide films without impairment of the merits imparted thereto by the initial sealing treatment with the heated aqueous solution of a phosphorus compound.

The invention is hereinafter described more specifically in terms of several Inventive Examples, which, however, are meant purely to illustrate or explain and not to impose limitations upon the invention. Also given hereinbelow are some Comparative Examples which are intended to make clear the advantages of the inventive process.

Inventive Examples 1-10.

Specimens each consisting of an aluminum extrusion sized 150 millimeters by 70 by 1.3 were degreased, etched and desmutted in the

usual manner. Each specimen which had been pretreated as above was made anodic in an aqueous solution of 17.5 W/V% sulfuric acid, which had a temperature of 20° C, and a direct current voltage of 16 volts was impressed for 30 minutes between the anodic specimen and an aluminum cathode also immersed in the bath as the counter electrode. The current density was 1.3 amperes per square decimeter. An oxide film with a thickness of about 12 microns was thus formed on each specimen, which was then rinsed.

For sealing treatment, the anodized specimens were immersed in respective heated solutions which had been prepared by dissolving in pure water the phosphorus compounds listed in Table 1 below. The specimens were then rinsed and dried at room temperature. The specific conditions of the sealing treatment are given also in Table 1. The specimens of only Inventive Examples 8 and 9 were subjected to additional sealing treatment by live steam, under pressure of five kilograms per square centimeter, for 30 minutes.

Table 2 below gives the test results of the sealed oxide films on the various specimens. The tests were conducted as follows:

Alkaline dropping corrosion resistance test.

This test was effected in accordance with the Japanese Industrial Standard (JIS) H 8681 specification. Sodium hydroxide was dissolved in desalted water, with a concentration of exactly 10 W/V percent. This reagent was dropped on the cleaned surface of each specimen at constant intervals of five seconds, with each drop weighing about 16 milligrams, until the basis metal was exposed. Both specimen, reagent and ambience were held at a temperature of 35° C. Table 2 gives the length of time in seconds until the basis metal of each specimen was exposed.

CASS test.

This test was also effected in accordance with the JIS H 8681 specification. For preparation of a reagent, sodium chloride was dissolved in desalted water, with a concentration of four W/V percent, and cupric chloride was further dissolved in the solution, without a concentration of 0.26 gram per liter. Acetic acid was then added to the solution to reduce its pH to three. By use of compressed air under pressure of one kilogram per square centimeter, the thus prepared reagent was sprayed for eight hours onto each specimen at a rate of from one to two milliliters per 80 square centimeters per hour. Both specimen and reagent were held at a temperature of 50° C. Table 2 gives the consequent degrees of corrosion of the various specimens in "rating numbers" as provided for by JIS H 8681.

Kape's test.

To an aqueous solution containing 10 grams per liter of sodium sulfite was added glacial acetic acid to regulate the pH of the solution to 3.75, and to this solution was further added 5N sulfuric acid to reduce its pH to 2.5. The solution was then heated to a temperature of 92° C. The specimens were immersed for 30 minutes in this heated solution, and the consequent changes in their surface conditions were observed.

Coatings were then applied to the sealed oxide films on the specimens of each Example by the electrophoretic, dip and electrostatic coating methods, in accordance with the following procedures:

Electrophoretic coating.

Each specimen was made anodic in a 12 weight percent aqueous solution of electrophoretic coating material (thermosetting acrylic resin paint) having a temperature of 22° C, and a direct current voltage ranging from 140 to 180 volts was applied for two minutes between the anodic specimen and a stainless steel cathode immersed in the solution as the counter electrode. The thus coated specimen was rinsed and then dried at a temperature of 180° C for 40 minutes. A coating with a thickness of about seven microns was thus formed on each specimen.

Dip coating.

Each specimen was immersed in a 26 weight percent aqueous solution of dip coating material (thermosetting acrylic resin paint) having a temperature of 40° C. The specimen was withdrawn from the solution at a speed of about one meter per minute. After having been allowed to stand for 10 minutes at an ambient temperature of 35° C, the coated specimen was dried at a temperature of 180° C for 40 minutes. A coating with a thickness of about seven microns was thus formed on each specimen.

Electrostatic coating.

A thermosetting acrylic resin paint was thinned with a thinner at a ratio of one to one. The thinned paint was air sprayed at a pressure of four kilograms per square centimeter onto each specimen. A voltage of 60,000 to 90,000 volts was applied between the air spray nozzle and the specimen. The thus coated specimen was allowed to stand for 10 minutes and was then dried at a temperature of 180° C for 20 minutes. A coating with a thickness of about seven microns was thus formed on each specimen.

Table 2 also shows the presence or absence of cracks in the thus coated oxide films on the various specimens. Also given in Table 2

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are the test results as to the adhesiveness of the coatings to the basis metal. The adhesiveness of the coatings was determined in accordance with the Dupont impact test (1/4"R x 500g x 50cm) and the JIS H 4706 adhesion test. In the latter test, crisscross cuts were made on the coating of each specimen by means of a razor to form 100 squares each measuring one millimeter by one. An adhesive tape of the material sold under the Trade Mark "CELLOPHANE" with a width of 12 millimeters was stuck on the crisscrossed surface portion of the specimen and was immediately raised off the surface to see if the squares would peel off.

Comparative Example 1.

The procedure of Inventive Example 1 was repeated except that pure water at a temperature of 95° C was used instead of the aqueous solution of phosphoric acid for seal-

ing the pores in the anodic oxide films. The results are as given in Tables 1 and 2.

Comparative Example 2.

The procedure of Inventive Example 1 was repeated except that the sealing treatment was effected for 30 minutes by use of live steam under pressure of five kilograms per square centimeter, instead of the aqueous solution of phosphoric acid. The results are as given in Tables 1 and 2.

Comparative Example 3.

The procedure of Inventive Example 1 was repeated except that an aqueous solution containing 5.6 grams per liter of nickel acetate and 1.0 grams per liter of cobalt acetate and 814 grams per liter of boric acid was used instead of the aqueous solution of phosphoric acid. The results are as given in Tables 1 and 2.

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TABLE 1

Example	Sealing treatment			Temp. (°C)	Time (min.)	Sealing by live steam
	Agent	Concentration (g/l)	pH			
Inventive Example 1	Phosphoric acid	0.01	6	95	25	
" 2	"	0.1	6	95	25	
" 3	Diammonium hydrogen phosphate	1	6	95	25	
" 4	"	1	8	95	25	
" 5	"	10	6	95	25	
" 6	"	1	6	80	25	
" 7	"	1	6	95	25	
" 8	"	1	6	80	25	5 kg/cm ² × 30 min.
" 9	"	1	6	95	25	5 kg/cm ² × 30 min.
" 10	Phosphorous acid	1	6	95	25	
Comparative Example 1	Pure water		...	95	25	
" 2	Live steam		...			5 kg/cm ² × 30 min.
" 3	Chemicals*	*	6	95	25	

*As set forth in Comparative Example 3 above.

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TABLE 2

Example	Alkaline dropping test (sec.)	CASS test (RN)	Kape's test	Cracks			Adhesion
				Electro-phoretic coating	Dip coating	Electro-static coating	
Inventive Example 1	70	9.5	Affected	No	No	No	Excellent
" 2	75	9.8	Slightly affected	No	No	No	Excellent
" 3	70	9.8	Slightly affected	No	No	No	Excellent
" 4	70	9.8	Slightly affected	No	No	No	Excellent
" 5	65	9.8	Slightly affected	No	No	No	Excellent
" 6	50	9.6	Affected	No	No	No	Excellent
" 7	75	10	Slightly affected	No	No	No	Excellent
" 8	80	10	Slightly affected	No	No	No	Excellent
" 9	170	10	Slightly affected	No	No	No	Excellent
" 10	60	10	Slightly affected	No	No	No	Excellent
Comparative Example 1	70	9.5	Slightly affected	Yes	Yes	Yes	
" 2	180	10	Slightly affected	Yes	Yes	Yes	
" 3	70	9.8	Slightly affected	Yes	Yes	Yes	

WHAT WE CLAIM IS:—

1. A process for coating aluminium and aluminium alloys comprising the steps of:—

- 5 (a) anodising a workpiece of aluminium or an aluminium alloy to form an oxide film thereon;
 (b) sealing pores in the oxide film formed by immersing the workpiece in an aqueous solution of a phosphorus compound or compounds only at a temperature of at least 80° C for at least 10 minutes;
 10 (c) applying a coating material to the sealed anodised surface of said workpiece to form a coating thereon.

15 2. A process as claimed in Claim 1, wherein the phosphorus compound is selected from phosphoric acid, potassium phosphate, sodium dihydrogen phosphate, sodium ammonium hydrogen phosphate, diammonium hydrogen phosphate, disodium hydrogen phosphate, tetracalcium phosphate, potassium dihydrogen phosphate, phosphotungstic acid, sodium phosphotungstate, phosphomolybdic

acid, sodium phosphomolybdate, phosphorous acid, sodium phosphite, potassium phosphite, sodium hydrogen phosphite, ammonium hydrogen phosphite, triethyl phosphate, and aniline phosphate.

3. A process as claimed in Claim 1 or Claim 2, wherein the concentration of the phosphorus compound in the aqueous solution is in the range of from 0.005 to 100 grams per litre.

4. A process as claimed in any one of Claims 1 to 3, wherein the anodised metal workpiece is immersed in said aqueous solution for 10 to 60 minutes.

5. A process as claimed in Claim 1, for coating aluminium and aluminium alloys, substantially as hereinbefore described with reference to the examples.

6. Aluminium and aluminium alloys coated by a process as claimed in any one of Claims 1 to 5.

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(c) applying a coating material to the sealed anodised surface of said workpiece to form a coating thereon.

2. A process as claimed in Claim 1, wherein the phosphorus compound is selected from phosphoric acid, potassium phosphate, sodium dihydrogen phosphate, sodium ammonium hydrogen phosphate, diammonium hydrogen phosphate, disodium hydrogen phosphate, tetracalcium phosphate, potassium dihydrogen phosphate, phosphotungstic acid, sodium phosphotungstate, phosphomolybdic

acid, sodium phosphomolybdate, phosphorous acid, sodium phosphite, potassium phosphite, sodium hydrogen phosphite, ammonium hydrogen phosphite, triethyl phosphate, and aniline phosphate.

3. A process as claimed in Claim 1 or Claim 2, wherein the concentration of the phosphorus compound in the aqueous solution is in the range of from 0.005 to 100 grams per litre.

4. A process as claimed in any one of Claims 1 to 3, wherein the anodised metal workpiece is immersed in said aqueous solution for 10 to 60 minutes.

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