

[54] **METHOD FOR THE ANODIZATION AND
RESIN-COATING OF ALUMINOUS
ARTICLES**

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[57]

ABSTRACT

A method for treating the surface of an aluminous article is provided which comprises conducting the electrolysis with the aluminous article as the anode and in a single electrolytic bath containing

1. at least one strong acid known per se for the anodization of an aluminous material;
2. at least one polybasic organic acid; and
3. at least one cationic type resin prepolymer or precondensate in an aqueous system wherein said cationic type resin prepolymer or precondensate is anionized at least partly, so that the anodization and electrodeposition of the resin prepolymer or precondensate are effected on the surface of the aluminous article in said single bath.

11 Claims, No Drawings

METHOD FOR THE ANODIZATION AND RESIN-COATING OF ALUMINOUS ARTICLES

This invention relates to the surface treatment of an aluminous article. More particularly this invention relates to a method for effecting the anodization and electrodeposition resin coating on the surface of an aluminous article in a single electrolytic bath.

Throughout the specification and claims the term "aluminous" means aluminum and its alloy, particularly aluminum base alloy which is capable of being anodized. It is known to produce a porous film or layer on the surface of an aluminous article by conducting the electrolytic anodization with the use of an electrolyte containing sulfuric acid, chromic acid, oxalic acid or the like.

It is also known to apply a resin coating on the surface of an aluminous article by the so-called electrodeposition. In such electrodeposition it has been conventional to employ an anionic type resin which shows behavior as anions in an aqueous bath of paint and is deposited on the anode by passing a current through the bath, or a cationic type resin which shows behavior as cations in an aqueous bath and is deposited on the cathode upon passage of a current through the bath.

In applying a resin coating by electrodeposition on an anodized aluminous article it has been considered essential to first conduct the anodization in a first bath of an electrolyte, and then wash the anodized article and then conduct the electrodeposition in a second or separate bath of paint. Thus there were required two separate baths and two separate operative stages. Further, between these two separate operative stages it was considered indispensable to wash the article.

Therefore it is an object of this invention to effect the anodization and electrodeposition resin coating on the surface of an aluminous article in a single bath and in a single operative stage.

Other objects of this invention will become apparent from the following description.

Briefly this invention provides a method for treating the surface of an aluminous article which comprises conducting the electrolysis with the aluminous article as the anode and in a single electrolytic bath containing (1) at least one strong acid known per se for the anodization of an aluminous material, (2) at least one polybasic organic acid and (3) at least one cationic type resin prepolymer or precondensate in an aqueous system wherein the cationic type resin prepolymer or precondensate is anionized at least partly, so that the anodization and electrodeposition of the resin are effected on the surface of the aluminous article in said single bath.

This invention is based on our unexpected finding that when a certain acidic electrolyte is selected for the anodization a cationic resin prepolymer or precondensate can be at least partly anionized in such electrolyte so that, upon electrolysis with an aluminous article as the anode, both anodization and electrodeposition of the resin on the surface of the aluminous article can be effected in the single electrolytic bath in a single operative stage.

In carrying out the method of this invention there can be used any kind of cationic type resin prepolymers or precondensates insofar as these are film-forming. For example, resins having amino groups (including primary amino group, secondary amino group, tertiary amino group and quaternary ammonium group) in the

molecule may be used. More particular examples thereof are vinyl or acrylic copolymers having dependent amino groups; epoxy resins (containing two or more epoxy groups in the molecule) treated with dialkylamines or dialkanolamines to introduce amino groups in the resins; polyester resins obtained by the condensation of alkanolamines with other polyols, polybasic acids, etc.; polyurethane resins obtained by the condensation of alkanolamines with other polyols, polyisocyanates, etc.; amino-terminated polyamide resins obtained by the condensation of an excess amount of polyamines with polybasic acids. These amino group-containing resins, when dissolved or dispersed in an acidic aqueous solution, show behavior as cationic ions and therefore are referred to as cationic type resins. If desired, the amino groups in these resins may be alkylated or quaternized in a monomer well known in the art.

It is preferable that these resins are used in thermosetting form. For this purpose, if necessary, self cross-linkable functional groups may be introduced into the resin itself or it is possible to mix the resin with a cross-linking agent such as condensates of formaldehyde with phenol, melamine, urea or the like, epoxy compounds, blocked isocyanates, etc.

According to this invention these resins are used in the form of prepolymer or precondensate which is curable by itself or cross-linking agent upon the subsequent heat treatment. If desired, a mixture of two or more of these resin prepolymers or precondensates may be used.

The important feature of this invention is to solubilize or disperse such cationic type resin and to anionize the same at least partly in an electrolytic bath which is useful also for the anodic oxidation (anodization) of an aluminous article. Thus the electrolytic solution to be used in this invention has two different functions i.e. anionization of the cationic type resin and anodization of an aluminous article. For this purpose an aqueous solution of a mixture of two or more acids is used as the electrolytic solution.

More particularly the electrolytic solution to be used in this invention should contain at least one strong acid which is known per se for the anodization of an aluminous article. The acid is sometimes referred to as acid (1). Examples of such strong acids are sulfuric acid, sulfaminic acid, sulfophthalic acid, sulfosalicylic acid, etc. These acids are useful not only for the anodization (anodic oxidation) but also for facilitating the deposition over the entire surface of an article, i.e. increasing the ability of resin to deposit completely on the recessed areas or shielded portions or the inside of the box section of the aluminous article as the anode (therein after referred to as throwing powder). Generally, the concentration of such strong acid in the electrolytic bath is at least about 0.05 percent. It is preferable however that sulfaminic acid, sulfophthalic acid, sulfosalicylic acid, etc. is used in an amount somewhat larger than sulfuric acid.

Another essential acid in the acidic electrolytic bath to be used in this invention is a polybasic organic acid, which will sometimes be referred to as acid (2). Examples of such polybasic organic acids are oxalic acid, malonic acid, tartaric acid, citric acid, malic acid, maleic acid, phthalic acid, etc., among them most preferable is oxalic acid. A mixture of two or more of these acids may also be used. These organic acids are useful not

only for solubilizing and anionizing the cationic resin but also for facilitating the anodization. Generally, the concentration of such organic acid in the electrolytic solution is at least about 0.3 percent. It is preferably however that malonic acid is used in a higher concentration, i.e. about 5 percent or higher.

The upper limit of the concentration of the acid (1) and acid (2) is not critical so far as the anodization of an aluminous article is possible. However, since the electrolytic solution contains a resin and therefore may sometimes become high in the viscosity which is not suitable for the anodization. In such case the acid concentration may be somewhat lowered by diluting the electrolytic bath to such extent under which the anodization can be satisfactorily effected. Thus, the upper limit of the total acid concentration may vary depending upon the particular conditions (kinds of acids used, kind and amount of the resin used, etc.) but it can be easily determined by those skilled in the art.

The concentration of the resin in the electrolytic bath is generally 1 - 40 percent, preferably 3 - 15 percent by weight.

In carrying out the method of this invention the resin prepolymer or precondensate may be put into an aqueous electrolytic solution containing both acid (1) and organic acid (2) for ionization therein. However it is preferable that the resin is first mixed with a part of the organic acid (2) to solubilize and ionize the resin and then mixed with the acid (1) and remaining portion of the acid (2).

When the resin is mixed with the acidic electrolyte it is rendered soluble or dispersable in water due to the reaction of the resin with the acid groups. In this case, a small amount of a hydrophilic organic solvent may also be used in order to facilitate the solubilization of the resin. Examples of such solvents are alcohols such as isopropyl alcohol, ter-butyl alcohol, glycolethers such as ethyleneglycol monobutyl ether, diethyleneglycol monobutyl ether, esters such as methyl formate, ethyl lactate, and ketones such as methyl ethyl ketone, methyl n-propyl ketone.

In the above manner there is obtained a uniform solution or dispersion of the resin in the acidic electrolytic aqueous solution containing both the strong acid (1) and organic polybasic acid (2). It should be noted that in such aqueous system the cationic type resin prepolymer or precondensate is anionized at least partly and shows behavior as anions even though the resin itself is initially cationic. This invention is to utilize this surprising phenomenon in the simultaneous anodization and resin-deposition.

Thus according to the invention an electrolysis is conducted with an aluminous article as the anode in the above prepared resin-containing acidic electrolytic bath. An electric current may be passed through the electrolytic system in a manner well known in the art of the anodization of aluminous article. When the electrolysis is conducted the aluminous article forming the anode is electrolytically oxidized at the surface to form an oxide film or layer on the surface. This phenomenon is the same as in the conventional anodization of an aluminous article well known in the art. The important feature of this invention is that, at the same time, the resin prepolymer or precondensate now in the form of anions as explained above will be deposited on the surface of the anode, i.e. aluminous article to form a resinous film or layer thereon. A further important feature

is that the resinous film or layer once deposited on the surface of the aluminous article is not substantially dissolved in the acidic electrolytic solution and is satisfactorily adhered on the aluminous article. Thus, according to this invention both anodization and electrodeposition of resin can be effected in the same and single bath in a single operative stage. When a direct current is to be passed any suitable material (e.g. carbon, lead, stainless steel, etc.) may be used as the cathode. It is preferable to conduct the electrolysis while stirring the electrolytic bath. The anodization occurs first and then anionized resin is deposited on the anode. After a predetermined period of time the aluminous article is taken out of the electrolytic bath, washed with water and baked to cure the deposited resinous layer. It is sometimes preferable to conduct a certain after-treatment before baking. Such after-treatment will be explained hereinafter.

Sometimes the cationic type resin is not completely anionized and therefore shows behavior partly as cations. In such case the cationic resin will be deposited on the surface of the cathode during the electrolysis so that the efficiency of the cathode will be impaired. In order to avoid this difficulty, it is preferable to employ a semipermeable membrane. Thus, the electrolytic cell is divided into two by a semipermeable membrane (e.g. cellophane) through which the acidic electrolyte can pass but the resin in the form of cations can not pass. In the anode compartment there is placed an acidic electrolytic solution containing the resin while in the cathode compartment there is placed an acidic electrolytic solution not containing the resin. By this measure the cathode is protected against the deposition of the resin thereon. In this case, during the electrolysis, a small amount of the cationic resin will be deposited on the surface of the membrane but such resin in the form of cations is easily redissolved in the acidic electrolytic solution and therefore there will cause no trouble.

When an alternating electric current is to be used it is preferable to use the aluminous articles for both cathode and anode. In this case it is strongly recommended to employ an electrolytic solution wherein all the cationic type resin is anionized as completely as possible.

The conditions for the electrolysis may be varied depending upon the particular electrolytic solution. Generally, however, the electrolysis is conducted at a current density of $0.1 \text{ A/dm}^2 - 2 \text{ A/dm}^2$ for 3 - 20 minutes at a bath temperature of $5^\circ - 30^\circ \text{ C}$.

After the electrolysis the anodized and resin-coated aluminous article is taken out of the bath and washed with water and then heated or baked for curing the resinous layer. However, as explained hereinbefore, it is sometimes preferable to conduct an after-treatment before the heat treatment.

The after-treatment is conducted by washing the resin-coated article with an aqueous solution containing an organic solvent. This treatment is useful to improve the smoothness and abrasion resistance of the resin coating and also to prevent undesired yellow coloration of the resin coating during the subsequent baking or heat treatment. The organic solvent to be used here is for example a hydrophilic high boiling point organic solvent such as ethylene glycol ether or diethyleneglycol ether. If desired a small amount of a hydrophobic organic solvent may also be added. Further, a slight amount of a surface active agent such as silicone type

surfactant, anionic surfactant, cationic surfactant, non-ionic surfactant and amphoteric surfactant may be added. Generally, the concentration of the organic solvent in the aqueous treating solution is 1 – 99 percent, preferably 5 – 70 percent by weight, while that of the surfactant is 1 percent by weight or less.

Further when the nitrogen content in the resin is large there is a possibility that the resin coating is colored to yellow during the baking due to the oxidation of such nitrogen. In order to prevent this coloration it is preferable to add a small amount (e.g. 1 percent or less) of an antioxidant (such as phenol derivatives, phosphite compounds, etc.) to the aqueous solution for the after-treatment.

Mostly the resin prepolymer or precondensate deposited on the aluminous article is thermo-setting and therefore is cured upon baking or heat-treatment. Such baking may be conducted in a well known manner. Thus, for example, the resinous coating may be baked at a temperature of 120° – 200° C. for 10 – 60 minutes.

If it is desired to form a colored resinous coating it is possible to add a dye or pigment to the electrolytic solution.

According to the invention the fiber or layer of a resin prepolymer or precondensate deposited on an aluminous article by the electrodeposition upon electrolysis is not substantially redissolved into the acidic electrolytic solution. Therefore there is no troublesome problem in this connection, and the electrolytic condition should be taken care to satisfactorily effect the anodization. For example, the electrolytic condition should be so selected that the anodization occurs first and then the resin electrodeposition takes place. The proper condition (e.g. kind of resin, composition of the electrolyte, bath temperature, current density, etc.) can be easily determined by a simple preliminary test.

The invention will be further explained by referring to the following Examples which are given for the purpose of illustration only and not for limiting the scope of the invention. In these Examples all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Each of a pure aluminum panel 1S - 1/2 H and a corrosion-resistant aluminum alloy panel 52S was degreased with an organic solvent and immersed in 10 percent aqueous solution of sodium hydroxide at 60° C. for 3 minutes, then washed with hot water and then immersed in 10 percent aqueous solution of nitric acid for 5 minutes, and then well washed with water.

A commercial Epon resin was reacted with di-n-propylamine in 1:1 mixture of butylcellosolve and isopropyl alcohol to obtain 154 parts of a viscous substance containing 65 percent (as solid) of a resinous prepolymer. To this solution were added 200 parts of 25 percent aqueous solution of citric acid and 50 parts of butylcellosolve to form a uniform solution. To this solution were gradually added 400 parts of 5 percent aqueous solution of oxalic acid and 20 parts of 10 percent aqueous solution of sulfuric acid and then 176 parts of ion-exchanged water were added for dilution to prepare an electrolytic solution.

An electrolytic cell made of polyvinyl chloride was divided by a cellophane sheet into 9 volume compartment and 1 volume compartment. Into the larger compartment there was placed the above prepared electrolytic solution while the smaller compartment was filled

with an aqueous solution containing 5 percent citric acid, 2 percent oxalic acid and 0.2 percent sulfuric acid. The whole solution was stirred and maintained at a temperature of 20° C.

A cathode made of a stainless steel was put into the smaller compartment and the aluminum sheet (or aluminum alloy sheet) was put into the larger compartment as the anode. The surface area ratio between the cathode and anode was approximately 1:1. The distance between the electrodes was 10 cm. The constant electrolysis was conducted at a voltage of 10 V. for 10 minutes. The current density varied from 0.5 A/dm² to 0.1 A/dm². During this electrolysis there were gradually formed on the surface of the anode an anodized film and resin film. After the electrolysis the anode was taken out of the cell and baked at 160° C. for 20 minutes to form a continuous and adherent resin coating (thickness 7 μ) on the aluminum (or aluminum alloy) sheet. Before the baking the resin coating was partly removed and it was observed that the exposed surface layer is an anodized yellowish layer of a thickness of about 0.5 – 1 μ .

EXAMPLE 2

98.5 parts of an acrylic copolymer (solid content 65 percent) having dependent amino groups introduced by the usual copolymerization with dimethylaminoethyl acrylate in isopropyl alcohol were mixed with 24.5 parts of water soluble melamine resin (solid content 65 percent) prepared by the methyl-etherization of a melamine-formaldehyde precondensate. To this resinous mixture were added 200 parts of 25 percent aqueous solution of citric acid, 400 parts of 10 percent aqueous solution of oxalic acid and 20 parts of 10 percent aqueous solution of sulfuric acid. Then 257 parts of ion-exchanged water were added for dilution to prepare an electrolytic solution.

The electrolytic solution was filled in an electrolytic cell of polyvinyl chloride and the bath temperature was maintained at 10° C. by external cooling while stirring. In this cell were placed a cathode (lead panel) and an anode (aluminum alloy panel of Example 1) with a distance of 15 cm. therebetween, the surface area ratio being 1:1. Initially the constant voltage electrolysis was conducted at 15 V for 5 minutes and then the voltage was increased to 30 V and the constant voltage electrolysis was conducted for 5 minutes at this higher voltage. The current density varied from 1 A/dm² to 0.1 A/dm².

After the electrolysis the aluminum alloy panel (anode) was taken out of the cell, washed with water to remove the electrolytic solution and then immersed in water containing 15 percent butylcellosolve. Then the sheet was baked at 180° C. for 30 minutes to obtain a continuous and adherent resin coating (thickness about 10 μ) on the alloy panel. Before the baking the resin coating was partly removed and it was observed that the exposed surface layer is an anodized light yellowish layer of a thickness of about 1 μ .

EXAMPLE 3

108 parts of a resinous material (solid content 65 percent) prepared by copolymerizing glycidyl methacrylate, butyl acrylate and methyl methacrylate in a conventional manner in butyl cellosolve, followed by the reaction with diethanolamine were mixed with 200 parts of 25 percent aqueous solution of citric acid and

60 parts of butylcellosolve to form a uniform solution. To this solution were gradually added 400 parts of 5 percent aqueous solution of oxalic acid and 20 parts of 10 percent aqueous solution of sulfuric acid. Then the solution was diluted with 212 parts of ion-exchanged water to prepare an electrolytic solution.

An electrolytic cell of polyvinyl chloride was filled with the electrolytic solution and the bath was maintained at 25° C. while stirring. In this cell were placed a cathode (carbon rod) and anode (aluminum panel of Example 1) with a distance of 15 cm. therebetween, the surface area ratio being 1:1. Initially the constant voltage electrolysis was conducted at 25 V for 2 minutes, during which the current density varied from 1.2 A/dm² to 0.2 A/dm². Then, further constant current electrolysis was conducted at 0.07 A/dm² for 6 minutes.

After the electrolysis the anode (aluminum panel) was taken out of the cell and washed with water to remove the electrolytic solution and then immersed in an aqueous solution containing 40 percent butyl cellosolve, 0.04 percent silicone surfactant, 0.3 percent anti-oxidant (phenol derivative) for 2 minutes. Then the panel was heated at 80° C. for 5 minutes and baked for 160° C. for 30 minutes to obtain a smooth, wear-resistant resin coating (thickness about 25 μ) on the aluminum panel. When the resin coating was removed it was observed that there had been formed a light yellow-purple colored anodized film of a thickness of 0.5 - 1 μ . The aluminum panel with this anodized film (the resin layer having been removed) was subjected to anti-corrosion test (CASS test - Copper-Accelerated Acetic Acid Salt Spray Testing ASTM B 368-62T, 3 hours) and it was observed that the corrosion is only about 1 mm. in diameter whereas the same aluminum sheet without the anodization of this invention shows a corrosion of about 5 mm. diameter.

EXAMPLE 4

123 parts of the resinous material used in Example 1 were dissolved in a mixture of 50 parts of butylcellosolve and 400 parts of 5 percent aqueous solution of oxalic acid. To this solution was further added 100 parts of 6 percent aqueous solution of sulfaminic acid and 327 parts of ion-exchanged water to prepare a resin-containing electrolytic solution.

An electrolytic cell was divided into two in the same manner as in Example 1 and the larger compartment was filled with the resin-containing solution while the smaller compartment was filled with an aqueous solution containing 2 percent oxalic acid and 0.6 percent sulfaminic acid. An aluminum anode same as in Example 1 and a stainless steel cathode were placed in the larger and smaller compartments respectively. The electrolysis was conducted at 25 V for 3 minutes during which the current density varied from 2 A/dm² to 0.1 A/dm². Then the constant current electrolysis at 0.1 A/dm² was continued for 10 minutes. The anode was taken out of the cell, washed with water and baked at 160° C. for 20 minutes to obtain a continuous, tough and adherent resin coating (thickness 10 μ) on the surface of the aluminum panel. The anodized film beneath the resin coating had a thickness of about 1 μ .

EXAMPLE 5

154 parts of a resinous material (solid content 65 percent) prepared in a manner similar to Example 1 by

reacting commercial Epon resin with diethanol amine were uniformly dissolved in 200 parts of 10 percent aqueous solution of malic acid. To this solution were added 400 parts of 5 percent aqueous solution of oxalic acid and 100 parts of 6 percent aqueous solution of sulfosalicylic acid. The resulting solution was diluted with 146 parts of ion-exchanged water to prepare a resin-containing electrolytic solution.

The apparatus same as in Example 2 was used and the electrolysis was conducted at 15 V for 10 minutes during which the current density varied from 0.6 A/dm² to 0.15 A/dm². The bath temperature was maintained at 10° C. After the electrolysis the aluminum alloy was taken out of the cell and baked at 160° C. for 20 minutes to obtain a continuous and firmly adherent resin coating of a thickness of 20 μ . The anodized surface layer beneath the resin layer was 0.5 - 1 μ in thickness.

EXAMPLE 6

167 parts of commercial acrylic cathionic resin (made by Mitsubishi-Gasukagaku Co.) of a solid content of 60 percent were mixed with 600 parts of 10 percent aqueous solution of malonic acid. To this solution were further added 10 parts of 10 percent aqueous solution of sulfuric acid and 223 parts of ion-exchanged water to prepare a resin-containing electrolytic solution.

An electrolytic cell was divided into two in the same manner as in Example 1 and the larger compartment was filled with the above prepared resin containing solution while the smaller compartment was filled with an aqueous solution containing 6 percent malonic acid and 0.1 percent sulfuric acid. The constant current electrolysis was conducted at a current density of 0.5 A/dm² for 10 minutes. The bath temperature was maintained at 20° C. The anode was the aluminum alloy panel of Example 1 in the larger compartment and the cathode was a stainless steel panel in the smaller compartment. After the electrolysis the aluminum alloy panel was taken out of the bath, washed with water and baked at 180° C. for 30 minutes to obtain a continuous resin coating layer (thickness 5 μ) on the surface of the alloy panel. The deep yellow anodized layer beneath the resin layer was about 1 μ in thickness.

EXAMPLE 7

Example 3 was repeated except that the aluminum panel of Example 1 was used for both cathode and anode and that the electrolysis was conducted with an alternating electric current at 30 V for 10 minutes. There was obtained anodized and resin-coated panel similar to the product of Example 3.

What we claim is:

1. A method for treating the surface of an aluminous article in a single electrolytic bath which comprises conducting the electrolysis with the aluminous article as the anode in said single electrolytic bath containing

1. at least one strong acid known per se for the anodization of an aluminous material;
2. at least one polybasic organic acid; and
3. at least one cationic type resin prepolymer or precondensate in an aqueous system wherein said cationic type resin prepolymer or precondensate is anionized at least partly, whereby the anodization and electrodeposition of the resin prepolymer or precondensate are effected on the surface of the aluminous article in said single electrolytic bath.

2. A method of claim 1 wherein said strong acid (1) is sulfuric acid, sulfaminic acid, sulfophthalic acid or sulfosalicylic acid.

3. A method of claim 2 wherein the concentration of said strong acid (1) in the electrolytic bath is at least 0.05 percent.

4. A method of claim 2 wherein the resin coating after the electrodeposition is heat-treated to cure the resin.

5. A method of claim 1 wherein said polybasic organic acid (2) is oxalic acid, tartaric acid, malonic acid, citric acid, maleic acid, phthalic acid or malic acid.

6. A method of claim 5 wherein the concentration of said polybasic organic acid (2) in the electrolytic bath is at least 0.3 percent.

7. A method of claim 1 wherein the aluminous article with the resin coating thereon is washed before the heat-treatment with an aqueous solution containing organic solvents.

8. A method of claim 7 wherein the aqueous solution further contains a small amount of at least one surfactant.

9. A method of claim 7 wherein the aqueous solution further contains an anti-oxidant.

10. A method of claim 1 wherein the concentration of said cationic type resin prepolymer or precondensate in the electrolytic bath is 1 - 40 percent by weight.

11. A method of claim 1 wherein said cationic type resin prepolymer or precondensate is thermo-setting.

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