PROCESS FOR TREATING ALUMINUM SURFACES

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ABSTRACT

In the process for treating the surface of aluminum or an aluminum alloy which comprises subjecting said surface to anodic oxidation and subsequently sealing with hot water or steam, the improvement which consists essentially of sealing said surface by applying an aqueous solution containing calcium ions and from 0.001 to 0.05 gm per liter of at least one acid selected from the group consisting of (A) a water-soluble phosphonic acid which forms a complex with a divalent metal, (B) a water soluble salt of said acid of (A), and (C) the mixtures thereof at a temperature ranging from 90°C to the solution boiling point temperature and at a pH of from 5 to 6.5, to the anodic oxidized surface, the molar ratio of calcium ions to phosphonic acid being at least 2:1.

5 Claims, No Drawings
PROCESS FOR TREATING ALUMINUM SURFACES

PRIOR ART

To protect aluminum or aluminum alloys against corrosion, anodically produced oxide layers are frequently applied to aluminum surfaces. These oxide layers protect the aluminum surfaces from the effects of the weather and other corroding media. Further, the anodic oxide layers are also applied in order to obtain a harder surface and therewith to give the aluminum an increased resistance to wear. In particular, decorative effects can be attained by the self coloring of the oxide layers or can be attained in part by their easy colorability.

A number of processes are known for the application of anodic oxide layers to aluminum. For example, the production of the oxide layers takes place using direct current in solutions of sulfuric acid (the direct current-sulfuric acid process). However, solutions of organic acids, such as in particular sulfophthalic acid or sulfanilic acid or mixtures of these organic acids with sulfuric acid, are also frequently used. The last named processes are particularly known as the autocolor processes.

These anodically applied oxide layers, however, do not fulfill all requirements with respect to protection against corrosion, since they have a porous structure. For this reason it is subsequently necessary to seal the oxide layers by after-sealing which is often effected with hot or boiling water or steam and is known as "sealing." This closes the pores and therefore considerably increases the corrosion protection.

During the subsequent consolidation of anodically applied oxide layers, however, not only are the pores closed, but a substantially thick and velvety film may also be formed over the whole surface. This velvety film is the so-called sealing coating and consists of amorphous aluminum hydroxide which is not resistant to handling, so that the decorative effect of the layer is thereby impaired. Furthermore, it reduces the adhesive strength during the bonding of such aluminum parts and, due to the increased effective surface, this sealing film promotes later soiling and corrosion. For these reasons it has previously been necessary to remove the coating by hand, mechanically or chemically.

It is already known to detach the film from sealed surfaces covered with a sealing film by a further mineral acid treatment. With this process, therefore, a further treatment step is needed, and moreover it necessitates a very careful treatment with the mineral acid in order to avoid damage to the oxide layer. Further, it is also known to prevent formation of sealing films by carrying out a sealing with solutions which contain nickel acetate and lignite sulfate. This method has the disadvantage that the oxide layers may become yellowed under the influence of light. Finally it is known from U.S. Pat. Nos. 3,672,966 and 3,657,077 to prevent the formation of sealing films without impairing the anodic oxide coating or the quality of the after-sealing by applying a solution of polycrylates or specified dextrins to the surface. These processes have proved satisfactory. In some cases, however, especially if not carefully carried out, it is possible that residues may remain upon drying. These are undesirable, but they can be removed by a further rinsing.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide a development in the process for treating the surface of aluminum or an aluminum alloy which comprises subjecting said surface to an anodic oxidation and subsequently sealing with hot water or steam, the improvement which consists essentially of sealing said surface by applying an aqueous solution containing calcium ions and from 0.001 to 0.05 gm per liter of at least one acid selected from the group consisting of (A) a water-soluble phosphonic acid which forms a complex with a divalent metal, (B) a water soluble salt of said acid of (A), and (C) the mixtures thereof at a temperature ranging from 90°C to the solution boiling point temperature and at a pH of from 5 to 6.5, to the anodic oxidized surface, the molar ratio of calcium ions to phosphonic acid being at least 2:1.

Other and further objects of the invention will become apparent as the description thereof proceeds.

DESCRIPTION OF THE INVENTION

The invention relates to a process for the treatment of surfaces of aluminum or aluminum alloys by anodic oxidation with a subsequent sealing step in aqueous solutions at elevated temperatures. In this manner, the formation of troublesome aluminum hydroxide coatings (sealing films) on the surfaces are prevented and difficulties caused by the salts producing hardness in the water are avoided by the addition of certain phosphonic acids.

The present invention is further directed to a development in the process for treating the surface of aluminum or an aluminum alloy which comprises subjecting said surface to an anodic oxidation and subsequently sealing with hot water or steam, the improvement which consists essentially of sealing said surface by applying an aqueous solution containing calcium ions and from 0.001 to 0.05 gm per liter of at least one acid selected from the group consisting of (A) a water-soluble phosphonic acid which forms a complex with a divalent metal, (B) a water soluble salt of said acid of (A), and (C) the mixtures thereof at a temperature ranging from 90°C to the solution boiling point temperature and at a pH of from 5 to 6.5, to the anodic oxidized surface, the molar ratio of calcium ions to phosphonic acid being at least 2:1.

A relatively large number of phosphonic acids is known which form complexes with divalent metals; and suitable examples of compounds to be utilized according to the present invention include those having the following formulae:

\[
R - H_{2}O_{2}P - C - PO_{2}H_{2} \quad (I)
\]

in which R represents phenyl or alkyl of 1 to 5 carbon atoms;

\[
\text{R}_{1}, \text{R}_{2}, \text{R}_{3}, \text{PO}_{2}H_{2} \quad (II)
\]
in which R₁ and R₂ each represent hydrogen or alkyl of 1 to 4 carbon atoms, R₃ represents hydrogen, alkyl of 1 to 4 carbon atoms, or phenyl;

$$R_1\text{-CXY} \quad N\text{-CXY} \quad PO_2H\text{H}$$

$$H_2PO_2\text{-CXY}$$

(III)

in which X and Y each represent hydrogen or an alkyl or 1 to 4 carbon atoms, R₄ represents —PO₃H₂ or a group of the formula:

(A) $$-CH_2-N\text{-CXY} \quad PO_2H\text{H}$$

(B) $$-CH_2-N\text{-CXY} \quad PO_2H\text{H}$$

(CXY-PO₂H₂)

in which X and Y each have the above-defined meaning; and

$$H_2PO_2\text{-CXY} \quad CH_2\text{-COOH}$$

(IV)

in which R₅ represents hydrogen, methyl or —CH₂—COOH.

Examples of 1-hydroxylalkane-1,1-diphosphonic acids of formula I which may be used are 1-hydroxypropane-1,1-diphosphonic acid, 1-hydroxypentane-1,1-diphosphonic acid, 1-hydroxyhexane-1,1-diphosphonic acid, as well as 1-hydroxy-1-phenylmethane-1,1-diphosphonic acid and preferably 1-hydroxyethane-1,1-diphosphonic acid.

Suitable examples of 1-aminoalkane-1,1-diphosphonic acids of formula II are 1-aminoethane-1,1-diphosphonic acid, 1-amino-1-phenylethyl-1,1-diphosphonic acid, 1-dimethylaminooctane-1,1-diphosphonic acid, 1-dimethylaminobutane-1,1-diphosphonic acid, 1-diethylaminomethane-1,1-diphosphonic acid, 1-propyl-aminomethane-1,1-diphosphonic acid, and 1-butyl-aminomethane-1,1-diphosphonic acid.

Suitable examples of aminopolymethylene phosphonic acids of the formula III include alaminotramethylene phosphonic acid, ethylenediaminotetramethylene phosphonic acid, diethylenetriaminopentamethylene phosphonic acid, aminotri(2-propylene-2-phosphonic acid).

Suitable examples of phosphono succinic acids of formula IV include phosphonosuccinic acid, 1-phosphono-1-methylsuccinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid.

Instead of the phosphonic acids mentioned above, their water-soluble salts may also be used, such as alkali metal salts especially the sodium salt or potassium salt, as well as the ammonium salts, or the lower alkanolamine salts for example triethanolamine salt. The phosphonic acids or their water-soluble salts are preferably employed in a concentration of 0.001 to 0.05 gm/liter of solution. They may be used singly or in mixtures thereof.

A mixture of 1-hydroxyethane-1,1-diphosphonic acid and aminotrimethylenephosphonic acid in the proportion by weight of 4:1 to 1:4 has been found to be preferred.

The solutions containing phosphonic acids or their salts are adjusted, where necessary, to a pH in the range of from 5 to 6.5. This adjustment may be effected with ammonia or acetic acid.

Ordinary water which is neither completely deionized or softened may be used for the solutions. If completely deionized water, distilled water, or very soft water is used for making the solutions, it is necessary to add calcium ions, and preferably, water-soluble calcium salts such as CuCl₂ or Ca(NO₃)₂ are used. The molar ratio of calcium ions to phosphonic acids should be at least 2:1. Generally it is advantageous to use a higher molar ratio of calcium ions to phosphonic acids of 5:1 to about 500:1.

A preferred form of the process comprises adding from 0.1 to 5 gm/liter, preferably from 0.1 to 2 gm/liter, of a dextrin additionally to the sealing solutions. For this purpose, those dextins are specially used which have a viscosity of 50 to 400 cP in 50% solution at 20°C, the viscosity being measured with a Brookfield rotary viscometer.

The advantages of the present invention include preventing the formation of a sealing coating without causing damage to the anodic oxide layer. Difficulties do not occur because of the water hardness components in the aqueous sealing solutions, so that deionized or softened water need not be used. Precipitates of water hardness causing components are usually avoided.

However in the case of water with a high degree of hardness, only flocculent heavy precipitates are formed; but these precipitates are not deposited on the sealed portions, instead however, they fall to the bottom of the bath and may be easily rinsed thereon. The appearance of the surface is not affected by the process of the invention; the effect obtained by the pre-treatment and anodization remain unchanged. Only very small amounts of additives are necessary for the process according to the invention.

The following examples are merely illustrative of the present invention without being deemed limiting in any manner thereof.

In the examples, the notation of the aluminum alloys is based upon nomenclature according to DIN 1,725. The quality of the oxide layers was determined by the so-called Testal value according to DIN 50,949 and by the loss factor d (Anostest apparatus) according to DIN 50,920 (design). Further, the products of the after-sealing were tested by means of the Green test according to DIN 50,146. DIN is the abbreviation for “Deutsche Industrie-Norm” representing a series of standard German published test procedures.

**EXAMPLE 1**

Aluminum sections (AlMg₃) degreased with an aqueous alkali metal hydroxide solution and pickled in the usual manner, were anodically oxidized in direct current-sulfuric acid process (layer thickness 22 μ) and were sealed at 100°C for 70 minutes with a solution of 0.003 gm/liter of 1-hydroxyethane-1,1-diphosphonic acid and 0.5 gm/liter of dextrin (viscosity 100 cP, measured in 50% solution at 20°C) in water of 15°C (Ger-
man hardness) which had been adjusted to pH 5.8 with ammonia prior to the sealing. The sections showed no sealing film. The layer thickness was unchanged after the sealing; and the Testal value of 8.5 and the loss factor $d$ of 0.41 both indicated a satisfactory sealing. After a relatively prolonged use of the sealing solution, no solid precipitates of the water hardness causing components appeared in the sealing solution. A flocculent heavy coating was formed on the bottom of the bath container, which was not deposited on the sections and could easily be removed from the bath by flushing it out.

The same result was obtained when, instead of 1-hydroxyethane-1,1-diphosphonic acid, an equivalent amount of its di-, tri- and tetrabasic potassium or ammonium salt or a triethanolamine salt was used. In the case of the alkaline salts the pH adjustment was carried out with acetic acid.

**EXAMPLE 2**

Aluminum sheets (AlSi$_3$), degreased in the usual manner, which had been anodically oxidized in the direct current-sulfuric acid-oxalic acid process (layer thickness 21 $\mu$), were sealed at 100°C for 60 minutes with a solution of 0.007 gm/liter of 1-hydroxyethane-1,1-diphosphonic acid in deionized water with the addition of 10 mgm/liter of calcium ions, which was adjusted with ammonia to pH 5.6 prior to the sealing. The sheets showed no sealing film. The Testal value of 12 and the loss factor $d$ of 0.49 both indicated a satisfactory sealing. The same results were obtained with di-, tri- and tetra-alkali metal salts or ammonium salts.

**EXAMPLE 3**

Aluminum sections (AlMgSi 0.5) degreased and pickled in the usual manner, which had been anodically oxidized by an autocolor process (layer thickness 18 $\mu$), were sealed at 100°C for 60 minutes in a solution of 0.005 gm/liter of 1-hydroxyethane-1,1-diphosphonic acid, 0.005 gm/liter of aminotrimethylenephosphonic acid and 1 gm/liter of dextrin (viscosity 200 cP, measured in 50% solution at 20°C) in water of 35 dH (German hardness), adjusted with ammonia to pH 5.9 prior to sealing. The sections showed no sealing film. A satisfactory sealing was indicated by the Testal value of 10.5 and by the loss factor $d$ of 0.47. The degree of water hardness was not noticeably objectionable, since the water hardness causing components were precipitated in a flocculent, easily removable, settling form.

The same results were obtained when, instead of the above-mentioned phosphonic acids, their alkaline metal salts or ammonium salts were used, while the alkaline salts were adjusted with acetic acid to a pH value between 5.8 and 6.0.

**EXAMPLE 4**

Aluminum sections (AlMgSi 0.5) which had been degreased with an aqueous alkali metal solution and pickled in the usual manner, were anodically oxidized in the direct current sulfuric acid process (layer thickness 20 $\mu$ to 22 $\mu$). The sections were then sealed at 98°C to 100°C for 60 minutes in a solution which contained 0.01 gm/liter of 1-hydroxyethane-1,1-diphosphonic acid and 2 gm/liter of dextrin (viscosity 150 cP, measured in 50% solution at 20°C), in water of 20° dH (German hardness) which was adjusted with ammonia to a pH of 5.8 prior to the sealing. The sections showed no sealing film; and the Testal value of 9.0 and the loss factor $d$ of 0.40 indicated a very satisfactory sealing. No difficulty resulted from the water hardness causing components of the sealing solution.

**EXAMPLE 5**

In a manner analogous to that described in Example 4, aluminum sections were sealed with solutions which contained,

- a. of the 1-hydroxyethane-1,1-diphosphonic acid, the equivalent amount of one of the following phosphonic acids:
  - 2. 1-hydroxypropane-1,1-diphosphonic acid,
  - b. 1-hydroxyhexane-1,1-diphosphonic acid,
  - c. 1-aminoethane-1,1-diphosphonic acid,
  - d. 1,1-diphosphonic acid,
  - e. ethylenediaminetetramethylephosphonic acid,
  - f. 2-phosphonobutane-1,2,4-tricarboxylic acid, or
  - g. 1-phosphono-1-methylsuccinic acid.

In all cases no sealing film was formed. No difficulty resulted from the hardness of the water. The Testal value ranged from 10 to 12 and the loss factor $d$ ranged from 0.43 to 0.52 both of which indicated a satisfactory consolidation.

The same results were obtained when, instead of the above-mentioned phosphonic acids, their alkaline metal salts or ammonium salts were used in equivalent amounts.

Although the present invention has been disclosed in connection with a few preferred embodiments thereof, variations and modifications may be resorted to by those skilled in the art without departing from the principles of the new invention. All of these variations and modifications are considered to be within the true spirit and scope of the present invention as disclosed in the foregoing description and defined by the appended claims.

We claim:

1. In the process for treating the surface of aluminum or an aluminum alloy which comprises subjecting said surface to an anodic oxidation and subsequently sealing with hot water or steam, the improvement which consists essentially of sealing said surface by applying an aqueous solution consisting essentially of water, calcium ions and from 0.001 to 0.05 gm per liter of at least one acid selected from the group consisting of (A) a water-soluble phosphonic acid which forms a complex with a divalent metal, said acid having the formula

\[
\text{H}_2\text{PO}_3\text{C}\text{PO}_3\text{H}_2
\]

in which R is selected from the group consisting of phenyl and alkyl of 1 to 5 carbon atoms, (B) a water-soluble salt of said acid of (A), and (C) the mixtures thereof at a temperature ranging from 90°C to the solution boiling point temperature and at a pH of from 5 to 6.5, to the anodic oxidized surface, the molar ratio of calcium ions to phosphonic acid being at least 2:1.

2. The process as claimed in claim 1 in which the ratio of calcium ions to phosphonic acid is from 5:1 to 500:1.

3. The process as claimed in claim 1 in which said salt of (B) is selected from the group consisting of alkali...
metal salts, ammonium salts, and lower alkanolamine salts.
4. The process as claimed in claim 1 in which said solution additionally contains from 0.1 to 5 gm per liter of dextrin.
5. The process as claimed in claim 4 in which said solution contains from 0.01 to 2 gm per liter of dextrin.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,900,370 Dated August 19, 1975

Inventor(s) Hans Gunther Germscheid et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet, second column, at the end of the Abstract, "5 Claims, No Drawings" should read -- 6 Claims, No Drawings --.

Column 6, line 10, "a." should read -- instead --.

Column 6, line 13, "2." should read -- a. --.

Column 6, line 16, "1,1-diphosphonic acid" should read -- dimethylaminomethane-1-diphosphonic acid --.

line 19, A hyphen (-) should be between "phosphono" and "1", ie, -- phosphono-1 --.

Signed and Sealed this Third Day of August 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks