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DUAL-SEAL ANODIZED ALUMINUM
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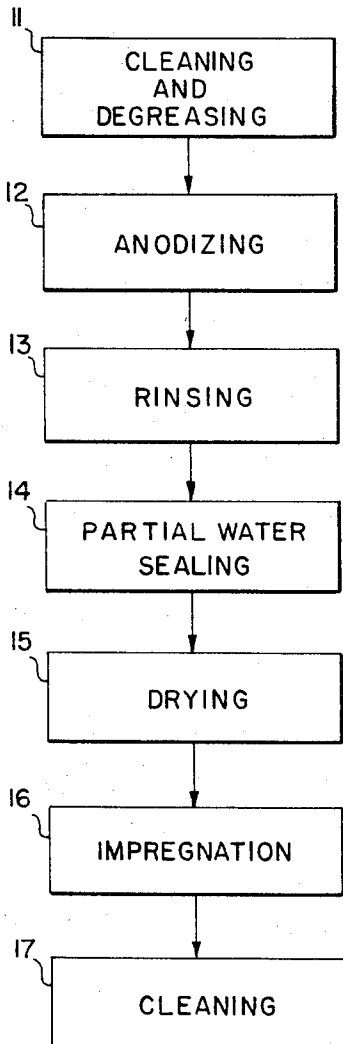
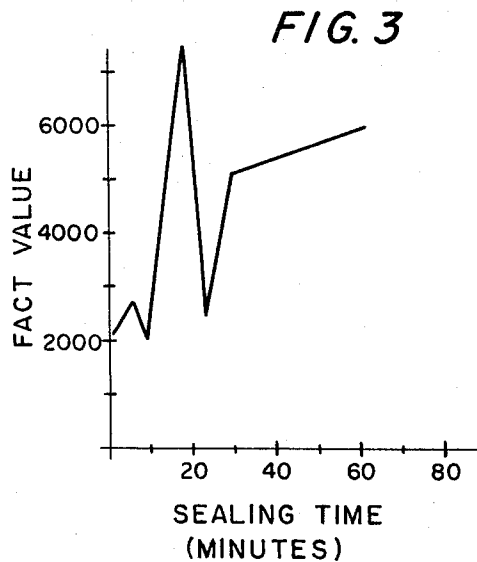
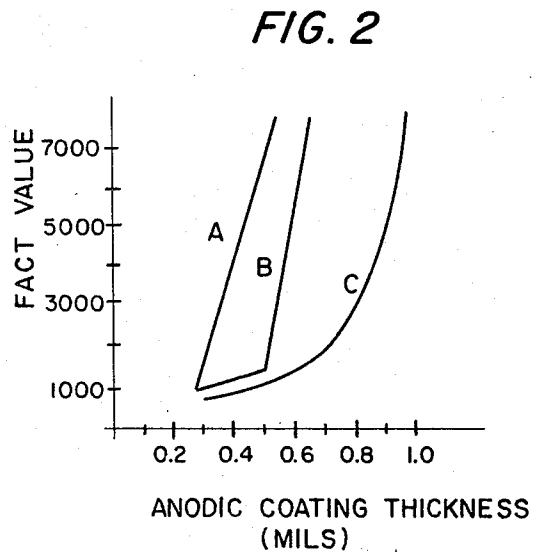


FIG. 1



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DUAL-SEAL ANODIZED ALUMINUM

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9 Claims

ABSTRACT OF THE DISCLOSURE

A process for enhancing the corrosion resistance of aluminum and aluminum alloys of low alloy content comprising the steps of

(1) Anodizing to provide a porous oxidic anodized surface at least 0.3 mil thick;

(2) Partially water sealing this anodized surface; and

(3) Impregnating the partially sealed pores with an aliphatic acid, alcohol or amine such as behenic acid, stearyl alcohol or stearamide.

The present invention is concerned with providing corrosion protection for metals and, more particularly, with providing low-alloy-content aluminum with a surface having corrosion-resistant characteristics.

It is known to provide lean-alloy content aluminum with a corrosion-resistant surface by anodizing articles made of such metal in an anodizing bath and thereafter sealing said anodized coating by treatment with hot water. This is the process conventionally employed to impart corrosion resistance to such an aluminum alloy. In our copending U.S. patent applications Ser. Nos. 242,080 and 361,252 a different anodizing and sealing process is disclosed and claimed. This different process involves the use of an organic impregnant in an anodized layer, which organic impregnant is potentially reactive with aluminum to form a chemical compound. It has now been found that improved corrosion protection can be imparted to anodized, lean-alloy-content aluminum by the use of a combination of anodizing, sealing and impregnating techniques.

It is an object of the present invention to provide a novel process for imparting corrosion resistance to lean-alloy-content anodized aluminum.

Another object of the present invention is to provide lean-alloy-content aluminum objects having good resistance to corrosion.

A further object of the invention is to provide novel means and methods for improving the corrosion resistance of anodized lean-alloy-content aluminum objects.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawing in which:

FIGURE 1 is a schematic outline of the process in accordance with the present invention;

FIGURE 2 is a graph interrelating Fact Values and anodic coating thickness; and

FIGURE 3 is a graph interrelating Fact Values and sealing time.

Generally speaking, the present invention contemplates a process wherein an object having a surface made of lean-alloy-content aluminum is anodized under carefully controlled conditions to provide an anodized metal object, the anodized metal object is then partly sealed by means of water and thereafter the anodized surface of the partly water-sealed anodized metal object is impregnated with a molten, substantially undiluted polar, organic substance selected from the group consisting of saturated aliphatic alcohols, acids, amines and mixtures

thereof having at least about 10 carbon atoms in the aliphatic chain.

In order to describe the process of the present invention with particularity, it is necessary to incorporate herein the definitions of certain terms and expressions employed in the specifications and claims. When such terms are employed in this specification and claims, it is understood that they have the meaning hereinafter assigned.

For purposes of this specification and claims "lean"-alloy-content aluminum includes high-purity aluminum, commercially pure aluminum and conventional aluminum alloys with varying alloy contents. In other words, lean-alloy-content aluminum includes deleted, solid-solution aluminum alloys. Such alloys include those designated by the following numbers according to the American Standards Association (ASA): 5557, 6063, EC, 2EC, 1060, 1100, 3003, 5052, 5357, 5457, 5454, 5657, 5557, 6061, 6063, 2014 alc., 2024 alc., and 7075 alc.

The term "anodized" is employed in this specification and claims as including all forms of surface treatment which will produce on the lean-alloy-content aluminum surface an oxidic layer at least about 0.3 mil thick and having the chemical and physical characteristics of a layer produced on alloy ASA 5557 by anodizing in an aqueous solution containing 15% (by weight) of sulfuric acid at a temperature of about 85° F. for at least about 10 minutes.

"Sealing by means of water" includes for purposes of this specification and claims the conventional processes whereby anodically produced oxidic products on aluminum surfaces are reacted with water to seal same. Thus sealing by means of water includes sealing at the boiling point of pure or slightly acidic water, sealing in steam at temperatures above the boiling point of water, and also sealing at about 200° F. using dilute solution of nickel and/or cobalt acetate. Partly sealing by means of water includes the application of the afore-defined water-sealing processes for a critical length of time from about 10 minutes minimum up to about 30 minutes maximum so that pores originally present in the anodized layer are partly, but not completely, closed. It is to be noted that since the pore structure normally present in an anodized layer is microscopic in nature, one cannot readily determine by direct means as to whether or not the pores are only partly closed. Accordingly, for purposes of this invention, one can ascertain that the proper, partly closed pore condition has been achieved by checking with anthraquinone violet dyestuff. If the pores are not sufficiently closed, a dark dye stain will be evident. On the other hand, if the pores are closed too much, the dye stain will be completely removed.

In carrying the invention into practice one can advantageously anodize a lean-alloy-content aluminum in an aqueous acid bath containing about 10% to about 45% by weight of sulfuric acid. The anodization is advantageously carried out at a temperature of about 65° F. to about 90° F. However, each individual metal or alloy responds best to a very narrow range of anodization temperature within the afore-stated range. In order to achieve an anodic layer thickness of greater than about 0.3 mil, it is usually necessary to anodize for at least about 10 minutes. After anodization is complete, the anodized surface is rinsed in water and then partially water sealed, advantageously by immersion in slightly acidified (pH 6), boiling water for about 10 minutes to about 30 minutes. It is critical to the operability of the present invention that the water seal be only partial (as defined hereinbefore) in order that subsequent processing will be effective.

When partial water sealing is completed, the anodized object is removed from the boiling water, dried and then

immersed in or otherwise subjected to the action of a molten aliphatic acid, alcohol or amine. Advantageously the aliphatic compound comprises a saturated chain of at least about 10 carbon atoms attached to a terminal polar carboxylic, hydroxy or amine group. Satisfactory aliphatic compounds for use in the present invention include docosanoic acid (behenic acid), stearic acid, arachidic acid, ligoceric acid, behenyl alcohol, stearyl alcohol, stearamide, behenamide and mixtures thereof. These are used in the substantially undiluted condition, i.e., containing no more than about 10% in the aggregate of diluent, or additives such as antioxidants, chelating agents, and the like normally employed in small but effective amounts. With acids, alcohols and amines containing more than about 10 carbon atoms, it is advantageous to impregnate the partially water-sealed, anodized surface at a temperature of at least about 190° F. In any event, however, it is usually not necessary to employ a temperature in excess of about 300° F. for impregnation. Since the pores existing in the original anodized surface have been partially closed by partial water sealing, it is usually necessary to maintain contact between the molten organic polar compound and the partially sealed anodized surface for at least about one minute after the metal has been heated to the temperature of the sealing bath, to insure adequate impregnation. Subsequent to impregnation, treatment of the anodized surface is usually completed by removal of excess organic compound, i.e. any organic compound which is on the surface of the anodized layer but not in the pores thereof. The schematic diagram in the drawing illustrates the sequence of operations in accordance with and ancillary to the present invention. Referring now thereto, in operation 11 an object made at least in part of a lean-alloy-aluminum is cleaned and degreased. Subsequent thereto in operation 12, the object is anodized to provide an anodic layer at least about 0.3 mil and up to about 0.8 mil thick. Thereafter in sequence, in operations 13, 14, 15, 16 and 17 the object is rinsed, partially water sealed, dried, impregnated and finally cleaned to remove excess impregnant.

In order to give those skilled in the art a better appreciation of the advantages of the invention, the following examples are given.

Sheet specimens of alloys identified by ASA numbers were anodized as set forth in Table I wherein examples, Nos. 1 to 3, identify examples of the present invention and examples, Nos. A to F, identify processes outside the scope of the present invention.

TABLE I

Example No.	Alloy No.	Anodic Bath, Percent Sulf. Acid	Temp., ° F.	Anode C.D., amps./sq. ft.	Time, min.
1	5557 H25	15	85	15	27
2	6063	15	85	15	18
3	7075-T6 Alclad	15	70	15	30
A	5557 H25	15	85	15	27
B	6063	15	85	15	18
C	7075-T6 Alclad	15	70	15	30
D	5557 H25	15	85	15	27
E	6063	15	85	15	18
F	7075-T6 Alclad	15	70	15	30

The sheet specimens were then sealed as set forth in Table II.

TABLE II

Example No.:	Type of Seal	Aluminum Alloy	Oxide Film Thickness (Mils)	Rinse Time (Min.)	Dry Time (Min.)	Water, pH	Water Temp., ° F.	Water Sealing Time (Min.)	Aliphatic Material	Acid Sealing Temp., ° F.	Acid Sealing Time (Min.)	Fact Value
1	Dual	5557	.5	30	30	6	212	20	Behenic acid	230	20	7,567+
2	do.	6063	.7	30	30	6	212	20	do.	230	20	7,576+
3	do.	7075 Ale.	.8	30	30	6	212	20	do.	212	20	7,478+
A	Water	5557	.5	30	-----	6	212	20	-----	-----	-----	1,067
B	do.	6063	.7	30	-----	6	212	20	-----	-----	-----	1,643
C	do.	7075 Ale.	.8	30	-----	6	212	20	-----	-----	-----	1,220
D	-----	5557	.5	30	30	-----	-----	-----	Behenic acid	230	20	1,093
E	-----	6063	.7	30	30	-----	-----	-----	do.	230	20	1,322
F	-----	7075 Ale.	.8	30	30	-----	-----	-----	do.	212	20	1,630

+ Indicates no failure after 3-minute test.

Comparison tests to determine the relative corrosion resistance of the specimens treated in Examples 1 to 3 and A to F were conducted. These tests are essentially a salt-spray-fog test, two accelerated corrosion tests (i.e. the Cass Test and the Fact Test) and outdoor-exposure tests in a middle-Atlantic marine atmosphere. After 984 hours in salt-spray fog, specimens treated in accordance with Example 1 were bright with no corrosion evident. Fact tests (Ford Motor Company Specification BQ 7-1) based upon Examples 1, A, D and other specimens of alloy 5557-H25 with differing anodic thicknesses resulted in curves as depicted in FIGURE 2 of the drawing. In explanation, it is to be noted that essentially the Fact Test is a measure of electrical resistance of the anodized layer on an aluminum specimen employing a specific copper-acetic-acid-salt electrolyte. The higher the Fact Value, the higher the corrosion resistance can be expected to be. Referring now to FIGURE 2 of the drawing, curve A represents the results obtained when testing specimens treated in accordance with the present invention, curve B represents results obtained when testing specimens sealed only with water and curve C represents results obtained when testing specimens sealed only with long-chain, saturated, polar, aliphatic compounds. From the curves of FIGURE 2, treatment in accordance with the present invention is shown to result in higher Fact Values as contrasted to the results obtained with other treatments when specimens are compared on a basis of equal anodic thicknesses in excess of about 0.3 mil. The Fact Value data plotted in FIGURE 3 indicates the criticality of partial water sealing in the process of the present invention on a 0.5 mil thick anodic coating produced on alloy 5557-H25. Sealing time (minutes) is time of sealing in boiling water (pH 6). The curve of FIGURE 3 shows that under the specific circumstance of the test, partial water sealing for about 20 minutes is critical to achieve high Fact Values.

The improvement achieved employing the dual-seal process of the present invention with a low-alloy-content aluminum alloy is shown by the Cass Test data set forth in Table III. The Cass Test is a standard accelerated-corrosion test defined in ASTM Procedure No. B368-62T. Again, as in the Fact Test, high Cass Values indicate high resistance to corrosion. The data set forth in Table III for each exposure period was obtained on groups of five test panels selected from a group having an average anodic film thickness not significantly divergent from 0.55 mil with average deviations of less than about 0.03 mil.

TABLE III

Type of Sealing	20 Hours	Cass Value, ¹ 60 Hours	80 Hours
Water alone	9.0	-----	7.2
Aliphatic compound alone	8.7	-----	6.8
Dual seal of present invention	9.6	8.7	8.6

¹ Cass value is based on number of corrosion pits over a given area with test time. ASTM rating is a logarithmic scale. Therefore, the water-sealed specimen had more than twice the number of pits as the dual-seal specimen.

The data in Table III demonstrates that the dual-seal process of the present invention, when applied to a proper anodic film about 0.5 mil thick, is highly effective in im-

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parting excellent corrosion resistance to lean-alloy-content aluminum.

The corrosion resistance of the dual-seal-treated specimens is greatly enhanced when antioxidant and chelating agents are added. The data in Table II is based on the use of behenic acid containing 0.25% triphenyl phosphate and 0.1% tetraethanol. The effectiveness of the antioxidants and chelating agents used in conjunction with an aliphatic acid in the treatment of alloy 6063 is shown by Table IV.

TABLE IV

Aluminum Alloy	Anodic Film Thickness (Mils)	Sealing Treatment	Fact Value
6063-----	.8	Distilled water, pH6, 212° F., 20 min-----	6,217
6063-----	.8	Behenic acid, 212° F.-----	1,173
6063-----	.8	Behenic acid plus additives, 212° F., 20 min-----	1,023
6063-----	.8	Dual seal, water plus behenic acid without additives-----	5,392
6063-----	.8	Dual seal, water plus behenic acid with additives-----	7,520+

+ Indicates no failure.

While the present invention has been described in conjunction with advantageous embodiments, those skilled in the art will recognize that modifications and variations may be resorted to without departing from the spirit and scope of the invention. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

We claim:

1. A process for enhancing the corrosion resistance of an object having a surface of lean-alloy-content aluminum which comprises anodizing said lean-alloy-content aluminum to provide a porous anodic layer at least about 0.3 mil thick, partially water sealing said porous anodic layer for about 10 to about 30 minutes at a temperature of at least about 200° F. to only partially close the pores therein and thereafter impregnating the thus produced partially closed pores with a molten, substantially undiluted, polar organic substance selected from the group consisting of saturated aliphatic alcohols, acids, amines and mixtures thereof having at least about 10 carbon atoms in the aliphatic chain.

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2. A process as in claim 1, wherein the anodized layer is about 0.3 mil to about 0.8 mil thick.

3. A process as in claim 1, wherein the polar organic substance is a saturated aliphatic acid containing a single carboxy group at least about 10 carbon atoms in the chain attached thereto.

4. A process as in claim 1, wherein the impregnation is conducted at a temperature in excess of about 90° C. for at least about one minute.

5. A process as in claim 1, wherein subsequent to im-

pregnation excess polar organic substance is removed from the anodized surface of the lean-alloy-content aluminum.

6. A process as in claim 1, wherein the anodizing is conducted in an aqueous sulfuric-acid bath.

7. A process as in claim 1, wherein the partial water sealing is conducted in slightly acidic water at the boiling point thereof.

8. A process as in claim 1, wherein the substantially undiluted polar organic substance contains small but effective amounts of an antioxidant and a chelating agent.

9. A lean-alloy-content aluminum object treated in accordance with the process of claim 1.

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