

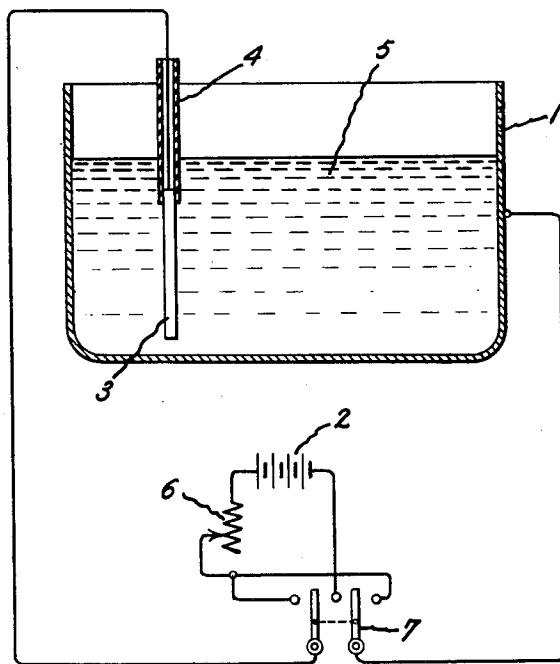
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K. P. ZEMAN

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ELECTROLYTIC METHOD OF PRODUCING THIN SHEETS OF ALUMINUM OXIDE

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Inventor:
Kenneth P. Zeman,
by *Paul A. Frank*
His Attorney.

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ELECTROLYTIC METHOD OF PRODUCING THIN SHEETS OF ALUMINUM OXIDE

Kenneth P. Zeman, Schenectady, N.Y., assignor to General Electric Company, a corporation of New York
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This invention relates to a method of producing a predetermined sheet-like form of aluminum oxide, and more particularly to the combined method of anodizing aluminum and subsequently thereto removing predetermined forms of coherent amorphous alumina from the aluminum body being anodized.

A protective film of oxide is always formed on aluminum surfaces which are exposed to the air; however, anodizing is a method of producing oxide films many times thicker than the natural film, and as such, is well known in the prior art in many and diverse forms. For example, if aluminum is made the anode in a solution of boric acid, the current falls off rapidly as the thickness of the film increases, until the resistance becomes so high that the current is practically stopped. Electrolytic condensers used in many radio circuits depend upon this type of film.

The properties of anodically produced films are to a great extent dependent upon the oxidation process. According to the type of current, the current density or voltage, the nature, concentration and temperature of the electrolyte, and the period of treatment, the films obtained on aluminum may be thin or thick, hard or soft, and possessed of a very high or very low rectifying effect. The oxide film resulting from an anodized process may generally be regarded as hard, somewhat inflexible and quite resistant to high temperatures, and if formed thick enough to be removable from the aluminum metal in coherent form, provides many possible applications such as insulators, a substitute for quartz, tubing for making lamps for very high temperature operation, and various other practical possibilities.

It is an object of this invention to provide an anodizing process which produces relatively thick oxide film on the order of 0.005 inch thick.

It is another object of this invention to provide in combination with an anodizing process a novel method of removing the oxide film thus formed.

It is still another object of this invention to provide an economical and efficient method of producing various configurations of oxide film free from the metal it is formed upon.

Briefly described, this invention in one form contemplates forming anodic coatings on aluminum on the order of 0.005 inch in thickness in a relatively short period of time, and thereafter by suitable polarity control removing the oxide coating from the base metal in sheet or other diverse forms.

The more common anodization processes usually employed are referred to as the chromic acid method, the oxalic acid method, and the sulfuric acid method. In the chromic acid process, the films of aluminum oxide are heavily discolored, and are generally preferred for anodizing assembled aircraft parts having seams and recesses which entrap the electrolyte. Entrapped chromic acid does no harm to the aluminum alloys commonly used in aircraft as it is an inhibitor which retards chemical reaction. The oxalic acid process is somewhat similar to the chromic acid process, and also produces a relatively thin and yellow colored coating.

For the purposes of this invention, the sulfuric acid process is the more desirable in that not only is a thicker coating produced, but the coating is transparent and glass-

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like in appearance. In the drawing there is illustrated a schematic representation of the rather simple apparatus utilized in the sulfuric acid process. In the drawing lead tank 1 is connected as cathode to a source of electrical power 2 while the aluminum work piece 3 is positioned within the tank by means of a non-conducting projection tube 4, to be hereafter described, and connected as the anode. Alternatively, however, where applicable, work piece 3 may be maintained submerged by a suitable metal support which becomes incidentally anodized during the process. Electrolyte 5 in tank 1 consists of approximately 15 to 18% by weight of concentrated sulfuric acid diluted with water, and its temperature is maintained at about 78° F. In order to commence anodizing of work piece 3, there is impressed between the cathode and anode a starting voltage of approximately 5 volts which is gradually increased by means of a suitable voltage control 6, over a period of 3 to 5 minutes to about 18 volts. The voltage is maintained at 18 volts for 30 minutes or more. Thereafter, the anodized work piece is usually given a sealing treatment in boiling water for 10 to 20 minutes. The above description describes generally the process used to anodize various commercial items, with the coating being on the order of 0.0015 inch thick. A 0.0015 inch thick oxide coating is comparably speaking the maximum thickness coating generally employed since greater thicknesses are not economically feasible, nor adaptable for normal anodizing operations.

The adherence of the oxide film to the base metal, if the oxidation is properly carried out, is so good that it is scarcely possible to separate the film from the underlying surface by mechanical means, for the film is actually intergrown during oxidation in the metal. Special chemical or electrochemical means are necessary to remove the film.

A method frequently used to bring about separation for the purposes of analysis consists in heating the oxidized test piece in a current of dry hydrogen chloride or chlorine. The aluminum is therefore converted into aluminum chloride, which volatilizes at the high temperature employed, and sublimates in the cold portion of the reaction tube. In another method, the test piece with the film on it is first immersed in a saturated mercuric chloride solution and then for a few seconds in metallic mercury, after which it is immersed in distilled water in which part of the film separates off after some hours.

This invention discloses a method of forming an extremely thick coating of 0.005 and more inches of aluminum oxide on high purity aluminum, and then a removal of the coating in a thin amorphous coherent sheet form which may suitably be employed for various applications such as insulators, a substitute for quartz and mica, and various other related possibilities. The process includes the utilization of high purity aluminum on the order of 99.99 purity and connecting the aluminum in the apparatus disclosed in the drawing as an anode. The electrolyte 5 in this invention is a 5-10% sulfuric acid solution and the current density applied is approximately 0.33 ampere per square inch. After the aforementioned current density is maintained for about 60 minutes an anodized coating of about 0.005 inch thick is formed on the high purity anode. The specimen is then removed from the anodizing tank, washed with water for about 10 minutes and then returned to the anodizing solution. By a suitable reverse voltage control such as switch 7 in the drawing, the polarity of the anodizing cell is reversed for a period of time of about 10 minutes. After polarity reversal, the aluminum oxide coating becomes detached from the high purity aluminum anode in the form of a thin coherent structure. During the anodizing process and the current reversal, the aluminum

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anode is maintained submerged in the electrolyte so that no air to solution interface is presented. Tube 4 is employed to maintain the submerged condition while preventing total surface anodizing which would hinder oxide removal. Where the surface is to be partly anodized and thus not completely submerged, tube 4 prevents air to solution interfaces at exposed surfaces which would give poor and difficult-to-remove coatings.

For the removal of the oxide coating it is not necessary that the polarity reversal take place in the anodizing solution. It is believed that the oxide removal is a result of the formation of hydrogen between the oxide surface and the base metal and accordingly a solution which is electrically conductive, capable of furnishing hydrogen ions, and in which the oxide coating is not readily dissolved, would provide a removed oxide coating upon the application of the polarity reversal method.

The following procedure is given as one example of this invention, and not by way of limitation.

(1) A specimen of high purity aluminum on the order of 99.99 pure was cleaned by submersion in a 10% sodium hydroxide solution at a temperature sufficient to cause rapid reaction with the aluminum. (2) The specimen was washed with water to remove the sodium hydroxide. (3) The specimen was anodized for 1 hour in a sulfuric acid-water solution of about 10% sulfuric acid. (4) The temperature of the anodizing solution was maintained about 10° C. (5) The current density was applied and maintained at about 0.33 ampere per square inch. (6) The specimen was removed from the anodizing solution and washed for 10 minutes with water at a temperature of about 10 to 15° C. higher than the anodizing solution. (7) After the washing, the specimen was placed in the anodizing solution and the current reversed. (8) During the current reversal, the current density employed is the same as that during the anodizing. (9) The temperature of the anodizing solution during current reversal was 5 to 10° C. higher than that for anodizing.

The above procedure produced an integral aluminum oxide film of approximately 0.005 inch thick which, upon current reversal, become removed from the anode in a thin coherent sheet form. By way of additional information, it should be noted that in step 3 of the above process, the temperature of the bath may be maintained 5 to 10° C. higher if suitable stirring or solution agitation is employed. Similarly, in step 6, the water temperature may also be 5° C. higher if suitable stirring is employed, and furthermore, in step 8 above, the anodizing solution temperature may be 2 or 3° C. higher if stirring is employed.

The following table provides a relationship between bath or solution temperature and average film thickness.

Bath temperature, °C.	Average film thickness, inches
0	0.0046
5	0.0046
10	0.0044
15	0.0038
20	0.0029
25	0.0015

From the above table, it may be seen that a lower anodizing temperature produces a thicker film, and the thickness of the film appears to maintain constant at below 5° C. It was also noted that the film became increasingly difficult to remove below about 10° C. bath temperature.

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The following table gives the relationship between current density and average film thickness.

Current density	Average film thickness
0.13	0.0016
0.18	0.0023
0.23	0.0029
0.28	0.0034
0.33	0.0038
0.38	0.0039

While it was concluded that the film thickness increases as a non-linear function of the current density, it was also learned that, with current densities above 0.33 ampere per square inch, a pitting of the coating was encountered. This pitting appears to be caused by the formation of tiny oxygen bubbles under the skin or film, which isolate the film from the middle at that point, and as a result, keeps the film from becoming thicker in those areas.

The following table illustrates the relationship between washing temperature and average film thickness.

Washing temperature, °C.	Average film thickness
0	0.0040
15	0.0038
28	0.0041
55	0.0037
100	-----

The washing temperature did not appear to have a substantial effect on the film thickness obtained. However, a washing temperature as high as 100° C. made film removal exceedingly difficult.

The following table provides the relationship between the effect of the percent anodizing solution and the average film thickness.

Percent sulfuric acid by volume	Average film thickness in inches
2	0.0062
5	0.0046
10	0.0045
15	0.0038
20	0.0036
25	0.0035

In the anodizing solution it was shown that the weaker solutions, those less than 15% of sulfuric acid by volume, give thicker films, and that the films formed in the weaker solutions appear easier to remove.

There is thus illustrated and described by this invention a method of forming a relatively thick oxide coating on a substantially pure aluminum base by the anodization method, and thereafter removing the oxide coating in the form of a thin and coherent structure of a predetermined shape or configuration of the anode.

While other modifications of this invention and variations of apparatus which may be employed within the scope of the invention have not been described, the invention is intended to include all such as may be embraced within the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of producing an integral amorphous coherent aluminum oxide form which comprises anodizing a high purity aluminum body of at least 99.95+ % purity with direct current in an acid bath, and reversing the polarity of the aluminum body at the finish of the anodizing process to remove the oxide form.

2. The invention as claimed in claim 1 wherein said

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reversal process is carried out in a further solution different from the anodizing solution, said further solution being characterized by being electrically conductive, substantially non-dissolving with respect to the oxide coating, and capable of forming hydrogen ions.

3. A method of producing an integral amorphous coherent aluminum oxide form which comprises, anodizing with direct current a high purity aluminum body of at least 99.95+ % purity in an acid bath, preventing air to solution interface between the aluminum body and the acid bath during the anodizing process, and reversing the polarity of the aluminum body at the finish of the anodizing process to remove the oxide form.

4. A method of producing integral amorphous coherent aluminum oxide forms which comprises, employing a high purity aluminum body of about 99.5% purity, anodizing said aluminum body with direct current in an acid bath, preventing air to solution interface between the aluminum body and the bath, and reversing the polarity of the aluminum body at the finish of the anodizing process to remove the oxide form.

5. A method of producing integral amorphous coherent aluminum oxide forms which comprises employing a high purity aluminum body of about 99.95% purity, anodizing said aluminum body with direct current in a sulfuric acid bath, preventing air to solution interface between the aluminum body and the bath, and reversing the polarity of the aluminum body at the finish of the anodizing process to remove the oxide form.

6. The process as recited in claim 5 wherein said sulfuric acid bath contains 10% or less sulfuric acid.

7. The process as described in claim 5 wherein said

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sulfuric acid bath is maintained at a temperature of about 10° C.

8. The process as described in claim 5 wherein the current density employed in the anodizing process is about 0.33 ampere per square inch.

9. The invention as described in claim 5 wherein the current density after reversal is substantially equal to the applied current density in the anodizing process.

10. A method of producing integral amorphous coherent aluminum oxide forms of about 0.005 inch thickness which comprises employing an aluminum anode of about 99.95+ % purity, anodizing said aluminum anode with direct current in a sulfuric acid bath of approximately 10% or lower sulfuric acid content, applying a current density about 0.33 ampere per square inch, maintaining said current density for a period of about one hour, reversing the polarity of said anode, and maintaining a current density of approximately 0.33 ampere per square inch thereupon to remove the anodized coating.

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