PROCESS FOR PRODUCING OXIDE COATINGS ON ALUMINUM AND ALUMINUM ALLOYS

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This application is a continuation-in-part of my co-endeping applications Serial No. 438,349, filed June 21, 1954 (now Patent 2,897,125), and Serial No. 614,388, filed Dec. 9, 1954 (now Patent 2,905,600).

This invention relates to the production of hard, dense, smooth and corrosion resistant aluminum oxide films having good dielectric properties on aluminum, particularly high copper bearing aluminum alloys, by electrolytic oxidation of such alloys. The term "aluminum" employed herein, unless otherwise indicated, is intended to include pure aluminum, commercial grade aluminum containing small amounts of other materials, and aluminum alloys.

In my above copending application, Serial No. 438,349, I have disclosed and claimed a process capable of making thicker, denser and harder oxide coatings on aluminum and aluminum alloys than prior art processes, and which also produces thick, dense, hard oxide coatings on aluminum alloys which prior art processes are incapable of coating and which process is substantially insensitive to the presence of copper and iron ions in the bath. Thus, according to the process of such application oxide coating thicknesses up to .010" or more can be obtained. Improved bonding of the oxide coating to the metal is also obtained, and the coating is deposited more rapidly than heretofore in prior art processes.

In my above copending application Serial No. 614,388 I have now disclosed a substantially improved procedure over those disclosed in my above copending applications, which is particularly advantageous for high copper bearing aluminum alloys. According to the instant invention, I have now found that by commencing the electrolytic oxidation at a bath temperature of about 40 to about 65° F., and maintaining such temperature until a coating of at least about .0002" and not more than about .002" is produced, and then continuing the anodizing process in an electrolyte at a lower temperature than about 40° F., but not less than about 0° F., and preferably employing at this lower temperature the voltage increment technique of my copending application, Serial No. 438,349, the overall time required to produce a coating of a given thickness can be materially reduced.

I have now developed a still further improved procedure over those disclosed in my above copending applications, which is particularly advantageous for high copper bearing aluminum alloys. According to the instant invention, I have now found that the time required for obtaining an oxide coating on aluminum can in many cases be reduced still further, and denser, smoother, harder and thicker coatings can be obtained, especially on high copper bearing aluminum alloys containing more than 3% copper, such as 11S, 14S, 17S and 24S, with practically no defective parts or rejects, by commencing the electrolytic oxidation in an acidic electrolyte having relatively high acid concentration and forming therein an oxide coating of at least about .0005" thickness, preferably at least about .0007" thick, and continuing to electrolytically oxidize the aluminum article in an acidic electrolyte having a lower acid concentration than said first mentioned electrolyte, and forming additional oxide coating in the electrolyte of lower acid concentration until the desired coating thickness is obtained.

Electrolytic oxidation of the aluminum in the first bath at relatively high acid concentration can be continued until an oxide coating .003" thick is obtained. However, it is preferred to form an oxide coat not greater than about .0015" in such electrolyte and most desirably between about .0007" and .001". Coatings in excess of about .0015" when obtained in the initial electrolyte at the higher acid concentration have a tendency toward softness and are thus less desirable. This tendency toward softness of coatings between .0015" and .003" obtained in the first electrolyte can be alleviated to some degree by employing in the initial electrolyte an acid concentration in the range given below, for example, an electrolyte containing an acid concentration equivalent to 16 to 18% by volume of the solution, of 66 Bauman sulfuric acid (93% H₂SO₄).

When the aluminum containing the initial coating produced in the first electrolyte is treated in the second electrolyte at lower acid concentration, electrolytic oxidation can be continued therein up to the desired thickness, for example, from .003" to .015" or higher. The initial oxide coating formed in the first electrolyte at higher acid concentration is preferably formed within a relatively short period of time, for example, 15 minutes or less, and does not remain in such electrolyte for any extended period. It is preferred to produce only relatively thin coatings in the initial electrolyte.

Briefly, then, according to a preferred embodiment, particularly for production of oxide coatings on high copper bearing aluminum alloys, my process involves anodizing the aluminum part in an electrolyte bath containing sulfuric acid at a concentration equivalent to about 17% by volume of the solution, of 66 Bauman acid in water, and maintaining at a temperature between about 25 and 35° F. until a .0007" oxide coat is formed. The part is then transferred to another electrolyte bath containing sulfuric acid at a concentration equivalent to about 10% by volume of solution, of 66 Bauman acid in water, with temperature of the electrolyte maintained about the same as in the first electrolyte, and the part anodized to the desired thickness of coating. During the anodizing period in the initial electrolyte at the higher acid concentration, voltage is raised while current density is also permitted to rise. During formation of oxide coating in the second electrolyte at the lower acid concentration, voltage is increased while the current density value is controlled to prevent its rise above a desired maximum value, as described more fully below. By employment of the above two-stage process I can deposit the initial oxide coat in a short time in the higher acid concentration bath of the first stage, since the employment of a first stage electrolyte of this type permits rapid increase of voltage and deposition of a high density coating before substantial dissolution of oxide takes place, after which time the remainder of the coat to the desired thickness can be readily deposited in the second electrolyte bath at lower acid concentration.

Where, for example, the final coating desired is greater than .005" thickness, the temperature in the second electrolyte bath of lower acid concentration can be reduced below the temperature maintained in the first electrolyte bath, so as to facilitate obtaining the increased coating thickness without danger of "burning" the coating and to produce the desired hardness of coating.

In preparing the electrolyte I may employ any of the acids usually employed in making up the electrolyte for electrolytic oxidation of aluminum such as sulfuric acid, chromic acid, oxalic acid, phosphoric acid or mixtures thereof. The latter acids can be employed for the anodic oxidation of aluminum in the instant process, and are termed electro anodizing acids herein. Other acids, in addition to sulfuric, oxalic, chromic and phosphoric acids, have been suggested by the prior art
for the anodic oxidation of aluminum, and those skilled in the art will understand the nature and type of such acids contemplated herein. I prefer, however, to employ sulfuric acid as the electrolyte in both baths or in both baths of the invention process.

In the first stage electrolyte I employ an acid concentration equivalent to that produced by adding to water 66 Baumé sulfuric acid in an amount of between about 16 and 20% by volume of the solution, or in other words, equivalent to between 16 and 20 parts by volume of 66 Baumé sulfuric acid per 100 parts by volume of total solution volume. Preferably I employ in the initial bath a concentration of acid equivalent to between about 16 and 18% by volume of solution of 66 Baumé sulfuric acid in water, most desirably about 17%.

In the second electrolyte I employ a lower acid concentration equivalent to between about 7 and 12% of 66 Baumé sulfuric acid by volume in water, preferably about 10%, based on total volume of the solution.

I also employ in both electrolytes of my process from about 1 to 10%, preferably about 2 to about 6%, by volume of the aqueous electrolyte solution, of an aqueous extract of peat.

It is understood that the above proportions of ingredients in the electrolytes may be varied if desired.

The extract additive can be obtained by extracting peat obtained from various localities, with water. The extraction is particularly made more rapid and yield increased by extraction at elevated temperature, preferably atmospheric boiling temperature or more elevated temperature, and most desirably by extraction at elevated temperature under pressure for a period sufficient to produce an aqueous acid solution. The peat used in practice of my invention may be derived from various locations in the United States, for example, from Georgia, Florida, etc.

This extract additive and its mode of preparation are described and claimed in Sanford Patent No. 2,743,221.

In practice, the peat is first mixed with water in a proportion of say one part by weight of the ground, flaked or fibrous peat with, for example, six parts by weight of water. These proportions may vary, however. This aqueous mixture is then fed to an autoclave when high extraction temperatures are desired for practical reasons and wherein the mixture is cooked at atmospheric pressure and at temperature above its normal boiling point (i.e., the boiling point of the mixture at atmospheric pressure)

In this respect, I have found that satisfactory results according to the invention are obtained by cooking the peat at a temperature of from about the boiling point of the mixture at atmospheric pressure, to about 290°F or higher, e.g., between about 250°F and about 350°F, and at pressures up to about 140 p.s.i. for from about 6 to 100 hours or more, but preferably less than 100 hours.

While the above described high pressure and high temperature method for producing the extract is preferred, I can also obtain such extract by refluxing the aqueous mixture of peat at atmospheric pressure over an extended period say over 100 hours. After extraction, the undissolved residue may be separated from the extract.

Preferably, I employ an aqueous extract of Georgia peat made according to the example described below, by volume of Georgia peat ground and mixed is added to 10 parts by volume of water and the resulting mixture is cooked at superatmospheric pressure between 5 and 20 pounds gage pressure for about 72 hours. The resulting material is cooled and allowed to settle. The liquid is decanted from the insoluble residue and forms the peat extract additive which is incorporated in the electrolyte according to the invention.

This extract is in the form of an aqueous solution of organic acids of a complex nature, and is characterized by the following properties. The aqueous extract has a pH of from about 4 to about 6 and may contain as little as 2% of dissolved or dispersed solids, depending on the amount of dilution of the material. The extract upon evaporation to dryness leaves a dark brown, glossy residue which is amorphous and has a total nitrogen content of about 4.5 to 5.5% as determined by the Kjeldahl method. The extract solids are essentially water soluble and form a clear brown solution or dispersion. The aqueous extract is preferably kept refrigerated or a minor portion of sulfuric acid can be added or a fungicidal material such as Dowfax 3A4 to be essentially sodium. In the event of phenoxy may be added to prevent mold growth. For this purpose I preferably add, for example, about 1 gallon of 66 Baumé sulfuric acid to 5 gallons of the aqueous peat extract.

The part to be coated is connected to the anode of an electrolytic cell and immersed in the first electrolyte bath which is maintained during the first stage of the reaction at the above noted relatively high acid concentration equivalent to between about 16 and 20% by volume of 66 Baumé sulfuric acid, with temperature maintained between about 0 and 50°F preferably about 20 to 40°F. Direct current is applied in the electrolyte in both the first and second stages. If desired, however, alternating current alone or superimposed on direct current can also be employed.

As the coating becomes thicker, its electrical resistance requires higher voltages for penetration. I have found that the addition of peat extract to the electrolyte is necessary in the mixture with my technique for obtaining the improved results noted herein. The presence of the peat extract aids in preventing burning of the part at high voltages and amperages, and also permits use of lower electrolyte temperatures. The rapid increase of voltage at the end of the coating period to the electrolyte to facilitate the production of thickness quickly with little softening or solution of the aluminum oxide coating, and denser, thicker and harder coatings are obtained by my process than are obtainable by the prior art.

In operation of my process I raise the voltage from zero to say about 20 volts in a period of about a minute in the first electrolyte. As the voltage is raised gradually during this period current density rises. When a voltage of 20 volts is reached the voltage can thereafter be raised in one volt increments, maintaining the voltage substantially constant for one minute after each voltage rise. This procedure is continued until the current density has increased to about 32 volts. However, I can alternatively operate by raising the voltage from about 20 to 25 volts in a period of about 3 minutes and then proceed in one volt steps, each step maintained constant for a period of about one minute, up to 32 volts.

When the voltage has been raised to 20 volts current density may be about 5 amperes/sq. ft. During the stepwise voltage procedure above 20 volts, current density also continues to increase. At the beginning of each voltage step current density increases above the value at the end of the preceding voltage step, and then decreases until at the end of the constant voltage period, it is only slightly higher than it was at the commencement of such period. Thus, for example, when the voltage is raised from 20 to 21 volts and maintained at 21 volts for a minute, the current density may increase say from 5 to 8 amperes/sq. ft. at the beginning of this constant voltage period and then decreases gradually during this period to, for example, 6 amperes/sq. ft. at the end of the period, and when going from 21 to 22 volts, the current density may increase say from 6 to 9 amperes/sq. ft. at the beginning of this constant voltage step and decrease to 7 amperes/sq. ft. at the end of this step.

Hence it will be noted that while the current density during the raising of the voltages from 20 to 32 volts increases and then decreases during each constant voltage period, the overall value of current density, as voltage increases, also increases until at about 32 volts the cur-
rent density may be, for example, 20 to 30 amps./sq. ft. The coating commences to form during the above noted period as the voltage is raised from 20 to 32 volts and at about 32 volts the coating thickness on most high copper bearing alloys, the preferred materials coated in my process, is about .0005". The anodic part can at this point be transferred to the second stage electrolyte described below. I prefer to continue coating in the first stage electrolyte described above until a .0007" coat is formed. To attain such coating thickness in the first electrolyte, after a voltage of 32 volts is reached in the first stage electrolyte at the voltage in a stepwise fashion. In constant voltage increments of one volt for every one minute until a voltage of about 35 volts is reached, at which point a coating thickness of about .007" is obtained on most of the above noted high copper bearing alloys. Formation of such .0007" coating may require only about 12 to 15 minutes from the start whereas in conventional procedures formation of such a coating thickness requires 20 to 30 minutes.

During the latter portion of the operation from 32 to 35 volts, current density increases during each of the constant voltage stages and then decreases to a value at the end of each increment which is somewhat higher than the current density at the beginning of the corresponding period, similar to the manner in which current density varies in each of the constant voltage steps during the period of coating between 20 and 32 volts above. Hence there is an overall increase in current density during the 32 to 35 volt operation until at 35 volts the current density may be between 30 and 35 amps./sq. ft. depending on various factors such as the type of casting, i.e., whether permanent mold, die cast, etc., the particular alloy used, the concentration of acid in the bath and other variables. If a coating thickness of .001" is desired to be obtained in the first electrolyte procedure is continued up to about 38 volts instead of only up to about 35 volts. If a coating thickness of .0015" is desired to be obtained in the first stage electrolyte, the stepwise voltage technique described immediately above, i.e., the application of one volt increments, each increment maintained constant for one minute, can be continued above 38 volts, until such a thickness of .0015" is obtained, usually at a voltage between about 44 and 48 volts. During this period of voltage increase from about 38 to about 44 and 48 volts, current density is maintained between about 30 and 35 amps./sq. ft.

If a coating thickness greater than .0015" is desired to be obtained in the first stage electrolyte, the above noted procedure is repeated at about 40 volts corresponding to a coating thickness of about .0011" to .0012", and the current density is decreased to about 15 amps./sq. ft. Then I proceed by increasing the voltage in one volt constant voltage increments each of 2 minutes duration until the desired coating thickness up to as high as .003" is obtained. During this period current density should not be permitted to exceed 25 amps./sq. ft. At high acid concentrations equivalent to about 18 to 20% by volume of 66 Baumé sulfuric acid in the first stage electrolyte, it is feasible to coat only up to .0015" thickness in the first stage, while at acid concentrations somewhat lower, equivalent to about 16 to 17% by volume of 66 Baumé sulfuric acid based on the volume of the first solution, it is feasible to obtain a greater thickness say up to .003" in the first stage. However, as noted above, production of such a coating thickness in the excess of about .0015" in the first stage electrolyte even at the above noted lower acid concentrations equivalent to about 16 to 17% by volume of 66 Baumé sulfuric acid, are not as satisfactory as coatings of .0015" or less formed therein, due to sacrifice in hardness of coat when coatings greater than .0015" are produced in the initial electrolyte at the relatively high acid concentration thereof.

When the initial coat preferably between about .0007" to .0011" is formed in the first electrolyte, the part being treated is preferably removed to another tank of electrolyte of a composition similar to that employed in the initial stage described above but having a lower acid concentration equivalent to between about 7 to 12%, preferably 10%, of 66 Baumé sulfuric acid by volume of solution. The aqueous peat extract and also coating in the second stage electrolyte is present in a concentration substantially the same as in the first stage electrolyte, although if desired a higher or lower concentration of peat extract may be employed in the second stage electrolyte than in the first stage electrolyte. For example, the first stage electrolyte, the part is now preferably transferred to the second stage electrolyte and is then subjected to a voltage technique in the second electrolyte which involves first raising the voltage to about 28 volts and then continuing at constant voltage increments of about one volt per minute until "breakthrough" which takes place between about 33 and 38 volts or higher, usually about 35 for high copper bearing alloys. The term "breakthrough" is intended herein to denote the voltage at which the oxide coat obtained in the first electrolyte commences to increase in thickness in the second electrolyte above the thickness of coat (.0007" in the instant case) obtained in the first stage electrolyte. During each of the voltage steps from 28 volts to about 32 to 38 volts and just before breakthrough, the current density rises say from about 5 amps./sq. ft. or higher at the beginning of each voltage increment to about 8, and then drops back to about 5 amps./sq. ft. or somewhat less at the end of the voltage increment. Current density at the start and at the end of each voltage increment during this portion of the operation may be substantially constant. Although substantially no coating forms in the second stage electrolyte at voltages below breakthrough, it has been found advantageous to pass through the above noted constant voltage increments between about 28 and about 32 to 38 volts in order to keep the current density at a low level so as to insure that the breakthrough voltage is reached without permitting the current density to rise markedly to a value which might cause burning of the part.

At breakthrough, say between about 32 and 38 volts, current density may increase up to about 20 amps./sq. ft. in a fraction of a minute, during which period the voltage may drop say about 3 volts below the voltage at the breakthrough, from say 35 volts down to about 32 volts. The current density attained just after breakthrough, for example, about 20 amps./sq. ft. is controlled by permitting the voltage to decrease sufficiently, that is, say, about 2.5 volts. The breakthrough voltage, at which the current density may increase to a maximum as noted above, may occur in about 5 minutes after the start of the second stage operation. After breakthrough and at the commencement of coating in the second stage electrolyte, voltage may be increased in constant voltage increments of 2 volts each for a duration of 2 minutes,
However, during each of these constant voltage increments current density may vary from about 20 amps./sq. ft. at the commencement of each voltage increment to a maximum of 25 amps./sq. ft. and then decrease again to about 20 amps./sq. ft. by the end of each voltage increment. Thus, during this period current density is preferably not permitted to increase above about 25 amps./sq. ft. to prevent burning. This voltage-current density technique may be continued up to about 40 to 45 volts to produce a coating thickness of about .0012" to about .0015". Thereafter the voltage may be increased by means of constant voltage increments of one volt each for a period of one minute with current density varying from about 20 to about 25 amps./sq. ft. during each constant voltage increment, the current density reaching about 30 shortly after commencement of each voltage step and decreasing to 25 amps./sq. ft. at the end of each voltage step. This is continued until the desired coating thickness is obtained up to a thickness of about .005" in the second electrolyte in one volt constant voltage increments above the voltage of 80 to 85 volts required for production of a .005" coat. It is preferred to maintain a lower current density during production of coating thicknesses above .005" than during production of coating thicknesses up to or below .003", in order to deposit the greater thicknesses of coating under the most favorable conditions without danger of destruction or burning of the coating.

Assuming now that a coating thickness of .0015" is obtained in the first electrolyte instead of only a .0007" oxide coat as described above, the part is immersed in the second electrolyte and voltage raised therein to 28 volts. At this point I proceed in one volt per minute constant voltage increments to breakthrough which, in this instance, occurs at a voltage between about 40 and about 45 volts as compared to the 32 to 38 volt breakthrough range noted above, since the coating on the instant part following its removal from the first electrolyte is greater than the .0007" coating as described above. At breakthrough the current density increases to about 20 amps./sq. ft. with the voltage decreasing about 3 volts, say from about 45 volts to about 42 volts. Thereafter I again proceed at one volt per minute constant voltage increments up to a voltage of between about 50 and 55 volts. During this period current density is permitted to vary between 20 and 25 amps./sq. ft. in each voltage step. At 50 to 55 volts a coating thickness of about .0017" is obtained. Thereafter I proceed in 2 volt constant voltage steps each for a duration of 2 minutes with the current density varying during each constant voltage increment between 25 and 30 amps./sq. ft. until the desired coating thickness, e.g., .005" is obtained, if coating thicknesses greater than .005" are desired I proceed above .005" by 2 volt per minute constant voltage increments, with current density varying during each of such voltage increments between about 15 and 20 amps./sq. ft. Should the part be burned during the initial electrolyte up to a coating thickness of .003" and the part then transferred to the second stage electrolyte, the voltage may be raised therein to about 30 volts and then increased slowly up to about 50 to 55 volts, during which time care is taken that the current density does not exceed about 10 amps./sq. ft. until breakthrough takes place at a voltage in the second tank approximately equal to the final voltage applied in the first electrolyte bath for obtaining a .003" coat, which may be between about 60 and 65 volts. At breakthrough current density may increase to about 15 amps./sq. ft.

Thereafter voltage can be increased at about 5/ volt per minute constant voltage increments, while maintaining during this period the current density between about 10 and 15 amps./sq. ft. The operation may be continued in this fashion up to about 75 volts at which time I can proceed in one volt per minute constant voltage increments with current density varying between 20 and 25 amps./sq. ft. during each voltage step; that is, during each voltage step, current density increases to about 25 amps./sq. ft. and then drops back at the end of the step to about 20 amps./sq. ft. This technique is continued until the desired coating thickness is obtained, which may be as high as .010" or higher. Thus, for example, by means of this technique a coating thickness of .005" is obtained at a voltage of about 80 to 85 volts.

Oxide coatings according to the invention can be produced on various types of aluminum alloys. The invention process is particularly advantageous for anodizing high copper aluminum alloys, and compositions of a few examples of such alloys are illustrated below.

<table>
<thead>
<tr>
<th>Aluminum Alloy Designation</th>
<th>Approximate Composition</th>
</tr>
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<tbody>
<tr>
<td>148</td>
<td>94% Al, 4.8% Cu, 0.8% Sn</td>
</tr>
<tr>
<td>218</td>
<td>94% Al, 4.8% Cu, 0.6% Mg, 0.5% Mn, 0.2% Si</td>
</tr>
<tr>
<td>115</td>
<td>98% Al, 0.4% Si, 0.2% Cu, 0.0% Fe</td>
</tr>
<tr>
<td>178</td>
<td>99.5% Al, 0.5% Sn, 1% Fe, 0.1% Cu, 0.7% Mn, 0.0% Mg</td>
</tr>
<tr>
<td>0.1% Cu, 0.5% Sn</td>
<td></td>
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The following examples are given as illustrative but not as limitations of my invention:

Example 1

A 4" x 4" x 1/4" test panel of 24S aluminum alloy is connected to the anode of an electrolytic cell comprising a stainless steel tank which forms the anode. The electrolyte is prepared by adding about 5% by volume of the aqueous extract of Georgia peat as described above employing 4 parts of Georgia peat by volume and 10 parts by volume of water, to a water solution of sulfuric acid formed by the addition of 17 parts by volume of 66 Baumé sulfuric acid to about 80 parts by volume of water. The temperature of the electrolyte is maintained between 28 and 32° F.

The voltage is raised from 0 to about 20 volts in about one minute and then increased to from 20 volts to 25 volts in 3 minutes. Thereafter voltage is raised in one volt constant voltage increments each lasting a period of one minute up to about 32 volts. During each of these constant voltage increments the current density increases at the commencement of each new voltage step and then decreases during such voltage step to a current density somewhat greater than that at the beginning of each voltage step. Thus, the current density in the first voltage step may increase initially from about 5 to 8 amps./sq. ft. and then decrease to a final current density at the end of the first one minute constant voltage step of about 6 amps./sq. ft. This general pattern is repeated during each of the subsequent constant voltage increments up to about 32 volts, at which voltage the current density is between 25 and 30 amps./sq. ft. with a coating thickness of about .0005" obtained. Voltage is then raised in voltage steps of one volt, each voltage step being held substantially constant for one minute until a voltage of about 35 volts is reached at which time a coating of .0007" is formed. The current density between 32 and 35 volts increases and then decreases during each of the constant voltage increments but with an overall increase in current density up to about 50 to 35 amps./sq. ft. at about 35 volts.
The part is then removed from the electrolyte described above and made the anode of a second electrolytic cell containing an electrolyte formed by adding 3 parts by volume of Georgia peat extract obtained as described above to an acid aqueous solution formed by adding 10 parts by volume of 66 Baumé sulfuric acid to 87 parts by volume of water. The temperature of the solution is maintained between 28 and 32°F. The voltage is then raised to about 28 volts in the second tank and is thereafter increased in constant voltage increments of one volt per minute up to about 35 volts. During this period the current density varies during each constant voltage increment to about 2.5 and 3 amps./sq. ft.

At about 35 volts current density increases up to about 20 amps./sq. ft. This corresponds to breakthrough. Thereafter I proceed by 2 volt constant voltage increments each for a period of 2 minutes up to a voltage 44 to 46 volts to a coat thickness of about .0015". Current density in each of the latter constant voltage increments varies between about 20 and 25 amps./sq. ft.

I thereafter proceed in 2 volt per 2 minute constant voltage increments up to formation of a coating thickness of .003" at about 65 volts, current density during this period varying between 25 and 30 amps./sq. ft. during each constant voltage increment. Total time for formation of the .003" coat is on the order of about 45 minutes.

Example 2

The procedure of Example 1 in the first stage electrolyte thereof is carried out, except that instead of discontinuing coating when a voltage of 35 volts is reached, the operation is continued employing the one volt constant voltage increments each for a one minute interval employed in the latter portion of the first electrolyte stage in Example 1, up to a voltage of between 44 and 48 volts to attain a coat thickness of .0015".

The panel is then immersed in the second stage electrolyte bath, described above in Example 1, and the voltage is raised to 28 volts and thereafter increased in one volt per minute constant voltage increments to between 42 and 45 volts, current density varying between about 5 and 8 amps./sq. ft. between each such constant voltage increment. At between 42 and 45 volts current density increases from about 5 to 8 amps./sq. ft. Voltage is then increased in one volt per minute constant voltage increments up to between 52 and 55 volts, the current density varying during each of the latter constant voltage increments between about 20 and 25 amps./sq. ft. A coating thickness of about .0017" is reached at between 52 and 55 volts, and thereafter voltage again is increased in 2 volt increments each for a duration of 2 minutes up to formation of a coating having a thickness of about .005", which is formed at about 80 to 85 volts, current density during each of the latter 2 minute constant voltage steps being maintained between about 25 and 30 amps./sq. ft.

Example 3

The procedure of Example 1 is repeated, except that the temperature in the second electrolyte bath is maintained at about 20°F. Results similar to those noted in Example 1 are obtainable.

Example 4

The procedure of Example 1 is repeated, except that the concentration of the aqueous peat extract employed in the first electrolyte bath is about 4% by volume of the solution instead of about 3%. Results similar to those noted above in Example 1 are obtainable.

Instead of using the aqueous extract of peat as additive in the electrolyte employed in the invention process, other additives may be used which permit the technique and procedure of the invention as described above to be employed. Other suitable additives include, for example, 2-aminoethyl sulfuric acid, taurine, and alkyl taurines, as for example, N-methyl taurine and N-cyclo-hexyl taurine, and sulfamic acid. The use of the latter specific compounds as additives in electrolytes for the electrolytic oxidation of aluminum and its alloys is described and claimed in the applications of Robert Ernst, Serial Nos. 457,314, 457,315 and 457,316, all filed September 20, 1954 (Patents 2,855,350, 2,855,351 and 2,855,352 respectively).

Such additives should function to permit substantially increasing the voltage in the manner described above without substantial increase in current to a value producing burning, while operating at reduced electrolyte temperatures, to obtain oxide coatings on high copper alloys, which are thick, hard and dense, according to the invention. These additives permit such increase in voltage and consequent increase in coating thickness in a shorter period of time than in the absence of such additives, and hence such additives when used in my process are termed oxide coating accelerators. By this term is meant that the additive functions to increase the rate of growth of oxide coating by permitting increased voltage without producing burning, when employed in conjunction with the two-stage electrolyte feature of my invention employing a higher acid concentration in the first stage electrolyte than in the second stage electrolyte.

In accordance with the instant process, a reduction in time is achieved in forming a desired thickness of coat, in comparison to the prior art; for example, oxide coatings according to the instant process, having a thickness of .001" , .002" or .003", can be formed in one-half or less the time required by conventional procedure. Further, I can form thicker oxide coatings up to .015" or greater, as well as denser coats, as compared to those obtained by the prior art, particularly on high copper alloys. The treatment of the aluminum part in an initial stage electrolyte of high acid concentration for a relatively short period permits rapid deposition of the initial oxide coat without the danger of dissolving any substantial amount of the oxide film. Due to the increase in voltage in both electrolyte baths, which is permitted while maintaining current density at a value at which burning or destruction of the coat does not occur, hardness and density of the oxide coat are enhanced. Further, anodic coating according to the two-stage procedure described herein, I can anodize in a single operation a full tank load of parts, for example, 5,000 parts, of high copper alloy per tank. The anodizing of such large numbers of parts, especially high copper alloy parts, in a single tank is generally not possible in conventional practice. From the above it is seen that the instant process is an improved two-stage operation for electrolytic anodizing of aluminum, preferably aluminum alloys of high copper content, particularly for formation of a hard, dense, anodic oxide coating of a given thickness on such high copper alloys in a relatively short period of treatment.

While I have described a particular embodiment of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

1 claim:
1. A process for coating aluminum articles with a hard and dense coating of oxide of aluminum which comprises passing an electric current at increasing voltage through an electrolytic cell containing an electrolyte with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid having an acid concentration equivalent to between about 16 and 20% by volume of solution of 66 Baumé sulfuric acid and an oxide coating accelerator as additive, until an oxide coating of at least about .0002" and not greater than .003" thick is formed and continuously growing to electrolytic coating a water solution of sulfuric acid having an acid concentration equivalent to between about 7 and 12% by volume.
2,977,294

volume of solution of 66 Baumé sulfuric acid and an oxide coating accelerator as additive, until a desired increase in oxide coating thickness substantially greater than the coating thickness produced in said first electrolyte is formed.

2. The process as defined in claim 1, wherein said electrolytes are maintained at temperature between about 0 and 50° F.

3. The process as defined in claim 1, wherein said oxide coating accelerator is an aqueous extract of peat.

4. The process as defined in claim 1, wherein the temperature of said electrolytes are maintained between about 20 and about 40° F.

5. A process for coating an aluminum alloy metal article having in excess of about 3% copper, with a hard and dense coating of oxide of aluminum which comprises passing an electric current in a series of increasing voltage steps through an electrolytic cell containing a first electrolyte with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to between about 16 and 20% by volume of solution of 66 Baumé sulfuric acid and an aqueous extract of peat, until an oxide coating of at least about .0007" and not greater than about .003" thick is formed, continuing to electrolytically oxidize said article in a second electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to between about 7 and 12% by volume of solution of 66 Baumé sulfuric acid and an aqueous extract of peat, and forming oxide coating until a desired coating thickness substantially greater than the coating thickness produced in said first electrolyte is formed, the temperature of said electrolytes being maintained between about 0 and 50° F.

6. A process as defined in claim 5, wherein from about 1 to about 10% of aqueous peat extract by volume of the solution is employed in each of said electrolytes.

7. A process as defined in claim 6, wherein temperature of said electrolytes is maintained between about 20 and 40° F.

8. A process for coating aluminum articles with a hard and dense coating of oxide of aluminum which comprises passing an electric current through an electrolytic cell containing a first electrolyte with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to between about 16 and 20% by volume of solution of 66 Baumé sulfuric acid and 1 to 10% by volume of said first named solution of an aqueous extract of peat, and raising the voltage until an oxide coating at least about .0007" thick and not greater than about .0015" thick is formed, continuing to electrolytically oxidize said article in a second electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to between about 7 and 12% by volume of solution of 66 Baumé sulfuric acid and an oxide coating until a desired increase in oxide coating thickness greater than the coating thickness produced in said first electrolyte is formed.

9. A process as defined in claim 8, wherein the sulfuric acid concentration in said first electrolyte solution is equivalent to between about 16 and 18% by volume of said solution of 66 Baumé sulfuric acid, and the amount of aqueous peat extract employed in each of the electrolyte solutions is between about 2 and 6% by volume of each of said solutions.

10. A process for coating aluminum alloy metal articles having in excess of about 3% copper, with a hard and dense coating of oxide of aluminum which comprises passing an electric current through an electrolytic cell containing a first electrolyte with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to about 17% by volume of solution of 66 Baumé sulfuric acid and about 3% by volume of said solution of an aqueous extract of peat, raising the voltage until an oxide coating of between about .0007" and .001" thick is formed, continuing to electrolytically oxidize said article in a second electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to about 10% by volume of solution of 66 Baumé sulfuric acid and about 3% by volume of said solution of an aqueous extract of peat, and raising the voltage and forming oxide coating until a desired increase in oxide coating thickness greater than the coating thickness produced in said first electrolyte is formed, the temperature of said electrolytes being maintained at about 30° F.

11. A process for coating aluminum articles to form a hard and dense oxide coating, which comprises passing an electric current through a first electrolytic cell containing an electrolyte maintained at a temperature between about 0 and 50° F., with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid in a concentration equivalent to between about 16 and 20% by volume of a solution of 66 Baumé sulfuric acid, and an aqueous extract of peat in an amount of about 1 to about 10% by volume of said solution, said extract being obtained by extracting a mixture of said peat with water at elevated temperature raising the voltage until an oxide coating having a thickness of about 32 volts in a series of substantially constant voltage increments, and raising the current density during this period, and forming an oxide coating at least about .0005" and not greater than about .003" thick, transferring said article to a second electrolytic cell containing an electrolyte having the aforementioned composition and temperature ranges but having a lower sulfuric acid concentration equivalent to between about 7 and 12% by volume of solution of 66 Baumé sulfuric acid, with said article forming the anode, passing an electric current through said second cell, increasing the voltage above the highest voltage applied in said first electrolytic cell by a plurality of increasing voltage steps, the voltage at each said step being maintained substantially constant, and oxidizing said article to form a desired increase in oxide coating thickness in excess of .001" thickness and substantially greater than the coating thickness produced in said first electrolyte.

12. A process for coating aluminum articles to form a hard and dense oxide coating, which comprises passing an electric current through a first electrolytic cell containing an electrolyte maintained at a temperature between about 0 and 50° F. with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid in a concentration equivalent to between about 16 and 18% by volume of solution of 66 Baumé sulfuric acid, and an aqueous extract of peat in an amount of about 2 to 6% by volume of said solution, said extract being obtained by extracting a mixture of said peat with water at elevated temperature, raising the voltage to at least about 35 volts in a series of substantially constant voltage increments, and raising the current density during this period, and forming an oxide coating at least about .0007" and not greater than .003" thick, transferring said article to a second electrolytic cell containing an electrolyte having the aforementioned composition and temperature ranges, but having a lower sulfuric acid concentration equivalent to between about 16 and 18% by volume of solution of 66 Baumé sulfuric acid, and an aqueous extract of peat in an amount of about 1 to about 10% by volume of said solution, said extract being obtained by extracting a mixture of said peat with water at elevated temperature raising the voltage until an oxide coating having a thickness of at least about .0007" thick and not greater than .0015" thick is formed, continuing to electrolytically oxidize said article in a second electrolyte comprising a water solution of sulfuric acid having a concentration equivalent to between about 7 and 12% by volume of solution of 66 Baumé sulfuric acid and an oxide coating until a desired increase in oxide coating thickness greater than the coating thickness produced in said first electrolyte is formed.

13. A process for coating articles composed of an aluminum alloy containing in excess of 3% copper, to form...
a hard and dense oxide coating, which comprises passing an electric current through a first electrolytic cell containing an electrolyte maintained at a temperature between about 20 and 40° F., with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid in a concentration equivalent to between about 0.8% and 10% by volume of solution of 66 Baumé sulfuric acid, and an aqueous extract of peat in an amount of about 2 to 6% by volume of said solution, said extract being obtained by extracting a mixture of said peat with water at elevated temperature, raising the voltage from between about 20 and 25 volts to at least about 35 volts in a series of substantially constant voltage increments, and raising the current density during this period, and forming an oxide coating at least about .0007" thick and not greater than about .0015" thick, transferring said article to a second electrolytic cell containing an electrolyte having the aforementioned composition and temperature but having a lower sulfuric acid concentration equivalent to about 10% by volume of solution of 66 Baumé sulfuric acid, with said article forming the anode, passing an electric current through said second cell, increasing the voltage above the highest voltage of at least about 35 volts applied in said first electrolytic cell by a plurality of increasing voltage steps, the voltage at each step being maintained substantially constant, with current density maintained between predetermined limits during this period, and oxidizing said article to form a desired increase in oxide coating thickness of at least about .003" thickness.

16. A process for coating articles composed of an aluminum alloy containing in excess of 3% copper, to form a hard and dense oxide coating, which comprises passing an electric current through a first electrolytic cell containing an electrolyte maintained at a temperature of about 30° F. with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid in a concentration equivalent to about 17% by volume of solution of 66 Baumé sulfuric acid, and an aqueous extract of peat in an amount of about 3% by volume of said solution, said extract being obtained by extracting a mixture of said peat with water at elevated temperature, raising the voltage from between about 20 and 25 volts to about 35 volts in a series of substantially constant voltage increments, and raising the current density during this period, and forming an oxide coating at least about .0007" thick and not greater than about .0015" thick, transferring said article to a second electrolytic cell containing an electrolyte having the aforementioned composition and temperature but having a lower sulfuric acid concentration equivalent to about 10% by volume of solution of 66 Baumé sulfuric acid, and an aqueous extract of peat in an amount of about 3% by volume of said solution, said extract being obtained by extracting a mixture of said peat with water at elevated temperature, raising the voltage from between about 20 and 25 volts to about 35 volts in a series of substantially constant voltage increments, and raising the current density during this period, and forming an oxide coating at least about .0007" thick and not greater than about .0015" thick, transferring said article to a second electrolytic cell containing an electrolyte having the aforementioned composition and temperature but having a lower sulfuric acid concentration equivalent to about 10% by volume of solution of 66 Baumé sulfuric acid, with said article forming the anode, passing an electric current through said second cell, increasing the voltage above the highest voltage of at least about 35 volts applied in said first electrolytic cell by a plurality of increasing voltage steps, the voltage at each step being maintained substantially constant, with current density maintained between predetermined limits during this period, and oxidizing said article to form a desired increase in oxide coating thickness of at least about .003" thickness.

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