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ANODIZING ELECTROLYTE AND METHOD

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This invention relates to a novel anodizing electrolyte and method for anodizing aluminum, and particularly to producing anodic oxide coatings on aluminum by making an aluminum article the anode in an electrolytic cell employing an aqueous acid electrolyte. As generally used herein, the word "aluminum" includes high purity aluminum, aluminum in various commercial grades, and aluminum base alloys.

Decorative and protective oxide coatings on aluminum have long been made by anodizing in electrolytes consisting of aqueous solutions of sulfuric acid. Such electrolytes are usually employed at a temperature near room temperature, and must be cooled to maintain such temperature. The anodic oxide coatings, as so produced, are usually relatively clear or colorless, although on some alloys they may be tinnted or colored by some constituents.

In recent years, "hard" anodic oxide coatings which are more abrasion resistant, have been produced by anodizing in aqueous sulfuric acid electrolytes at extremely low temperatures, e.g., 25 to 32° F., requiring much more cooling, with consequent increased equipment and operating expense. Such coattings, as so produced, in addition to being abrasion resistant, are colored in metallic gray, brownish gray and dark brown colors, which are attractive for architectural and other uses of aluminum. Consequently, more practical methods of producing similarly colored anodic oxide coatings are demanded.

It is a general object of this invention to provide, for use in an electrolytic cell for anodizing aluminum, a novel electrolyte and anodizing process or method for producing oxide coatings on aluminum, particularly colored oxide coatings. Another object is to provide such an electrolyte and process for use under a wide range of practical operating conditions. A particular object is to provide such an electrolyte and process for anodizing aluminum which requires no more than moderate cooling of the electrolyte, and in which small changes in electrolyte composition during use do not have a critical effect on anodizing results. Another object is to produce abrasion resistant, colored anodic oxide coatings on aluminum at moderate cost, particularly at moderate electrolyte cost. A specific object of the invention is to produce uniform, abrasion-resistant, lightfast colored anodic oxide coatings on aluminum, with moderate electrolyte cost, voltage and cooling requirements.

In accordance with the invention, it has been found that an electrolyte consisting essentially of lignosulfonic acid, together with sulfate provided by at least one compound selected from the group consisting of sulfuric acid and water soluble sulfates and bisulfates, and water, may be advantageously used in an electrolytic cell for anodizing aluminum. As generally used herein, the expression "lignosulfonic acid" refers to the sulfonic acid form of sulfonated lignin, as distinguished from alkali and alkaline earth sulfonate forms. A high purity or a low-sugar

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lignosulfonic acid may be used in accordance with the invention, but various crude and sugar-containing lignosulfonic acid products may also be used, particularly sulfite process crude lignosulfonic acid.

As indicated above, lignosulfonic acid may be obtained as a by-product of wood pulping processes. The cellulose pulp desired for paper-making is commonly obtained by digesting wood in a cooking liquor which dissolves lignin and some other non-cellulosic material. With an alkali or alkaline earth bisulfite cooking liquor, the resulting sulfite spent liquor typically contains about 8 to 14 percent dissolved solids. These solids may, for example, consist of about 65 to 70 percent sulfonated lignin, about 20 to 25% wood sugars and the like, and about 10% inorganic material. Since large volumes of sulfite spent liquors are generated, lignosulfonic acid is available therefrom, either directly or by conversion from lignosulfonate forms, at moderate cost. Commonly available lignosulfonate forms of sulfite spent liquors may be readily converted to the acid form, for use in accordance with the present invention, by replacing the cations of lignosulfonates with hydrogen. A conventional ion-exchange or other suitable procedure may be used. Lignin from other pulping processes may also be converted to lignosulfonic acid by conventional procedures, for use in accordance with this invention.

Lignin itself is a water-insoluble polymer whose complex organic structure is still not completely known. It is considered as made up of a group of high molecular, amorphous compounds which are chemically very closely related, but of somewhat varying molecular weight. The monomeric lignin building unit is reported to be a substituted phenyl propane, with a methoxyl group meta to the side chain, and with a hydroxyl group para to the side chain (this hydroxyl group providing a point of linkage to the next monomer unit in a lignin molecule). Lignin molecules are readily sulfonated, as in the sulfite pulping processes, reportedly at one or more alpha carbon positions on the side chains. Thus, a sulfite spent liquor is an inexpenisve source of crude lignosulfonic acid. The crude product may be refined by removal of sugars and other matter if desired.

Lignosulfonates and lignosulfonic acid may be fractionated, to provide various molecular weight fractions. In one classification, alpha-lignosulfonic acid has an average molecular weight of about 15,000, and beta-lignosulfonic acid has an average molecular weight of about 5000, for example. Other fractions are also offered by the pulp industry. Lignosulfonic acid obtained from sulfite pulping processes may vary somewhat as to degree of sulfonation, but commonly has about one sulfonic acid group for every two phenyl-propane units (sometimes expressed as about one sulfuric acid group for every two methoxyl groups), the acid being essentially water soluble even though it has a high molecular weight. This acid may usually be further sulfonated, or partially desulfonated, if desired, nad yet remain water soluble. The commonly available by-products of the sulfite process which contain lignosulfonic acid, or which contain lignosulfonates convertible to lignosulfonic acid, may be used in the practice of the invention. Various lignosulfonate products which may be converted to the acid form by an ion-exchange or like treatment are listed in the following table, together with descriptive information concerning the same.

I. *Lignosulfonate Products Convertible to Acid Form*

Product	Product name	Descriptive information
A	Norlig MC	Relatively crude, very low molecular weight (about 1,000), 60% calcium lignosulfonate, 3% reducing sugars and other organics and inorganics.
B	Norlig A	Relatively crude, very low molecular weight (about 1,000), calcium containing, with about 20% reducing sugars and some other matter including inorganics.
C	Marathon B 35 L	High purity (95%) sodium lignosulfonate, average molecular weight 1,000–1,500, sugar-free, 4.5% volatile acids, 0.5% sodium sulfate.
D	Marasperse C	Fractionated, higher molecular weight, sugar-free, sodium calcium and magnesium containing.
E	Marasperse N	Fractionated, higher molecular weight, sugar-free, sodium containing.
F	Marasperse CE	Fractionated, higher molecular weight, sugar-free, sodium and calcium containing.
G	Maracarb NC	Mixed lower molecular weight salts, sugar-free, calcium and sodium containing, and formate, acetate and lactate containing.
H	Bindarene Flour	70% calcium lignosulfonate, 20% sugars, 10% inorganics.
I	Goulac	A sulfite process lignosulfonate.
J	Glutrin	Do.

The products listed in Table I are available as powders (except for product J which is available in an aqueous solution). While the powders may contain as much as 5 to 8 percent moisture, the composition data are herein reported on a moisture-free basis. Further, all of these products, prior to conversion to the acid form, are either alkaline or insufficiently acid to be employed directly in the practice of the invention. They contain primarily, lignosulfonates rather than lignosulfonic acid. Product C was found to contain some chloride ions (presumably remaining from the purification process), and such ions are desirably precipitated out with silver sulfates, for example. Alternatively to the conversion of lignosulfonate, a suitable lignosulfonic acid product may be obtained directly as a digester strength sulfite spent liquor, such as Norlig 10% Solids—Unneutralized (hereinafter referred to as product K). It is not necessary for this acid product to undergo an ion-exchange or like treatment prior to use in accordance with the invention. Additional data on several of the commercial products mentioned are contained in Bulletin No. 130 and other data sheets of Marathon Division of American Can Company. Product H is described in the Bindarene Data Sheets of International Paper Company. Products I and J are sold by Robeson Process Company as core binders.

The lignosulfonic acid content of solutions employed as electrolytes in accordance with the invention may be a small amount, e.g., about 25 grams per liter. Somewhat higher lignosulfonic acid contents, preferably at least 60 grams per liter or more, impart greater electrolyte conductivity and are easier to control. Because the solution viscosity increases with total solids content, however, it is desirable to employ solutions with a total solids content of less than about one kilogram per liter, preferably less than 600 grams per liter. For production of colored coatings at or near room temperature, satisfactory results have been most readily obtained when the lignosulfonic acid content is about 60 to 500 grams per liter.

The sulfate content of the solutions employed as electrolytes may be small, e.g., about 3 grams per liter (total sulfate calcuated as H_2SO_4, including any sulfate content of the lignosulfonic acid product used). Somewhat higher sulfate contents, preferably at least 4 grams per liter or more, will ordinarily be employed, since the voltage requirements for the same anodizing current density (with consequent electrical equipment and electrolyte cooling cost factors to be considered) are reduced in such cases. However, an increase in the sulfate content tends

to reduce the depth of color obtained in the anodic coating. For the production of the most satisfactory colored coatings at or near room temperature, therefore, a sulfate content of less than 13 grams per liter is desirable. The sulfate content may conveniently be substantially all sulfuric acid, but an alkali metal or ammonium sulfate or bisulfate such as sodium sulfate, sodium bisulfate or ammonium bisulfate, a heavy metal sulfate or bisulfate such as ferrous sulfate, an organic sulfate or bisulfate such as aniline sulfate, or any other water soluble sulfate or bisulfate such as hydrazine sulfate may be used. Double sulfates may also be used.

While various proportions of lignosulfonic acid and sulfate may be used, it has been found that the production of uniform, colored coatings at or near room temperature is most readily obtained when the lignosulfonic acid content is greater than the sulfate content. However, electrolytes with higher amounts of sulfate than lignosulfonic acid are also useful. Generally, the higher the sulfate content the lighter the color obtained in the coatings. However, even with high sulfate containing electrolytes, abrasion resistant coatings are obtained at lower temperatures which need not, nevertheless, be as low as with sulfuric acid electrolytes devoid of lignosulfonic acid.

A specific example of electrolyte make up for use in accordance with the invention is as follows. First, a lignosulfonate product (such as product A of Table I) is dissolved in water, in a concentration of 200 grams (moisture-free basis) per liter, for example. If the dissolved product contains 60% calcium lignosulfonate (as reported for product A), such a solution contains 120 grams per liter of calcium lignosulfonate and 80 grams per liter of other solids. The solution is run through a cation-exchange column to replace metal ions with hydrogen ions. If the solid product (prior to ion-exchange) contained nearly 8% metal ions (as calculated for product A), removal of the metal ions produces an acid-containing solution having a dissolved solids content of about 185 grams per liter (see Table II). However, the lignosulfonic acid content thereof (from the calcium lignosulfonate) is smaller, i.e., about 110 grams per liter. To this solution, which may contain on the order of one gram per liter of sulfate carried over from the starting lignosulfonate product, 10 grams per liter of sulfuric acid may be added, producing a sulfate content of about 11 grams per liter, for example (see Table II).

II. *Electrolyte Compositions*

Acid form of product used	Grams per liter acid form of product (total, moisture-free basis)	Grams per liter sulfate (total)
A	185	11
B	270	8
C	265	10
D	85	8
E	70	8
F	65	6
G	160	6
H	210	6
I	200	10
J	190	10
K	100	8

In this table, the composition of each electrolyte example is given in grams per liter of two components providing a desired lignosulfonic acid content and a desired sulfate content, in aqueous solution. For each of electrolytes A through J, a correspondingly identified lignosulfonate product from Table I was used following an ion-exchange treatment to produce the acid form of such product as herein described. The indicated amount of each acid form of product is the total amount, on a moisture free basis, after adjustment for cation exchange (and after chloride ion removal, in the case of Electrolyte C, as described hereinbefore). For Electrolyte K, the lignosulfonic acid product K was used directly to pro-

vide approximately the indicated amount of dissolved lignosulfonic acid containing solids. For each electrolyte example sulfuric acid was added to produce the indicated sulfate content (total sulfate, calculated as H_2SO_4).

A specific example of an electrolyte suitable for producing a lightly colored coating at room temperature, or a darker colored coating at lower temperatures, e.g., 50° F., is one made up with 133 grams per liter of the acid form a product A, 60 grams per liter sulfuric acid, and water.

As indicated above, electrolytes for use in accordance with the invention may be employed under a wide variety of operating conditions. A temperature at or near room temperature, e.g., 75° F., may be employed. However, either extremely low temperatures or rather high temperatures may also be employed, i.e., temperatures between about 40 and 110° F. Very satisfactory results in producing colored coatings with Electrolyte A, for example, with a moderate amount of cooling being required, may be obtained with temperatures between about 60 and 90° F.

Current densities may extend over a wide range, for practical purposes as low as 9 amperes per square foot or even less, and as high as 144 amperes per square foot or even more, depending on size, shape and composition of the aluminum article. Preferably, the current density is between 12 and 36 amperes per square foot. The current may be either A.C. or D.C., or a current of undulating characteristics, but D.C. is quite satisfactory.

Time of treatment depends upon current density and thickness of coating desired, as coating thickness is generally a function of anodizing current density and time. Abrasion resistant coatings for outdoor service are often made in a thickness of 0.4 to 1 mil (0.0004 to 0.001 inch). However, coatings may be made in any substantial thickness desired, e.g., 0.1 mil or greater.

Illustrative of particularly suitable operating conditions, Electrolyte A above mentioned has been operated at 75° F., at 24 amperes per square foot, with voltages starting at about 30 volts and generally extending up to about 75 volts over a 30 minute period, depending on the composition of the aluminum being coated, to produce abrasion resistant, colored oxide coatings on a variety of aluminum articles. As examples of the colored coatings produced on various types of aluminum, it is noted that Electrolyte A, operated under the conditions just noted, for time sufficient to produce coatings about 1 mil thick, produced the following results as to color:

Aluminum or aluminum alloy designations	Nominal constituents, percent	Color of coating
1100	Normal impurities	Dull yellow tan.
6061–T6	0.6 Si, 0.3 Cu, 1 Mg, 0.25 Cr.	Dark gray bronze.
6063–T5	0.4 Si, 0.7 Mg	Medium bronze.
6463–T5 (higher purity than 6063).	0.4 Si, 0.7 Mg	Light metallic bronze.

Color stability of the colored coatings was very high when tested in the Fade-O-Meter after 1000 hours of exposure. Lighter and darker shades of these colors were obtained with thinner and thicker coatings, respectively. Similar resutls were obtained on 6061–T6 and 6063–T5 alloys with the other electrolytes above discussed.

As an example of the abrasion resistance of the coatings, a coating produced on 1100–H18 aluminum under the specific conditions immediately above discussed for Electrolyte A, exhibited an abrasion resistance valve of 490 grams per mil, as obtained by the ASTM D658–44 method of test.

Coatings produced in accordance with the invention may be sealed, or dyed or pigmented and sealed, by conventional procedures. Thus, dyes or pigments may be used to modify the colors produced by the anodizing methods described herein. Etching or brightening treatments may be given the aluminum surfaces prior to anodizing, when desired. Further the aluminum article treated may, of course, be composed of aluminum alone, or it may be an aluminum coated or clad product, a composite aluminum product, or any other form of product presenting an aluminum surface for anodizing.

What is claimed is:

1. A method of anodizing aluminum, comprising making an aluminum article anode in an electrolyte consisting essentially of
at least 25 grams per liter of lignosulfonic acid,
at least 3 grams per liter and less than 13 grams per liter of sulfate (calculated as H_2SO_4) provided by at least one compound selected from the group consisting of sulfuric acid and water soluble sulfates and bisulfates, and
water,
for a time sufficient to produce a colored anodic oxide coating of substantial thickness.

2. A method of anodizing aluminum, comprising making an aluminum article anode in an electrolyte consisting essentially of
at least 60 grams per liter of lignosulfonic acid,
at least 4 grams per liter and less than 13 grams per liter of sulfate (calculated as H_2SO_4) provided by at least one compound selected from the group consisting of sulfuric acid and water soluble sulfates and bisulfates, and
water,
for a time sufficient to produce a colored anodic oxide coating of substantial thickness.

3. A method in accordance with claim 1 in which the electrolyte is maintained at a temperature between about 40 and 110° F. and
the current density is maintained between about 9 and 144 amperes per square foot.

4. A method in accordance with claim 1 in which the amount of lignosulfonic acid is less than about 600 grams per liter.

5. A method of anodizing aluminum, comprising making an aluminum article anode in an electrolyte consisting essentially of
about 60 to 500 grams per liter of lignosulfonic acid,
about 4 to 13 grams per liter of sulfate (calculated as H_2SO_4) provided by at least one compound selected from the group consisting of sulfuric acid and water soluble sulfates and bisulfates, and
water,
while the electrolyte is maintained at a temperature of between about 60 to 90° F., and
the current density is maintained between about 12 and 36 amperes per square foot,
for a time of treatment sufficient to produce an anodic oxide coating at least 0.1 mil thick,
whereby a colored anodic oxide coating is produced on the surface of the aluminum article.

6. A method of anodizing aluminum, comprising making an aluminum article anode in an electrolyte consisting essentially of
about 60 to 500 grams per liter of lignosulfonic acid,
about 4 to 13 grams per liter of sulfuric acid, and
water,
while the electrolyte is maintained at a temperature of between about 60 and 90° F., and
the current density is maintained between about 12 and 36 amperes per square foot,
for a time of treatment sufficient to produce an anodic oxide coating at least 0.1 mil thick,
whereby a colored anodic oxide coating is produced on the surface of the aluminum article.

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