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ELECTROLYTE COMPOSITION AND PROCESS FOR EMPLOYING SAME

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This application is a continuation-in-part of my copending applications Serial Nos. 237,361 filed July 18, 1951, (now abandoned), and 297,985, filed July 9, 1952.

This invention relates to electrolytes, and is particularly concerned with a novel composition of matter and with electrolytes containing such composition and which are especially useful for the production of hard wear and corrosion resistant aluminum oxide films or coatings on aluminum and aluminum alloys by electrolytic oxidation of the aluminum and such alloys. The invention is also concerned with a process for production of oxide coatings on aluminum and its alloys employing such electrolytes.

Inasmuch as aluminum in its pure or alloyed state is a comparatively soft metal and extremely susceptible to corrosive action, an attempt has been made in the aircraft and other industries to give the metal a protective plating, or "hard coat." The hardest and most resistant coating to wear and to the corrosive action of atmospheres containing salt, smoke and corrosive acids is the oxide of aluminum corresponding to corundum (Al_2O_3). By processes already known to the industry this coating in limited thickness, may be applied to pure aluminum and some of its alloys. However, some of the most important aluminum alloys used in the aircraft and other industries have resisted all previously known processes for the successful application of a hard coating because of the higher percentages of alloying elements, e. g., copper and silicon, present in these alloys.

As is well known in this art, the anodic oxidation of aluminum to create oxide films in acid electrolytes, such as chromic acid, sulphuric acid, or oxalic acid now generally employed, is limited to the production of thin films of oxide. Such films may not practically be in excess of about .001" in thickness. The denseness of these films is also of moderate nature; being porous especially when approaching in thickness the dimension of .001". An additional limitation lies in the fact that the processes of the prior art are limited in their application to certain only of the aluminum alloys. Thus it has been reported that alloys containing zinc or high percentages of copper and silicon will not produce dense coatings of uniform thickness by such prior art processes.

The process of my invention employing the electrolyte hereof, is capable of making thicker, denser and harder oxide coatings on aluminum and aluminus alloys than prior art processes known to me, and also produces thick, dense, hard oxide coatings on aluminum alloys which prior art processes are incapable of coating. Improved bonding of the oxide coating to the metal is also obtained, and the coating is deposited more rapidly than heretofore.

An objection of this invention is the provision of a novel composition of matter of particular use in electrolytes.

Another object is the provision of a process for the preparation of such a composition.

Another object of this invention is to provide novel

electrolytes, particularly aqueous acidic solutions for use in electrolytic oxidation of aluminum and its alloys to produce a protective oxide coating thereon.

Still another aim of the invention is to afford procedure for applying a tough, hard wear resistant oxide coating on aluminum and its alloys by electrolytic oxidation employing the foregoing aqueous acidic solutions as electrolytes.

Another object is to produce such coatings on aluminum alloys containing substantial amounts of copper and/or silicon.

A still further object is to afford a process providing a hard coating on aluminum and its alloys, which are highly resistant to the corrosive action of atmospheres containing salt, smoke and acids.

Other objects and advantages of the invention will be apparent from the following description of my invention.

I have discovered a novel composition in the form of an aqueous extract of brown or low grade coal, lignite or peat, which can be obtained by extracting brown or low grade coal, lignite or peat obtained from various localities, with water. The extraction is particularly made more rapid and yield is increased by extraction at elevated temperature, preferably the atmospheric boiling point of the mixture or more elevated temperature, e. g. up to 290° F. or higher, and most desirably by extraction at elevated temperature under pressure for a period sufficient to produce an aqueous acid solution. I have found peat to be partcularly suitable for this purpose and this is the preferred raw material. The peat used in practice of my invention may be derived from various locations in the United States, for example, from Georgia, Florida, Californit or Michigan.

In practice, the starting material, e. g., lignite or Georgia peat is first mixed with water in a proportion of say one part by weight of the ground, flaked or fibrous lignite, peat or brown or low grade coal with, for example, six parts of water. These proportions may vary, however. This aqueous mixture is then fed to an autoclave where high extraction temperatures are desired for practical reasons and wherein the mixture is cooked at autogenous 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 brown coal, peat or lignite at temperatures between about 250° F. and about 350° F. and at pressures between about 10 and about 140 p. s. i. gage for from about 6 to say 50 hours or more, the time required to process the organic starting material being less as the temperature and pressure are increased.

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 brown coal, lignite or peat at atmospheric pressure over an extended period of say 24 hours.

After an extraction the undissolved residue may be separated from the extract.

In accordance with the invention I add the aqueous extract of brown coal, peat or lignite to sulphuric, chromic or oxalic acid, or mixtures thereof. The latter acids are considered equivalents for the anodic oxidation of aluminum and its alloys, and are termed electro-anodizing acids herein. Other acids in addition to sulphuric, oxalic and chromic 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 have obtained denser, harder and thicker oxide coatings employing my extract according to the invention than heretofore obtainable using aqueous acid solutions without my ex-

tract additive. Also the aqueous extract-containing electrolyte of my invention has the important advantage of permitting formation of protective oxide coatings on a wide variety of aluminum alloys, particularly high silicon or copper alloys of aluminum containing, for example, as much at 4% copper or more, when employed in the electroyltic oxidation process, whereas commercial oxide coatings on such alloys have not been possible in the prior art.

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 sulphuric acid, chromic acid, or oxalic acid or mixture thereof. Thus, I may use up to say about 70% H_2SO_4 in the electrolyte, but I prefer to use dilute H_2SO_4 in an amount corresponding to a range of from about 1 part to 20 parts by volume of concentrated (100%) sulphuric acid dissolved in 100 parts by volume of water. For example, I may employ an amount of H_2SO_4 in the electrolyte corresponding to from about 5 to 7% by volume of 66 Baumé sulphuric acid per 100 parts by volume of water. I generally add to this bath from 1 to 6 parts, preferably about 3 to about 6 parts, by volume of the aqueous extract of brown coal, lignite or peat per 100 parts by volume of water in the electro-anodizing acid solution. It is understood, however, that these proportions are not critical and may be varied.

The electrolytic oxidation of aluminum and its alloys to produce an oxide coating thereon is carried out according to the invention by cleaning the aluminum or aluminum alloy article to be coated and making it the anode of an electrolytic cell which may be in the form of a stainless steel case which acts as the cathode, the cell containing as electrolyte an aqueous electro-anodizing acid solution including my extract. Sufficient voltage and current density is applied to the cell for a period of time varying from 1 to 120 minutes depending on the thickness and hardness of coat desired. The coated aluminum or aluminum alloy article is then removed from the electrolyte, rinsed in clear water and drain dried.

I may operate my process at the relatively low temperatures conventionally used in oxidation of the aluminum and aluminum alloys, using the conventional electro-anodizing acids as employed in the prior art as described above, and obtain the previously noted improvements by the addition thereto of the extracts described above. I may employ temperatures in the range of about 10° F. to about 70° F., but prefer to use as low temperatures as convenient, for example, about 20° F. to about 30° F.

The following are examples illustrating preparation of my extract and novel electrolytes containing such extract for the formation of oxide coatings on aluminum and aluminum alloys, and also illustrating the application of such electrolytes in my electrolytic oxidation process.

Example 1

An aqueous extract of the preferred starting material, peat, for use in the invention, can be produced as follows:

One part by volume of Georgia peat ground and mixed is added to 5 parts of water, and the resulting mixture is cooked at 20 lbs. gage pressure for 48 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 upon the amount of dilution of the material. The extract upon evaporation to dryness forms a dark brown, glossy residue which is amorphous and has a total nitrogen content of about 4.5 to 5%, for example, 4.8% as determined by the Kjeldahl method. The extract solids are essentially water soluble and form a clear dark brown solution or dispersion. The aqueous extract is preferably kept refrigerated or a fungicidal material such as 2% by volume of 66 Baumé H_2SO_4 is added.

Example 2

One part by weight of ground peat is mixed with six parts of water and the mixture is fed to an autoclave. The mixture is cooked therein at about 290° F. and at autogenous pressure for six hours. The liquid is decanted and forms an acidic aqueous extract containing complex organic acids, and having a pH of about 4.5 to about 5.5.

Example 3

A .002 inch tough hard coating of oxide of aluminum can be produced on the high copper alloy of aluminum designated 24S and containing about 4.5% copper, by applying a 44 to 48 ampere per square foot current density for 20 minutes to a part formed from such alloy and submerged as the anode in an electrolyte composed of 1.25% by volume of the aqueous extract of Example 2 added to 12% by volume of 100% sulphuric acid in water solution, the temperature of the electrolyte being maintained between about 20° F. and about 30° F. The coating of oxide of aluminum thus formed will resist 40,000 revolutions of Taber abraser #17 wheels, a standard abrasion testing device, without noticeable effect on the coating. A conventional chromic acid anodize coating on 24S alloy obtained employing an electrolyte not containing the aqueous extract of the invention, fails at 100 revolutions in a similar test, and a conventional hard chrome electroplate coating of .0015" thickness on 24S alloy similarly tested fails at 1000 revolutions, failure being considered any visual destruction of the coating.

Example 4

In using lignite extract, the extract is formed by the process of Example 1 or 2, substituting ground lignite for the peat and employing the extract in the manner set forth in Example 3.

Example 5

A hard, tough coating of oxide of aluminum is formed on a part composed of a high copper, silicon alloy of aluminum designated as 14S, and containing about 4.4% copper and about 0.8% silicon, by subjecting the clean alloy part to 10 volts of direct current for one minute and then to 80 volts of direct current for 20 minutes while the part is immersed as anode in an agitated bath in the form of an aqueous solution consisting of 10% by weight of sulphuric acid and 3% by volume of such solution, of the aqueous extract of Example 1 or Example 2.

I have found that my process is applicable to aluminum and to a wide variety of aluminum alloys containing copper, silicon and other metals such as zinc and nickel. The following are examples of such alloys in addition to 14S and 24S noted above:

Alloy Designation	Composition
356S	92.7% Al, 7% Si, .3% Mn.
142	92.5% Al, 4% Cu, 2% Ni, 1.5% Mn.
75S	90% Al, 1.6% Cu, 2.5% Mn, 5.6% Zn, 0.3% Cr.

The omission of the extract from the electrolyte bath and employment only of H_2SO_4 or other electro-anodizing acid does not produce coatings of comparable hardness, density and thickness as is obtained by the addition of the foregoing extract to such baths. By employing the aqueous extract as an additive to the anodizing electro-

lyte bath, I may obtain oxide coating thicknesses up to and above .002 inch.

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.

I claim:

1. A novel composition of matter: an acidic extract of a substance chosen from the group consisting of low grade coal, lignite and peat, said extract being obtained by cooking a mixture of said substance with water at a temperature of from about the boiling point of said mixture at atmospheric pressure to about 350° F.

2. A composition of matter as set forth in claim 1, and wherein said cooking temperature is from about the boiling point of the mixture at atmospheric pressure to about 290° F.

3. A composition of matter as set forth in claim 2, and wherein said substance is peat.

4. A composition of matter as set forth in claim 1, and wherein said cooking is carried out at superatmospheric pressure.

5. A composition of matter as set forth in claim 1, and wherein said substance is peat.

6. A composition of matter as set forth in claim 5, and wherein said cooking is had for a period of at least 48 hours.

7. An electrolyte composition of matter consisting essentially of an aqueous solution of an electro-anodizing acid and an acidic extract of a substance chosen from the group consisting of low grade coal, lignite, and peat, said extract being obtained by cooking a mixture of said substance with water at a temperature of from about the boiling point of said mixture at atmospheric pressure to about 350° F.

8. A composition of matter as defined in claim 7, and wherein said cooking temperature is from about the boiling point of said mixture at atmospheric pressure to about 290° F.

9. A composition of matter as defined in claim 8, and wherein said electro-anodizing acid is sulfuric acid.

10. A composition of matter as defined in claim 8, and wherein said substance is peat.

11. A composition of matter as defined in claim 10, and wherein said electro-anodizing acid is sulfuric acid.

12. A composition of matter as defined in claim 7, and wherein said cooking is had at superatmospheric pressure.

13. A composition of matter as defined in claim 12, and wherein said electro-anodizing acid is sulfuric acid.

14. A composition of matter as set forth in claim 12, and wherein said substance is peat.

15. A composition of matter as set forth in claim 14, wherein said electro-anodizing acid is sulfuric acid, and said cooking is had for a period of at least 48 hours.

16. A process of coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum which comprises passing an electric current through an electrolytic cell with said article forming the anode, and containing an electrolyte consisting essentially of an aqueous solution of an electro-anodizing acid and an acidic extract of a substance chosen from the group consisting of low grade coal, lignite and peat, said extract being obtained by cooking a mixture of said substance with water at a temperature of from about the boiling point of said mixture at atmospheric pressure to about 350° F.

17. A process as set forth in claim 16, and wherein the cooking temperature is from about the boiling point of said mixture at atmospheric pressure to about 290° F.

18. A process as set forth in claim 17, and wherein said electro-anodizing acid is sulfuric acid.

19. A process as set forth in claim 17, and wherein said substance is peat.

20. A process as set forth in claim 19, and wherein said electro-anodizing acid is sulfuric acid.

21. A process as set forth in claim 16, and wherein said electro-anodizing acid is sulfuric acid and said cooking is had at superatmospheric pressure.

22. A process as set forth in claim 21, wherein said substance is peat.

23. A process as set forth in claim 22, and wherein said cooking is had for a period of at least 48 hours.

24. A composition of matter as defined in claim 7, and wherein said substance is peat.

25. A composition of matter as defined in claim 7, and wherein said electro-anodizing acid is sulfuric acid and said substance is peat.

26. A composition of matter as defined in claim 7, and wherein said electro-anodizing acid is sulfuric acid, said substance is peat, and said cooking is had at superatmospheric pressure.

27. A process as set forth in claim 16, and wherein said substance is peat.

28. A process as set forth in claim 27, and wherein said electro-anodizing acid is sulfuric acid.

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