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ANODIC OXIDATION OF ALUMINUM

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This invention relates to the surface treatment of aluminum and aluminum alloys and more particularly to the electrolytic formation thereon of a coating layer mainly comprising oxides.

This application is a continuation in part of my co-pending application, now abandoned, Serial No. 607,267, filed July 26, 1945.

The invention of the applicant provides for the formation on aluminum and aluminum articles of a substantial coating which is mostly oxide and which protects the articles from corrosive agents, which acts as an electrical and thermal insulation, which forms a base for the application of paints, oils, and varnishes, and which serves many other functions.

In addition, the instant invention enables such a coating to be obtained in a much shorter length of time than obtainable by previously-known methods, processes, and apparatus.

Furthermore, by the practice of the instant invention, such a coating may be deposited with a high degree of regularity and control.

The coating obtained by use of the applicant's invention has superior qualities of flexibility, adsorbtion, and electrical insulation.

With the foregoing and other objects in view which will appear as the description proceeds, the invention resides in the methods, processes, and compositions used therein and hereinafter described and claimed, it being understood that changes in the precise embodiment of the invention herein disclosed may be made without departing from the spirit of the invention.

The general characteristics of oxide coatings on aluminum and aluminum alloy articles are well known, and they are greatly used for protecting the surface of such articles against attack by corrosive and solvent agents, for insulating the articles thermally and electrically, and for backing layers for impregnation, etc. In the past, such coatings have been produced by treating the metal in a sulphuric acid bath and with salts of sulphuric acid. The expression "sulphuric bath" will be employed hereinafter to designate baths containing sulphuric acid or a mixture of said acid with the salts thereof. The above-recited treatment requires an extremely long time because of the high resistivity of such prior-art baths, which makes high current densities impractical, because they would cause the coating to be re-dissolved as fast as it was formed. Furthermore, it has been generally recognized that the addition of traces of halides to the sulphuric bath inhibits the formation of an oxide coating, and, in fact, may even cause partial or total dissolution of the layer. Furthermore, sulphuric baths containing halides are commonly used with direct current as electrolytic pickling baths for aluminum and its alloys.

The applicant has discovered the surprising

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fact that by adding to a sulphuric bath a certain amount of one or more compounds, selected from the class consisting of alkali and alkaline-earth chlorides, bromides, and iodides, and hydrochloric, hydrobromic, and hydroiodic acids, and by using high current densities in alternating or pulsating current having a negative wave component and a positive wave component, an oxide coating forms with a high degree of regularity which coating has remarkable characteristics of flexibility, adsorption, and electrical insulation. Generally speaking, the bath used in the practice of the instant invention is an electrolyte containing from 3% to 70% by weight of sulphuric acid with the addition of such amounts of one or more of the compounds selected from the class consisting of alkali chlorides, bromides, and iodides, alkali-earth chlorides, bromides, and iodides, hydrochloric, hydrobromic, and hydroiodic acids as to obtain such a bath wherein the concentration of the halogen elements themselves is within the range of 0.1% to 20% by weight. Mixtures of the salts and acids recited as in the above class may be used in proportions consistent with their solubility in the sulphuric bath. The most desirable proportions are those in which the ratio by weight of sulphuric acid to the amount of the combined halogen elements is in the range which extends from 6 to 60.

For example, if the bath, according to the invention, contains KCl, HCl, NaBr, and CaI_2, the total Cl, Br, and I should be from 0.1% to 20% by weight of the entire bath, and, preferably, the ratio of H_2SO_4 to the total of Cl, Br, and I should be in the range from 6 to 60. This and following examples are in no way restrictive, and are merely given to indicate more clearly how the invention may be applied to any conceivable mixture of the alkali and alkaline-earth metal salts of HCl, HBr, and HI, and the acids themselves.

The bath prepared according to the above recitation has a low electrical resistivity, whereby high current densities may be used. The amount of oxide coating formed will be about the same as for an equivalent amount of electrical power expended in the conventional sulphuric bath, so that the result is that, for an equal thickness of coating, the time of treatment by use of the applicant's invention will be very much shorter than by use of previously-known techniques.

The anodic oxidation of aluminum articles according to the applicant's invention should be carried out under the following general conditions: the bath temperature should be within the range from 15° C. to 25° C., the electrical current used should be alternating or pulsating and comprise, in any case, both a negative and a positive component, of a frequency similar to that used in industrial applications, the voltage of

the current used should be from 10 to 25 volts. In addition, the current density may be in the range from 14 to 300 R. M. S. amps./sq. dm. when alternating current is used, and, when pulsating current is used, the alternating component density may be in the range from 14 to 250 R. M. S. amps./sq. dm. and the superposed direct current density from 5 to 70 amps./sq. dm. The treatment time under the above conditions may be anywhere from 20 seconds to 2 minutes.

As in previously-known procedures for the production of an oxide coating or other surface treatment of the surface of aluminum and aluminum alloy articles, the article is first subjected to a surface conditioning process intended to confer on it an attractive or artistic quality or to bring about other desirable properties such as high reflective power, or deep pitting to enable subsequent coatings or plating to better grip the surface. To that end, the articles may be buffed, brushed, sand-blasted, or pickled, depending on the final effect that must be achieved. The article is next carefully cleaned to remove any dirt, polishing residue, or the like which may have been retained from previous steps, or from storage. The article is then thoroughly degreased by any suitable method such as electrolytic de-greasing, or by immersion in an alkaline bath (soda or hot or cold carbonate of soda, etc.) and then the article is ready for treatment according to the instant invention.

It is customary in treating articles by this general method to suspend the article in the electrolyte and make it an electrode in the electrolytic action by connecting it to one pole of the power source; if pulsating alternating-current is used, the article is connected to the positive pole of the source of the direct-current component.

To bring out clearly the advantages to be obtained from the practice of the applicant's invention, the data given below enables a direct comparison of the techniques under the previously-known systems with that of the applicant.

Example I (ordinary sulphuric bath)

An ordinary sulphuric bath contained 20% by weight of sulphuric acid and was operated at 23° C. The alternating current density for anodic oxidation was from 1 to 1.5 R. M. S. amps./sq. dm. The operation was carried on for 30 minutes. The oxide coating obtained a thickness of 8 microns.

Example II (according to applicant's invention)

Bath contained:

	Percent by weight
Sulphuric acid	30.7
Sodium chloride	1.67
Potassium chloride	0.63
Magnesium chloride	0.042

and the remainder water.

In the above electrolytic bath, there is a total of 1.36% Cl, with a ratio of H_2SO_4 to Cl of 22.6. The bath was operated at a temperature of 23° C. with an alternating current voltage of 12 volts and a current density of 180 R. M. S. amps./sq. dm. The operation was continued for 30 seconds. The resulting oxide coat had a thickness of 8 microns.

Example III (according to the applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	20
Magnesium chloride	3.5

and the remainder water.

This means that the Cl content was 2.6% and the ratio of H_2SO_4 to Cl was 7.7. The bath was used at a temperature of 20° C. with an alternating current density of 150 R. M. S. amps./sq. dm. The operation was allowed to proceed for from 30 to 45 seconds. The oxide coating obtained had a thickness of 5 to 6 microns and had a breaking voltage of 120 volts.

Example IV (according to applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	20
Magnesium chloride	3.5

and the remainder water.

This meant that the Cl content was 2.6% and the ratio of H_2SO_4 to Cl was 7.7. The bath temperature was 20° C. and a pulsating current was used having an alternating current density of 150 R. M. S. amps./sq. dm. and a direct current density of 30 amps./sq. dm. The operation was allowed to proceed for from 30 to 45 seconds. The obtained oxide coating had a thickness of 8 microns and a breaking voltage of 160 to 180 volts.

Example V (according to applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	70
Sodium chloride	15

and the remainder water.

In this bath, there was 9.1% Cl and the ratio of H_2SO_4 to Cl was 7.7. The bath was operated under alternating current density of 200 R. M. S. amps./sq. dm. and the treatment was allowed to continue for 20 to 30 seconds with excellent results.

Example VI (according to applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	20
Hydrochloric acid	0.4

and the remainder was water.

This amounts to 0.39% Cl and a ratio of H_2SO_4 to Cl of 51.3. The bath was used with an alternating current density of 27 R. M. S. amps./sq. dm. at the start of the oxidation and 16 R. M. S. amps./sq. dm. toward the end of the oxidation, with a voltage of 12 at the beginning and 20 at the end. The operation was allowed to proceed for 90 seconds with excellent results.

Example VII (according to applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	15
Magnesium chloride	3

and the remainder water.

This bath contained, therefore, 2.25% Cl and had a ratio of H_2SO_4 to Cl of 6.7. The bath was used at 20° C. with an alternating current density of 100 R. M. S. amps./sq. dm. Excellent results were obtained in from 1 to 2 minutes of operation.

Example VIII (according to applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	20
Magnesium bromide	3

and the remainder water.

This amounts to 2.6% Br and a ratio of H_2SO_4 to Br of 7.7. The bath was used at 20° C. with an alternating current density of 45 R. M. S. amps./sq. dm. under a voltage of 12.5 volts. The operation was allowed to proceed for 50 seconds and the oxide coating produced then had a breaking voltage of 45 volts. When the time of treatment was increased to 2 minutes and 30 seconds, the characteristics of the coating were enhanced, so that its breaking voltage was 130 volts.

Example IX (according to applicant's invention)

The bath contained:

	Percent by weight
Sulphuric acid	20
Potassium iodide	1.5

and the remainder water.

This meant that the I content was 1.15% and the ratio of H_2SO_4 to I was 17.4. The bath was operated at 20° C. with an alternating current density of 45 R. M. S. amps./sq. dm. and a voltage of 16 to 17 volts. At the end of 2 minutes and 30 seconds, a coat was obtained which showed a breaking voltage of 50 volts.

In addition to the above examples, an aluminum alloy containing 0.36% Fe, 0.63% Si, 4.25% Cu, 0.66% Mg, and 0.66% Mn was oxidized by the practice of the invention of the applicant and an oxide layer was obtained which had a breaking voltage of 130 volts. Also, a breaking voltage of 150 volts was obtained on an alloy containing 0.28% Fe, 0.20% Si, 2.93% Mg, and 0.46% Mn, and in both cases the treatment lasted only 60 seconds.

Several other aluminum alloys containing 90% or more of aluminum can be oxidized in this way and particularly good results are obtained when the alloy contains copper or magnesium or both of these metals.

For a given thickness, the coatings obtained by the practice of the instant invention are much more flexible than those obtained by previously-known methods. Such greater flexibility is a distinct advantage in connection with electrical insulation for aluminum or aluminum alloy wires. In addition, the coatings of the invention are easier to dye. At the same time, all the other physical and chemical characteristics of the applicant's coatings are at least as desirable as those of similar layers obtained by use of straight sulphuric baths and the like. For instance, it has been found that the breaking voltages in wire conductors respectively treated in both types of baths and under the conditions recited in the above examples equal:

90 to 100 volts for the ordinary sulphuric bath, and 120 to 200 volts for baths following Example II, III, and IV, say, and following the teaching of the applicant.

Furthermore, the oxide coatings produced by the practice of the applicant's invention are particularly adaptable to being subjected to any of the known improving or conditioning treatments, such as filling in boiling water, oxidizing salts, hydrolysable metal salts, etc., as well as impregnation with waxes, oils, varnishes, and the like, and various heat treatments.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A method for the electrolytic superficial oxidation of aluminum and alloys containing at least 90% aluminum which consists in immersing the article to be oxidized in a bath through which is passed an electrical current having an alternating component, said bath containing sulphuric acid and at least one compound selected from the class consisting of alkali metal chlorides, bromides, and iodides, alkaline-earth metal chlorides, bromides, and iodides, and hydrochloric, hydrobromic, and hydroiodic acid in such proportions that the total content of halogen elements in said bath is in the range from 0.1% to 20% by weight.

2. A method of providing aluminum and alloys containing at least 90% of aluminum with a coating of oxide consisting in subjecting the article to be coated to immersion in a bath through which passes an electric current having an alternating component, said bath containing from 3 to 70% sulphuric acid by weight, at least one compound selected from the class consisting of alkali metal chlorides, bromides, and iodides, alkaline-earth metal chlorides, bromides, and iodides, and hydrochloric, hydrobromic and hydroiodic acid in such proportions that the total content of halogen elements in said bath is in the range from 0.1% to 20% by weight, and the remainder made up of water.

3. A method of producing by electrolytic oxidation a very flexible insulating oxide coating on articles formed of aluminum and alloys of aluminum containing at least 90% aluminum comprising the steps of immersing the article to be coated in an aqueous bath containing 3 to 70% by weight of sulphuric acid and at least one compound selected from the class consisting of alkali metal chlorides, bromides and iodides, alkaline-earth metal chlorides, bromides and iodides, hydrochloric, hydrobromic and hydroiodic acid in such amount that there be 0.1 to 20% by weight of halogen in the bath, and passing through the bath an electric current having an alternating component, the article forming the anode.

4. A method as recited in claim 3 wherein the bath is maintained at a temperature in the range from 15 to 25 degrees C.

5. A method as recited in claim 3 wherein the voltage is maintained in the range from 10 to 25 volts.

6. A method as recited in claim 3 wherein the current has an alternating current density of from 14 to 250 R. M. S. amperes per square decimeter, a direct current density of from 5 to 70 amperes per square decimeter and a voltage of from 10 to 25 volts.

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