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METHOD OF PROTECTIVELY COATING ALUMINUM OR ALUMINUM ALLOYS

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This invention relates broadly to a method of protectively coating aluminum or aluminum alloys. More particularly, the invention is concerned with, and has as a main object to provide a hard, dense, wear- and corrosion-resistant, tenaciously adhering, electrically insulating protective covering for surfaces of aluminum and aluminum base alloys, hereinafter for brevity collectively designated as aluminum. In accordance with this invention a coating of the kind described is produced by first forming a permeable or porous aluminum oxide deposit on clean aluminum, preferably, although not necessarily, by electrolytically treating such aluminum in a bath of a dibasic organic acid compound such as oxalic acid. The oxide-coated aluminum is then electrolytically treated in a solution of alkali-metal silicate, for example, sodium or potassium silicate, to form the protective coating of this invention.

Prior to our invention aluminum oxide coatings have been formed on aluminum by electrolyzing a solution of oxalic acid in contact with aluminum. It also has been known that aluminum surfaces may be rendered corrosion-resistant by anodically oxidizing such surfaces in an electrolyte to form a porous coating of aluminum oxide and subsequently impregnating such an oxide coating with soluble silicate, for example, with sodium or potassium silicate, by immersion in a hot solution of such silicate.

Single- or multiple-layered coatings of aluminum oxide, or coatings comprising aluminum oxide impregnated with a soluble silicate, have been only partly satisfactory in meeting the various service requirements of such films. In other words, they have not had the combined properties of hardness, mechanical strength, adhesiveness, corrosion resistance and insulating value to and in the degree that such coatings must possess in order to meet fully all kinds of service conditions. The present invention, on the other hand, provides an improved coating that is able to meet satisfactorily the widest variety of service requirements.

For a consideration of what is believed to be novel and the invention, attention is directed to the following specification and to the claims appended thereto.

In carrying our invention into effect the aluminum article to be coated is first subjected to a cleansing operation in order to free the surfaces of substances that would, or might, interfere with the efficient formation of the desired coating. Any suitable means for eliminating films of grease, impermeable aluminum oxide, and other undesirable ingredients and impurities from the starting aluminum material may be employed. Advantageously, however, this cleansing treatment comprises immersing the aluminum article in a hot solution of sodium hydroxide containing, for example, from about 1 to 20 per cent by weight of NaOH, preferably containing from about 3 to 5 per cent of NaOH. The time of dipping is carefully controlled by the operator and is stopped when the surface of the aluminum has been freed of grease film.

After washing with water to remove excess alkali the article is dipped in a dilute acid solution, preferably in dilute nitric acid, and advantageously in a bath comprising nitric acid and ammonium sulphocyanate, the latter serving to improve the efficiency of the treatment. The acid dip is for the purpose of removing from the aluminum surface other impurities, for example, metallic impurities that are not removed by a preceding treatment such as the sodium hydroxide treatment above-described. An acid bath of any suitable concentration may be employed, but preferably one containing less than about 20 per cent by weight of acid, for instance about 10 per cent, is used. If desired, other mineral acids such as hydrochloric acid may be utilized. After treatment in an acid bath, the article is water washed to remove excess acid and adhering acid-soluble impurities. If pure aluminum is being coated, its treatment in an acid bath is often not necessary.

The cleansing treatment has a beneficial effect in obtaining the hard, dense, wear- and corrosion-resistant, tenaciously adhering insulating coating of this invention.

The clean aluminum surface is now ready for the deposition of a coating of porous aluminum oxide thereon. Such a coating may be formed by immersing the aluminum article in a hot solution of sodium carbonate and alkali chromate for a short period of time. Another method comprises anodically treating the aluminum in an electrolyte such as sulfuric or chromic acids in aqueous solutions, or in a sulfuric acid-dibasic organic electrolyte of any suitable concentration (for example, an electrolyte containing from about 1 to 15 per cent by weight of sulfuric acid and about 1 to 10 per cent by weight of a dibasic organic acid such as oxalic acid), using aluminum, lead or other suitable metal as the cathode. We prefer, however, to form the aluminum oxide coating by electrolysis in an aqueous bath containing a dibasic organic acid such as oxalic, malonic, suc-

cinic, maleic, malic, and the like, or water-soluble salts of such acids such, for instance, as sodium or potassium oxalate or malonate, since coatings so formed are not only permeable, but also are harder than oxide coatings otherwise prepared. Advantageously oxalic acid is used and the process of forming the aluminum oxide coating is, for example, as follows:

An aqueous bath is prepared by dissolving about 3 parts by weight of oxalic acid in 97 parts by weight of distilled water. The bath is placed in an aluminum receptacle which serves both as the cathode and as a container for the bath. To cool the bath during electrolysis the aluminum receptacle is either jacketed and cooling water passed therethrough, or it is partly submerged in a water bath. The aluminum articles to be coated serve as the anode. Maximum rapidity in coating consistent with homogeneousness of film is obtained under working voltages of 60 to 70 volts (direct current) and at bath temperatures below about 50° C., preferably below about 40° C., for instance at about 30° C. Working voltages above 70 volts, for example, as high as about 90 to 100 volts, may be employed if the bath is cooled to the temperatures just mentioned. Artificial refrigeration may be used, if necessary, to keep down the temperature. The temperature of the bath is a matter of importance, since the lower the temperature the harder is the resultant film. The strength of the oxalic acid bath may be varied over a substantial range, for example between about 1 and 10 per cent, without detrimentally affecting the results.

Table I shows the results of coating five pieces of commercial hard aluminum, 1 inch by 1 inch by ⅛ inch, in a 3 per cent oxalic acid solution under a working voltage of 70 volts and at a temperature not exceeding 30° C. The aluminum article was the anode and an aluminum container for the bath, the cathode. Time of exposure of the aluminum to electrolysis was as shown:

Table I

Sample No.	Time of exposure to electrolysis in minutes	Average of breakdown tests, 60 cycles, in volts
1	30	1796
2	45	1875
3	60	1763
4	90	1707
5	120	2150

When starting the plating of these samples the current inrush was off the meter when 70 volts was first applied, but dropped to approximately 4 amperes after about 2 seconds and remained constant in proportion to the cathode area thereafter. The resultant ovide coatings were porous. They varied in color from light grey for coatings produced by the shorter periods of electrolysis to bluish-white for coatings produced by prolonged electrolysis.

The aluminum article, coated with a film of aluminum oxide integral with the surface of the said article, is water washed. It is then placed in an electrolytic bath comprising an aqueous solution of an alkali-metal silicate such as sodium silicate. Most practically satisfactory results are obtained if the silica to soda (SiO_2 to Na_2O) ratio, in the sodium silicate used, is not less than about 2:1 and, preferably, above about 2.7:1, for example between about 2.8:1 to 4:1, since it is definitely advantageous and desirable to introduce, that is, to pack by the process hereinafter more fully described, a maximum amount of silica into the coating. Thus, commercial sodium silicates that have silica to soda (SiO_2 to Na_2O) ratios of about 2.8:1, 3.3:1 and 3.9:1 may be employed satisfactorily in practicing this invention. The concentration of the solution may be varied within wide limits, for example, from very dilute solutions containing by weight as little as about 2 to 3 per cent alkali-metal silicate to concentrated solutions containing as much as about 30 to 40 per cent silicate. Advantageously an aqueous solution comprising from about 15 to 25 per cent by weight of sodium silicate in which the ratio of silica to soda (SiO_2 to Na_2O) is not less than about 2:1 is used. The oxide-coated aluminum is subjected to electrolysis in the silicate solution using, for example, an iron cathode. The aluminum article serves as the anode. The voltage (direct current) is raised gradually, that is, in steps, above about 60 volts, for example to about 250 volts. Within about 5 to 15 minutes the current flow drops to zero and the operation is completed. For the production of films of increased insulating value, a voltage as high as about 800 volts may be used if desired.

Table II shows the results of the anodic treatment of the five oxide-coated samples shown in Table I in a 20 per cent sodium silicate solution at a starting voltage of about 60 volts and a maximum voltage of about 250 volts (direct current).

Table II

Sample No.	Time of exposure to electrolysis	Average of breakdown tests, 60 cycles, in volts
1	Within about 15 minutes current flow was reduced to zero and operation was completed.	1650
2		1825
3		1762
4		1944
5		2001

By the process of forming a film or covering on an aluminum surface hereinbefore described, a hard, dense coating is obtained that is highly resistant to corrosion and abrasion, of good electrical insulating properties, and one that adheres very tenaciously to the underlying aluminum surface.

The formation of this film probably takes place in some such manner as the following:

In the anodic treatment of an aluminum article in a solution of sodium silicate, the action of the current is to cause enrichment of the anolyte in silicic acid and impoverishment of it in the base, Na_2O, thus bringing about a change in the alkaline silicate environment in the direction of a more acid silicate. In other words, the positively charged sodium ions migrate toward the cathode and the negatively charged silica ions toward the anode. Since the solution is not agitated the silica-ion concentration at the anode surface soon reaches a point at which the sol is no longer stable, and a thin transparent film of silica gel is formed. As this gel is porous, contact can be maintained through it and the main body of electrolyte. Bearing in mind that the anode is aluminum, that the oxide coating is porous, and that the aluminum is attacked in varying degrees by sodium silicates of varying silica to soda (SiO_2 to Na_2O) ratios, even by those having a silica to soda (SiO_2 to Na_2O) ratio of 4.2:1, one would expect an action such as aforedescribed to be accompanied with some attack of the metal.

Examination of samples of non-oxide-coated aluminum anodized in sodium silicate solution supports such hypothesis. Attack of the aluminum surface is evident from a visual examination of the sample, and an extremely thin silicate film can also be demonstrated chemically. Tests show the presence of no water-soluble alkaline silicate. That the film formed by anodizing oxide-coated aluminum in sodium silicate solution is at least mainly aluminum silicate, and not simply a film of substantially pure silica or a high ratio silica-soda (SiO_2–Na_2O) gel, may reasonably be deduced from the fact that the evident attack of the metal must have formed soluble sodium aluminate, and that this must have reacted at once with the sodium silicate present to form insoluble aluminum silicate. This mechanism of reaction, and not the direct union of free or colloidal silicic acid and aluminum oxide, is to be assumed because no such action of free silicic acid in solution is known except with very powerful bases, and even then it is slow. It is important further to note that a film formed by anodizing non-oxide-coated aluminum in sodium silicate solution, although very dense, is poorly adherent and easily abraded.

Since coatings produced in accordance with this invention have physical properties so strikingly different from coatings produced by merely anodizing non-oxide-coated aluminum in alakli-metal silicate solution or by mere immersion of oxide-coated aluminum in such solution, the difference in properties must be due to the anodic treatment of the oxide-coated aluminum in a solution of alkali-metal silicate. As indicated hereinbefore, the effect of electrolysis apparently is (1) the increased formation of aluminum silicate in the oxide layer in a manner such as previously described and (2) the migration of dissolved or colloidal silicic acid into the layer and sodium oxide out of it with resultant silica gel deposited within the layer. Both of these processes would be expected to continue so long as any current flowed. As the voltage across the layer rises, there is probably a substantial temperature increase within the layer that tends to dehydrate the deposit.

Regardless of what the exact mechanism of the process may be, the fact remains that the present invention provides a protective coating for aluminum bodies of outstanding and surprising physical properties. It is very hard, dense, coherent, adheres very firmly to the underlying aluminum, and is extraordinarily resistant to mechanical and chemical attack. For example, a sample of oxide-coated aluminum immersed in a hot sodium silicate solution of high silica to soda (SiO_2 to Na_2O) ratio for, say, 20 minutes, then rinsed in water and baked, was easily abraded by a piece of "Pyrex" glass roughened by grinding. An aluminum sample coated in accordance with this invention was not at all abraded under a like abrasion test. The former coating was immediately stripped off the aluminum base upon applying thereto a 2:1 water-hydrofluoric acid solution which, as is well known, is a mineral acid, but it took many times as long for such a solution merely to penetrate the protective coating of this invention.

The remarkable properties possessed by the coating of this invention may be explained as due to the presence in the coating of a substantial amount of dense silica, initially deposited anodically as colloidal silicic acid, as well as to the presence of aluminum silicate, both of which are brought into intimate association with, and firmly held by the initially formed porous, adsorbent oxide coating. The coating of this invention therefore, in our opinion, comprises aluminum oxide, aluminum silicate and silica, which components may be at least in part united chemically. A coating having the composition and properties of the coating produced in accordance with this invention is not formed by mere immersion of an oxide-coated aluminum article in a hot solution of sodium silicate or other alkali-metal silicate.

Articles of aluminum or having aluminum surfaces, coated as hereinbefore described, if desired may be rendered even more resistant to moisture and to corrosion and abrasion by treatment with waxes, resins, and the like, or with mixtures thereof, for example, with carnauba wax, paraffin wax of high melting point, mixtures of carnauba and paraffin wax, alkyd resin varnishes, et cetera.

Although not limited thereto, articles of aluminum alloys protectively covered in accordance with this invention are especially suitable for use in the construction of switchboards. In one such use an aluminum strip is perforated and the insulated wires are drawn through it. By providing an insulating film on the aluminum, rupture of the wire insulation will not result in breakdown during use, through the establishment of contact between the conducting wire and the aluminum itself. For the purpose described it is necessary that the protective coating on the perforated aluminum strips be very adhering, so that it will not chip off or crack, and it must also successfully withstand mechanical wear encountered during assembly operations. A protective coating fully able to meet these requirements is produced by this invention.

Metallic articles, for example, copper conductors, coated with essentially pure aluminum or with an aluminum alloy containing a preponderant amount of pure aluminum may have applied to the aluminum surface a protective covering produced in accordance with this invention. For instance, a copper wire having a covering of aluminum and insulated as herein described is especially suitable for use in electrical applications where high temperatures encountered in service operation result in the breakdown of organic insulating coatings such as the various resinous and other insulating enamels and the like.

Either direct current or alternating current may be used in forming the initial oxide coating by electrolytic means or in producing the final coating of this invention, but such coatings in all cases are formed anodically.

The term "oxide coating" as used hereinbefore, and in the claims which follow, means a layer of aluminum oxide artifically produced on the aluminum or aluminum alloy surfaces, with or without the use of applied electrical energy, but does not include the thin film of aluminum oxide which is naturally formed upon the metal by contact with air. By the term "aluminum alloys" as used herein is meant an alloy containing a preponderant amount of aluminum, for example, an alloy containing about 1.25 per cent manganese and about 1 per cent magnesium and the remainder consisting essentially of aluminum.

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

1. In the art of forming protective coatings

on aluminum articles, the process of providing such article with a coating integral therewith and consisting of an initially porous layer of aluminum oxide impregnated with a dense mass of silica firmly united to said oxide, said process comprising removing surface impurities from such article, forming a coating of porous aluminum oxide integral with the surface of the cleaned article by anodic oxidation of the surface in an aqueous solution of oxalic acid, and introducing into and firmly uniting with the said oxide coating a dense mass of silica by anodically treating the oxide-coated article in an aqueous solution of sodium silicate in which the ratio of silica to sodium oxide is not less than about 2 to 1.

2. A process of forming on an aluminum surface a hard, dense, wear- and corrosion-resistant coating integral with said surface and consisting of an initially porous layer of aluminum oxide impregnated with densely packed silica firmly bound to said oxide, said process comprising treating said surface for the removal of impurities, forming a permeable coating of aluminum oxide integral with the cleaned surface by anodic oxidation of the surface in an aqueous solution containing less than about 10 per cent by weight of oxalic acid and maintaining the bath temperature below about 50° C. during the formation of said oxide coating, and densely packing silica into the said oxide coating and firmly bonding the same therewith by electrolytically treating said oxide-coated aluminum surface as anode in an aqueous solution of sodium silicate in which the ratio of silica to sodium oxide is above about 2.7 to 1.

3. A process of providing an aluminum article with a hard, dense, wear- and corrosion-resistant, electrically insulating covering integral with the surface of said article and consisting of an initially porous layer of aluminum oxide impregnated with dense silica firmly united to said oxide, said process consisting in the steps of removing surface impurities from said article, forming a coating of porous aluminum oxide integral with the surface thereof by anodically treating said article in a bath consisting essentially of about 1 to 10 per cent by weight of oxalic acid and the remainder water, using a direct current operating voltage below about 100 volts and maintaining the bath temperature below about 40° C. during the formation of said oxide coating, washing the oxide-coated article with water, and anodically treating the water-washed article in a bath consisting essentially of about 15 to 25 per cent by weight of sodium silicate in which the ratio of silica to sodium oxide is above about 2.7 to 1 and the remainder water, using during said anodic treatment a direct-current operating voltage starting at about 60 volts and ending below about 800 volts, the said last-mentioned anodic treatment introducing a dense mass of silica into the porous aluminum oxide and firmly uniting the same thereto.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 60, for "ovide" read oxide; page 3, second column, line 23, before the word "alloys" insert or aluminum; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of July, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.