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METHOD FOR PROVIDING OXIDE COATING ON ALUMINUM AND ITS ALLOYS

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This invention relates to the treatment of aluminum or aluminum alloy surfaces to provide aluminum oxide coatings thereon for the purpose of increasing resistance to corrosion, of insulation, of dyeing, or for other usual purposes of such type of treatment.

This application is in part a continuation of my application, Serial No. 543,046, filed June 30, 1944, now abandoned.

Many methods have been proposed for the treatment of aluminum and its alloys involving generally the formation on the aluminum or alloy surface of a hard film of oxide which is resistant to abrasion and also serves to prevent, to a reasonable degree, chemical corrosion of the aluminum material.

The best results in the direction of providing aluminum oxide films on aluminum or alloy surfaces are attained by anodizing and in particular by two classes of anodizing which give rather different results.

One type of anodizing is the so-called chromic acid anodizing which as known and commonly practiced in the art produces a quite thin oxide coat in a given length of time as compared with other baths, such as sulphuric or oxalic acid, in the same length of time. This oxide coat produced through the use of chromic acid has greater corrosion resistance than the oxide coats produced by various other methods due to its nonporous nature and in spite of its thinness. On the other hand, it has relatively low abrasion resistance and in view of its lack of porosity it results in relatively poor dyeing. This anodized coat produced by the use of chromic acid is accordingly used in practice mainly for corrosion resistance or as a paint base. Similar thin, impervious coatings may be produced by other treatments as described hereafter.

In contrast with the above, the oxide coats formed by anodizing using sulphuric acid or oxalic acid electrolytes are thicker and more abrasion resistant but are substantially more porous. It is customary and generally necessary to seal these pores by plugging them with waxes or oils or by the chemical deposition of insoluble metallic compounds by immersion of the coat in a hot solution of some weak metallic base or in a hot solution of an alkali bichromate to precipitate an insoluble chromate. These various methods of sealing have various disadvantages. Discoloration of the oxide coat generally takes place to an appreciable extent and in the case of chromate sealing to a very marked extent. A long immersion period in a hot solution is required. While

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the corrosion resistance is increased the ultimate resistance secured is usually not as good as that attainable by chromic acid anodizing.

In accordance with the present invention the aluminum or aluminum alloy is subjected to an anodizing treatment of conventional type using as the electrolyte a sulphuric or oxalic acid solution or one of the various other known electrolytes which give rise to a porous oxide coat. This conventional oxide-forming treatment is not, alone, a part of the present invention and need not be further specifically described except to note that it may equally well be carried out through the use of either direct or alternating current in accordance with the usual practices in this art. Sulphuric-chromic acid mixtures may also be used at this stage since they will give rise to porous, thick coats. To produce these porous coats there may also be used such electrolytes as phosphoric acid, malonic acid, hydrofluosilicic acid, manganic acid, various sulphonic and sulphamic acids, potassium bisulphate and others known to the art. The electrolytes may contain metallic salts or other constituents as are known in the art and may be used under conventional conditions of times, temperatures, current densities, voltages, concentrations, etc.

As an example of the anodic treatment just described there may be cited anodic treatment in a conventional sulphuric acid electrolyte comprising, for example, a 10% sulphuric acid solution, the anodic treatment being carried out for twenty minutes at fifteen volts at temperatures ranging from 70° F. to 95° F. Wide variations in these values are permissible as will be evident by reference to prior patents and publications in this art.

Following the formation of a porous coat by the conventional anodic treatment indicated above, which porous coat is generally desirably thick, though it may be thin in particular cases, the aluminum or aluminum alloy surfaces which have been coated are subjected, in accordance with the invention, to anodic electrochemical action in a solution which, preferably, may be one which gives rise to formation of chromic acid at the anode. This anodic treatment, for example, may be carried out in a 1% to 50% aqueous solution of chromium trioxide, preferably about 10% (or in a solution of equivalent anion content) for one to three minutes at twenty to fifty volts and at a temperature ranging from room temperature to about 130° F. This forms a thin impervious coating which, alternatively, may be formed by other methods, known to the art, giving rise

to similar thin, impervious coatings, for example, using sodium silicate, boric acid, borates such as ammonium borate or borax, sodium carbonate, ammonium bicarbonate, sodium bicarbonate, acetic acid and other known materials. The electrolyte should be free of substantial amounts of free sulphuric acid which would produce porous coatings.

While anodic after treatment has been referred to, it is not intended to imply that this can be carried out solely by the use of direct current. It has been found possible to use unrectified alternating current under approximately corresponding conditions of voltage, time and temperature, those half cycles being effective which correspond to an anodic condition of the material being treated. In fact, with the use of alternating current it is possible to treat two articles or groups of articles simultaneously, these articles or groups forming the two electrodes in the treating bath. As each article or group alternately becomes the anode its treatment occurs. It will, of course, be obvious that pulsating direct current as well as substantially constant direct current may be used.

A study of the procedure just described indicates what happens to render it highly effective. The originally formed coating (produced in a sulphuric acid, oxalic acid or equivalent electrolyte) is porous so that in the second chromicion containing, or equivalent, bath the electrolyte may readily penetrate the pores and the current reaches the metal surface through these pores. Accordingly, the further coating of oxide produced in the second treatment builds up directly on the aluminum or alloy surface with the result that the coating finally produced consists of a thin non-porous layer directly in contact with the metal surface, covered by the relatively porous, and generally relatively thick, coating produced by the first treatment which has now been pushed away from the metal surface. It is to be stressed that this second treatment does not involve sealing in the usual fashion characterized by the mere plugging of the pores of the porous coat. Rather the effect is to produce two distinct oxide layers of different characteristics, the inner involving a high degree of corrosion resistance and the outer a high degree of abrasion resistance and with other advantages attendant upon thickness and porosity.

That the outer layer remains porous, and is not merely plugged, is quite evident from the fact that it has substantially the dye absorbing properties characteristic of a coating produced by the first type of treatment (sulphuric or oxalic acid or the like) alone. The porous coating absorbs dye uninhibited by the relatively impervious coating which lies between it and the surface of the metal. While this relatively impervious coating does not absorb a substantial quantity of dye, that condition is not detrimental.

The process is, in fact, particularly advantageous when a dyed coating is to be produced having a high resistance to corrosion and also having high electrical resistance or abrasion resistance qualities. Dyeing may be carried out in any of the usual fashions well known in the art. Then the pores of the porous coating may be sealed in conventional fashion using, for example, nickel acetate, sodium aluminate, alkali silicates, or the like. While the underlying impervious coat takes care of corrosion resistance to a much greater extent than the sealing material, the seal is desirable to insure that the dye remains in the coat and cannot be washed out if the surface becomes wet. In fact, even without dyeing such sealing may be used to add somewhat to the corrosion resistance. When dyeing is not effected and coloration is not objectionable this sealing may be performed through the use of an alkali bichromate in the usual fashion.

The invention, as will be clear from the above, involves, fundamentally, first the formation of a porous coating followed by the formation of an impervious thin coating which underlies the porous coating, being formed through the pores thereof on the metal surface. It may be noted that a reversal of the order of formation of these coatings is quite ineffective: if the impervious coating is first formed, not only is a pervious coating formed with difficulty but, if formed (by prolonged treatment), the impervious coating is destroyed from the standpoint of effectiveness by being pushed away from the metal surface. At best, the result is about equivalent to that resulting from the formation of only a pervious coating, with inferior dye absorption characteristics.

One exception to the last exists, however: porous castings of aluminum or aluminum alloys may be advantageously subjected to a triple treatment, first involving formation of an impervious film, secondly formation of a porous film and thirdly formation of a final impervious film. The first is a pretreatment which may be carried out either chemically or anodically.

In accordance with the chemical method, a porous casting which has been previously cleaned is immersed for a period of about 5 to 40 minutes, and preferably about 30 minutes, in a hot solution containing about 1% to 7% by weight of a bichromate such as sodium, potassium or ammonium bichromate. The conditions of this treatment are not particularly critical. As to the time, 5 minutes' treatment is apparently about an effective minimum while 40 minutes results in a condition which is not susceptible to substantial improvement by longer treatment. While the desired action takes place at lower temperatures, it is substantially accelerated by using temperatures of about 150° F. to boiling of the solution. The content of chromate or bichromate (the essential of the solution being solely that it contains chromic acid anions) may be varied through a considerable range, even beyond the limits just indicated, but it appears that about 5% by weight of sodium bichromate is optimum.

Even more desirable, however, is a pre-treatment giving rise to very similar results comprising the anodic treatment of porous castings of the type indicated, this treatment being carried out in a solution containing chromic acid anions which may comprise either a solution of chromic acid or solutions of chromates or bichromates which will give rise in electrolytic treatment to the formation of chromic acid at the anode. The solution in which treatment is effected is preferably about a 1% to 50% aqueous solution of chromium trioxide (1.35 ounces to 135 ounces chromium trioxide per gallon of water) or a solution of chromate or bichromate having the equivalent chromic acid content. A 10% solution of chromium trioxide appears to give the best results, but this is not critical. The treatment is carried out with the material to be treated forming the anode and with an applied voltage of 20 to 50 volts, preferably about 40 volts, at a tem-

perature which may range from ordinary room temperature to about 130° F., though the temperature limits are not critical. The time of such anodic treatment may be quite short, and, in fact, 1 to 3 minutes will generally suffice to give substantially as good results as may be accomplished by much longer treatment.

This pre-treatment has the effect of producing a coating deep in the pores of the casting. This is then followed by formation of a porous film as described above which, while it does not penetrate the pores and does not destroy or substantially modify the coating therein, in effect lifts the surface film resulting from the pretreatment and destroys its impervious nature. Then the third treatment effects the same results as the last treatment above described for aluminum and its alloys generally. The second and third treatments are identical with the two earlier mentioned and the final results are quite similar, the only overall difference being more effective plugging of the casting pores.

Where "aluminum" is hereafter referred to it will be understood to include aluminum and alloys containing as their major constituent aluminum on which oxide coatings may be formed in accordance with the prior art procedures above referred to.

What I claim and desire to protect by Letters Patent is:

1. The method of treating aluminum comprising essentially the steps of successively forming anodically thereon a relatively pervious aluminum oxide coating and then anodically, in an electrolyte containing a substantial quantity of anions of chromic acid and substantially free of free sulphuric acid, a relatively impervious aluminum oxide coating underlying the relatively pervious coating.

2. The method of treating an aluminum casting comprising essentially the steps of successively pretreating the casting with a solution containing a substantial quantity of anions of chromic acid, forming anodically on the casting a relatively pervious aluminum oxide coating, and then anodically a relatively impervious aluminum oxide coating underlying the relatively pervious coating.

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