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PROCESS FOR PRODUCING REFLECTIVE ALUMINUM SURFACES

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This application is a continuation-in-part of my copending application, Serial No. 55,275, for Process of producing reflective aluminum surfaces, filed December 19, 1935.

The invention relates to the production of reflecting surfaces on aluminum, and it is particularly concerned with an improved method of treating aluminum surfaces to produce bright oxide-coated aluminum surfaces of improved reflectivity.

The application of aluminum, that is to say, aluminum and aluminum base alloys, to uses in which a bright reflective surface of substantial permanence is necessary or desirable has been considerably retarded because of the tendency of unprotected aluminum surfaces to oxidize when exposed to the atmosphere. This natural oxidation of aluminum produces on its surface a film which is more or less translucent and which substantially detracts from the reflecting power of the surface. In attempts to adapt aluminum and its alloys tc such uses, several methods have been devised for the treatment of aluminum reflecting surfaces to produce on them artificial oxide coatings of substantial thickness which are substantially transparent.

One of the most successful of these methods is disclosed in Patent No. 2,108,603 to Mason. This method, in one form, comprises an electrolytic brightening step followed by an anodic oxidation treatment of the brightened surface. The first step may be carried out in a solution of a fluoborate. The anodic oxidation may be carried out in a solution of sulfuric or oxalic acid. Any porosity of the oxide coating may be decreased by treatment in hot water at or near the boiling point. Finally, any undesirable superficial surface film or deposit which may have formed during these steps is removed mechanically. In general, brightening electrolytes made with hydrofluoric acid or its compounds have been preferred, such as mixtures of sulfuric and hydrofluoric acids, and chromic and hydroflouric acids. However, other brightening electrolytes having substantially the same characteristics are known in the art.

Some difficulty has been encountered in the commercial operations of these methods, all of which leave a thin film on the surface of a nature apt to smudge on rubbing or handling, and the removal of such film on an oxide-coated surface has proved a tedious, costly task undesirable for use in commercial production.

During the electrolytic brightening treatment, a soft superficial film consisting essentially of aluminum oxide is formed on the aluminum surface which is substantially transparent and at times invisible. In some instances this film becomes faintly visible, particularly by reflected light. Such a film does not affect to any substantial degree the reflectivity of the surface when formed. However, if the surface is rubbed or handled, the surface smudges, which is highly undesirable in reflecting surfaces. During the subsequent anodizing or oxide-coating treatment, if unremoved, this film apparently acts as a permeable membrane and a hard oxide coating is formed beneath it upon the surface of the metal. Thus, this film remains on the outer surface of the finished article unless it is removed. Furthermore, during the treatment of the oxide coating in hot water to make it impervious, the tendency to smudge is increased owing to the action of the hot water on outer portions of the coating. It is the removal of this superficial film which causes the above-mentioned difficulties in commercial production.

The chief object of the present invention is to overcome these difficulties and to provide an improved process for the production of aluminum reflecting surfaces. A further object is to provide an improved, rapid method of removing a superficial film of undesirable nature from aluminum reflecting surfaces. These and other objects will be apparent from the following description.

I have found that it is possible and practical to remove this superficial smudge-forming film from aluminum reflecting surfaces which have been chemically or electrolytically brightened, and particularly from reflecting surfaces which have been brightened by anodic treatment in brightening electrolytes. While my invention is described in connection with the anodic treatment of aluminum surfaces in brightening electrolytes containing hydrofluoboric acid or salts thereof as one constituent, I contemplate the treatment of surfaces treated in other known types of brightening electrolytes. My invention consists in removing the smudge-forming superficial film from electrolytically brightened aluminum surfaces by chemical solution or partial solution or loosening of this film by treatment with a solution of a solvent for aluminum oxide which exhibits preferential attack on aluminum oxide when controlled as to concentration, temperature and time of treatment. I have found that this solution or loosening and removal of the deposit can be carried out rapidly and with uniformly excellent results without the

employment of highly skilled operators. I have also found, contrary to expectations, that the film or deposit may be removed from the finest specular reflecting surfaces without damage or impairment of their reflecting quality. Such film solvent solutions, however, will attack an oxide coating on the aluminum and therefore their use is limited to the removal of film from the aluminum surface and are not suitable for the removal of superficial film from an oxide-coated aluminum surface. In case the reflecting surface is oxide-coated and the oxide coating treated in hot water to impermeabilize it, as is customary, it has been found that film formations ordinarily resulting from this treatment may be substantially avoided by controlling the maximum temperature employed in impermeabilizing the oxide coating. Thus, by a novel combination of steps, including the control of the temperature in the finishing step, I am able to produce an abrasion-resistant reflecting surface upon aluminum without employing a mechanical cleaning or buffing step to remove superficial smudge-producing film, and by the simple means of a brightening step and a film-removing step produce an aluminum reflecting surface which will not smudge on rubbing or handling.

The present invention consists in the application of these discoveries to the problem of commercially producing aluminum reflecting surfaces of a uniformly high quality at a minimum expense. Stated broadly, my invention comprises the substitution of a chemical means of removing film or smudge for a mechanical means, and a change in the sequence of steps in the process for the production of reflecting aluminum surfaces which are protected by transparent impermeabilized oxide coatings, and, further, the additional step of the control of temperature during the impermeabilization of the oxide coating with hot water so that further film formation is inhibited. As explained heretofore, this film does not decrease to any substantial extent the reflecting power of the surface in its original form but does, upon the slightest rubbing action, produce a non-transparent smudge which seriously interferes with the appearance of the surface and its reflecting properties. One form of my invention comprises the removal of this smudge-forming film from electrolytically brightened aluminum reflecting surfaces by treatment with an alkaline chromate solution.

In the practice of my invention I anodically treat the surface of aluminum sheet which has been thoroughly cleansed of grease and other matter in a known brightening electrolytic bath. If a diffuse reflecting surface is desired, I etch or otherwise roughen the surface, preferably finally cleaning in a 50% solution of nitric acid. If a specular surface is desired, I start with a polished aluminum surface. The brightening electrolyte is preferably an aqueous solution of hydrofluoboric acid or compounds of that acid having a concentration of fluoboric acid of from ½ to 1 per cent (HBF_4); the impressed voltage may be from 5 to 35 or more and the current density from 3 amperes per square foot upward, 10 to 20 amperes being normal, using direct current. The time of treatment is usually 4 to 16 minutes. The desirable temperature is from 20 to 60° C. As examples of alternative brightening electrolytes, one composed of chromic acid and hydrofluoric acid may be used. This electrolyte, according to Patent No. 2,040,617 to Mason et al., is composed of from 1 to 25 per cent of chromic acid and from 0.2 to 1.5 per cent hydrofluoric acid. The electrolyte is used at a temperature of 30 to 70° C. and with a current density of from 20 to 140 amperes per square foot of anode. Another suitable electrolyte is disclosed in Patent No. 2,040,618 to Mason et al., which is composed of sulfuric acid 5 to 35 per cent, and hydrofluoric acid 0.2 to 1.5 per cent. This electrolyte is preferably used at a temperature of 30 to 70° C., and at a current density of 10 to 100 amperes per square foot of anode surface treated. The term "brightening electrolyte" as used herein and in the appended claims comprehends that class of electrolytes in which aluminum surfaces are rendered bright and highly reflective by anodic treatment.

After the surface of the article is brightened, the extremely thin, transparent film which is simultaneously formed on the surface may be removed by the action of an alkaline or acid solvent for aluminum oxide. Any solvent may be used which will attack or so loosen the deposit that it may be removed by washing and which at the same time does not attack the delicate brightened surface of the metal. Exemplifying a suitable film solvent for use in my invention, an alkaline solution of a chromate, such as sodium chromate, or other alkali metal chromate in a solution containing an alkali metal carbonate may be used. In research directed towards determination of the most desirable solution concentration and conditions of use, it has been found that the presence of the chromate salt retards or controls, for the purposes of this invention, the action of the carbonate solution over a substantially wide range. It has been found desirable, however, to have the chromate somewhat in excess of the carbonate content. The conditions of use control to a large extent the concentration chosen. A solution high in carbonate dissolves a film more readily, but continued contact with such a solution at times impairs the brightened surface beneath the film. In solutions in which the chromate is high in proportion to the carbonate the action becomes unsatisfactorily retarded. The speed of the solution is also governed by the temperature. In general, the higher the temperature the more rapid the action. In practice it is desirable to choose a solution concentration which, when used at a temperature somewhat above room temperature but preferably not above the boiling point of water, a temperature of 70–95° C. is preferred, will remove the film in a reasonable length of time. An extremely rapid action or short time of solution is undesirable in many cases owing to the close supervision which it necessitates. On the other hand, an unreasonably long time is expensive in commercial production and tends to produce less satisfactory results. In answer to these practical aspects I have found that solutions prepared by dissolving from 0.5 to 3.0 per cent of sodium dichromate and 1.0 to 8.0 per cent of sodium carbonate in water are satisfactory used at a temperature substantially above room temperature and remove substantially all surface film in about 15 seconds to 3 minutes. Potassium salts may be used in equivalent amounts instead of sodium. A solution prepared by dissolving 1.5 per cent of sodium dichromate and 2.0 per cent of sodium carbonate, corresponding to about 1.8 per cent sodium chromate and 1.5 per cent sodium carbonate, is preferred. The dichromate salt is preferred for use on account of its availability and cost, but the direct addition of the chromate salt is, of course, per-

missible. If the article is treated by immersion in the film solvent, it is desirable that the solvent be agitated during treatment in order that the material which is loosened but not completely dissolved may be removed from the surface as soon as possible. Agitation also prevents any possibility of local depletion of the solvent solution. A convenient method of agitation is to blow air or steam into the solution. However, any other suitable method may be used. The surface, free from film, is thoroughly washed in water, preferably running water, so that all the solvent and loose solid material, if present, may be thoroughly removed before further treatment.

Other solvent solutions which have been found to be satisfactory for the removal of these superficial smudge-forming films on anodically brightened surfaces are solutions of sulfuric and phosphoric acids preferably containing chromic acid to control the action of the solution on the aluminum surface. For example, an aqueous solution containing 1 per cent phosphoric acid and 0.5 per cent chromic acid, and an aqueous solution of 1 per cent sulfuric acid and 0.5 per cent chromic acid were found to remove the superficial film in 30 seconds at a temperature of about 96° C.; a 1 per cent solution of chromic acid was found to remove the superficial smudge-forming film from an electrolytically brightened surface in 1½ minutes at a temperature of about 82° C.; an aqueous solution containing 2 per cent citric acid and 0.15 per cent quinine sulfate was found to remove the superficial film from an electrolytically brightened aluminum surface in 3 minutes at a temperature of about 93° C. All of these solvent solutions, under the conditions specified, remove the superficial film without damage to the brightened aluminum surface or substantial impairment of its reflecting properties.

In the preferred practice of my invention, the brightened film-free surface is treated by known methods to produce thereon a transparent oxide coating which will, to a large extent, preserve the desirable qualities of the brightened surface and which will resist abrading or scratching. These coatings, however, do impair to some extent the reflecting power of the surface. This impairment will vary with the particular process and electrolyte used in forming the coating, and with the aluminum or aluminum alloy treated. In treating high purity aluminum surfaces, for example, an electrolyte of 15 per cent sulfuric acid may be used. Oxidation may be carried on in this electrolyte at about 12 amperes per square foot for a period of from 4 to 20 minutes without decreasing the reflectivity of the surface more than a few per cent. In oxide-coating aluminum base alloy surfaces, the coating is apt to be colored or less transparent than the coating formed on high purity aluminum, and for this reason it is preferable to reduce the time of oxidation to four or five minutes. Therefore, the degree of reflectivity obtained by the practice of that process in its preferred form will vary somewhat, depending upon the exact treatment of the oxide coating applied and upon the composition of the alloy treated. These oxide coatings are, in general, not entirely suitable for use until treated to impermeabilize or render stain-proof and impervious. The step of impermeabilizing the oxide coating as a step in my preferred practice necessitates a treatment which in itself produces no superficial film on the oxide coating which will smudge upon handling or rubbing or otherwise interfere with the reflecting properties of the surface. In the present invention, the method of rendering the oxide coating impervious while retaining its other desirable features consists in treating in hot water at a temperature from 70 to 85° C. The preferred time of treatment will vary somewhat with the thickness of the oxide coating. The thicker the oxide coating, the longer the time required for impermeabilization. As the thickness of the oxide coating bears a direct relationship, under most conditions, to the time of anodic oxidation, it can be generally stated that the time of anodic oxidation controls almost entirely the time of impermeabilization. For example, in treating high purity aluminum surfaces by my process, the step of anodic oxidation may be carried out in a sulfuric acid bath containing 15 per cent sulfuric acid with a current density of from 12 to 14 amperes per square foot for a period of about eight minutes. This oxidation step results in a transparent oxide coating of medium thickness which may be impermeabilized by immersing in water held at a temperature of from 75° to 80° C. for fifteen minutes. If a heavier coating is desired, the oxidation time is extended to fifteen minutes under the above conditions, and the treatment in hot water extended to about thirty minutes. Water temperatures higher than 85° impermeabilize the coating somewhat more rapidly, but tend to form a superficial film upon the surface of the coating. Water temperatures less than 70° consume an excessive time in the higher ranges, and are ineffective in the lower ranges. After the oxide coating has been impermeabilized, the process is completed by drying the surface by any convenient means.

Exemplifying the treatment of high purity aluminum sheet to produce thereon a specular reflecting surface according to my preferred practice, the surface is first cleansed with an appropriate cleaning solution to remove grease and other foreign matter which may have been introduced during a preliminary polishing operation or other previous treatments. The cleaning solution preferably should be of a nature which has no action upon the aluminum itself. After cleansing, the surface is thoroughly rinsed in cold water. The clean surface is then made anode in an electrolyte containing about 1.25 per cent hydrofluoboric acid. A current of about 10 to 20 amperes per square foot is passed for from 10 to 12 minutes. It is desirable to use initially, that is, from the first minute or two, a somewhat higher current density, 18–20 amperes per square foot. The thus brightened surface is then dipped or otherwise treated in a solution prepared by dissolving 20 parts sodium carbonate and 15 parts sodium dichromate in 1000 parts water. During the removal of the smudge-forming film or deposit formed on the surface during the brightening step, this solution is held at a temperature of from about 70° to 95° C. and agitated against the surface of the aluminum for a period of about two minutes. The sheet is then rinsed in cold running or otherwise agitated water. It is then made anode in an electrolyte of 15 per cent sulfuric acid and anodized at a current density of about 12–14 amperes per foot at a temperature of 72° for about eight minutes. The surface is thoroughly rinsed and then placed in water held at a temperature of from 75° to 80° for a period of fifteen minutes. It is then dried on a steam table.

By the removal of superficial surface film pro-

duced in the electrolytic brightening bath and the prevention of further superficial smudge-forming film depositing upon the oxide coating during the impermeabilizing step, no further treatment of the surface is necessary. By this combination of steps I am able to produce a hard, bright, specular, abrasion-resistant reflecting surface upon aluminum by electrolytic and chemical means, and eliminate costly steps of mechanical cleaning and finishing the reflective surface. It is also possible to produce specular reflecting surfaces on polished aluminum simply by an electrolytic brightening step and removing the smudge-forming film from the reflecting surface by a subsequent treatment in an aqueous solution of a solvent which will preferentially attack aluminum oxide and controlling the time of treatment and the temperature and concentration of the solution to effect removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties. It is generally desirable to protect such surfaces by some subsequent treatment, such as lacquering. It has been impossible heretofore to produce such reflecting surfaces free from smudge-forming film owing to the fact that methods ordinarily adaptable would, in the absence of a hard oxide coating, damage the underlying delicate reflector surface. Specular reflector surfaces formed on high purity aluminum by the brightening and film-removing steps herein described may attain a reflecting power as high as 87 per cent. Similar reflecting surfaces anodically treated to form a hard, transparent oxide coating may attain a reflecting power of as high as 85%. Aluminum of commercial purity gives somewhat lower figures. Aluminum base alloys in general do not produce reflectors of this order, but may be usefully employed in many cases. The term "aluminum" as used herein and in the appended claims comprehends aluminum and aluminum base alloys.

I claim:

1. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of a solvent which will preferentially attack aluminum oxide, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties.

2. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of a solvent which will preferentially attack aluminum oxide, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties, and thereafter anodically producing on said surface a transparent oxide coating.

3. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of a solvent which will preferentially attack aluminum oxide, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties, thereafter anodically producing on said surface a transparent oxide coating, and subsequently treating said coating with water at a temperature of 70 to 85° centigrade to render it impermeable.

4. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of an alkaline solvent which will preferentially attack aluminum oxide, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties.

5. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of an alkaline solvent which will preferentially attack aluminum oxide, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties, and thereafter anodically producing on said surface a transparent oxide coating.

6. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of an alkaline solvent which will preferentially attack aluminum oxide, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties, thereafter anodically producing on said surface a transparent oxide coating, and subsequently treating said coating with water at a temperature of 70 to 85° centigrade to render it impermeable.

7. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of an alkali metal carbonate containing a chromate, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or

substantial impairment of its reflecting properties.

8. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with a solution containing about 2 parts of an alkali metal carbonate and 1½ parts of an alkali metal dichromate in 100 parts of water at a temperature of about 70 to 95° centigrade for a period of 15 seconds to 3 minutes.

9. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with a solution containing about 2 parts sodium carbonate and 1½ parts sodium dichromate in 100 parts of water at a temperature of about 70 to 95° centigrade for a period of 15 seconds to 3 minutes.

10. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with an aqueous solution of an alkali metal carbonate containing a chromate, and controlling the time of treatment and the temperature and concentration of the solution to effect the removal of the film without damage to the brightened surface or substantial impairment of its reflecting properties, and thereafter anodically producing on said surface a transparent oxide coating.

11. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with a solution containing about 2 parts of an alkali metal carbonate and 1½ parts of an alkali metal dichromate in 100 parts of water, at a temperature of about 70 to 95° centigrade for a period of 15 seconds to 3 minutes, and thereafter anodically producing on said surface a transparent oxide coating.

12. In a process of producing a highly reflective surface on aluminum in which the aluminum surface is brightened and a superficial film is simultaneously produced thereon by anodic treatment of said surface in an aluminum brightening electrolyte, the step comprising removing said superficial film by treating the brightened surface with a solution containing about 2 parts sodium carbonate and 1½ parts sodium dichromate in 100 parts of water at a temperature of about 70 to 95° centigrade for a period of 15 seconds to 3 minutes, and thereafter anodically producing on said surface a transparent oxide coating.

13. A method of producing highly reflective, abrasion-resistant and stain-proof aluminum surfaces, comprising anodically treating said aluminum in a fluoborate electrolyte and then subjecting said aluminum to the action of a solvent consisting of 2 parts sodium carbonate, 1½ parts sodium dichromate and 100 parts water, heated to a temperature of from 70 to 95° C. for a period of from ¼ to 3 minutes, thereafter anodically producing thereon a transparent oxide coating, and treating said oxide coating with water at a temperature of from 75 to 80° centigrade to render it impermeable.

14. A method of producing highly reflective surfaces on aluminum, comprising removing impurities from the aluminum surface and simultaneously forming thereon a superficial film by treating said aluminum surface as the anode in an electrolyte of the class consisting of solutions of fluoborates, solutions of sulfuric acid and hydrofluoric acid, and solutions of chromic acid and hydrofluoric acid, and subsequently dissolving the film from said surface by treatment with a solution containing from about 1 to 8 per cent of an alkali metal carbonate and from about 0.5 to 3.0 per cent of an alkali metal dichromate at a temperature substantially above room temperature for a period of 15 seconds to 3 minutes.

15. A method of producing highly reflective surfaces on aluminum, comprising removing impurities from the aluminum surface and simultaneously forming thereon a superficial film by treating said aluminum surface as the anode in an electrolyte of the class consisting of solutions of fluoborates, solutions of sulfuric acid and hydrofluoric acid, and solutions of chromic acid and hydrofluoric acid, and subsequently dissolving the film from said surface by treatment with a solution containing 2 parts sodium carbonate and 1½ parts sodium dichromate in 100 parts water at a temperature substantially above room temperature for a period of 15 seconds to 3 minutes.

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