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PRODUCTION OF ALUMINUM REFLECTING SURFACES

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This invention relates to the treatment of reflecting aluminum surfaces and to the production of aluminum articles having a durable reflecting surface.

The reflecting surfaces herein referred to are those designed to reflect radiant energy of any sort, and particularly light-reflecting surfaces adapted to the diffuse or specular reflection of light. Thus the invention herein described is directed to the general object of increasing and preserving the power of an aluminum surface to reflect radiant energy of any sort, although it finds greatest usefulness in the processing of aluminum surfaces designed to specularly reflect light.

In the production of various aluminum articles having reflecting surfaces, the reflecting surface is usually produced either by etching, as in the case of surfaces designed to diffusely reflect light, or by mechanically polishing or buffing, as where specular surfaces are desired. Such surfaces are subject to deterioration in reflectivity during handling and use, and are difficult to maintain or restore to their original efficiency.

It is a leading object of the present invention to provide methods by which durable reflecting aluminum surfaces may be produced. A further object of my invention is to provide methods for the electrolytic treatment of aluminum surfaces to remove dirt and impurities therefrom. Other objects of the invention will become apparent in the following description thereof.

To the end that the reflecting power of an aluminum surface be made stable and durable, it has been proposed to provide the prepared aluminum surface with a protective coating such as, for example, an oxide coating or a transparent varnish or lacquer coating. Prior to my invention, however, methods have not been known by which the reflecting surface may be oxide-coated without materially decreasing its reflectivity, for the reason, apparently, that the resulting oxide coating is foggy and translucent. I have found that the impurities which are usually present in an aluminum surface, particularly in a mechanically polished aluminum surface, are apparently in large part the cause of foggy or translucent coatings. I have further discovered that such impurities and foreign matter as may be present in the metal surface may be removed from the metal by electrolytic treatment in certain electrolytes, and that if in accordance with the electrolytic brightening methods of my invention a substantially clean aluminum surface is obtained, it may thereafter be anodically oxidized without seriously impairing its reflectivity. Other forms of protective coatings may also be applied to the improved reflecting surfaces obtained by the electrolytic brightening methods of my invention, such, for example, as clear transparent coatings, such as lacquer or varnish coatings.

In practicing my invention the reflecting surface is submitted to a cleaning and brightening step which comprises electrolytically treating the aluminum article in an electrolyte containing a fluoborate. This procedure may or may not, according to the surface conditions of the metal, be preceded by a preliminary cleaning step to remove any superficial dirt and grease which may be present upon the metal surface as a result of the preliminary polishing operation, or whatever operation is originally employed to produce the reflecting surface. Any convenient method of preliminary cleaning may be employed, but a cleaning with a solvent or a chemical without objectionable attack upon the metal is preferable to any preliminary cleaning operation which involves rubbing the surface, since the original surface may be, if it is of the specular variety, highly polished, and any frictional preliminary cleaning operation may mar this polished surface.

The metal surface is materially brightened by this treatment in the fluoborate electrolyte and is apparently covered with a thin transparent coating. This coating offers some protection to the bright reflecting surface against deterioration by handling or atmospheric influences. Thus an article is obtained having a clean bright reflecting surface provided with a thin protective film which is useful as a reflector, particularly where the reflector will not be subject to excessive handling or severe exposure.

However, in the preferred practice of my invention the reflecting surface is again electrolytically treated to build thereon by anodic oxidation a comparatively thick, dense oxide coating. By the term "oxide coating" as used herein and in the appended claims is meant such coatings concurrently so designated in the art, which consist in substantial part of aluminum oxide, and which are produced by the anodic oxidation of aluminum in electrolytes such as sulfuric acid, chromic acid, or oxalic acid. The oxide-coated reflecting surface may then be subjected to a hot water treatment to make the coating impervious. The oxide-coated surface thus produced retains the brightness imparted to it by the electrolytic brightening step and is substantially proof against permanent staining and

marking by exposure to the weather or by handling, or when being recleaned during use, for example by washing with soap and water. The hot water treatment is, however, not necessary to the production of useful reflecting surfaces, and satisfactory oxide-coated reflecting surfaces may be produced in accordance with my invention without this treatment. As a final treatment, and particularly in the case where the hot water treatment has been employed, a very light polishing with materials such as magnesia, silver polish, or the like, may be desirable, and such polishing treatment may be applied to the oxide-coated reflecting surface to advantage without impairing its reflecting power.

There is thus produced an aluminum article having a clean bright surface of high reflectivity and provided with a hard, transparent, impervious coating consisting substantially of aluminum oxide formed integral with the bright metal surface, which imparts properties of durability and permanence to the bright reflecting surface of the article.

When a specular reflecting surface is desired, a mechanically polished aluminum surface is, in the preferred practice of my invention, first subjected to the preliminary cleaning step to remove surface grease and dirt by means of a solvent or a chemical cleaner which does not objectionably attack or pit the metal; then to the electrolytic brightening step of my invention, in which the polished aluminum article is made an electrode in an electrolytic cell containing a fluoborate solution; then to a coating step in which the now electrolytically brightened aluminum reflecting surface is made the anode in the solution of an electrolyte which will form upon the surface of the metal a comparatively thick and dense oxide coating; and thereafter to a treatment in water at 80° to 100° centigrade to impermeabilize the oxide coating and make it non-adsorptive; and finally to a light polishing operation to remove any superficial deposit which may have been formed upon the reflecting surface by reason of any of the previous operations. Where a diffusely reflecting surface is desired, the procedure is the same as in the preferred practice of my invention except that the metal is etched or mechanically abraded to produce the diffusing surface instead of being mechanically polished prior to the steps above named, and the preliminary cleaning step to remove superficial grease and dirt may usually be eliminated.

The above is the preferred practice of my invention, but the electrolytic brightening step where the aluminum article is made an anode in a cell containing a solution of fluoborate as electrolyte may be practiced without reference to any preliminary cleaning step and without further treatment to produce on the reflecting surface a dense oxide coating or any other form of coating, and likewise the reflecting surface may be electrolytically treated in the fluoborate solution and thereafter anodically treated in another solution to form an oxide coating on its surface without a following treatment in hot water or without a final polishing operation. The preliminary cleaning step, the step of impermeabilizing the oxide coating by treating it in hot water, and the final polishing step are merely preferred steps which are not at all times necessary to realize the benefits of my invention.

In treating the aluminum reflecting surface in a solution of a fluoborate in accordance with the basic principles of my invention, the aluminum article is made an electrode in an electrolytic cleaning cell which contains a fluoborate electrolyte. The current impressed upon the cell may be either alternating or direct current. It is preferable, however, to use direct current, as the process may be more readily controlled with this type of current. When direct current is used, it is essential that the aluminum article be made the anode in the electrolytic cell. Graphite cathodes may be used with advantage. Satisfactory operation is usually obtained with direct current under a potential of about 5 to 25 volts. The voltage used, however, is largely dependent upon the conductivity of the electrolyte, which will vary with its exact composition, concentration, and temperature. Consequently, it may in some cases be desirable to use voltages outside this range, the lesser voltages being used with electrolytes of high conductivity and the greater voltages being used with electrolytes of low conductivity. The desirable temperatures of operation lie usually between about 20 and 60° centigrade, although it may be advantageous to use temperatures outside this range with electrolytes of unusually high or low activity. To obtain the best results I have found that a current density of about 10 to 80 amperes per square foot of anode surface is suitable, although substantially any current density above about 3 amperes per square foot may be used. The time of treatment in the fluoborate electrolyte is not critical and will vary with the current density and the amount of brightening desired. A treatment of 5 to 15 minutes will generally give adequate results, but longer or shorter treatments may be used. When alternating current is used, the same operating conditions of voltages, temperature, and current density will produce satisfactory results. However, the concentration of the electrolyte should, in general, be lower than that used with direct current, and the time of treatment required to obtain equivalent results is generally somewhat longer.

The fluoborate electrolytes referred to are formed by dissolving in water, compounds of the class composed of hydrofluoboric acid, and the compounds of that acid, such as, for instance, ammonium fluoborate, lead fluoborate, acetofluoboric acid, which class is generally herein and in the appended claims termed "fluoborate". A convenient way of forming a suitable electrolyte for use in my process, particularly where fluoborates are not immediately available, is to mix hydrofluoric acid and boric acid. For the best results when the electrolyte is made in this way, the respective acids should be mixed in combining proportions, though either the boric acid or the hydrofluoric acid may be present in moderate excess in the electrolyte. If after mixing the acids the solution is allowed to stand for some time, the solution behaves more satisfactorily as an electrolyte. In forming the fluoborate electrolytes, compounds of relatively high purity are preferably used. The presence of some impurities in the electrolyte tends to reduce its useful life and impairs the quality of the results obtained. Sulfates, which are common impurities in commercial hydrofluoric acid, particularly show this property; and it is preferred that they be substantially removed when such acid is used in forming a fluoborate electrolyte. Certain components may also be added to the electrolyte in small amounts which do not deleteriously affect the action of the fluoborate in brightening the metal surface. For example, a small amount of

a salt such as ammonium fluoride may be added to increase the conductivity of the electrolyte.

The concentration of the fluoborate in the electrolyte will vary with the particular fluoborate used and depending upon the type of current to be used. In general the concentration of a fluoborate solution for use in connection with alternating current is preferably considerably less than the concentration of a solution of the same fluoborate for use with direct current. When an electrolyte containing hydrofluoboric acid is used in connection with direct current, good results are obtained, for instance, with a concentration of 2.5 per cent of that acid, and an electrolyte having a content of about 0.5 to 5.0 per cent of hydrofluoboric acid (HBF_4) is particularly advantageous in the production of specularly reflecting aluminum surfaces. With alternating current a hydrofluoboric acid electrolyte containing about 0.8 per cent HBF_4 gave good results in the production of specular reflecting surfaces.

The result of treating the aluminum reflecting surface in an electrolyte of fluoborate according to my invention is to brighten and improve the reflecting power of the surface. The treatment appears to involve some solution of the aluminum surface. However, the attack of the surface by this electrochemical treatment is so regular that when a specular reflecting surface is treated the specular property of the surface is not appreciably impaired. The fluoborate solution is, however, capable of direct chemical attack on the aluminum surface if maintained in contact with it without the application of the electric current. In such case the attack is, however, not regular. Care should be taken, therefore, particularly where specular surfaces are treated, that the current is maintained throughout the period of the contact of the aluminum surface with the electrolyte. Furthermore, the bright reflecting surface obtained by my electrochemical treatment is coated with a transparent film which is quite thin and, as judged by commercial standards, is relatively soft, but which affords some protection for the bright metal surface.

By anodic oxidation of the surface thus obtained in suitable known electrolytes, such as oxalic acid or sulfuric acid, a hard, protective oxide coating of substantial thickness may be formed integral with the reflecting surface with only a slight reduction in reflectivity. For this purpose I prefer to carry out the anodic oxidation reaction in sulfuric acid electrolytes, since the coatings obtained are substantially colorless, clear, and transparent, and this result is desirable in order that the reflectivity will be reduced as little as possible. But other oxide coat-forming electrolytes may be used, the main desideratum being to avoid the formation of a colored, cloudy or translucent oxide coating. Instead of the hard protective oxide coating, other forms of protective coatings may be applied to the bright surface obtained by treatment in fluoborate electrolytes, such as, for example, clear lacquer coatings. While in such case the reflectivity is somewhat reduced, the resulting coated surface, when the coating medium is itself clear, will generally have a high reflectivity and will be satisfactory for many purposes.

The provision of a hard, adherent comparatively thick and dense oxide coating on the reflecting surface which has been treated in the fluoborate electrolyte is, however, the preferable procedure, particularly since it is possible in this manner to place upon the reflecting surface a coating which is thoroughly protective without decreasing substantially the reflectivity of the resulting surface, and a coating which is substantially resistant to deterioration by handling and exposure, since it can be readily washed or otherwise cleaned to restore it to its original brilliance. The amount of reduction in reflectivity caused by placing upon the prepared reflecting surface the oxide coatings in question varies with the thickness of the coating and with the purity of the aluminum surface itself. With pure aluminum surfaces, for example, oxidation in a 7 per cent sulfuric acid electrolyte may be carried on for about 15 to 20 minutes at about 12 amperes per square foot current density without decreasing the reflectivity of the surface more than a few per cent, while a less pure aluminum surface will have its reflectivity substantially decreased if the oxidation is allowed to proceed for longer than about 4 or 5 minutes. Therefore, the degree of reflectivity obtained by the practice of my invention in its preferred form will vary somewhat, depending upon the exact treatment applied and upon the composition of the aluminum treated.

On high purity aluminum I have obtained specularly reflecting surfaces having a light reflection factor as high as 87 per cent after anodically treating the polished surface in a fluoborate electrolyte, but these surfaces are of course not as durable as desired for many types of service. However, when the surface is anodically treated in a fluoborate electrolyte in accordance with my invention, and by subsequent treatment in an oxide coat-forming solution a substantial oxide coating is placed upon the metal, I have obtained surfaces having a light reflection factor as high as 85 per cent. Upon aluminum sheet of commercial purity, surfaces having light reflection factors of about 80 per cent may be obtained. In general, aluminum alloys, when treated by the methods of my invention, do not give reflection factors of this order. However, the method of my invention is applicable to many aluminum base alloys with advantage, and the term "aluminum" as used throughout this specification and in the appended claims is to be understood to include both aluminum and aluminum base alloys. In measuring the light reflection factor of the surface treated by my electrolytic brightening method I have used the Taylor reflectometer devised by A. H. Taylor of the National Bureau of Standards and described in the Scientific Papers of the Bureau of Standards Nos. S.391 and 405.

The following specific examples clearly illustrate the advantageous results obtained by the methods of my invention.

A solution of hydrofluoboric acid was first prepared by adding 40 grams of boric acid to 100 grams of concentrated hydrofluoric acid, containing about 48 per cent of HF, while the solution was kept cold. This amount of boric acid gives an excess of about 7.5 per cent over that required to combine with all of the hydrofluoric acid. The resulting solution contained about 37.7 per cent of hydrofluoboric acid and a slight excess of boric acid. The brightening electrolyte was then made up by diluting about 15 cc. of this hydrofluoboric acid solution to about 300 cc., thus producing an electrolyte containing about 2.5 per cent of hydrofluoboric acid and a trace of boric acid in excess. A sample of aluminum sheet of high purity (99.85 per cent aluminum)

was polished and cleaned with acetone to remove surface grease. The reflection factor of the polished surface thus obtained was about 75 per cent. The aluminum sheet was then made the anode in an electrolytic cell, using as the electrolyte the above described 2.5 per cent solution of hydrofluoboric acid. A current density of about 20 amperes per square foot was employed at a potential of about 10 to 12 volts and with an electrolyte temperature of about 31 to 33° centigrade. After a treatment for 5 minutes in this manner the aluminum sheet was removed and the reflection factor of its surface again measured. The surface now had a reflection factor of 87 per cent. The sample was then subjected to anodic oxidation in an electrolyte containing 7 per cent sulfuric acid by weight, using a current density of 12 amperes per square foot at a potential of 20 volts and at a temperature of 25 to 26° centigrade. After treatment for 10 minutes the sample was removed and was boiled in pure water for 15 minutes. It was then polished with a mildly abrasive polishing cream and its reflection factor again measured. The final sample had a reflection factor of 85 per cent. The article could be handled without permanent marking or staining and could be readily washed or wiped without depreciation of its reflecting power.

A similar sample of aluminum sheet of high purity prepared as above was made an electrode in an electrolytic cell containing as electrolyte a hydrofluoboric acid solution containing 0.8 per cent HBF_4. A 60-cycle alternating current was impressed upon this cell, using a current density of about 20 amperes per square foot at a potential of 8 to 11 volts and a temperature of 30° centigrade. After a treatment for 20 minutes in this manner the aluminum sheet was removed. The surface had a reflection factor of about 85 per cent. The sample was then subjected to anodic oxidation in an electrolyte containing 7 per cent sulfuric acid by weight, using a current density of 12 amperes per square foot at a potential of 20 volts and at a temperature of 22° centigrade. After treatment for about 10 minutes, the sample was removed and was boiled in pure water for 15 minutes. It was then polished with a mildly abrasive polishing cream and its reflection factor measured. The final sample had a reflection factor of 83 per cent.

To illustrate the benefits obtained by the use in the above process of the step of anodically brightening the reflecting surface in a fluoborate electrolyte, there may be cited the case of a similar sample which was subjected to exactly the same treatment as above described in connection with the direct current, with the exception that the step of brightening the reflecting surface in the fluoborate electrolyte was omitted. In the case of this sample, the final reflecting surface had a reflection factor of only 79 per cent.

I claim:

1. A method of producing an aluminum article having a durable reflecting surface, comprising electrolytically treating the aluminum article in an electrolyte containing fluoborate as a major active constituent thereof, and thereafter producing on said surface by anodic oxidation a clear, transparent coating consisting substantially of aluminum oxide.

2. A method of producing an aluminum article having a durable light-reflecting surface, comprising anodically treating the aluminum article in an electrolyte containing fluoborate as a major active constituent thereof, and thereafter producing on said surface by anodic oxidation a clear, transparent coating consisting substantially of aluminum oxide.

3. A method of producing an aluminum article having a durable reflecting surface, comprising electrolytically treating the aluminum article in an electrolyte containing fluoborate as a major active constituent thereof, and thereafter producing on said surface by anodic oxidation a clear, transparent coating consisting substantially of aluminum oxide, and impermeabilizing the oxide-coated surface by treating with hot water.

4. A method of producing an aluminum article having a durable reflecting surface, comprising anodically treating the aluminum article in an electrolyte containing fluoborate as a major active constituent thereof, and thereafter producing on said surface by anodic oxidation a clear, transparent coating consisting substantially of aluminum oxide, and impermeabilizing the oxide-coated surface by treating with hot water.

5. A method of producing a durable, specular reflecting surface on aluminum, comprising treating a polished aluminum reflecting surface electrolytically in an electrolyte containing fluoborate as a major active constituent thereof, and thereafter anodically oxidizing the clean, bright surface obtained.

6. A method of producing a durable, specular reflecting surface on aluminum, comprising treating a polished aluminum reflecting surface electrolytically in an electrolyte containing fluoborate as a major active constituent thereof, thereafter anodically oxidizing the clean, bright surface obtained, and treating the oxide-coated surface with water at 80 to 100° centigrade.

7. Method of brightening aluminum surfaces and simultaneously producing thereon a clear, transparent film comprising treating the surface electrolytically in an electrolyte containing a fluoborate as a major active constituent thereof.

8. The method of brightening aluminum surfaces and simultaneously producing thereon a clear, transparent current-permeable electrolytic film, which comprises removing impurities from the aluminum surface by treating the same electrolytically as an anode in an electrolyte containing a fluoborate as a major active constituent thereof, said electrolyte being effectively free from ingredients active to produce a current impermeable film upon said surface.

9. A method of brightening an aluminum surface and simultaneously producing thereon a transparent electrolytic film, which includes treating the same electrolytically as the anode in an electrolyte containing a fluoborate as a major active constituent, and continuing such treatment for a period of time sufficient to effect removal of impurities from said surface.

10. The method of producing an aluminum article having a durable surface, which comprises removing impurities from the surface of said article by electrolytically treating the same as an anode in an electrolyte containing a fluoborate as a major active constituent thereof, to form upon said surface a current-permeable, transparent electrolytic film, and thereafter producing on said surface a clear, transparent impermeable coating.

11. The method of producing an aluminum article having a durable reflecting surface, which comprises first electrolytically treating the article as an anode in an electrolyte containing fluoborate as a major active constituent thereof, said

electrolyte being substantially free from ingredients tending to produce a current impermeable film, and thereafter coating said surface with a clear, transparent lacquer.

12. The method of producing a specular, highly reflecting surface on aluminum, comprising treating a polished aluminum reflecting surface electrolytically as an anode in an electrolyte containing fluoborate as a major active ingredient thereof.

13. The process of increasing the reflection factor of an aluminum surface which comprises removing impurities from the surface by treating the same electrolytically as an anode in an electrolyte solution having a fluoborate as a major active constituent thereof for producing said reflecting surface.

14. The method of brightening aluminum surfaces and simultaneously producing thereon a clear, transparent film comprising treating the surface electrolytically in an electrolyte consisting substantially of a fluoborate.

15. The method of producing an aluminum article having a durable surface which comprises removing impurities from the surface of said article by electrolytically treating the same as an anode in an electrolyte consisting substantially of a fluoborate, and thereafter producing on said surface a clear transparent impermeable coating.

16. A process of increasing the reflection factor of an aluminum surface which comprises removing impurities from the surface by treating the same electrolytically as an anode in an electrolyte solution consisting substantially of a fluoborate.

17. The method of brightening aluminum surfaces and simultaneously producing thereon a clear transparent current permeable electrolytic film which comprises treating said surface electrolytically as the anode in an electrolyte consisting substantially of a fluoborate.

18. The method of brightening aluminum surfaces and simultaneously producing thereon a clear, transparent film comprising treating the surface electrolytically in an electrolyte containing hydrofluoboric acid as a major active constituent thereof.

19. The method of producing an aluminum article having a durable light-reflecting surface, comprising anodically treating the aluminum article in an electrolyte containing hydrofluoboric acid as a major active constituent thereof, and thereafter producing on said surface, by anodic oxidation, a clear, transparent coating consisting substantially of aluminum oxide.

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