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TREATING ALUMINUM AND ALUMINUM
ALLOY SURFACES

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This invention relates to the treatment of aluminum and aluminum alloy surfaces to produce thereon colored coatings, particularly colored coatings possessing good resistance to corrosion. The term "aluminum", as used herein and in the appended claims, includes that metal in every degree of purity. The term "aluminum alloy" or "alloy", as used herein and in the appended claims, includes all aluminum alloys having an aluminum content of 50 per cent or more.

It is very often desirable to durably color metal surfaces. It is further desirable to obtain metal having prepared surfaces which resist the attack of corrosive agents. Aluminum and aluminum alloys have been the subject of numerous investigations directed toward the development of colored coatings on the metal surface, and attempts have been made to develop, chemically, coatings on aluminum and its alloys which are resistant to corrosion. Although such efforts have met with some success, no process heretofore developed is entirely satisfactory for coating aluminum with even and permanent colors, while the many investigations directed toward the covering of this metal and its alloys with a chemically applied, corrosion-resistant coating have left much to be desired.

It is an object of this invention to provide a process by which aluminum and its alloys may have affixed upon their surfaces colors of substantially any hue which are uniform and of a permanent nature.

It is a further object of this invention to provide a process of so treating aluminum and its alloys that a chemically produced, corrosion-resistant coating may be obtained on the surfaces thereof.

Another object of the invention is the provision of an aluminum or aluminum alloy article, the surfaces of which are covered with a chemically produced coating in which is deposited an insoluble, inorganic compound.

I have discovered that when aluminum or aluminum alloy is first provided on its surface with a hard and substantially adsorbent oxide coating, by subsequent treatment there may be deposited in the said oxide coating an insoluble, inorganic compound which, by means of its characteristic color, will produce a uniformly and permanently colored surface of pleasing appearance. I have further discovered that when, in the aforesaid oxide coating, certain inorganic compounds are deposited, the corrosion-resistance of the coating, and consequently of the coated aluminum, is substantially increased.

According to the present invention and as the first part thereof, the aluminum or aluminum alloy article is treated to produce upon its surface an oxide coating which is hard and dense and which has sufficient adsorbent qualities to retain, when immersed in a liquid, an appreciable quantity of such liquid within and upon it. The term "oxide coating", as used herein and in the appended claims, is a well known designation of the art which describes a layer of aluminum oxide artificially produced on the aluminum or aluminum alloy surfaces by treatment of the metal surfaces with acids, such as sulfuric, chromic, etc., or alkalis, such as sodium carbonate or the alkali sulfates and acid sulfates such as sodium sulfate or sodium acid sulfate, etc., all with or without the addition of other substances and with or without the use of externally-applied electrical energy. The term "oxide coating" does not include the very thin film of aluminum oxide which is naturally formed upon that metal or its alloys by reason of contact with the air.

After an oxide-coated aluminum or aluminum alloy has been prepared, I employ the novel methods of my invention to deposit in the oxide coating an insoluble, inorganic compound. My novel methods comprise in part, the placing of an oxide-coated aluminum or aluminum alloy in contact with a solution, preferably but not necessarily aqueous, of a soluble compound, the inorganic anion or cation of which will, when combined with the inorganic cation or anion of another soluble compound, produce an inorganic compound of a characteristic color and/or of corrosion-inhibitive properties. I have discovered that when the oxide-coated metal is placed in contact with or immersed in a solution, an inorganic anion or cation present in that solution will be adsorbed in and on the oxide coating, and that when an inorganic anion or cation is so adsorbed by the oxide coating, a subsequent and separate treatment of the oxide-coated metal with a solution of another soluble compound, the inorganic cation or anion of which is capable of combining with the inorganic anion or cation adsorbed in the coating to form an insoluble, inorganic compound, will cause the precipitation of the insoluble compound so formed in and on the oxide coating. I have further discovered that the insoluble, inorganic compound precipitated is so firmly and adherently deposited in the oxide coating as to become in effect if not actually integral with the coating and to remain as a permanent part thereof. In the above I speak of an

anion or cation being adsorbed from a solution, and it is my belief that it is the anion or cation which is adsorbed, rather than the entire compound, but I do not want to be bound by such theory. In the appended claims I have referred to the compound being adsorbed. It is to be understood, however, that the term is used to mean the entire compound or an ion thereof, as the case may be.

When the inorganic compound so precipitated in the oxide coating has a characteristic color, that color or some hue thereof is imparted to the oxide coating with the result that by the use of the method of my invention there may be produced aluminum or aluminum alloy articles having uniformly and permanently colored surfaces of substantially any desired shade. Also, if the insoluble, inorganic compound so precipitated is of a corrosion-inhibitive nature, the oxide coating containing it affords substantially greater protection to the coated aluminum or aluminum alloy article. It will now be apparent that by use of my invention an aluminum or aluminum alloy article may be provided with a coating which may at once serve both as a colored surface and as a means of protection against corrosion; or, on the other hand, the coating may not be colored but yet may protect the metal against corrosive influences.

In practicing my invention in the preferred manner the aluminum or aluminum alloy which is to be treated is first provided with an oxide coating of certain characteristics. In order that the coating will not later separate from the metal surface, it is necessary that it be hard, dense, and adherent. Of great importance, however, is the adsorbent nature of the coating. In order to obtain the most satisfactory results the oxide coating should be adapted to adsorb a substantial amount of the solution with which, as above mentioned, it later comes in contact. A further desirable quality of the oxide coating is its thickness, a comparatively thick coating being preferable. However, the thickness of the coating is not a controlling factor, and some comparatively thin coatings, artificially produced, will give good results. Being adsorbent, the coating is necessarily porous.

To produce adsorbent oxide coatings of a nature suitable to the purpose of my invention, I have used a large number of solutions, among which are included solutions of sulfuric acid, chromic acid, sodium carbonate and potassium dichromate, phosphoric acid and the salts thereof, ammonium citrate or lactate, citric acid and the salts thereof, and sodium carbonate. The treatment of the aluminum or aluminum alloy with these solutions to produce the desired oxide coating may consist in either immersing the metal in the solution and allowing the coating to be formed by the action of the solution, or by supplementing the action of the solution by making the metal to be coated the anode of a cell in which the solution serves as the electrolyte, and then impressing external electrical energy upon the electrodes of the cell. The manner and detail of forming oxide coatings on aluminum and aluminum alloys by means of the solutions and methods above mentioned are well known and sufficiently described in the art, and consequently only my preferred solutions and methods will be specifically described. The solutions which I prefer to use in the preparation of an oxide-coated aluminum or aluminum alloy article are three, viz: sulfuric acid, chromic acid, or sodium bicarbonate and potassium dichromate.

In forming an oxide coating on aluminum or its alloys by the use of solutions of sulfuric acid, aqueous solutions are preferably used, the concentration of the acid ranging from about 1 to 70 per cent. The metal article to be coated is placed in the bath and made the anode of an electric circuit of which another aluminum object or lead or other metal may be the cathode. When a solution of 7 per cent sulfuric acid is used, a current of from about 0.01 to 0.4 amperes per square inch is impressed upon the circuit and the action of the acid solution on the aluminum or aluminum alloy is allowed to continue for about thirty minutes. When lower concentrations of acid are used, heating of the solution is preferred to increase the rapidity of action. With higher concentrations of acid, lower current densities are preferably impressed on the anode.

When chromic acid is used as the oxide coating solution, the conditions named in the case 20 of sulfuric acid may be followed substantially. In my preferred practice, I have found a three per cent solution of chromic acid to give excellent results. The solution, during the coating process, should be heated to about 40° C.

When a solution of sodium carbonate and potassium dichromate is used to produce an oxide coating on aluminum or aluminum alloys, I have found it preferable to simply immerse the piece to be coated in the solution without applying any external electrical energy. I also prefer to heat the solution to boiling during the coating process. A solution containing about 0.5 to 6 per cent of sodium carbonate and about 0.1 to 1 per cent of potassium dichromate will give good results, but as a specific solution, I prefer one containing about 2 per cent of sodium carbonate and 0.5 per cent of potassium dichromate.

After an oxide coating has been satisfactorily formed on the aluminum or aluminum alloy surface I treat the coated metal to deposit therein an insoluble, inorganic compound. The term "inorganic compound", as used herein and in the appended claims, includes, in addition to those compounds which are strictly inorganic, the metallic ferri-cyanides and ferro cyanides. The term "insoluble inorganic compound", as used herein and in the appended claims, refers to a compound of the defined nature which is substantially insoluble in water. The method of introducing these insoluble inorganic compounds into the preformed oxide coating consists of two steps. The first step consists in placing the oxide-coated metal surface in contact with or immersing it in a solution containing either the anion or the cation of the insoluble inorganic compound which it is desired to deposit in the oxide coating. The oxide-coated metal is held in contact with or immersed in the solution for a sufficient time to allow the solution to be adsorbed in or on the oxide coating. The second step consists in bringing the oxide-coated metal, which now, as the result of the first step, has adsorbed in or on its oxide coating the solution used in the first step, in contact with a second solution, containing the cation or anion which, by combining with the anion or cation present in the first and adsorbed solution, will produce the insoluble, inorganic compound desired. The oxide-coated metal with the solution adsorbed from the first step in its oxide coating now adsorbs part of the solution used in the second step with the result that the insoluble inorganic compound desired is precipitated from the adsorbed solution in and on the oxide coating of the metal. The inorganic compound so deposited is in effect inte-

gral with or permanently affixed in the oxide coating.

An important utilization of my invention concerns the coloring of aluminum or aluminum alloy articles which are to be used in various applications where certain colors are desirable. The following may be cited as specific examples of the exact manner in which my invention may be practiced to obtain a number of different colors and shades thereof. In these examples the oxide coating may be formed on the aluminum or aluminum alloy by any of the methods heretofore mentioned but it is preferred to use solutions of sulfuric acid or solutions of chromic acid or solutions of sodium carbonate and potassium dichromate.

Example 1

Brown colors may be obtained thus: For a light brown, the oxide-coated metal is first immersed in a solution of potassium bichromate ($K_2Cr_2O_7$) and is thereafter immersed in a solution of silver nitrate ($AgNO_3$). To produce a reddish brown color the oxide-coated metal is immersed in a solution of a soluble copper salt such as copper sulfate ($CuSO_4$) and is thereafter immersed in a solution of potassium ferro cyanide ($K_4Fe(CN)_6$). To obtain a dark brown, the oxide-coated metal is immersed in a solution of lead acetate ($Pb[C_2H_3O_2]_2$) and is thereafter immersed in a solution of ammonium sulfide ($(NH_4)_2S$).

Example 2

A red color may be obtained on aluminum and aluminum alloys by immersing the oxide-coated metal in a solution of uranyl acetate ($UO_2[C_2H_3O_2]_2$) or uranyl nitrate ($UO_2(NO_3)_2$) and thereafter immersing the oxide-coated metal in a solution of potassium ferro cyanide ($K_4Fe(CN)_6$).

Example 3

A yellow color may be obtained upon aluminum and aluminum alloys by immersing the oxide-coated metal in cadmium acetate ($Cd[C_2H_3O_2]_2$), cadmium nitrate ($Cd(NO_3)_2$), or cadmium chloride ($CdCl_2$), and thereafter immersing the metal in ammonium sulfide ($(NH_4)_2S$), hydrogen sulfide (H_2S), or an alkali sulfide such as sodium or potassium sulfide. Yellow colors may also be obtained by immersing the oxide-coated aluminum or aluminum alloys in a solution of lead acetate ($Pb[C_2H_3O_2]_2$) and thereafter immersing the metal in potassium dichromate ($K_2Cr_2O_7$) or potassium chromate (K_2CrO_4). Yellow colors may also be obtained by the use of zinc acetate ($Zn[C_2H_3O_2]_2$) as an initial solution and potassium dichromate ($K_2Cr_2O_7$) or a similar alkaline dichromate or chromate as a second solution. Yellow colors may also be obtained by using barium nitrate ($Ba(NO_3)_2$) or barium acetate ($Ba[C_2H_3O_2]_2$) as the initial solution and an alkaline dichromate or chromate as the subsequent solution.

Example 4

The surfaces of aluminum or aluminum alloys may be whitened by immersing the oxide-coated metal into an initial solution of lead acetate ($Pb[C_2H_3O_2]_2$) and thereafter immersing the metal in a solution of sodium sulfate (Na_2SO_4). Aluminum and its alloys may also be whitened by immersing the oxide-coated metal in an initial solution of lead acetate ($Pb[C_2H_3O_2]_2$) and

thereafter immersing the metal in a solution of sodium arsenate (Na_3AsO_4).

Example 5

A black surface may be readily produced on aluminum and aluminum alloys by immersing the oxide-coated metal in a solution of cobalt acetate ($Co[C_2H_3O_2]_2$) or in a solution of a nitrate or chloride of that metal and thereafter immersing the aluminum or aluminum alloy in a solution of ammonium sulfide ($(NH_4)_2S$). Black surfaces may also be obtained by immersing the oxide-coated metal in an initial solution of nickel acetate ($Ni[C_2H_3O_2]_2$) and thereafter immersing the metal in a solution of ammonium sulfide ($(NH_4)_2S$).

Example 6

Blue colors, for example the deep color known as Prussian blue may be produced upon aluminum or its alloys by initially immersing the oxide-coated metal in a solution of potassium ferro cyanide ($K_4Fe(CN)_6$) and thereafter immersing the metal in a solution of ferric sulfate ($Fe_2(SO_4)_3$) or ferric chloride ($FeCl_3$). Other blue colors may be obtained by initially immersing the oxide-coated metal in a solution of ferrous sulfate ($FeSO_4$) or ferrous chloride ($FeCl_2$) and thereafter immersing the metal in potassium ferri-cyanide ($K_3Fe(CN)_6$).

Example 7

An orange color may be produced upon the surface of aluminum and its alloys by immersing the oxide-coated metal in an initial solution of antimony potassium tartrate ($K[SbO]C_4H_4O_6$) and thereafter immersing the oxide-coated metal in a solution of hydrogen sulfide (H_2S).

Example 8

A green color may be placed upon aluminum and its alloys by immersing the oxide-coated metal in a solution of copper sulfate ($CuSO_4$) and thereafter immersing the metal in a solution of sodium arsenite (Na_2HASO_3).

In the above examples the color is produced in each case by the precipitation in the oxide coating of the oxide-coated aluminum or aluminum alloy of an insoluble, inorganic compound. Thus, in Example 1, silver bichromate ($Ag_2Cr_2O_7$), copper ferro cyanide ($Cu_2Fe(CN)_6$), or lead sulfide (PbS) is precipitated in the oxide coating, according to the reagents used. In Example 2, uranium ferro cyanide is precipitated to form a red colored coating. In Example 3, a precipitate of cadmium sulfide, lead chromate, zinc chromate, or barium chromate, respectively, is deposited in the oxide coating to form various shades of yellow. In Example 4, lead sulfate and lead arsenite respectively are precipitated in the oxide coating with the result that a white color is produced. In Example 5, cobalt sulfide and nickel sulfide are respectively deposited in the oxide coating to produce a black surface on the aluminum and its alloys. In Example 6, ferric ferro-cyanide and ferro-ferri cyanide are respectively precipitated in the oxide coating to form various shades of blue. In Example 7, antimony sulfide is precipitated in the oxide coating and imparts to the surface of aluminum and its alloys an orange color. In Example 8, the oxide coating on aluminum and its alloys is colored green by the precipitation of cupric arsenite. In the examples above given and in all cases where an insoluble inorganic compound is deposited in the oxide coating of an oxide-coated aluminum or

aluminum alloy article in accordance with my invention, the depth and intensity of the color produced may be increased by repeating the treatment with various soluble compounds. Thus, for instance, in Example 8, the light green color, which is imparted to the oxide-coated aluminum or aluminum alloy by first immersing the metal in copper sulfate and then immersing it in sodium arsenite, may be increased in depth and intensity by again immersing the colored, oxide-coated metal in copper sulfate followed by an immersion in sodium arsenite.

In practicing the steps of my novel process I have determined that the concentration of the solutions in which the oxide-coated metal is immersed is not a critical factor and that solutions containing as little as 1 per cent of the soluble compounds used or solutions which are completely saturated with the soluble compounds will produce the colors desired. However, I prefer to use concentrated solutions since I have observed that in more concentrated solutions, the adsorption of the solution by the oxide coating of the oxide-coated metal is more rapid than in dilute solutions. I have further determined that the temperature of the solutions at the time at which the oxide-coated metal is introduced therein is not a governing factor and that satisfactory colors may be produced whether the solution be cold or hot.

Although my invention is extremely useful in the coloring of aluminum and aluminum alloy articles, the article so produced is in many cases more resistant to corrosion than is the untreated oxide-coated metal. This is particularly true when, as in Examples 1 and 3, an insoluble inorganic compound containing a chromate ion is deposited in the oxide coating. The corrosion-inhibiting effect of the chromate adds further efficiency to the protective action of the original oxide coating with the result that the coated and colored article is very resistant to corrosive agencies.

It is to be understood that the invention is not limited to the specific details herein described, since these can be varied without departure from the spirit of the invention.

I claim—

1. Method of providing the surface of aluminum and aluminum-alloy articles with color of uniform and permanent characteristics by forming on the surface of the aluminum or aluminum-alloy adsorbent oxide coating and adsorbing in said coating inorganic compounds separately from solutions thereof, said compounds being adapted to react to precipitate an insoluble inorganic compound of characteristic color.

2. The method of coloring the surface of an aluminum or aluminum-alloy article having on the surface to be colored an adsorbent oxide coating, comprising treating such coating with separate solutions of inorganic compounds whereby said compounds are successively adsorbed by the coating, such compounds being adapted to react to produce a colored inorganic precipitate.

3. The method of coloring the surface of an aluminum or aluminum-alloy article having on the surface to be colored an adsorbent oxide coating, comprising treating such coating with a solution containing a soluble lead compound and a solution containing a soluble salt of chromic acid whereby said compound and salt are successively adsorbed by the coating, said compound and salt being adapted to react to precipitate a yellow lead-chromium compound.

4. The method of coloring the surface of an aluminum or aluminum-alloy article having on the surface to be colored an adsorbent oxide coating, comprising treating such coating with a solution of lead acetate and with a solution of an alkali metal salt of chromic acid whereby the reagents named are adsorbed by the oxide coating and react to precipitate a yellow lead-chromium compound.

5. The method of coloring black the surface of an aluminum or an aluminum-alloy article having on the surface to be colored an adsorbent oxide coating, comprising treating such coating with a solution of a cobalt or equivalent nickel compound and with a solution of ammonium sulphide whereby the reagents are adsorbed by the oxide coating and react to precipitate an insoluble black sulphide.

6. The method of coloring blue the surface of an aluminum or an aluminum-alloy article having on the surface to be colored an adsorbent oxide coating, comprising treating such coating with a solution of an alkali metal-iron cyanide and with a solution of another iron compound whereby the reagents are adsorbed by the oxide coating, said reagents being adapted to react to precipitate an insoluble blue compound.

7. The method of coloring blue the surface of an aluminum or an aluminum-alloy article having on the surface to be colored an adsorbent oxide coating, comprising treating such coating with a solution of an alkali metal-iron cyanide and with a solution of iron sulphate or the equivalent chloride whereby the reagents are adsorbed in the oxide coating and react to precipitate an insoluble blue compound.

8. The method of coloring the surface of aluminum and aluminum-alloy articles, comprising making the article anode in a sulphuric acid electrolyte and forming thereby on the article a porous adsorbent oxide coating, and thereafter depositing in the coating by metathetical reaction therein an insoluble inorganic compound of permanent color.

9. The method comprising forming on the surface of an aluminum or aluminum-alloy article a porous adsorbent oxide coating, and thereafter by metathetical reaction depositing in the pores of the coating an insoluble inorganic precipitate of permanent color.

10. An aluminum or aluminum-alloy article having an adsorbent oxide coating containing an insoluble colored inorganic compound precipitated therein.

11. An aluminum or aluminum-alloy article having an adsorbent oxide coating containing a yellow lead-chromium compound such as is precipitated by the reaction of a soluble lead compound and a soluble salt of chromic acid adsorbed by the coating.

12. An aluminum or aluminum-alloy article having an adsorbent oxide coating containing a black sulphide such as is precipitated by the reaction of a soluble cobalt or equivalent nickel compound and soluble ammonium sulphide adsorbed by the coating.

13. An aluminum or aluminum-alloy article having an adsorbent oxide coating containing a blue compound such as is precipitated by the reaction of a soluble alkali metal-iron cyanide and another soluble iron compound adsorbed by the coating.

14. An article of aluminum or aluminum-alloy having on its surface an adsorbent anodic oxide

coating containing in its pores an insoluble inorganic precipitate of permanent color.

15. An article of aluminum or aluminum-alloy having on its surface an adsorbent anodic oxide
5 coating containing in its pores a precipitate of Prussian blue.

16. An article of aluminum or aluminum-alloy having on its surface an adsorbent anodic oxide

coating containing in its pores a precipitate of lead chromate.

17. An article of aluminum or aluminum-alloy having on its surface an adsorbent anodic oxide coating containing in its pores a precipitate of
black sulphide. 5

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