United States Patent

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[31] **53698/67**

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[54] **METHOD OF PRODUCING COLORED COATINGS ON ALUMINUM**
14 Claims, No Drawings

[52] **U.S. Cl.** **204/58**
[51] **Int. Cl.** **C23b 9/02**
[50] **Field of Search** 204/58, 35

[56] **References Cited**

UNITED STATES PATENTS

3,475,167	10/1969	Beatty et al.	204/58
3,382,160	5/1968	Asada	204/58
3,280,013	10/1966	Economy	204/58
2,930,951	3/1960	Burger et al.	204/58

FOREIGN PATENTS

662,063	4/1963	Canada	204/42
741,753	11/1943	Germany	204/58

OTHER REFERENCES

The Surface Trentment of Aluminum, by Wermick & Pinner, 3rd edition, 1964, p. 348.

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ABSTRACT: In procedure for producing colored coatings on aluminum by first anodizing the aluminum surface and then treating such anodically coated surface with alternating current in an acidic bath containing metal ions selected from the group consisting of the following cations and anions: NI^{++}, Co^{++}, Cu^{++}, Ag^{+}, Pb^{++}, and anions consisting of oxygen combined with one of the metals Se, Te and Mn, to produce a colored deposit in the coating, improved coloring results notably in avoiding or inhibiting occurrence of localized nonunifomity, especially with darker or more intense tones, are achieved by maintaining a content of magnesium ions in the bath.

METHOD OF PRODUCING COLORED COATINGS ON ALUMINUM

BACKGROUND OF THE INVENTION

The present invention relates to a process for producing colored coatings on aluminum, and more particularly relates to the production of inorganic-colored coatings on aluminum articles. References to aluminum herein will be understood to include aluminum of ordinary commercial purity and aluminum-base alloys that are suitable for conventional anodizing treatments. The term aluminum article as used herein is intended to include semifabricated products, such as rolled aluminum sheet and aluminum extruded sections.

The present invention relates to improvements in a previously described two-stage process for producing a colored coating which comprises anodically oxidizing an aluminum article and thereafter treating the anodized article by passing an alternating current between such aluminum article and a counterelectrode, while such aluminum article and electrode are immersed in a bath that contains a dissolved compound of a selected metal in an aqueous acidic medium. Under these circumstances the anodic oxide coating on the aluminum article becomes colored. More particularly, the invention is concerned with such process wherein the acidic bath of the alternating current treatment contains metal ions selected from the group consisting of the following cations and anions: Ni^{++}, Co^{++}, Cu^{++}, Ag^{+}, Pb^{++}, and anions consisting of oxygen combined with one of the metals Se, Te and Mn. Procedures of this sort are included in the description of U.S. Pat. No. 3,382,160, granted May 7, 1968 to Tahei Asada.

In the above, known process in which the aluminum article is in the first stage subjected to anodizing, preferably with direct current, for example in a sulfuric acid electrolyte, i.e. under conditions known for the production of an anodic oxide film of the so-called porous type, the counterelectrode in the alternating current step may be a material, such as graphite (i.e. carbon), which is inert to the electrolyte, or may be formed of other conductive composition, e.g. metal, which may advantageously be selected among metals having a solution potential more noble than aluminum in the conventional series of electrode potentials, and which can preferably be the same metal, if available, as constituted by the selected ions in solution in the electrolyte, all as explained in the previous disclosure. For instance, where the bath electrolyte contains nickel dissolved therein, a nickel counterelectrode may be very effectively employed.

As stated, it is known by the foregoing procedure to produce colored deposits in the anodic coating, being understood to be a deposit of the selected metal in chemical combination with oxygen, i.e. a compound of the class of oxide or hydroxide, it having been further indicated that depending on the selected metal and intensity or duration of treatment, a variety of colors are obtainable, including gold or other yellow tones, various shades of red and brown, bronze and like deep colors, including black.

In the known process certain difficulties have been experienced especially when the treatment time or conditions are adjusted to give darker shades, associated with a relatively large or intense deposition of the metallic material, presently understood to be metallic oxide, in the anodic oxide film on the aluminum. In particular there is an increased tendency to so-called spalling, i.e. local flaking or like modification of the anodic oxide film, this effect being to produce colorless or pale local spots in the coating, which may be of minute size but are nevertheless extremely objectionable.

A chief object of the present invention is to reduce the incidence of spalling. A further and more specific object is to improve the operation of the above process utilizing metal ions selected from the stated group, notably the second or alternating current treatment stage of such process, so that a full range of tones or shades may be obtained by employing a given bath, including the darker tones that are achieved with higher voltages or longer times or both, while in all cases there is desirable avoidance of deterioration of the colored coating as by spalling or the like.

SUMMARY OF THE INVENTION

With one or more of the foregoing aims in view, it is found that more uniform results, and specifically an inhibition or avoidance of spalling and like deterioration, can be obtained by the introduction of magnesium, as in the form of magnesium compounds, into solution in the electrolyte, i.e. the acidic bath employed in the alternating current step. More particularly a significant content of magnesium ions is achieved and maintained in the bath, as by incorporating a magnesium salt such as magnesium sulfate or other appropriate compound, the process being otherwise generally performed as heretofore disclosed. Under these circumstances relatively very dark or intense shades or tones can generally be achieved without spalling or like deterioration; or at least, it is possible to obtain darker shades, without the risk of spalling, than has heretofore been uniformly or reliably attainable.

The complete procedure includes first anodizing the aluminum surface to produce the anodic coating thereon, and then subjecting the coated surface to alternating current in an aqueous bath containing the selected metal ions, such bath also containing magnesium ions, as for example in amount represented by at least about one gram per liter of magnesium sulfate (calculated as $MgSO_4.7H_2O$), or more generally stated at least about 100 p.p.m. Mg^{++} ions. Thus a typical bath may constitute the salt of the metal selected for coloring function, appropriate acidic and related constituents, and a magnesium compound which in dissolved form is in effect a magnesium salt, advantageously containing an anion otherwise present in the electrolyte.

The underlying, known method of producing colored coatings has been found of special practical value as utilizing nickel-containing or copper-containing baths, and it has correspondingly been noted that such operations are markedly improved by the maintenance of combined magnesium in solution. A special advantage of the present invention is that a given electrolyte can be employed to provide a wide range of shades or tones, notably up to the darkest values, without difficulty, so that the process has improved flexibility in practice, to accommodate a wide variety of color requirements. Moreover, it has been noted, for example in the nickel-containing and copper-containing solutions, and others, that more intensely colored and spall-free surfaces are obtainable from the magnesium-bearing electrolyte under otherwise identical conditions.

DETAILED DESCRIPTION

As stated, the complete process of producing a colored coating on an aluminum surface of an article involves first anodizing the surface in conventional manner to produce an anodic oxide coating, e.g. of a type customarily applied for protective or like purposes. While any of a number of known operations may be employed, notably with electrolytes of a group which may be defined as consisting of aqueous solutions of sulfuric acid, chromic acid, or a sulfonic acid such as sulfosalicylic acid, and suitable mixtures of these with other acids or compounds, and while in some cases AC anodizing treatment may be feasible, effective results are obtained by anodizing the work with direct current, as for periods of 20 minutes to 60 minutes, in an aqueous solution of sulfuric acid, e.g. 15 percent acid by weight. The operating conditions of the anodizing step do not appear to be very critical, being selected largely to suit the thickness and other characteristics of anodic coating desired; the requirements of the subsequent coloring step are satisfied over a considerable range of thicknesses of porous oxide coating on aluminum.

The second step of the process, to which the present improvements are specifically directed, then involves submerging the anodized aluminum article, if desired after suitable rinsing, in an acidic bath in which a counterelectrode is

likewise submerged, such bath comprising an aqueous acidic solution containing the metal selected for coloring function, specifically metal ions selected from the group consisting of the following cations and anions: Ni^{++}, Co^{++}, Cu^{++}, Ag^{+}, Pb^{++}, and anions consisting of oxygen combined with one of the metals Se, Te and Mn. Thereupon alternating current is passed through the solution between the article and the counterelectrode, for sufficient time to effect the desired colored deposit in the oxide coating, e.g. a deposit understood to consist of metal, of the selected ions, which is in chemical combination with oxygen, such as oxide or hydroxide, conveniently herein considered to be oxide.

It is in this acidic bath that a content of magnesium ions is maintained in accordance with the present invention, preferably by adding a quantity of suitable magnesium salt (or other compound which becomes dissolved) in substantial excess so as to accommodate a slow but continuing depletion of such ions as the bath is repeatedly used, i.e. to avoid need for frequent replenishment of the Mg. content.

As will be apparent from the prior disclosure mentioned above, the basic requirement of the process is that the bath should be a water solution containing the metal ions selected for coloring function, and an acidic constituent, the dissolved compounds being all in relatively low concentration. Thus the bath constituents, including nonmetallic anionic constituents, may be variously selected to provide the desired solubility of metal ions and suitable acidity of the electrolyte, and supplemental or further salts and the like may be incorporated, as desired for supplemental purposes that do not interfere with the formation of the colored deposit, or as may result from initial or subsequent pH adjustment. Thus sulfate, borate, acetate, tartrate, phosphate, sulfamate and other common ions have been found appropriate for solutions of one metal or another, e.g. with respect to salts of the selected metal or as forming the chosen acidic component. It will be readily apparent that the constituents will depend on solubility and like requirements of the metal ions, as for example in the case of lead ions, substances such as sulfamic acid and acetic acid and their salts should be utilized instead of sulfate. Where the metal ions are of anionic nature, compounds appropriately soluble in the acidic bath should be employed, such as alkali metal selenites, selenium oxide, selenic acid, alkali metal tellurites, permanganates, and the like.

Numerous examples of suitable metal-containing baths and types of compounds therein are set forth in the above-cited U.S. Pat. No. 3,382,160, to which reference may be had for such information, as indeed likewise for inherent or other indication of generally preferable conditions of acidity. For instance, notably good results have been attained in baths containing nickel ions or cobalt ions with the pH adjusted to the range of about 4 to about 4.5, while in the case of other metal ions of the group named herein above, presently preferable operation has been in a pH range of about 0.5 to about 2.

For the purposes of this invention, magnesium is preferably added to the electrolyte in the form of a salt, the anion of which is already present in the bath or is otherwise compatible as will be understood or may be readily determined. Thus for example a presently preferred nickel electrolyte contains nickel sulfate and boric acid, to which the magnesium may be added as magnesium sulfate or borate. Alternatively, the magnesium can actually be supplied as a soluble form of magnesium oxide or magnesium hydroxide, then becoming a corresponding dissolved salt in the presence of acidic constituents. Necessary adjustments of acidity for this and other purposes are made by suitable additions such as sulfuric acid, boric acid, ammonium hydroxide and the like. While some anions, such as halides (except perhaps chlorides in small concentration) are not presently recommended, the essential requirement is to have dissolved magnesium ions present and selection of a suitable and commonly available salt presents no problem in the light of the foregoing.

In general the amount of magnesium present should be sufficient to provide significant inhibition of spalling, i.e. to avoid or materially reduce the occurrence or tendency toward occurrence of minute spots or flaked-off areas, or like spots or defects in the colored product, e.g. in the darker or very dark tones, obtainable with the selected metal. Although such spalling is often represented by colorless or pale spots, it may sometimes occur otherwise, as for instance where flaking near the outset of the alternating current treatment leads to a more intense tone due to preferential flow of current to the spalled area. Although some utility has been noted for lesser amounts, in general at least about 100 p.p.m. of magnesium (measured as such, by weight) should be present for good results, and indeed preferably at least somewhat more, such as represented by about 2 grams per liter of conventional magnesium sulfate (200 p.p.m. Mg. Most preferably the magnesium compound is added in amount to provide from approximately 1,000 to 2,500 p.p.m. of Mg. as for example about 10 to 25 grams per liter of $MgSO_4 \cdot 7H_2O$, especially to avoid unduly rapid depletion. Even considerably greater amounts, as up to 40 grams per liter of the magnesium salt (4,000 p.p.m. Mg.), have shown no adverse effect, so that the upper limit appears primarily economic.

The exact effect of adding magnesium sulfate or other magnesium compound to the electrolyte is not known. However, a possible belief is that spalling is due to local differences in the resistance of the anodic oxide film, or more particularly that spalling may be related to the evolution of hydrogen where the oxide layer at the bottom of one or more pores of the coating is thin in a local area. It is believed that the incorporation of magnesium sulfate, for example, in the electrolyte leads to some co-deposition of magnesium oxide with the colored oxide or the like in the pores of the anodic oxide film and that such deposition increases the thickness of electrically resistant oxide at the bottom of the pores, thus removing the postulated cause of spalling and permitting the development of darker colors therein. Stated in another way, this hypothesis is that magnesium oxide or hydroxide is coprecipitated with the colored oxide or hydroxide of the metal of which ions are present from the above-defined group, to provide a more electrically resistant deposit, a present theory being that the relatively larger flow of current during that part of the AC cycle when the anodized article is the cathode results in depletion of hydrogen ions at the base of the pores, causing localized rise in pH (greater alkalinity) and consequently the desired precipitation of the metal oxide or hydroxide, and in the present process, of magnesium oxide or hydroxide as well. However, the beneficial effects of this invention have been abundantly demonstrated and it is not to be understood as dependent on the above or any other theories.

Referring to the following specific examples of the process, aluminum articles were first anodized by conventional anodic treatment with direct current, e.g. for periods upwards of 20 minutes in the 15 percent aqueous sulfuric acid solution at an ordinary temperature, for example selected in the range of 20° C. to 25° C., conveniently 21° C. It will be understood that other strengths of acid solution, or indeed solutions of other acids as mentioned above, and likewise other modifications of condition as to suit the protective or like requirements of the coating may be employed. Conveniently operation under the first-named conditions, with a current density of about 15 amperes per square foot (1.3 amperes per square decimeter) of work surface is very satisfactory, for a time selected to yield a desired film thickness, normally from 0.4 to 1.0 mil or more. As will be understood, the anodized article is then suitably rinsed and submerged in the selected acidic bath which contains the appropriate counterelectrode. In general, the alternating current is passed, between the article and the electrode, at a conveniently moderate voltage, say from 5 to 20 volts, for a correspondingly appropriate time, e.g. from a few minutes up to 10 to 15 minutes, sometimes with increasing voltage or other suitable electrical control. Generally, the shade of color achieved depends on the time of treatment and on electrical conditions; for instance, lighter shades are produced by relatively brief treatment with lower voltages, whereas darker or

stronger or very dark colors require a longer time or greater electrical values.

EXAMPLE 1

Aluminum articles, e.g. aluminum sheets, were first anodized in the conventional 15 percent sulfuric acid solution and after rinsing were then subjected to the alternating current treatment, with a counterelectrode of metallic nickel in a bath (adjusted to pH 4.0 to 4.5) having the following composition:

$NiSO_4.7H_2O$ 25 g.p.l.
$MgSO_4.H_2O$ 20 g.p.l.
H_3BO_3 25 g.p.l.
$(NH_4)_2SO_4$ 15 g.p.l.

Aluminum articles, as anodized, were respectively treated for different times and under different voltages in this bath, yielding a range of colors from light bronze to very dark bronze or nearly black. In these and in other examples herein, the treated articles were preferably subjected to conventional sealing treatment, as in very hot or boiling water, for usual purposes. Whereas the AC treatment in the stated bath for 5 minutes yielded light and medium bronze tones at AC voltages of 10 and 12 respectively, a dark bronze was achieved at 15 volts. An operation for 5 minutes at 13 volts, followed by 5 minutes more at 17 volts, yielded a very dark bronze color. For comparison, operation of such bath lacking the magnesium sulfate occasioned spalling difficulty in endeavors to produce the dark and especially the very dark tones.

EXAMPLE 2

Anodized articles treated with alternating current in baths comprising copper sulfate and sulfuric acid in aqueous solution having a pH of about 1.3, and containing magnesium sulfate addition of about 20 grams per liter yielded a range of colored coatings, including pink, light maroon, dark maroon and black, depending on voltage and treatment time. Copper sulfate ($CuSO_4.5H_2O$) was used, for example, in various concentrations from 25 to 50 grams per liter, and sulfuric acid in amounts of 5 to 6 g.p.l. As one specific instance, the electrolyte contained 25 g.p.l. copper sulfate, sulfuric acid as last noted and from 1 to 3 g.p.l. magnesium sulfate ($MgSO_4.7H_2O$). Using a graphite counterelectrode an operation was effected at 8 volts AC for 3 minutes, followed by 12 volts AC for 9 minutes. A uniform, essentially black color was produced, whereas comparable treatment without magnesium sulfate addition generally resulted in spalling defects.

EXAMPLE 3

In this instance a sheet of uniformly oxide coated aluminum (anodized in 15 percent sulfuric acid for 40 minutes), was submerged, with a nickel counterelectrode, in a bath of 2.5 percent boric acid solution, containing 4.0 percent nickel ammonium sulfate and 3.5 percent magnesium sulfate, this bath being at a pH of 4.5. With the bath at room temperature alternating current was passed for 10 minutes at a potential of 15 volts. The product was sealed in boiling water for about 30 minutes and had a very dark brown color, free of coating defects.

EXAMPLE 4

A sheet of aluminum anodized as in example 3 was similarly treated with alternating current, except for the use of a graphite counterelectrode and the use of 2.5 percent magnesium sulfate in the electrolyte. After passage of the alternating current for 13 minutes at a potential of about 16 volts, and sealing as before, the aluminum sheet was found to have a permanent oxide coating characterized by a uniform, essentially black color.

EXAMPLE 5

In this instance aluminum articles were first anodized by conventional treatment as indicated in other examples, and then subjected to the alternating current treatment, with a graphite counterelectrode, in a bath containing from 25 to 30 g.p.l. of lead acetate, 20 to 25 g.p.l. of acetic acid and 20 g.p.l. of magnesium acetate ($Mg[C_2H_3O_2]_2.4H_2O$). Alternating current was passed at 23 volts for about 5 minutes. A uniform black coating was produced, whereas similar operation without the magnesium addition tended to exhibit some spalling or like difficulty.

Further instances of baths to which magnesium ion additions, usually effected by inclusion of 2 to 30 g.p.l. magnesium sulfate, have been found beneficial, are solutions of 2.5 g.p.l. selenium oxide (SeO_2) in aqueous sulfuric acid at pH 0.8, one g.p.l. sodium tellurite (Na_2TeO_3) in aqueous sulfuric acid at pH 0.6 and 1 g.p.l. silver nitrate ($AgNO_3$) in aqueous sulfuric acid at pH 1.2, yielding respectively reddish gold, dark gold and yellow-green colors in the oxide coating.

Extended tests have also indicated that magnesium ion additions, for example by employment of appropriate magnesium salts in amounts of the order indicated in the above specific examples, are also advantageous for the purposes of the present invention, in the baths for alternating current treatment in each of those of the examples of the above-cited U.S. Pat. No. 3,382,160 which relate to the employment of metal ions (whether cations or anions) of the specific group hereinabove set forth.

It is to be understood that the invention is not limited to the particular compounds and operations herein set forth but may be carried out in other ways without departure from its spirit.

We claim:

1. In a method of producing an inorganically colored anodic coating on an aluminum surface of an article wherein said surface has first been anodized to produce an anodic coating thereon and wherein alternating current is passed between said anodized surface and an electrode while both are immersed in an aqueous acidic bath containing metal ions selected from the group consisting of: the cations Ni^{++}, Co^{++}, Cu^{++}, Ag^{+}, Pb^{++}, and anions consisting of oxygen combined with one of the metals Se, Te and Mn, for producing a colored deposit in the coating, the procedure comprising adding to said bath a magnesium compound in an amount to provide in solution in said bath at least about 100 p.p.m. of magnesium ions and effecting said alternating current treatment while maintaining said magnesium ion content of at least about 100 p.p.m. in said bath to inhibit occurrence of localized nonuniformity of the colored coating.

2. A method as defined in claim 1, in which the metal ions are Ni^{++} ions or Cu^{++} ions.

3. A method as defined in claim 1, in which said step of adding the magnesium compound consists in adding a magnesium salt to the bath in amount of at least about 2 grams per liter.

4. A method as defined in claim 1, which includes the step of first anodizing said aluminum surface of the article with direct current between said article as anode and a cathode in an aqueous solution of sulfuric acid to produce said anodic coating.

5. A method as defined in claim 4, in which in the bath through which alternating current is passed to said anodized surface the metal ions are Ni^{++} ions or Cu^{++} ions, and said magnesium compound is incorporated in the bath in amount of at least about 2 grams per liter.

6. A method as defined in claim 1, in which the metal ions selected from said group consist essentially of Ni^{++} ions.

7. A method as defined in claim 6, in which said treatment in the bath is effected by passing said alternating current between said anodized aluminum surface and an electrode of nickel.

8. A method as defined in claim 6, in which said bath contains nickel sulfate and boric acid and in which magnesium sulfate is added to the bath to provide said magnesium ions.

9. In a method of producing an inorganically colored anodic coating on an aluminum surface of an article wherein said surface has first been anodized to produce an anodic coating thereon and wherein alternating current is passed between said anodized surface and an electrode while both are immersed in an aqueous acidic bath containing metal ions selected from the group consisting of: the cations Ni^{++}, Co^{++}, Cu^{++}, Ag^{+}, Pb^{++}, and anions consisting of oxygen combined with one of the metals Se, Te and Mn, for producing a colored deposit in the coating, the procedure comprising adding to said bath a magnesium compound in an amount to provide in solution in said bath at least about 200 p.p.m. of magnesium ions and effecting said alternating current treatment while maintaining magnesium ions in said bath in amount of at least about 200 p.p.m.

10. A method as defined in claim 9, in which the metal ions selected from said group consist essentially of Pb^{++} ions, said bath consists essentially of, acetic acid and magnesium acetate.

11. A method as defined in claim 9, in which the metal ions are Ni^{++} or Cu^{++} ions and which comprises adding $MgSO_4 \cdot 7H_2O$ to the bath in amount of at least about 10 grams per liter to provide said magnesium ions.

12. A method as defined in claim 11, in which the metal ions selected from said group consist essentially of Cu^{++} ions.

13. A method as defined in claim 9, which includes the step of first anodizing said aluminum surface of the article with direct current between said article as anode and a cathode in an aqueous solution of sulfuric acid to produce said anodic coating, and in which in the bath through which alternating current is passed to said anodized surface the metal ions selected from said group consist essentially of Ni^{++} ions and said treatment in the bath is effected by passing said alternating current between said anodized aluminum surface and an electrode of nickel.

14. A method as defined in claim 13, in which said alternating current treatment bath consists essentially of nickel sulfate, ammonium sulfate, boric acid and magnesium sulfate, said bath being maintained at a pH of at least about 4.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,616,309 Dated October 26, 1971

Inventor(s) TAHEI ASADA; WILLIAM ERNEST COOKE and PAUL JOHN SAJBEN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4, line 54, "the" should read --a--

Col. 6, line 9, "23" should read --13--

Col. 7, line 18, after "of" and before comma (,), add

--lead acetate--

Signed and sealed this 16th day of May 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334