COLORING ANODIZED ALUMINUM

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The present invention is related to the coloring of anodized aluminum and, more particularly, to the production of a black color on anodized aluminum.

It has been proposed that there be a number of processes for producing colored anodized metal, especially black colored aluminum. These processes are generally of two kinds. First a color may be introduced into the pores of an anodic film on the surface of anodized aluminum by the use of one or more colored dyes carried in an aqueous bath or alcoholic vehicle. The second kind of coloration involves the formation of a colored precipitate in the pores of the anodic film. Such a colored precipitate is often a metallic sulfide and, more particularly, is produced by a metathetical reaction wherein a metal ion is absorbed into the anodic pores followed by the subsequent absorption of sulfide ion therein.

The aforementioned prior art processes have certain disadvantages. With very few exceptions, organic colorations are subject to fading through the action of light, oxidation, and the like. With respect to the prior art metallic sulfide colors, it is very difficult to obtain uniform coloration in any reasonable length of time. Since the depth of color is dependent upon the completeness of diffusion, time, often amounting to up to about one hour, must be allowed to permit diffusion to occur. The fact that a solid product, i.e., the sulfide precipitate, is formed in narrow pores of the anodized layer during diffusion slow down the rate at which the color develops. In view thereof it is difficult to achieve a uniform, deeply colored aluminum by the usual metathetical reactions proposed heretofore. As far as is known, the art has not been provided with a commercially acceptable process whereby the disadvantages enumerated hereinbefore can be overcome.

It has now been discovered that by means of a novel composition of ingredients employed in a novel manner, deep, commercially satisfactory, black colorations can be produced in anodized metal. It is an object of the present invention to provide a novel process for the production of black-colored anodized metal.

Another object of the present invention is to provide a novel composition of matter useful in the formation of black-colored anodized aluminum.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawings in which the figure shows a schematic outline of an anodizing and coloring process involving use of the present invention.

Generally speaking, the present invention contemplates a coloring process wherein a porous anodized surface is impregnated with an aqueous solution containing a substance capable of donating a precipitating ion (e.g., sulfide ion) at temperatures in excess of about 200° F. and stable in aqueous solution at temperatures below about 200° F., and an ion capable of reacting with the precipitating ion to form a colored precipitate which is insoluble in water and heating the thus impregnated anodized surface to a temperature in excess of about 250° F. for at least about one or two minutes whereby the anodized surface is colored. Heating times can be up to any practical length of time and are principally dependent upon temperature. Longer times are employed at lower temperatures and shorter times are employed with higher temperatures.

The present invention further contemplates as a composition of matter a coloring impregnant for coloring anodized metal comprising an aqueous solution containing in solution metalliferous ion capable of reacting with the sulfide ion to form a colored sulfide which is insoluble in water, at least an amount of a substance capable of donating sulfide ion at temperatures in excess of about 200° F. and stable in aqueous solution at temperatures below about 100° F. effective to provide sufficient sulfide ion under reaction conditions to react with said metalliferous ion, a thickening agent in an amount effective to induce in the aqueous solution a workable viscosity for the means by which the coloring impregnant is applied to the anodized metal and a stabilizing agent. In addition, the aqueous solutions can contain dispersed therein an insoluble substance designated in this specification and claims as a flattening agent.

The ion capable of reacting with the precipitant sulfide ion used in the coloring process of the present invention is at least one member of the group consisting of the ions of cobalt, copper, antimony, nickel, molybdenum, iron, and bismuth. In order to obtain a stable black coloration in the anodized surface, it is advantageous to employ ions of cobalt, nickel, or iron. It is pertinent to note that the ion employed in solution can be not only a simple hydrated ion of a metal mentioned hereinbefore but also a complex ion which contains as a part thereof a metal mentioned hereinbefore. When a complex ion is employed, it is necessary that the complex ion be capable of thermal degradation at a temperature below about the heating temperature. The use of the term “precipitant ion” in this specification and claims is not intended to imply that color formation is a precipitation in the usual sense. The substance causing the color in the final product is usually a water-insoluble substance but is not necessarily produced in the presence of water.

The substance capable of donating sulfide ion at temperatures in excess of about 200° F. and stable in aqueous solution at temperatures below about 100° F. (hereinafter called “sulfide donor”) is advantageously sodium thiosulfate. The sulfide donor is generally a sulfur-containing substance capable of dissolving in water in an amount to provide at least about 0.1% of sulfur available for reaction. Operable sulfide donors include ammonium thiosulfate, potassium thiosulfate, thiourea (thiocarbamide), and substituted thioamides in addition to sodium thiosulfate.

Thickening agents operable in the present invention include a colloidal suspension of boehmite-type aluminum oxide known in the trade as “Baymal,” soluble starches such as arrowroot starch, hydroxyl alkyl celluloses (e.g. hydroxethyl cellulose), polyvinyl alcohol, polyacrylamide, methyl vinyl ether copolymer with maleic anhydride sold under the trade name “Gantrez AN,” polyvinylpyrrolidone and an ethylene oxide polymer such as sold under the trade name “Polyox WSR Resin.” Such thickening agents are employed in amounts of about 0.1 and up to about 20 or even 50 or more parts by weight of thickening agent per 100 parts by weight of solution. Because of ionic effects on the viscosity of a colloidal suspension, it is impossible to specify with accuracy the exact amount of thickening agent needed to achieve the required viscosity without specifying the character and amount of each ionic species present in the impregnating composition of the present invention. It will be found, however, that an amount of thickening agent in the range of parts by weight, as specified hereinafter, will usually suffice to achieve the required viscosity.
The use of a stabilizing agent in the coloring solutions of the present invention which contain sodium thioureaate is highly advantageous and in some instances essential if one is to be assured that the coloring bath is to be stable for even short periods of time. It is possible for unstable solutions to exist for a measurable period of time without the appearance of precipitated sulfide. Such solutions can be used, for example, by being mixed in a spraying device immediately prior to spray application. In some instances where a bath life in excess of about 15 minutes or a half hour is not necessary, unstabilized baths may be used for dip, roller or other types of coating. In the usual case, however, it is highly advantageous to employ at least about 0.1% by weight of sodium or potassium bisulfite in the bath as a stabilizing agent. It is even more advantageous to employ at least about 0.3% of such stabilizing agent in the bath. Normally no more than about 1% of stabilizing agent is necessary but up to about 5% by weight or more can be used if desired. In the case of sodium thioureaate solutions containing the cuprous ion as the sole coloring ion, the presence of at least about 0.3% by weight of stabilizing agent is a practical necessity since such solutions often can deteriorate by precipitation in very short spaces of time. Except for molybdenum solutions, all the sodium thioureaate solutions of the present invention appear to be stable at the pH produced by the ingredients, which pH’s are normally slightly acidic (i.e., a pH of 4 to 6). The pH of molybdenum-containing solutions must be adjusted to at least as high as about 7. Impregnating (coloring) compositions or solutions of the present invention containing thiourea appear to be shelf stable at least for several months without any stabilizing addition.

Optionally, but nevertheless highly advantageous, one can employ up to about 50% by weight or more (based on weight of bath not included therein) of a flattening agent. A flattening agent for purposes of this specification and claims is a finely divided, essentially inert substance such as titanium dioxide (pigment grade), rouge (iron oxide), finely ground mica, finely divided chemically stabilized clay or the like. For dipping or spraying purposes, the use of a flattening agent in an amount within the aforesaid range and more particularly within about 5% to 20% by weight dispersed in the coloring solution is highly advantageous. The flattening agent enhances even more the adhesion of the metal to be colored and in general, improves the workability of the coloring compositions.

As is obvious to one skilled in the art, the impregnating composition will contain addition ions balancing the color-producing ions (stochiometrically equivalent amounts) to permit electronic balance in the aqueous solution of the impregnating composition. These complementing ions necessarily are such that, together with the metal-bearing ion, they will produce a water soluble material stable in aqueous solution. Where mixtures of metallic species are employed, it is necessary to avoid mutually incompatible ions. For instance, one could not employ cobalt sulfate and lead acetate together in the same aqueous solution since lead sulfate is an undesirable, substantially water-insoluble material. In like manner, salts, such as cobalt chloride and silver sulfate, are also mutually incompatible in an aqueous solution.

The base metal which is colored by means of the present invention is usually aluminum (including for purposes of this specification and claims anodizable alloys containing more than about 80% aluminum) but can be another anodizable metal such as titanium. In preparing aluminum for the coloring process of the present invention, it is usually necessary to anodize in such fashion as to produce a surface anodic film at least about 0.1 mil thick. For architectural purposes it is advantageous that the anodic film be at least about 0.5 mil thick, for example about 0.7 mil or thicker. Those skilled in the art will recognize that such anodic films may be produced in a number of different ways. In order to describe the invention in the utmost particularity, however, details concerning satisfactory anodizing conditions in aqueous, acidic baths are set forth in Table I.

<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of electrolyte</strong></td>
</tr>
<tr>
<td><strong>Concentration of electrolyte</strong></td>
</tr>
<tr>
<td><strong>Anodic C.D.</strong></td>
</tr>
<tr>
<td><strong>Time</strong></td>
</tr>
</tbody>
</table>

* 1 Ampere = 0.256 square foot

It is to be noted that while preferred conditions of anodizing have been set forth in Table I under the heading "Preferred Aspect," these preferred conditions are, in truth, designed to provide a satisfactory anodizing coating about 0.7 mil thick on an aluminum alloy known to the art as grade 6063 containing nominally in percent by weight about 0.45 to 0.90% magnesium, about 0.2 to 0.5% silicon, not more than 0.35% iron, 0.1% each of copper, manganese, chromium, zinc and titanium in addition to aluminum. As those skilled in the art will recognize, each aluminum alloy will require subtle adjustments of the anodizing conditions within the broad range set forth in Table I to produce an equivalent coating. Since it may be possible to produce equivalent coatings in a non-electrolytic manner, the term "anodizing" is used in this specification and claims to include any and all means of forming a porous, adherent surface coating at least about 0.1 mil thick, which coating is substantially equivalent to those coatings produced under the broad conditions set forth in Table I.

Once the anodizing has been completed, the anodized object is rinsed and allowed to dry at about room temperature. The thickened solution of the coloring impregnant of the present invention is then applied to the anodized surface. While the thickened solution can be applied in any fashion which will produce an evenly distributed wet coating, it has been found to be advantageous to spray the thickened solution onto substantially horizontally oriented surfaces. It is possible and may at times be advantageous to arrange matters such that thickening of the solution occurs immediately prior to or simultaneously with the spraying. In this manner it is possible to employ thickening agents which, after a time, will become unstable in the presence of ionic solutions. After the freshly anodized surface has been sprayed with the thickened solution, it is immediately heated to a temperature of about 250° F. to about 1000° F. for about 15 to 60 minutes. Generally it is advantageous to heat within the range of about 300° F. to about 600° F. with the greatest amount of control and flexibility being obtained when heating is conducted within the range of 350° F. to 450° F. It has been found satisfactory to heat to a temperature of about 400° F. for about 15 minutes. The heating can be accomplished by using an oven, by induction heating or by any other heating means known to the art, which heating means will not disturb the treated surface of the anodized metal.

In further explanation of the heating operation, it is to be understood that when it is stated that a treated surface is heated to a temperature of about 400° F. for 15 minutes, this procedure is carried out when a wet, treated sheet metal object is introduced into an oven having an ambient temperature maintained within plus or minus 10° in Fahrenheit units of 400° F. It is recognized that attainment of the oven temperature by an object introduced therein is subject to a lag, especially when the surface of the object is wetted with an aqueous solution. Further, it is recognized that the mass of an object introduced into an oven is a determinant of the rate at which the object attains oven temperature. Accordingly, for purposes of this specification, temperatures and times are given with the understanding that sheet metal objects are being treated and that the oven or other heating means is of a sufficient capacity to heat a sheet metal object without losing temperature to any substantial degree.
those skilled in the art will readily recognize, modifications of the time and/or temperature ranges may have to be made if conditions or situations other than those specifically described herein are encountered. After heating, anodized and colored aluminum is usually found to be sealed as shown by the ASTM Dye Test Designation B—336—63T—

"Resistance of Anodically Coated Aluminum to Staining by Dyes." In some instances, such as when treating 1100 alloy, only partial sealing is attained.

For further corrosion protection the anodized and colored aluminum can be treated with polar alicyclic compounds, lacquers, waxes, boiling water, heated aqueous metal salt baths such as sodium dichromate, nickel acetate, etc. Treating with boiling water gives a velvety appearance to a black colored aluminum which at times may be desirable.

In carrying the present invention into practice, the concentration of the various color forming metal salt and precipitant) and control agents may vary widely. For example, the color forming salt may be used from a 1% concentration up to saturation, about 5—15% being usually advantageous. The sulfide donor can be used from a 1% concentration up to saturation, about 15 to 50% being usual. The solution stabilizing agent can be used from 0.1% concentration up to about 3%, e.g. about 0.75 to about 1.25%. The flattening agent can be used from a 1% concentration up to 50% or more. About 2—8% of flattening agent is usually sufficient. The thickening agent concentration is governed by the ionic effects on the viscosity of a colloidal suspension. Thus, the thickening agent can sometimes be present in minute amounts or can be present up to concentrations that will form very viscous solutions. A particularly advantageous range for "Baymal" alumina is about 1 to 10%, e.g. 2—4%.

In carrying the present invention into practice, it is advantageous to employ as a blackening precipitant an aqueous composition made up with the following:

**Substance:**
- Amount in percent by weight
  - Cobalt chloride hexahydrate ———— 4 to 15
  - Sodium thiosulfate pentahydrate ———— 12 to 30
  - Sodium bisulfite ———— 0.5 to 1.25
  - Rouge (Fe₂O₃) ———— 2 to 8
  - "Baymal" ———— 1 to 4
  - Water ———— Balance

Blackening is accomplished by impregnating an anodized aluminum surface with the cobalt-containing ingredient and thereafter heating for about 15 minutes in an oven maintained at 400° F. The impregnated anodized sheet was then heated in an oven at 400° F. for about 15 minutes. After washing off excess material the anodized surface was found to be colored jet black. It is to be observed that the procedure followed in this and subsequent examples is that procedure illustrated in schematic form on the drawing. Referring now thereto, it is to be noted that the two-step process of the invention involving coating with impregnant (or more broadly speaking, impregnating), and heating is preceded by the conventional anodizing operations and followed by any necessary cleaning and sealing operations.

**EXAMPLE II**

Aluminum alloy 6063 is anodized as in Example I. A sample of the anodized alloy is impregnated by immersing in the coloring solution and withdrawn at the rate of about 2° per minute. Solution composition is as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₂.6H₂O</td>
<td>100</td>
</tr>
<tr>
<td>(NH₄)₂CS</td>
<td>100</td>
</tr>
<tr>
<td>Arrowroot starch</td>
<td>3% to 1 liter</td>
</tr>
</tbody>
</table>

Dissolve the above salts in approximately 700 ml. of 3% aqueous solution of arrowroot starch. When dissolved dilute to 1 liter with the starch.

Aluminum sheet after impregnation heated as in Example I.

**EXAMPLE III**

A bank sheet of aluminum alloy designated as grade 5457 and containing in addition to aluminum about 80—82% magnesium, about 15—45% manganese and about .20% copper, .10% iron and .08% silicon was anodized in a 15% H₂SO₄ water bath at 72° F. for about 40 minutes to produce an anodic film about .5 mil thick. The anodized alloy divided into two parts was then dried in air at room temperature, treated as in Examples I and II and heated to 400° F. for 15 minutes. Excess salts were removed by washing with water. A bright jet black color was obtained.

**EXAMPLE IV**

Aluminum alloy 6063, anodized as in Example I, was sprayed with an impregnating composition prepared as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₃·5H₂O</td>
<td>250</td>
</tr>
<tr>
<td>NaHSO₃</td>
<td>10</td>
</tr>
<tr>
<td>CuCl</td>
<td>50</td>
</tr>
</tbody>
</table>

Dissolve the Na₂SO₃·5H₂O and NaHSO₃ in approximately 700 ml. of H₂O. When dissolved add the CuCl and when dissolved dilute to 1 liter.

**Solution for spraying**

In a high speed blender, blend

- 300 ml. master solution
- 20 gm. rouge (Fe₂O₃)
- 200 ml. 10% "Baymal"

After heating and cleaning, as described in Example I, a dark green color was obtained in the anodized layer.

**EXAMPLE V**

Aluminum alloy 6063, anodized as in Example I, was sprayed with an impregnating composition prepared as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₃·5H₂O</td>
<td>250</td>
</tr>
<tr>
<td>NaHSO₃</td>
<td>10</td>
</tr>
<tr>
<td>CaCl₂·2½H₂O</td>
<td>100</td>
</tr>
</tbody>
</table>

Dissolve the above salts in approximately 700 ml. of demineralized H₂O. When dissolved dilute to 1 liter with H₂O.
Solution for spraying

In a high speed blender, blend

400 ml. master solution
20 gm. rouge (Fe₂O₃)
150 ml. 10% "Baymalt"

After heating and cleaning, as described in Example I, a bright canary yellow color was obtained in the anodized layer.

EXAMPLE VI

Aluminum alloy 6063 is anodized as in Example I. The anodized alloy was then sprayed with an impregnating composition prepared as follows:

<table>
<thead>
<tr>
<th>Master solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S₂O₅·5H₂O</td>
</tr>
<tr>
<td>NaHSO₃</td>
</tr>
<tr>
<td>CuCl</td>
</tr>
<tr>
<td>(NH₄)₆Mo₇O₂⁴⁻</td>
</tr>
</tbody>
</table>

Dissolve the first two salts in approximately 700 ml. deionized water. When dissolved, dissolve the third and then the fourth salt. When dissolved immediately, adjust pH to 7.0 with NH₄OH and dilute to 1 liter with H₂O.

Solving for spraying

In a high speed blender, blend

350 ml. master solution
20 gm. rouge (Fe₂O₃)
100 ml. 10% "Baymalt"

After heating and cleaning, as described in Example I, a red-brown color was obtained in the anodized layer.

Additional examples of anodized alloys treated in accordance with the present invention are set forth in the following table together with the colors produced.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solution</th>
<th>Heating temp., °F.</th>
<th>Time (min.)</th>
<th>Color produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>Solution of Example I.</td>
<td>600</td>
<td>15</td>
<td>Black.</td>
</tr>
<tr>
<td>Al Alloy 1100</td>
<td>Solution of Example IV.</td>
<td>600</td>
<td>15</td>
<td>Dark Green.</td>
</tr>
<tr>
<td>Al Alloy 7075</td>
<td>Solution of Example I.</td>
<td>600</td>
<td>15</td>
<td>Black.</td>
</tr>
<tr>
<td>Al Alloy 7075</td>
<td>Solution of Example I.</td>
<td>600</td>
<td>15</td>
<td>Yellow.</td>
</tr>
</tbody>
</table>

Colored anodized metal, e.g. aluminum, produced in accordance with the present invention, is particularly adapted for architectural uses on the exterior of buildings and in any other locations where exposure to sunlight exists. The colors produced are resistant to fading in sunlight and are resistant to the detrimental action many substances carried in normal urban atmospheres. Many other uses can be contemplated for aluminum colored in accordance with the present invention. For example, attractive effects can be produced by combining the coloring procedure of the present invention with other metal treatments such as pre-anodizing, texturing, partial masking of surfaces during impregnation of the coloring solutions of the present invention and the like, which effects can be employed wherever decorated metal is required. Above and beyond mere decoration, the process of the present invention can be employed to provide surfaces which absorb or radiate moderate amounts of heat and thus provide utilitarian as well as aesthetic effects.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand.

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JOHN H. MACK, Primary Examiner.
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