PROCESS FOR ELECTROLYTIC COLORING OF THE ANODIC OXIDE FILM ON A ALUMINUM OR ALUMINUM BASE ALLOYS

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ABSTRACT
In the process of coloring an anodized aluminum or aluminum alloy article by subjecting the anodized article to an electrolytic treatment with a direct current in an aqueous electrolytic coloring bath containing a metal salt, the oxide film on the article can be colored in a stable manner and in a deep color by applying repeatedly, after subjecting the article to a cathodic direct current electrolysis in an electrolytic coloring bath containing the metal salt, an anodic direct current electrolysis and then further a cathodic direct current electrolysis to the article.

11 Claims, No Drawings
PROCESS FOR ELECTROLYTIC COLORING OF THE ANODIC OXIDE FILM ON A ALUMINUM OR ALUMINUM BASE ALLOYS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for electrolytically coloring an anodic oxide coating on aluminum or an aluminum base alloy (for brevity the term “aluminum” in this description includes articles made of aluminum or aluminum alloys and hereinafter the term “aluminum” will be used throughout) and more particularly, the invention relates to an improvement in the process of coloring anodized aluminum by subjecting it as a cathode to an electrolytic treatment with direct current in an electrolytic coloring bath containing a water-soluble metal salt.

2. Description of the Prior Art

One of the known processes for producing electrolytically colored coatings on aluminum surfaces involves the anodic oxidation of aluminum in an aqueous solution containing an organic acid (for example, as disclosed in U.S. Pat. Nos. 3,031,327 and 3,486,991).

Another process comprises electrolyzing aluminum which has been subjected to a preliminary anodic oxidation in an electrolytic bath containing a water-soluble metal salt.

Examples of this later process include known processes such as the inorganic coloring process disclosed in U.S. Pat. No. 3,382,160 using an alternating current electrolysis, and a process as disclosed in German OLS 2,112,927 using a direct current electrolysis in an electrolytic coloring bath containing a metal salt. However, the process using direct current electrolysis is superior to the aforesaid other conventional processes in such points that (1) the aluminum article can be colored in a short period of time, (2) the cell voltage required for performing the electrolytic coloring is low, (3) the coloring is applicable to various aluminum articles including plates, extrusions, castings, etc., and (4) the coloring can be easily operated and a superior color is obtained.

In the electrolytic coloring process as described in German OLS 2,112,927, a bronze color is obtained when anodized aluminum is electrolyzed in an aqueous solution containing a water-soluble nickel salt, a red-brown color is obtained in an aqueous solution of a copper salt, bronze to black colors are obtained in aqueous solutions of tin salts, a bronze color is obtained in an aqueous solution of a cobalt salt, and a yellow color is obtained in an aqueous solution of an iron salt.

However, in practicing this process on an industrial scale, the coloring is not stable and a defect that might be called “oxide spalling” may occur. This renders it difficult to obtain a uniformly colored oxide film on aluminum in a stable manner.

This phenomenon also occurs in the electrolytic coloring process as described in Japanese Patent Publication No. 28,585/1972 wherein anodized aluminum is subjected to alternating current electrolysis prior to the application of a direct current electrolytic coloring.

As a result of various investigations on elucidating the cause of the aforesaid difficulty, it has been found that the cause of the difficulty lies in the presence of impurities such as sodium ion, potassium ion, etc., dissolved in the electrolytic coloring bath and the variation in the pH value of the electrolytic coloring bath. That is, in practicing the aforesaid process on an industrial scale, the electrolytic coloring bath is contaminated by a build-up of various impurities which may arise from the water for the coloring bath, chemicals added to the coloring bath, and aluminum articles treated in the coloring bath as well as from the surroundings in an anodizing treatment plant. However, it is difficult to avoid completely contamination of the electrolytic coloring bath with such impurities.

SUMMARY OF THE INVENTION

An object of this invention is, therefore, to provide an improved process for electrolytically coloring anodized aluminum which can provide a superior and uniformly deeply-colored oxide coating on the aluminum without the above-described difficulty induced from contamination of the electrolytic coloring bath and variation in the pH value.

Another object of this invention is to provide an economically improved electrolytic coloring process for anodized aluminum employing an electrolytic coloring bath which does not require repeatedly purifying the bath of contamination and frequently reconstituting the bath.

Still another object of this invention is to improve the process for coloring an anodized aluminum using a direct current electrolysis in an electrolytic coloring bath containing a water-soluble metal salt so that the anodized aluminum can be uniformly colored in a stable manner unaccompanied by the aforesaid difficulty.

As a result of various investigations, it has been found that the aforesaid objects of this invention can be attained by the following process.

That is, the present invention provides an electrolytic coloring process for the anodized oxide film formed on the surface of aluminum by subjecting the aluminum having the anodized oxide film in a thickness of at least 6 microns to a direct current electrolysis in an aqueous electrolytic coloring bath containing a water-soluble metal salt, which comprises applying first to the anodized aluminum a cathodic electrolysis for coloring wherein the aluminum as the cathode is subjected to a direct current electrolysis and then applying to the aluminum alternatingly one or more times an anodic electrolysis wherein the aluminum as the anode is subjected to a direct electrolysis and further a cathodic electrolysis for coloring wherein the aluminum as the cathode is subjected to a direct current electrolysis.

DETAILED DESCRIPTION OF THE INVENTION

The invention is explained below in detail.

First of all, the anodization treatment or anodic oxidation treatment in this invention is conducted for forming an anodized oxide film on the surface of the aluminum and in this case, aluminum having thereon an oxide film of a thickness of at least 6 microns formed by the anodization in an anodic oxidation bath containing sulfuric acid and/or an aromatic sulfonic acid can be uniformly colored in the subsequent electrolytic coloring steps in a stable manner and further the colored oxide film thus formed on aluminum has high weatherability. Usually, an aqueous sulfuric acid solution having a concentration of from about 5 to 30% by weight, preferably 10 to 20% by weight, is used as the anodic oxidation bath and the anodic oxidation bath can further contain a small amount of an organic acid such as
oxalic acid, etc., or a salt of such an organic acid. It is
preferred, in this case, that the anodizing treatment
be conducted with direct current at room temperature
(about 20°-30°C) and a current density of about 1
amp./dm.² or, occasionally at a high current density
about 3.0 to 5.0 amp./dm.². However, the above-
described values of the sulfuric acid concentration,
the current density, and the bath temperature can be
changed to some extent with effective coloring, as the
case may be, if the thickness of the oxide film formed
is at least 6 microns. Furthermore, in using an anodic
oxidation bath containing an aromatic sulfonic acid
such as sulfosalicylic acid or sulfophthalic acid as the
main component, the anodization is preferably con-
ducted in an aqueous solution of the aromatic sulfonic
acid having a concentration of about 10% by superim-
posing an alternating current on a direct current.

According to the present invention, the thus anod-
ized aluminum is subjected to the first cathodic elec-
trolysis for coloring without applying a sealing treat-
ment of the micropores of the oxide film, in which the
anodized aluminum as the cathode is subjected to a
direct current electrolysis in an aqueous solution, as
an electrolytic coloring bath, containing a metal salt. The
electrolytic coloring bath used in the first cathodic
electrolysis contains generally, as the main component,
a water-soluble metal salt such as nickel salt, a copper
salt, a tin salt, a cobalt salt, or an iron salt and further
the bath can contain, if desired, a suitable amount of an
acid such as boric acid, sulfuric acid, etc., for adjusting
the pH and the electrolytic conductivity of the elec-
trolyte. Moreover, in order to obtain a desired color in the
anodized oxide film on the aluminum, the bath can also
contain an ammonium salt and/or one or more other
metal salts.

The first cathodic electrolysis will be explained more
specifically referring to an example using a water-
soluble nickel salt as the main component for the elec-
trolytic coloring bath. That is, in this case nickel sul-
fate, nickel chloride, nickel acetate, etc., can be used
as the water-soluble nickel salt and the concentration of
the nickel ions as the main component can vary over
a wide range. For example, when nickel sulfate is em-
ployed as the main component, a more desirable col-
ored oxide film is obtained at a nickel sulfate concen-
tration of about 15 to 100 g./liter. Sufficent coloring
is, of course, obtained using nickel sulfate concentra-
tions outside this general range.

Also, as described above, the electrolytic bath used in
this invention can contain further an acid such as, for
example, boric acid, for adjusting the electric conduc-
tivity of the bath and in this case the amount of the
boric acid is suitably about 10 to 50 g./liter for obtain-
ing a stable and uniform color.

The current density employed in the cathodic elec-
trolysis is usually about 0.05 to 3.0 amp./dm.², more
preferably about 0.1 to 2.0 amp./dm.². The tempera-
ture of the bath is usually at substantially room tempera-
ture (about 20° to 30°C) but can be selected appropri-
ately in the range of from about 0°C to 40°C.

The period of time required for the first cathodic electrolysis can be appropriately selected depending on the color of the anodized oxide film desired and the current density employed. That is, in general, as the pe-
riod of time of electrolysis increases, the color obtained
tends to become deeper. However, when a high current
density is employed in the electrolysis, sufficient color-
ing is obtained in a few seconds. Generally, a suitable
period of time for performing the cathodic electrolysis
is from about 2 seconds to 3 minutes.

The coloring mechanism of the cathodic electrolysis
has not yet been completely clarified but as the result
of various investigations, the following conclusions can
be drawn. These will be explained using a nickel salt,
for example, as the main component for the electrolytic
bath.

1. The anodized oxide film of the aluminum is col-
ored by the reduction of the nickel ions at the bottom
of the micropores of the oxide film, the reduced nickel
is present as metallic nickel and nickel compound, and
as the amount of the reduced nickel increases, the
color of the oxide film becomes deeper.

2. At the bottom of the micropores of the oxide film,
hydrogen gas is generated together with the coloring of
the oxide film by the reduction of the nickel ions and
when the volume of the hydrogen gas generated in the
micropores of the oxide film reaches a definite amount,
the coloring by the reduction of the nickel ions is com-
pleted at this point. If the electrolysis is further contin-
ued, only the generation of hydrogen gas occurs ulti-
mately resulting in a breaking and peeling of the oxide
film.

3. The elapsed period of time until the coloring is
completed depends upon the electrolyte composition
and the electrolytic conditions but when the electro-
lytic coloring bath contains impurities which hinder the
occurrence of coloring, such as, in particular, sodium
ions, potassium ions, and aluminum ions, the elapsed
period of time until the coloring is completed decreases
depending upon the concentration of the impurities.
Therefore, in such case, the amount of the reduced
nickel ions is less and hence faintly colored oxide coat-
ings on the aluminum are obtained.

4. When the aluminum thus subjected to the first ca-
thodic electrolysis is further treated with an anodic
electrolysis for a short period of time, it becomes possi-
ble to continue again the coloring of the oxide film of
the aluminum by a cathodic electrolysis and because in
the second cathodic electrolysis the concentration of nickel in the micropores of the oxide film is higher than
that in the first cathodic electrolysis, the color formed
by the second cathodic electrolysis is deeper than the
color obtained in the first cathodic electrolysis.

In addition, the end of the electrolytic coloring can be readily confirmed be detecting the condition when the cell voltage began to change greatly in employing a constant-current electrolysis or the condition when the electric current began to change greatly in em-
ploying a constant voltage electrolysis. When the elec-
trolysis is carried out at a low current density, the col-
oring of the oxide film is completed after a compara-
tively long period of time whereas when a high current
density is employed, the coloring is completed in a short period of time. If the electrolysis is continued fur-
ther beyond this point, only the generation of hydrogen
gas occurs and ultimately the oxide film will be peeled
and spalled.

In subjecting the faintly colored aluminum to an an-
odic electrolysis, when the electrolytic coloring of the
anodized aluminum is completed or during the ca-
thodic electrolysis for coloring the anodized aluminum,
the direction of the electric current from a D.C. power
source is changed using a change-over switch, whereby
a direct current electrolysis is conducted using the al-

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3,878,056

There is no particular limitation on the current density used in the anodic electrolysis but a better result is obtained by employing a current density substantially same as that used in the first cathodic electrolysis. Also, in the anodic electrolysis an effective result is obtained in a short period of time but when a low current density is employed, a comparatively longer period of time is required, for example, the period of time for electrolysis is about 5 to 30 seconds at a current density of 0.2 to 0.5 amp./dm², while when a high current density is employed, a shorter period of time is required, for example, the period of time for electrolysis is about 5 seconds at a current density of 1.0 to 1.5 amp./dm². These conditions are, however, selected depending to the color of the oxide film desired and the composition of the bath and, of course, a period of 1 to 2 minutes can be employed as the case may be.

The faintly colored aluminum treated with the above-described anodic electrolysis is subjected to a second cathodic electrolysis in, preferably, the same electrolytic coloring bath as used in the first cathodic electrolysis under electrolytic conditions which can be the same as or different from those conditions used in the first cathodic electrolysis. Thus, the anodized oxide film of the aluminum is colored more deeply than the colored coatings obtained in the first cathodic electrolysis.

If the color of the oxide film on the aluminum is lighter than the color desired, the aluminum is further subjected to a second anodic electrolysis and a third cathodic electrolysis, whereby the oxide film is colored more deeply. By further repeatedly applying the anodic electrolysis and the cathodic electrolysis to the anodized aluminum, the oxide film of the aluminum can be colored far more deeply.

Thus, the process of this invention is quite effective in obtaining a deeply colored anodized oxide coating on aluminum using an electrolytic coloring bath which results in only a light color using a conventional technique in the apparatus employed industrially caused by impurities present in the electrolytic bath. For example, when an electrolytic coloring bath containing a water-soluble nickel salt is employed, the electrolytic bath contains usually a large amount, e.g., about 15 to 30 ppm. of sodium ions and hence only a light color is obtained when the anodized aluminum is colored in the electrolytic coloring bath in a conventional manner. On the other hand, when the anodized aluminum is colored according to the process of this invention using the electrolytic coloring bath containing the above-described impurities, a deep bronze color is obtained and further the anodized aluminum can be readily colored black, which has not previously been possible using an electrolytic coloring bath containing a water-soluble nickel salt in a conventional manner.

In addition, the change from the cathodic electrolysis to the anodic electrolysis in an electrolytic coloring bath can be easily carried out by operating a change-over switch connected to a D.C. power source.

The above embodiment of this invention was explained for the use of one electrolytic coloring cell for conducting the cathodic electrolysis and the anodic electrolysis alternatingly but in the process of this invention, the cathodic electrolysis and the anodic electrolysis can be conducted in a different electrolytic cell. In the latter case the employment of the change-over switch is, of course, unnecessary and a great advantage is obtained in being able to treat a large amount of articles continuously. In conducting the cathodic electrolysis and the anodic electrolysis in separate electrolytic cells, it is preferable that the composition of the electrolytic bath for the anodic electrolysis be the same as the composition of the electrolytic coloring bath for the cathodic electrolysis but the electrolytic bath for the anodic electrolysis can have a different concentration and different composition than those of the electrolytic coloring bath for the cathodic electrolysis. However, if the solution in the electrolytic cell for the anodic electrolysis enters the electrolytic coloring cell for the cathodic electrolysis carried by aluminum articles treated in the latter electrolytic cell, the electrolytic coloring bath for the cathodic electrolysis is contaminated adversely affecting the coloring and hence adverse influences on the electrolytic coloring bath must be avoided by strictly controlling and managing the pH, the electric conductivity, and the composition of the electrolytic bath for the anodic electrolysis.

The invention is explained more specifically by the following examples but the invention is not to be construed as being limited to these examples.

Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

**EXAMPLE 1**

An extruded article of aluminum alloy 6063 (A.A. designation) was immersed in a 10% aqueous sodium hydroxide solution at 60°C. for 2 minutes and then subjected to a neutralization treatment for 3 minutes at room temperature using a 20% aqueous nitric acid solution. After washing the aluminum sample with water, the aluminum was anodized with direct current using a 15% aqueous sulfuric acid solution as an anodic oxidation bath for 15 minutes at a current density of 2.0 amp./dm² and at a bath temperature of 20°C ± 1°C, whereby an anodic oxide coating on the aluminum having a thickness of about 9 microns was formed. In the same manner, four samples, Samples 1, 2, 3, and 4, were prepared. After washing the samples with water, Sample 1 was placed as a cathode in an aqueous electrolytic coloring bath containing 50 g/liter of nickel sulfate and 30 g/liter of boric acid as well as sodium chloride (22 ppm. of sodium ions) and was electrolyzed by passing a direct current using a nickel plate as the anode for 30 seconds at a current density of 0.5 amp./dm² and a bath temperature of 20°C.

Sample 2 was also colored using the same direct electrolysis in an electrolytic coloring bath having the same composition as above for 20 seconds at a current density of 0.5 amp./dm² and a bath temperature of 20°C.

Sample 3 was subjected to a cathodic electrolysis under the same conditions as in the case of electrolyzing Sample 2, then subjected to an anodic electrolysis using a direct current in the same electrolytic coloring bath for 10 seconds at a current density of 0.5 amp./dm². using a change-over switch, and finally subjected again to a direct electrolysis for 20 seconds at a current density of 0.5 amp./dm² using the samples as the cathode.

Sample 4 was subjected to a series of electrolysis under the same conditions as in the case of treating Sample 3, then subjected to an anodic electrolysis in the same electrolytic coloring bath for 10 seconds at a current density of 0.5 amp./dm², and finally subjected...
again to a cathodic electrolysis using a direct current in the same electrolytic coloring bath for 20 seconds at a
current density of 0.5 amp./dm.².

The electrolytic coloring bath was always maintained
at 20°C. for Samples 3 and 4.

Each of the samples thus treated was washed with water and then sealed for 30 minutes in boiling water.

The shades of color of the samples thus treated were
evaluated with the lightness Y (%) being measured
using a color difference meter, and the results obtained
being shown in the following table.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Lightness Y (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.0</td>
</tr>
<tr>
<td>2</td>
<td>19.0</td>
</tr>
<tr>
<td>3</td>
<td>13.8</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
</tr>
</tbody>
</table>

As is clear from the results, in the first coloring treat-
ment or the first cathodic electrolysis, the coloring was
completed under the conditions applied to Sample 2
and even if the period of time of electrolysis was pro-
longed, no additional coloring occurred (see Sample
1).

Also, even Sample 2 for which only a light yellow-
brown color was obtained since the coloring had
reached the limit, could be colored more deeply by fur-
ther subjecting the sample to the anodic electrolysis
and the cathodic electrolysis as in Sample 3. Further-
more, it can be clearly understood from Sample 4 hav-
ing a dark-bronze color that by further repeating the
anodic treatment and the cathodic treatment, the color
of the oxide film of the sample became deeper and
deeper.

EXAMPLE 2

An aluminum plate (99.2% Al) was subjected to the
pretreatment as described in Example 1 and subjected
to an anodic oxidation treatment in a 15% aqueous sul-
furic acid solution for 50 minutes at a current density of
1.0 amp./dm.² and a bath temperature of 20°C. ±
1°C., whereby an oxide film having a thickness of about
15 microns was formed. In the same manner, three
samples, Samples 5, 6, and 7, were prepared. After
washing these samples with water, Sample 5 was placed
as a cathode in an aqueous electrolytic coloring bath
containing 35 g./liter of nickel sulfate and 35 g./liter of
boric acid as well as about 1 ppm. of sodium ions and
was electrolyzed by passing a direct current using a
nickel plate as the anode for 1.5 minutes at a current
density of 0.3 amp./dm.² and a bath temperature of
25°C.

Sample 6 was subjected to the same cathodic treat-
ment as described above under the same conditions as
in the case of treating Sample 5, then subjected to an
anodic electrolysis in the same electrolytic bath for 15
seconds at a current density of 0.3 amp./dm.², and fin-
ally subjected to a cathodic electrolysis for 1.5 minutes
at a current density of 0.3 amp./dm.².

Sample 7 was subjected to a series of treatments
under the same conditions as in treating Sample 6 and
further subjected to an anodic electrolysis for 15 sec-
onds at a current density of 0.3 amp./dm.² and further
to a cathodic electrolysis for 1.5 minutes at a current
density of 0.3 amp./dm.².

As is clear from the results shown in Table 2, from
the electrolytic coloring bath having a low sodium ion
content, a quite deep dark bronze color was obtained
as in Sample 5 but by applying the process of this inven-
tion, a deeper color was obtained and by applying re-
peatedly the coloring treatments further, a deep black
color was obtained for Sample 7.

As illustrated in the above-described examples, the
process of this invention can be quite effectively ap-
plied to the use of an electrolytic coloring bath contain-
ing, in particular, a water-soluble nickel salt and further
sodium ions as impurities to obtain a deep color
whereas only a light color is obtained using a conven-
tional process.

Thus, according to the process of this invention, a
uniformly and deeply colored oxide film can be formed
in a stable manner on aluminum without causing a
spalling of the oxide film which is quite important in-
dustrially.

While the invention has been described in detail and
with reference to specific embodiments thereof, it will
be apparent to one skilled in the art that various changes and modifications can be made therein with-
out departing from the spirit and scope thereof.

What is claimed is:

1. A process for electrolytically coloring an anodic
oxide coating on aluminum or an aluminum alloy arti-
cle by subjecting the article having an anodized oxide
film of a thickness of at least about 6 microns to a di-
rect current electrolysis in an aqueous electrolytic col-
oring bath containing a water-soluble metal salt, which
comprises applying first to the anodized article a ca-
thodic electrolysis wherein the aluminum article is sub-
jected to a direct current electrolysis as the cathode for
at least a few seconds and then applying alternatingly
at least once to the article an anodic electrolysis
wherein the article as the anode is subjected to a direct
current electrolysis and a cathodic electrolysis wherein
the article as the cathode is subjected to a direct cur-
rent electrolysis.

2. The process as claimed in claim 1, wherein the an-
odic oxide coating is obtained by anodically oxidizing
the article in an anodic oxidation bath containing sul-
furic acid or an aromatic sulfonic acid.

3. The process as claimed in claim 1, wherein said
first cathodic electrolysis for the article is conducted in
an aqueous electrolytic coloring bath containing a
watersoluble nickel salt.

4. The process as claimed in claim 3, wherein said
water-soluble nickel salt is nickel sulfate, nickel chlor-
ide, or nickel acetate.

5. The process as claimed in claim 1, wherein said
first cathodic electrolysis for the article is conducted in
an aqueous electrolytic coloring bath containing a cop-
per salt, a tin salt, a cobalt salt, or an iron salt.
6. The process as claimed in claim 1, wherein said electrolytic coloring bath used for the first cathodic electrolysis further contains boric acid or sulfuric acid for adjustment of the pH and electric conductivity of the electrolytic coloring bath.

7. The process as claimed in claim 1, wherein said first cathodic electrolysis for the article is conducted at a current density of about 0.05 to 3.0 amp./dm.², at a temperature of about 10 to 40°C, and for about 2 seconds to 3 minutes.

8. The process as claimed in claim 1, wherein said subsequent anodic electrolysis and the cathodic electrolysis are conducted in the same electrolytic coloring bath as used in the first cathodic electrolysis.

9. The process as claimed in claim 1, wherein said anodic electrolysis is conducted for about 5 to 30 seconds at a current density of about 0.2 to 1.5 amp./dm.² and at about room temperature.

10. The process as claimed in claim 1, wherein said second cathodic electrolysis is conducted under the same conditions as in the first cathodic electrolysis.

11. The process as claimed in claim 1, wherein said anodic electrolysis is conducted in an electrolytic bath different from the electrolytic coloring bath for the cathodic electrolysis.

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