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[54] **PROCESS FOR ELECTROLYTICALLY COLORING PREVIOUSLY ANODIZED ALUMINUM USING ALTERNATING CURRENT**

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[51] **Int. Cl.** **C23b 9/02,** C23f 17/00

[58] **Field of Search** ..... 204/96, 42, 58, 35 N

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

Anodized aluminum or aluminum alloy articles may be colored in blue tones by supplying alternating current to the articles in an aqueous acidic solution of silicomolybdic acid or silicotungstic acid.

6 Claims, No Drawings

PROCESS FOR ELECTROLYTICALLY COLORING PREVIOUSLY ANODIZED ALUMINUM USING ALTERNATING CURRENT

The invention relates to a process for obtaining colored coatings on anodized articles of aluminum or aluminum alloys, by supplying alternating current to the articles in aqueous acid-containing solutions of salts of molybdenum or tungsten in the presence of a suitable counter-electrode.

For electrolytic coloring of anodized articles of aluminum or aluminum alloys it has been suggested to use aqueous acid-containing solutions of salts of the metals iron, cobalt, nickel, manganese and chromium together with small auxiliary amounts of soluble compounds of arsenic, antimony, bismuth, selenium, tellurium and/or tin (Norwegian patent No. 69930).

British patent No. 1022927 relates to a similar process wherein an alternating current is passed between a previously anodically oxidized aluminum article and a counter-electrode of carbon, carborundum or aluminum in an aqueous bath containing a salt of a metal yielding a colored metal oxide or metal hydroxide in the aluminum oxide layer. As metal salts it is suggested to use small amounts of a salt of cadmium, chromium, cobalt, gold, iron, lead, nickel, silver or vanadium.

Moreover, according to German patent No. 741753 it has been generally suggested to use aqueous solutions of all metals which are more electro-positive than aluminum. However, it appears that not all of these metals are capable of yielding a color in this manner and, moreover, there may be only certain salts of the useful metals which will lead to the desired color.

Accordingly, from the large number of possibilities represented by the previous suggestion to use salts of metals in general which are more electro-positive than aluminum for electrolytic coloring of previously anodized aluminum or aluminum alloys using alternating current, it often has not been possible without considerable inventive effort among this large number of possibilities to arrive at the metals or the salts thereof which are capable of yielding a desired color in the previously anodized surface on the articles of aluminum or aluminum alloys.

The invention relates to a process for electrolytically coloring previously anodized articles of aluminum or aluminum alloys, by passing alternating current between a previously anodized article of aluminum or aluminum alloys and a counter-electrode, preferably consisting of molybdenum, tungsten or titanium, in an aqueous acidic solution of a salt of a metal capable of yielding a colored compound in the aluminum oxide layer, and the process is characterized in that as metal salt there is used a water-soluble salt of a metal selected from the group consisting of molybdenum and tungsten.

By the present process it has surprisingly been found that stable colors of various color tones can be obtained even when the multi-valent elements molybdenum and tungsten are present in the coloring compounds in a valency state other than their most stable valency state.

It has also been found possible by means of the present use of a water-soluble salt of molybdenum or tungsten that the anodized aluminum article may be colored in a separate electrolyte bath with salts of other metals and then by means of the present process in another

electrolyte bath using a salt of molybdenum or tungsten. The colors obtained by the use of a salt of molybdenum or tungsten will be superimposed on the already formed colors and thereby yield mixed colors in a number of attractive shades of e.g. grey, green, yellow-green and violet, and it has been found that these colors become very fast upon conventional sealing of the colored aluminum articles in boiling water.

In Norwegian patent specification No. 117398 and its patent of addition No. 119560 there are disclosed and claimed a process and an apparatus for electrolytic coloring of previously anodized aluminum articles by passing between the aluminum articles and a counter-electrode in an aqueous acidic electrolyte containing salts of metals capable of coloring the previously provided layer of aluminum oxide an alternating current which has been modified so as to become asymmetrical, in order to obtain an improvement and/or change of the coloring obtainable with the metal salts employed. The process and the apparatus disclosed in these patents have been proven to be very advantageous for the present electrolytic coloring with a salt of molybdenum or tungsten.

The concentration of the salt of molybdenum or tungsten in the electrolyte may vary within wide limits. However, it may generally be stated that a concentration of these salts of 0.5 to 20 percent by weight, preferably about 2.0 percent by weight, based on the electrolyte, is suitable. The pH in the electrolyte may vary considerably within the acid range but is preferably about 1.5. The alternating current may have a frequency of 10 to 500 periods per second, preferably 50 periods per second, and a voltage of 2 to 50 V, and a current density of 0.2 to 1.0 A/dm^2, based on the surface of the aluminum article, may be used. However, the stated upper limit may also be exceeded up to the current density which will cause destruction of the previously provided layer of aluminum oxide.

The material of the counter-electrode used in the present process is not of critical importance. However, it should preferably consist of molybdenum if a salt of molybdenum is used in the electrolyte or tungsten if a salt of tungsten is used. The counterelectrode employed ought otherwise to consist of a material which is not attacked by the electrolyte, e.g. stainless steel and titanium, in order to obtain an electrode which may be used for prolonged periods and in order to prevent contaminations due to the electrode from entering into the electrolyte. The counter-electrode employed in the present process preferably consists of molybdenum, tungsten or titanium.

It is of particular importance that when using silicomolybdic acid ($H_8SiMo_{12}O_{42}$) as the water-soluble molybdenum salt and silicotungstic acid ($H_8SiW_{12}O_{42}$) as the water-soluble tungsten salt various bluish shades are obtained which are very stable towards atmospheric influence and which, to the best of Applicant's knowledge, have not been obtainable by electrolytic coloring using the previously suggested metal salts.

EXAMPLE 1

An aluminum strip which had previously been anodically oxidized for 45 minutes in a 15 percent aqueous solution of sulfuric acid was electrolytically colored using an alternating voltage which was modulated so as to cut off the positive half period thereof with regard to the aluminum strip. The aqueous electrolyte con-

tained about 1.5 percent silicotungstic acid and 1.5 boric acid, and a strip of titanium was used as counter-electrode. The applied voltage was 16 V and the current density 0.4 to 0.5 A/dm². The coloring lasted for 5 minutes and a blue-violet color was obtained on the aluminum strip.

EXAMPLE 2

An aluminum strip which had previously been anodized in a 15 percent aqueous solution of sulfuric acid was subjected to an alternating voltage of about 16 V which was made asymmetrical so as to cut off the positive half period thereof with regard to the aluminum strip, titanium being used as the material for the counter-electrode. The electrolyte was a 2 percent aqueous solution of ammonium helptamolybdate and contained 2 percent sulfuric acid. The current density was 0.4 to 0.5 A/dm² and the colouring time was 4 minutes. There was obtained on the aluminum strip a deep blue color which upon sealing in boiling water was converted to a stable yellow color.

EXAMPLE 3

An aluminum strip which had previously been anodically oxidized in a 15 percent aqueous solution of sulfuric acid was subjected to an alternating voltage of 40 V, a counter-electrode of titanium being used. The electrolyte was a 1.5 percent aqueous solution of silicomolybdic acid and contained 1.5 percent boric acid. The current density was 0.4 to 0.5 A/dm². The coloring was carried out for 2 minutes. A deep blue color was obtained on the aluminum strip. This color was very stable and resistant towards atmospheric influence.

EXAMPLE 4

There was carried out an electrolytic coloring in a manner known per se of aluminum strips using alternating current and aqueous acidic electrolytes containing resp. various metal salts previously suggested for this purpose. The colored aluminum strips were removed from the resp. electrolytes, rinsed with water and placed in an electrolyte as used in example 3 and electrolytically colored in the manner described in example 3.

Dependent upon the metal salts used for the first coloring there were obtained mixed colors, like grey, green, yellow-green and violet in a number of attractive shades, and upon conventional sealing in boiling water the colors became very fast and resistant.

I claim:

1. A process for electrolytically coloring a previously anodized article of aluminum or aluminum alloy, comprising passing alternating current between said article and a counter-electrode in an aqueous acidic solution which comprises a water-soluble compound selected from the group consisting of silicomolybdic acid and silicotungstic acid.

2. A process as claimed in claim **1** wherein the compound is silicomolybdic acid.

3. A process as claimed in claim **1** wherein the compound is silicotungstic acid.

4. A method as claimed in claim **1** wherein the article has been previously anodized and then electrolytically colored using metal salts.

5. A process as claimed in claim **1** wherein the aqueous acidic solution also comprises a salt of a metal other than molybdenum and tungsten capable of yielding colored compounds in the aluminum oxide layer of the anodized article.

6. A process as claimed in claim **1** wherein the counter-electrode consists essentially of a metal selected from the group consisting of molybdenum, tungsten and titanium.

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