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1

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SELF-COLORING ANODIC OXIDATION PROCESS FOR ALUMINUM AND ITS ALLOYS

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ABSTRACT OF THE DISCLOSURE

An improved self-coloring anodic oxidizing process for aluminum and its alloys by means of electrolytic baths is disclosed, wherein in the electrolytic cells used for the oxidation there is used a cooled cathode system. Preferably, the cooling of the cathodes is achieved by circulating inside said cathodes a refrigerating fluid having an inflow temperature to the cathodes below 25° C. but higher than the temperature which would cause freezing of the electrolytic solution used in the cell.

The present invention relates to an improvement in the self-coloring anodic oxidation process for aluminum and its alloys, an improvement that allows one to reduce the consumption of the components constituting the electrolytic system and to reduce the formation of precipitates from that system.

It is well known that aluminum and its alloys may be coated with very resistant layers of oxide of quite a thickness, by means of an electrolytic treatment in aqueous solutions wherein the aluminum acts as an anode.

It is also well known that by using as electrolyte solutions based on carboxylic acids of the aliphatic series, it is possible to obtain self-colored layers through the transformation and incorporation in said layers of the constituents and alloying elements present in the material to be oxidized.

The self-coloring anodic oxidizing processes that have been suggested so far (among which may be recalled in particular the MS process based on a binary mixture of maleic acid and sulphuric acid, the MOS process based on a ternary mixture consisting of maleic acid, oxalic acid and sulphuric acid, as described in Italian Pat. No. 793,929 and in Belgian Pat. No. 660,867, and the TOS process based on a ternary mixture of tartaric acid, oxalic acid and sulphuric acid, as described in Italian Pat. No. 720,028) have in common a serious drawback: that is, the inconvenience of giving rise during the course of the oxidation to cathodic and/or anodic decomposition by-products of the carboxylic aliphatic acids used, with the consequentially heavy consumptions of the components involved, a rise in the costs of the treatments, and appreciable variations in the repeatability of the coloring.

The above-mentioned decomposition reactions lead, in some cases, to the complete fission of the carboxylic acid or to its conversion to soluble products (such as is the case with the oxalic acid in the TOS and MOS processes); in other cases, on the contrary, there occurs a transformation of the involved carboxylic acid to difficultly soluble products (as is the case with maleic acid in the MOS and MS processes), with the consequential formation of precipitates in the different parts of the installation and consequently with clogging phenomena (particularly of the perforated pipes used for the compressed air stirring of the electrolyte) and a lowering of the exchange capacity of the refrigerating equipment and of the resin columns used for the elimination of the aluminum in the baths.

2

An object of this invention is that of providing an improvement in the self-coloring anodic oxidizing process for aluminum and its alloys by which the previously-mentioned drawbacks will be eliminated or at least very considerably reduced.

More particularly, an object of the present invention is that of providing a process that will reduce to a minimum the formation of precipitates from the electrolytic solution and consequently will reduce the harmful cloggings of the installation and reduction of the exchange capacities of the refrigerating apparatus and of the ion-exchanging resin columns.

A further object of this invention is that of providing a process which will reduce the consumption of the components of the electrolytic system which is used, with considerable practical and economical advantages, thereby obtaining also an improved constancy of composition of the electrolytic system and therefore an improved reproducibility of the colorings obtained in the anodic coating, without requiring frequent and costly additions of electrolyte.

These and still other objects of the invention will become still more apparent to those skilled in the art through the detailed description that follows hereunder, and which is conveniently achieved by the improvement to the self-coloring anodic oxidizing process for aluminum and its alloys by means of electrolytic baths; an improvement that, according to this invention, consists in using a system of cooled cathodes in the electrolytic cells used for the oxidizing.

During the tests conducted in order to study the mechanisms of the cathodic and anodic reactions of the bi- and tri-acid baths suffering from the decomposition of the components thereof, it was in fact, surprisingly, found that whenever the temperature of the cathodes was kept below the temperature of the electrolyte, a heavy drop occurs in the decomposition kinetics of the electrolyte components subject to this phenomenon, and thus there results a heavy drop in the consumption of the bath components affected by these decomposition reactions.

The carboxylic acid component may be selected from maleic, oxalic or tartaric acid either alone or in a binary or ternary combination thereof, and generally also in the presence of sulphuric acid.

The cooling of the cathodes is generally carried out by circulating inside the cathodes a conventional refrigerating fluid, for instance by using hollow cathodes or cathodes provided with coils incorporated therein.

It has been found that, to obtain the best results, the refrigerating fluid must have an inflow temperature to the cathodes below 25° C.; such a temperature must however be higher than the temperature that would bring about freezing of the electrolytic solution used in the cell.

As material of construction for the cathode it is preferable to use stainless steel, graphite, aluminum or any other conductive material that resists the corrosive action of the electrolyte.

The tests carried out in connection with the present invention have revealed that the adoption of the above-described improvement offers considerable advantages without involving, on the other hand, excessive building and operating costs for the electrolytic plant. These advantages may be summarized as follows:

an appreciable reduction of precipitates from the electrolyte;

a reduced consumption of components affected by secondary reactions;

a reduction in the cost in dimensioning the ancillary equipment and of the maintenance connected therewith for the removal of the precipitates.

For a still more detailed illustration of this invention and of the advantages achieved thereby, the following detailed example of an embodiment of the invention is given:

EXAMPLE

The anodic oxidation was carried out in successive batches of 50 minutes each and at a temperature of 22° C. at 1.5 a./dm.^{2} through a self-coloring electrolyte of the MS-type consisting of an aqueous solution of maleic acid and sulphuric acid of the following composition:

	G./l.
Maleic acid	300
Sulphuric acid	3

For the test there was used a tank of about 150 liters capacity, fitted with an ion-exchange column and an external heat exchanger. Inside the electrolytic cell there were arranged six cathodes consisting of stainless steel pipes (AISI 316) with a surface such that the anodic current density amounts to at least 1.5 a./dm.^{2}. Running water was circulated within the pipes as refrigerating fluid, the running water having an inflow temperature of 12.5°–13° C.

A number of samples of a light aluminum alloy were oxidized in the bath, until one obtained an aging of the bath of about 12 a.h./l. after the bringing up of the bath to its duty operating conditions. After this aging, it will be observed that the modification introduced allows one to obtain the following advantages:

the formation of precipitates was reduced to about 0.8 g./a.h.;

the consumption of maleic acid amounts to about 1.5–2 g./a.h.

Practically, these values turn out to be lower by about 50% so far as the production of precipitates is concerned, while there is a drop of about 40% so far as the consumption of maleic acid is concerned, with respect to the production of precipitates and with regard to the consumption of maleic acid that would prevail were there no cooling of the cathodes.

In the following table the results of another series of tests are reported. These tests were carried out in a similar way as in the preceding example and using, as refrigerating fluid for the cathodes, water for tests Nos. 1 to 4 and an anti-freezing liquid (water/ethylene glycol in the volumetric ratio 2/1) for tests Nos. 5 and 6, at different inflow temperatures to the cathodes.

TABLE 1

	Inflow temperature to the cathodes of the refrigerating liquid (° C.)	Consumption of maleic acid (g./a.h.)	Formation of precipitate generating substances (g./a.h.)
Test number:			
1	25	3.5	1.5
2	20	1.5–2	0.8
3	17	1.5–2	0.8
4	13	1.5–2	0.8
5	0	1.5–2	0.8
6	−4	1.5–2	0.8

What is claimed is:

1. In the process for self-coloring anodic oxidation of aluminum and its alloys by means of an electrolytic bath consisting of an aqueous solution of maleic and sulfuric acid, the improvement comprising

cooling the cathode by circulating inside said cathode a refrigerating fluid having an inflow temperature to the cathode below 25° C. but higher than the temperature which would cause freezing of the electrolytic solution used in the cell and

applying direct current between the workpiece as the anode and said cathode.

2. The process of claim **1**, wherein said inflow temperature is 20° C.

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