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ANODISING OF ALUMINIUM AND ITS ALLOYS

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3 Claims

ABSTRACT OF THE DISCLOSURE

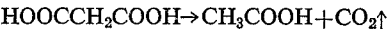
This invention relates to a method of anodising aluminium and its alloys in order to produce hard and coloured coatings using an electrolyte incorporating a first acid selected from dibasic and polybasic organic acids other than oxalic acid with the addition of either glyoxylic or oxalic acid.

This invention relates to a method of anodising aluminium and its alloys.

It is well known that if aluminium is made the anode in aqueous solutions of malonic acid and an electric current is passed under an applied potential an anodic oxide film is formed on the aluminium. Extremely hard anodic coatings may be produced which range in colour from deep yellow to sepia brown and which have been particularly described in an article by J. M. Kape on pages 181–191 of "Metallurgia" of November 1959.

Using the malonic acid electrolyte it is found that extremely high applied voltages (over 120 volts) are required to cause even small current densities (10–15 amperes per square foot) to pass at ambient temperatures in order to promote the formation of thick coloured anodic coatings.

Further, the use of the methods described in the literature mentioned above according to which the temperature of the electrolyte was raised to 40–60° C. (preferably 50–55° C.) in order to cause the production of current densities of 15–24 amperes per square foot at applied voltages of less than 100 volts, is disadvantageous in that the abrasion resistance of the anodic coating is substantially reduced and the density of colouration of the coating per unit film thickness is considerably reduced. Moreover, at these temperatures a considerable proportion of the malonic acid is decarboxylated according to the equation:



The chance of this reaction occurring is considerably minimised by reducing the temperature but at a temperature of 20° C. it is found that somewhat rough uneven coatings are produced on certain aluminium alloys—notably extrusions. In particular, on an alloy known under the nomenclature of British Standards specifications Nos. 1470 and 1490 as HE9 which is commonly used for building purposes, coatings are obtained which show up scratches and die lines as whitish streaks and thus are valueless for decorative applications.

If aqueous solutions of other organic dibasic or polybasic acids are used as the electrolyte then in general only thin anodic coatings are produced the thickness of such coatings being roughly proportional to the applied voltage. In some cases instead of forming an anodic coating aqueous solutions of certain dibasic or polybasic organic acids produce pitting of aluminium anodes under an applied potential.

It is also well known that if an aqueous solution of oxalic acid is used as the electrolyte then an anodic coating can be produced under favourable voltage and current density conditions on aluminium alloys which are free

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from copper, this coating being very hard and coloured pale yellow or brown the resultant anodised material having particular application architecturally.

It is an object of the present invention to provide an improved method of anodising aluminium and its alloys to produce particularly hard anodic coatings within acceptable limits of applied voltage and at adequate current densities with a wide range of colours.

According to the present invention there is provided a method of anodising aluminium and its alloys in which the anodising operation is carried out in an electrolyte comprising a first acid selected from dibasic and polybasic organic acids other than oxalic acid with the addition of a second acid different from said first acid and selected from oxalic acid and glyoxylic acid.

Preferably the first acid is selected from the group consisting of malonic acid, tartaric acid, citric acid, diglycollic acid, malic acid, succinic acid, glutaric acid, itaconic acid, maleic acid, pyromellitic acid, trimellitic acid, citraconic acid, thiomalic acid, thiodiglycollic acid, acetylene dicarboxylic acid, aconitic acid, glyoxylic acid and phthallic acid. In this specification glyoxylic acid is to be considered as a dibasic acid. The first acid may be a solution having a concentration ranging from 1% to saturation and the amount of the second acid incorporated in the electrolyte may vary between 0.1% and 10% by weight of the first acid.

The following examples illustrate the invention. Experiments were carried out using HE9 (British Standards specifications 1470 and 1490) test pieces, a current density of about 30 amperes per square foot for 1 hour and an electrolyte temperature of 20° C. Coating thicknesses of 30–40 microns were obtained and the results are tabulated below, M representing malonic acid and Ox representing oxalic acid.

Electrolyte	Voltage range	Type of Coating
10% M.....	125–135	Dark brown, non-uniform.
10% M+0.2% Ox.....	130–140	Dark brown, more uniform.
10% M+0.4% Ox.....	110–130	Dark bronze, fairly smooth.
10% M+0.6% Ox.....	110–135	Dark bronze, smooth.
10% M+1.0% Ox.....	100–115	Bronze, smooth, uniform.
10% M+3.0% Ox.....	85–100	Light bronze, smooth, uniform.
10% M+5.0% Ox.....	70–90	Very light bronze, smooth uniform.

When the additions of oxalic acid reached or exceeded 3.0% by weight, the coating produced resembled that produced with an electrolyte containing oxalic acid alone.

Similar experiments were carried out but modifying the malonic acid by an addition of glyoxylic acid (represented by G). The results are shown in the table below (HE9 material, 20° C., approximately 30 amperes per square foot for 1 hour, film thicknesses 30–40 microns).

Electrolyte	Voltage range	Type of Coating
10% M.....	130–145	Dark brown, non-uniform.
10% M+0.5% G.....	130–135	Dark brown more uniform.
10% M+1.0% G.....	125–135	Dark bronze, smoother.
10% M+2.0% G.....	125–140	Dark bronze smooth.
10% M 3.0% G.....	120–145	Do.

Whilst the additions of glyoxylic acid did not permit the voltage to be reduced, the colour of the malonic acid coating was preserved and the appearance much improved.

Abrasion-resistance measurements were carried out using the method O described in British Standards specifications 1615:1961, with an air flow rate of 70 litres/minute.

Comparative figures for the coatings produced in the malonic acid-oxalic acid mixture or the malonic acid-glyoxylic acid mixture and for other types of coating are given in the table below.

Electrolyte	Temperature of Electrolyte (° C.)	Typical specific abrasion resistance of a 25-35 micron thick coating gms./micron film thickness.
10% oxalic acid	20	3.7
10% malonic acid	20	6.6
10% malonic acid+0.2% oxalic acid	20	5.25
10% malonic acid+0.6% oxalic acid	20	5.0
10% malonic acid+1.0 glyoxylic acid	20	8.9
17.5% by vol. H ₂ SO ₄ +1% oxalic acid	0	4.0
7.0% by vol. sulphuric acid	20	2.0
10% sulphosalicylic acid+0.5% by wt. H ₂ SO ₄	25	4.0
10% sulphophthallic acid+0.5% by wt. H ₂ SO ₄	25	4.0

It can be seen that the malonic acid-oxalic acid electrolyte and the malonic acid-glyoxylic acid electrolyte each afford much more abrasion-resistant coatings than other processes used for architectural anodising and hard anodising.

Similar experiments were carried out using an electrolyte incorporating various other polybasic organic acids and the results are tabulated below with the inclusion of comparison figures for a sulphuric acid electrolyte:

Electrolyte	Voltage range	Colour of coating	Thickness of coating (microns)	Specific ¹ abrasion resistance
8% sulphuric acid	19-20	Silver	2-35	2.0
6% tartaric+1.5% oxalic	100-130	Brown-grey	20	7.5
5% tartaric+0.3 oxalic	110-155	Medium grey	20	6.75
5% citric+1.5% oxalic	85-104	Greenish-yellow	25	6.9
5% citric+0.3% oxalic	110-180	Grey-brown	15	8.3
5% itaconic+1.5% oxalic	120-150	Grey	25	6.9
5% maleic+1.5% oxalic	92-130	Grey-bronze	27	8.1
5% malic+1.5% oxalic	180-200	Dark grey	25	7.45
5% diglycollic+1.5% oxalic	100-130	Yellow grey	25	7.25
5% diglycollic+1.2% oxalic	100-140	Yellow-brown	30	10.5
5% thiomalic+1.5% oxalic	88-162	Grey-bronze	25.0	7.6
1% phthallic acid+2% oxalic acid	74-96	Medium grey to gold	25.0	9.0
2% trimellitic acid+0.75% oxalic acid	50-140	do	15.0	9.0
1% citraconic acid+2% oxalic acid	78-100	do	30.0	7.7
2% pyromellitic acid+0.3% oxalic acid	150-175	do	12.5	9.4

¹ After sealing—5 minutes in Nickel Acetate 8 grams/litre, 80° C. plus 60 minutes hot water 95° C.

In addition, it has been found that useful results can also be obtained with the following polybasic acids: succinic acid, glutaric acid, maleic acid, thiodiglycollic acid, acetylene dicarboxylic acid, aconitic acid and glyoxylic acid.

It has also been found that glyoxylic acid may be substituted for oxalic acid in admixture with all the polybasic acids (except glyoxylic acid itself) referred to above.

I claim:

1. A method of anodising aluminium and its alloys in which the anodising operation is carried out in an electrolyte consisting essentially of a first acid in a solution having a concentration ranging from 1% to saturation and selected from the group consisting of malonic acid, citric acid, diglycollic acid, malic acid, succinic acid, glutaric acid, itaconic acid, maleic acid, pyromellitic acid, trimellitic acid, citraconic acid, thiomalic acid, thiodiglycollic acid, acetylene dicarboxylic acid, aconitic acid, glyoxylic acid and phthallic acid with the addition of a second acid different from said first acid and selected from oxalic acid and glyoxylic acid in an amount which varies between 0.1% and 10% by weight of the first acid.

2. A method of anodising aluminium and its alloys in which the anodising operation is carried out in an electrolyte consisting essentially of malonic acid having a concentration of 10% with the addition of oxalic acid in an amount varying between 0.6% and 5% by weight of the malonic acid.

3. A method of anodising aluminium and its alloys in which the anodising operation is carried out in an electrolyte consisting essentially of malonic acid having a concentration of 10% with the addition of glyoxylic acid in an amount ranging between 0.5% and 3% by weight of the malonic acid.

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