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ANODISING TREATMENT FOR ALUMINIUM

Peter Geoffrey Sheasby, Banbury, Edward Percival Short, North Aston, and Roman Dominik Guminski, Banbury, England, assignors to Aluminium Laboratories Limited, Montreal, Quebec, Canada

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6 Claims

ABSTRACT OF THE DISCLOSURE

In procedure for producing coloured coatings on aluminium by anodising the aluminium in an oxalic acid solution, significantly deeper colours are obtained while providing an effective anodic oxide coating, by performing the anodic treatment with a pulsed direct current advantageously having stated characteristics, including defined values of the relative peak and means current density and of the pulse frequency, the pulses preferably being of approximately square wave form.

The present invention relates to the production of anodic oxide films on aluminium, including aluminium alloys and in particular it relates to a method of producing coloured anodised films.

It is well known that for external uses, such as window frames and curtain walling panels for buildings, aluminium alloys are often protected by a hard, low porosity, anodic oxide film to prevent corrosion.

It is also well known that colours can be developed in such films during the anodising process when certain acids are used in the anodising bath, the intensity and shade of the colour being dependent upon a number of factors, including the actual constituents of the aluminium alloy and the composition of the anodising bath. Thus it is known that very dark films are obtained with aluminium alloys having a high silicon content, and that bronze shades are obtained with many other aluminium alloys when the anodising is performed in a bath containing certain sulphonated organic acids, such as sulphophthalic acid and sulphosalicylic acid. Although the processes using these acids produce strongly coloured anodic oxide films, nevertheless they are expensive to operate because of the high cost of the electrolyte and because certain expensive auxiliary equipment, such as ion-exchange columns, are found to be necessary to avoid high electrolyte loss.

The use of oxalic acid as the electrolyte in an anodising process has already been described. With oxalic acid anodising, using direct current, a range of attractive colours can be developed in the anodic oxide film on certain aluminium alloys, but these are not of the same order of intensity (except on certain silicon-containing alloys) as is obtained with the sulphonated organic acids referred to above, operating under the same conditions of current density on the same alloys.

It is well known that the hardness of anodic oxide films depends to a large degree on the temperature at which the anodising process is performed. Aluminium, bearing an anodic oxide film which has become coloured during the anodising process, is mainly used for architectural purposes, such as window frames and shop front fittings produced from extruded aluminium sections. For these purposes it is important that the anodic oxide film should be hard and have low porosity, so that it may provide prolonged protection for the metal.

To ensure the production of anodic oxide films of this character it is found necessary to control the temperature

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of the acid anodising bath to a temperature of 30° C. at most; 20° C. being the temperature commonly used.

High current densities are employed in anodising baths and thus much heat is developed in the electrolyte. The temperature, to which the electrolyte can be held, depends upon the associated equipment for cooling the electrolyte and in practice, the cooling capacity of such equipment controls the total current capacity of an anodising bath of a given size. Beyond a certain size the capital cost of the associated equipment for cooling the electrolyte becomes prohibitive and thus the output of an anodising bath in terms of area of anodised aluminium is a function of the current density. Furthermore, the current density is also limited by the fact that under D.C. anodising conditions the heat produced in the pores must be dissipated to avoid "burning" of the film.

According to the present invention, as compared with normal direct current anodising, significant darkening of the colours developed in anodic oxide films may be achieved if the direct current applied to an anodising bath containing oxalic acid is pulsed without change of the average current density, so that during each pulse the maximum current density is appreciably increased as compared with operation under steady direct current conditions. The heat developed in the anodising bath is not much greater than if a steady direct current were passed, but the depth of the colour developed is increased on the aluminium-magnesium-silicon alloys conventionally employed in the production of extrusions for external use.

Although the anodising bath may contain mineral acid, salts of mineral acids or monocarboxylic acids to improve conductivity, oxalic acid must form the major proportion of the solute. One of the principal advantages of this method is that it permits a whole range of colours to be developed in an anodic oxide film of a given thickness by variation of the mark/space ratio of the pulses i.e. the ratio of the period during which the current flows to that where it is zero or substantially zero, without changing the average current density. The thickness of the anodic oxide film is a function of the product of the average current density and the treatment time.

It is found very desirable to avoid any negative component in the pulsed current, because this leads to soft anodic films.

From studies which we have carried out, we have concluded that the colours developed in anodic oxide films formed in organic electrolytes are mainly due to optical interference effects arising from the presence of fine particles dispersed in the anodic aluminium oxide. We have postulated that the colours developed in anodic films produced in baths containing oxalic acid are due, at least in part, to carbon particles produced by decomposition of the oxalic acid component of the anodising bath. We have further postulated that such decomposition is due to the development of localised high temperatures, resulting from high resistances in the oxide film at the bottom of the individual pores.

On the basis of these hypotheses it seems probable that deepening of the colour developed in the anodic oxide film is produced if such localised high temperatures are momentarily increased by pulsing the current, because during the pulses the current density at the surface of the aluminium is increased. Although it might be thought that the same result could be obtained by increasing the current density in a standard constant D.C. anodising process the greater amount of heat generated at the surface of the metal results in the metal itself becoming overheated and the occurrence of local "burning" of the anodic aluminium oxide film.

It is however found that the darkening of the colour developed in the anodic oxide film is not particularly significant unless the pulse frequency is less than a maxi-

imum value and the mark/space ratio of the pulses is below a maximum value. Thus it is believed that these conditions are required so that the increased current density at the metal surface is maintained during each pulse for a sufficient time interval to enable the local temperature at the bottom of the pores to increase significantly above the temperature in this region during steady current D.C. anodising.

It is found that the maximum frequency of the pulses is of the order of 50 pulses per second and preferably the pulse frequency is much lower than this, very satisfactory results being obtained when the pulse frequency is in the range of $1\frac{1}{2}$ –20 pulses per second.

Preferably the pulses are generated so as to have as square a wave form as possible and the maximum value of the mark/space ratio is about 50% to produce a darkening of the oxide film (as compared with direct current anodising under the same conditions). The conditions may be expressed alternatively by saying that the minimum ratio of the peak current density during a pulse to the mean current density is 3:1. Preferably the mark/space ratio is in the range of 6–33%, the lower value giving the most intense colours. Although it is believed that mark/space ratio of 3% could give even better results, the cost of the necessary equipment to produce D.C. power pulses of this order is probably so great as to render it uneconomic to do so.

The minimum mean anode current density is about 10 amps/square foot, with a maximum mean current density of about 36 amps/square foot. Above that value the cost of cooling equipment for the electrolyte becomes a major difficulty and little significant increase in darkening is achieved. Although the use of higher current density leads to the development of darker colours in a film of given thickness, the preferred operating range is 15–24 amps/square foot mean current density.

In one series of tests the D.C. current-pulses were generated by using thyristors in a three-phase half-wave rectifier system, the firing of the thyristors being controlled by means of a variable mark/space ratio pulser, which controls the time interval during which the thyristor remains conductive, the pulser also having a variable repetition period.

It was found that a considerable range of colours could be obtained on aluminium and aluminium alloys, when anodised in oxalic acid solution, by variation of the mark/space ratio and repetition period (pulse frequency). In addition to those factors, the colour obtained with an anodic film of a given thickness, depends on the alloy selected for treatment, the mean current density applied and the temperature of the electrolyte.

It is preferred that the temperature of the oxalic acid electrolyte should be in the range of 15–30° C. and that the aqueous electrolyte should contain at least 8% oxalic acid and should preferably constitute a saturated solution. In accordance with known practice, it is desirable to apply a reduced voltage at the beginning of the anodisation process to avoid uneven colour distribution; application of full process voltage at the beginning of the treatment leads to greater intensity of colour around the edges of the piece than in the middle of the surface.

In a series of tests carried out using a saturated oxalic acid anodising bath at 20° C. and a mean current density of 24 amps/sq. ft., the following process conditions were used:

Pulse frequency (cycles/second)	Mark/ space ratio, percent	Peak current density (a./sq. ft.)	Peak Voltage		Time (mins.)	Film (microns)
			Alloy HE9	Alloy HE20		
$1\frac{1}{2}$ -----	6	400	160	180	60	35
$1\frac{1}{2}$ -----	6	400	150	170	40	25
$1\frac{1}{2}$ -----	12	200	130	150	40	25
$1\frac{1}{2}$ -----	16	145	115	140	40	25

The first conditions given produced the darkest colour on all alloys tested. The colours became progressively

lighter as the peak current density was decreased. The time required to produce an anodic film of desired thickness varied a little from alloy to alloy, but the above time figure is typical.

Alloys HE9 and HE20 are aluminium alloys conventionally used for production of extrusions for architectural usage and have a nominal composition respectively as follows:

HE9—Si, 0.6%; Mg, 0.45; balance Al and impurities.

HE20—Si, 0.6%; Mg, 1.0%; Cu, 25%; Cr, 25%; balance Al and impurities.

Alloy HE20 cannot be extruded at the same high rate as the HE9 alloy and it is therefore more costly to produce extrusions in this alloy.

The peak current density employed can be as high as 500 amps/sq. foot without burning the anodic oxide film, which would occur with such high current density if a smooth D.C. current were applied.

No difficulties were experienced keeping the electrolyte at the desired operating temperature, using refrigeration and temperature controls normally available in a D.C. oxalic acid anodising tank for the production of hard, corrosion resistant anodic oxide films for external use. No abnormal signs of electrolyte deterioration were detected and the electrolyte has substantially the same service life as the oxalic acid electrolyte in the D.C. oxalic acid anodising process.

Physical examination of the anodic oxide films produced by the use of pulsed D.C. current with an oxalic acid anodising bath, operated under the conditions set forth above, shows no substantial difference, except colour, between these films and those produced by normal oxalic acid anodising using a smooth D.C. current. Accelerated corrosion tests have shown no difference in corrosion resistance between anodic oxide films obtained using pulsed D.C. and smooth D.C., other variable being the same.

Examination of the anodic films produced by pulsed D.C. has so far indicated that the colours have satisfactory light-fastness.

According to a further development of the invention, it has been found possible in some cases to obtain very dark colours in anodic films produced in an oxalic acid bath, using a relatively small peak current/mean current ratio of the order of 6:1 by treatment of the metal to develop the formation of fine particles which survive in the anodic oxide film.

In the case of the alloy HE9, referred to above, good results can be obtained by "overageing," that is to say by carrying out the normal "artificial ageing" heat treatment for a longer time and/or at a higher temperature than is required for the development of the optimum physical properties. The "overageing" heat treatment is believed to increase the development of particles of the Mg_2Si type.

Normal "ageing" treatment for the HE9 alloy is heating at 175° C. for 8 hours. Very significant darkening of the resultant oxide film is obtained if the alloy is "overaged" for a suitable time at a higher temperature, when using pulsed current. Most satisfactory results are obtained if "overageing" is carried out at $220\pm 5^\circ$ C. for 10 hours. Although this somewhat decreases the physical properties of alloy extrusions, it is not to such extent

that the extrusions become unacceptable on strength grounds. These treatment conditions have been selected

since they are found to produce reproducible colours, in spite of minor operational changes of the treatment conditions.

The use of "overaged" material allows the process to be operated with a less expensive source of pulsed D.C. current, capable of a maximum peak current/mean current ratio of 6:1.

Using such apparatus and anodising to a film thickness of 25-35 microns, generally considered necessary for external application of aluminium in the English climate we have produced the following range of colours on HE9 alloy overaged at 220° C. for 10 hours.

Sample No.	Peak to mean current ratio	Mean current density in amps/sq. ft.	Anodic film thickness in microns	Anodising time in min.	Electrolyte temperature in ° C.	Peak voltage	Approximate mean peak voltage	Colour
1-----	6:1	24	35	50	20	115-160	137	Black.
2-----	6:1	15	25	55	20	105-145	125	Brown-bronze.
3-----	3:1	15	25	55	20	90-130	110	Bronze.
4-----	6:1	24	35	50	25	105-155	130	Brown-bronze.
5-----	6:1	15	25	55	25	100-135	117	Bronze.
6-----	3:1	15	25	55	25	80-120	100	Light bronze.
7-----	6:1	24	35	50	30	100-125	112	Brown.
8-----	6:1	15	25	55	30	90-120	105	Gold-brown.
9-----	3:1	15	25	55	30	80-100	90	Gold-bronze.

The following table shows the mechanical properties of HE9 alloy "overaged" under varying conditions.

Alloy	Ageing temp., ° C.	Time in hours	0.1% proof stress	Ultimate tensile stress	Percent elongation on 2"
HE9-----	175	8	12.7	14.7	15
	205	6	14.0	15.6	12
	215	6	10.8	12.8	11
	225	6	10.7	13.0	14
	235	6	9.3	11.9	15
	220	10			

We have so far exemplified the process with reference to anodising baths containing oxalic acid alone.

Oxalic acid may have employed in conjunction with it a small proportion of another acid, either an inorganic acid, such as sulphuric acid, or an organic acid, such as formic acid, to improve the conductivity of the electrolyte. Alternatively a metal salt, such as ferrous sulphate, may be used for the same purpose. Such addition in the case of sulphuric acid or ferrous sulphate is not in excess of 1% and preferably much less so as not to interfere with the type of film formed by anodising in oxalic acid.

The table below summarises the results obtained using the pulse current anodising technique in various mixed electrolytes containing oxalic acid.

The same HE9 alloy was used for all the experiments and the anodising conditions used were kept constant at a mean current density of 24 a./sq. ft. and a time of 40 mins. A peak/mean current density ratio of 6:1 was used for the pulsed conditions.

All percentages for the electrolyte components are on a weight to volume basis.

Electrolyte	Electrolyte temperature (° C.)	D.C. anodised film thickness and colour	Pulsed current anodised film thickness and colour
(1) 8.0% oxalic acid, 5.5% formic acid.	23	45, rich gold-----	50, deep red-brown.
(2) 2.7% oxalic acid, 0.23% sulphuric acid.	20	35, light bronze-----	35, bronze.
(3) 10% sulphuric acid, 5% oxalic acid.	20	45, silver grey-----	45, bronze patchy film.
(4) 10% sulphuric acid, 10% oxalic acid.	20	40, silver grey-----	45, grey brown very patchy film.

odising is governed by the oxalic acid content of the electrolyte. Thus where the sulphuric acid content of an oxalic acid bath (result 2) was of the small order required to improve conductivity, improved results were obtained. With results 3 and 4 (which are outside the scope of the present invention) the large sulphuric acid content of the bath governed the character of the anodising.

We claim:

1. A process for producing a coloured anodic oxide coating on aluminium (including aluminium alloys) comprising suspending the material to be coated as an anode

in an aqueous electrolyte bath containing a solute of which a major proportion is oxalic acid and passing through said bath a pulsed direct current, in which the wave form of each current pulse is approximately square and the ratio of anode peak current density/anode mean current density is 3-6:1.

2. A process for producing a coloured anodic oxide coating on aluminium (including aluminium alloys) comprising suspending the material to be coated as an anode in an aqueous electrolyte bath containing a solute of which a major proportion is oxalic acid and passing through said bath a pulsed direct current, in which the pulse frequency is 1½-20 pulses per second and the ratio of anode peak current density to anode mean current density is at least 3:1.

3. A process according to claim 2, in which the wave form of each current pulse is approximately square.

4. A process according to claim 3, in which the mean anode current density is 10-36 amperes per square foot.

5. A process according to claim 3, in which the bath is a substantially saturated aqueous solution of oxalic acid.

6. A process according to claim 3, in which the material to be anodised is an aluminium alloy which consists essentially of about 0.6% Si and about 0.45% Mg, balance aluminium and impurities, and for which a normal ageing treatment is heating at 175° C. for 8 hours, said process further comprising, as a step preceding the aforesaid anodic treatment, subjecting the aforesaid alloy to a heat ageing treatment which in at least one of the respects

It will be seen from these results that a darkening of the film is obtained by the use of the pulsed current technique only in those cases where the character of the an-

of temperature and time exceeds the aforesaid normal ageing treatment.

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) PETER GEOFFREY SHEASBY; EDWARD PERCIVAL SHORT and
ROMAN DOMINIK GUMINSKI

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Column 4, line 10, "Cu. 25%; Cr, 25%" should read --Cu 0.25%;
Cr 0.25%--

SIGNED AND
SEALED
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(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents