

PATENT SPECIFICATION

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1,129,677

Index at Acceptance:—C7 B(2F, 13, 15X); C7 A(B249, B25Y, B25X, B289, B309, B319, B32Y, B333, B335, B349, B35Y, B363, B365, B37Y, B383, B385, B387, B399, B419, B42Y, B431, B433, B435, B459, B46Y, B489, B487, B50Y, B515, B517, B519, B539, B544, B547, B548, B549, B559, B610, B613, B616, B619, B62X, B620, B621, B624, B627, B630, B635, B66X, B661, B663, B665, B667, B669, B670, 741, 742, 743, 744, 745, 781).

vs

Int. Cl.:—C 23 b 9/02.

COMPLETE SPECIFICATION.

Improvements in or relating to Electrolytic Treatment of Aluminium.

We, KAISER ALUMINUM & CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 300 Lakeside Drive, Oakland, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing coloured anodic oxide coatings on aluminium extrusions and sheets, and to integrally coloured extrusions and sheets produced by such process.

It is now well known to colour-anodise aluminium by processes that produce integrally coloured coatings, as distinguished from colourless coatings that are later dyed or pigmented. Colour-anodising processes employ aqueous electrolytes containing sulphate ions and one or more aromatic sulphonic acids which are substituted with hydroxyl or carboxyl groups or combinations of hydroxyl and carboxyl groups. When aluminium is employed as the anode in an electric circuit which includes the electrolyte, integrally coloured anodic oxide coatings may be formed in colours ranging from light gold to black. The process may be applied to virtually any form of aluminium, but it is most often applied to sheets and extrusions, particularly sheets and extrusions employed for architectural pur-

poses. This invention deals with integrally coloured coatings, and the term *colour-anodised* or terms of similar import refer to integrally coloured coatings.

Although it is easy, on a laboratory scale, to produce coloured anodic oxide coatings, many difficulties arise when producing them for commerce. Among these difficulties are producing a series of colour-anodised articles which "match". For example, it is difficult repeatedly to produce a number of colour-anodised extrusions which have the same colour, texture, and glossiness; in other words, the same appearance so that when used side by side they will match one another. Another problem is to create colours which are usable with one another even though the alloys employed are different. Typical of this problem is employing colour-anodised sheets as curtain walls in conjunction with colour-anodised extrusions employed as door frames, spandrels, lintels, column sheaths or similar members.

Aluminium alloys suitable for extrusion usually have a different composition from alloys suitable for rolling, and they respond differently to anodising conditions. Even a series of articles made of the same alloy may respond to anodising differently due to different microstructures. A series of extrusions may differ due to slight differences in the thermal treatment of the extrusion or the billet from which it is formed, and these differences in structure produce different appearing anodised extrusions even though

[Price 4s. 6d.]



the billets from which the extrusions were formed had identical composition.

Generally speaking, it is difficult to anodise to obtain darker colours on alloys which are constituted to be suitable for extrusion. For example, the alloy designated as 6063 alloy by the "Aluminium Association" of America is a widely used extrusion alloy and has the following weight percentage composition: Si: 0.2—0.6, Fe: 0.35 max., Cu: 0.10 max., Mn: 0.10 max., Mg: 0.45—0.9, Cr: 0.10 max., Zn: 0.10 max., Ti: 0.10 max., others: each 0.05, others total 0.15, balance: aluminium. This alloy is very difficult to colour-anodise with black or other dark coatings. Another difficulty is that the appearance of anodised 6063 alloy is extremely sensitive to the thermal treatments to which the alloy is subjected before and during extrusion. In this regard, it should be pointed out that control of thermal conditions is extremely difficult. Even such a well known heat treatment as homogenising can create difficulties because ingots are generally homogenised in groups piled one upon another so that both the heating and the cooling rate of ingots in the interior of the pile is substantially slower than the heating and cooling rates of ingots on the exterior of the pile thereby producing a different internal structure which in turn produces a different response to colour-anodising.

Our copending Application No. 4847/66 (Specification No. 1,129,676) describes and claims an alloy suitable for extrusion and for accepting a range of colour-anodised coatings from light gold to dark colours on extruded aluminium. The present invention provides a method for colour-anodising aluminium base alloys and additionally provides a method for reducing the effect that variations in thermal treatments have on the response an alloy has to an anodising process. Stated differently, this invention provides a means for colour-anodising extruded and other aluminium products in such a way that the colour of the product will depend almost entirely on the composition of the alloy and the programme employed to anodise it thereby giving close control over reproducibility of appearance, and in addition it provides a means for obtaining dark coloured and even black anodic oxide coatings on extrusions while still retaining the ability to make light colours.

According to this invention, a process is provided for producing integrally-coloured anodic oxide coatings on aluminium extrusions, which comprises producing an extruded shape from an alloy which includes, by weight, 0.2% to 0.6% silicon, 0% to 0.35% iron, 0.15% to 0.5% copper, 0.1% to 0.4% manganese, 0.4% to 0.8% magnesium and the remainder aluminium and

impurities, and subjecting the extruded shape to electrolysis as an anode in an aqueous electrolyte containing sulphate ion equivalent to 0.1% to 4% sulphuric acid and 0.09 to 0.7 gram moles per litre of an aromatic sulphonic acid having two or more hydroxyl groups, two or more carboxyl groups or one or more hydroxyl groups together with one or more carboxyl groups, the electrolysis being effected by means of a direct current at a voltage of 30 to 130 volts and at a current density of 10 to 120 amperes per square foot of immersed anode area for a time sufficient to produce a coloured anodic oxide coating on the extruded shape.

Preferably, the weight ratio of magnesium to silicon in the alloy is from 1:1 to 2:1. Preferably, the alloy consists of 0.3% to 0.4% silicon, 0.15% to 0.25% iron, 0.15% to 0.25% copper, 0.1% to 0.2% manganese, 0.45% to 0.6% magnesium and the balance aluminium and impurities. All compositions stated in this specification and the following claims are on a weight percent basis unless stated otherwise.

The above-specified alloy is homogenised and formed into an extruded shape. The extruded shape is immersed as the anode in an aqueous electrolyte which contains in solution from 0.1% to 4% sulphuric acid or the equivalent amount of sulphate ion and from 0.09 to 0.7 gram moles per litre of an organic sulphonic acid substituted with at least two hydroxyl and/or carboxyl groups, i.e. with two or more hydroxyl groups, two or more carboxyl groups or one or more hydroxyl groups together with one or more carboxyl groups. Suitable organic acids include but are not limited to sulphosalicylic acid, sulphophthalic acid, sulphoresorcinol and lignosulphonic acid.

Anodising is effected at conditions now well known to the colour-anodising art. The temperature of the electrolyte may range from near its freezing point to 100°F. or substantially higher. The current density ranges from 10 to 120 amperes per square foot of surface being anodised, the voltage ranges from 30 to 130 volts and the time is that sufficient to produce the colour and thickness of coating that is desired; usually less than 120 minutes.

Following are several examples presented to illustrate the present invention with typical embodiments of it. The examples are intended to be illustrative and they have been selected as typical examples to demonstrate the invention rather than to limit it.

Extrusions were made from several alloys that are useful as extrusion alloys and capable of being colour-anodised. Prior to anodising the alloys were subjected to two tempers that differed substantially from one another in order to compare the difference

in colour-anodising response caused by varying thermal treatments of an alloy prior to extrusion. The alloys were also anodised by two different electrical programs which are both characteristic of those employed to colour-anodise extrusions.

The temper designated -T4 is one of the well known and standard tempers used throughout the aluminium industry with heat treatable aluminium alloys. The -T4 temper is obtained by solution heat treating (usually from 700° to 1000°F. for a time sufficient to place the hardening alloy components in solid solution) and rapidly cooling the alloy after which it is aged at room temperature to a stable condition. The temper designed as -T6 is also a standard temper well known to the aluminium industry for use with a heat treatable alloy. It is imparted by solution treating an alloy as described after which it is artificially aged to approximately maximum tensile properties thereby producing a very strong and stable alloy. Artificial ageing is accomplished by heating the alloy to a relatively low temperature usually from 300° to 475°F. until the hardening ingredients precipitate, usually 1 to 24 hours.

The alloy shown in Table 2 as 6063 alloy is a typical example of the 6063 alloy designated in the "Aluminium Association" of America classification of alloys. The specific alloy used contained 0.36% silicon, 0.2% iron, 0.005% copper, 0.004% manganese, 0.6% magnesium, 0.005% chromium, 0.01%

zinc, 0.004% titanium, and the remainder aluminium and impurities. The other alloys of the examples are the same 6063 composition with the specified amounts of additional elements. Thus, an alloy designated 6063 plus 0.4% manganese and 0.2% copper is the 6063 composition set forth above, but containing 0.4% manganese instead of 0.004% manganese and 0.2% copper instead of 0.005% copper.

In Table I two anodising programs are set forth. The first anodising program is employed in all cases in Example 1 and the second anodising program is employed in all cases in Example 2. Examples 1 and 2 set forth the response to various anodising treatments to the designated alloys in both the -T4 and the -T6 temper. The colour reported for the -T4 temper is a subjective observation which is accomplished by comparing the colours obtained with previously established colour standards. The colours obtained on the specimens with -T6 temper are comparative with respect to the colours on specimens with -T4 temper. Thus, if the -T4 temper produces a "bronze" colour and the -T6 temper produces a "lighter bronze" colour, the colour produced on the -T6 temper is reported as lighter with respect to the colour produced on the specimen with a -T4 temper.

The following Table 1 sets forth the anodising conditions employed in each of Examples 1 and 2:

TABLE 1

	Example 1	Example 2
Sulphuric acid (%)	0.5	0.5
Sulphosalicylic acid (gram moles/litre)	0.45	0.45
Temperature (°F.)	75	75
Initial current density (amperes/sq.ft.)	24	27
Maximum volts	65	60
Anodising time (minutes)	40	45
Total current quantity (amp.hrs/sq.ft.)	12.0	19

The results obtained in Example 1 are set forth in Table 2:

TABLE 2

Alloy	-T4 Temper	-T6 Temper
6063	Bronze	Much lighter bronze
6063 + 0.4% Mn + 0.2% Cu.	Black	Black

Example 1 above illustrates that the combined effect of the alloy of this invention and the colour-anodising process produces substantially darker colour-anodised coatings and coatings that are far less sensitive to thermal treatments. Although the difference between the colour produced in the -T4 temper and the -T6 temper in the manganese - copper - containing alloys is

noticeable except in the alloys producing black coatings, the amount of difference is very slight considering that the tempers employed were radically different from one another and that they were selected to exaggerate anodising response differences resulting from thermal history.

The results of anodising under conditions set forth in Table 3 below:

set forth for Example 2 as produced anodised alloys

Alloy	TABLE 3	-T4 Temper	-T6 Temper
6063		Bronze	Much lighter bronze
6063 + .4% Mn + .2% Cu		Black	Black

5 Example 2 also illustrates that the combination of the manganese-copper-containing extrusion alloy and the colour-anodising process of this invention can produce darker coloured anodised extrusions, and extrusions
10 which are for less sensitive to their thermal history with respect to colour-anodising response.

WHAT WE CLAIM IS:—

1. A process for producing integrally-
15 coloured anodic coatings on aluminium extrusions, which comprises producing an extruded shape from an alloy which includes, by weight, 0.2 % to 0.6% silicon, 0% to 0.35% iron, 0.15% to 0.5% copper, 0.1%
20 to 0.4% manganese, 0.4% to 0.8% magnesium and the remainder aluminium and impurities, and subjecting the extruded shape to electrolysis as an anode in an aqueous electrolyte containing sulphate ion equivalent to 0.1% to 4% sulphuric acid and 0.09
25 to 0.7 gram moles per litre of an aromatic sulphonc acid having two or more hydroxyl groups, two or more carboxyl groups or one or more hydroxyl groups together with one
30 or more carboxyl groups, the electrolysis being effected by means of a direct current at a voltage of 30 to 130 volts and at a current density of 10 to 120 amperes per square foot of immersed anode area for a
35 time sufficient to produce a coloured anodic oxide coating on the extruded shape.

2. A process according to claim 1, wherein the weight ratio of magnesium to silicon in the alloy is from 1:1 to 2:1.

3. A process according to claim 1 or 2, 40 wherein the alloy consists of 0.3% to 0.4% silicon, 0.15% to 0.25% iron, 0.15% to 0.25% copper, 0.1% to 0.2% manganese, 0.45% to 0.6% magnesium, and the balance aluminium and impurities. 45

4. A process according to claim 1, 2 or 3, wherein the sulphonic acid is sulphasalicyclic acid.

5. A process according to claim 1, 2 or 3, wherein the sulphonic acid is sulphonphthalic acid. 50

6. A process according to any preceding claim, wherein the sulphate ion is supplied from sulphuric acid.

7. A process according to claim 1, for 55 producing integrally-coloured anodic oxide coatings on aluminium extrusions, substantially as hereinbefore described.

8. An integrally-coloured aluminium extrusion, when prepared by a process according 60 to any of claims 1 to 7.

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Alloy	TABLE 3	
	-T4 Temper	-T6 Temper
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6063+.4% Mn+.2% Cu	Black	Black

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25 to 0.7 gram moles per litre of an aromatic sulphonic acid having two or more hydroxyl groups, two or more carboxyl groups or one or more hydroxyl groups together with one
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2. A process according to claim 1, wherein the weight ratio of magnesium to silicon in the alloy is from 1:1 to 2:1.

3. A process according to claim 1 or 2, 40 wherein the alloy consists of 0.3% to 0.4% silicon, 0.15% to 0.25% iron, 0.15% to 0.25% copper, 0.1% to 0.2% manganese, 0.45% to 0.6% magnesium, and the balance aluminium and impurities. 45

4. A process according to claim 1, 2 or 3, wherein the sulphonic acid is sulphonalcyclic acid.

5. A process according to claim 1, 2 or 3, wherein the sulphonic acid is sulphonthalic acid. 50

6. A process according to any preceding claim, wherein the sulphate ion is supplied from sulphuric acid.

7. A process according to claim 1, for 55 producing integrally-coloured anodic oxide coatings on aluminium extrusions, substantially as hereinbefore described.

8. An integrally-coloured aluminium extrusion, when prepared by a process according 60 to any of claims 1 to 7.

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