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(54) PROCESS FOR COLOURING ANODISED ALUMINIUM BY ELECTROLYTIC DEPOSITION

(71) We, ALCAN RESEARCH AND DEVELOPMENT LIMITED, (formerly ALUMINIUM LABORATORIES LIMITED,) a Company incorporated under the laws of the Dominion of Canada, of 1, Place Ville Marie, Montreal, Quebec, Canada, 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:—

The present invention relates to a process for producing coloured coatings on aluminium, and more particularly relates to the production of inorganic-coloured coatings on aluminium articles. References to aluminium herein will be understood to include aluminium of ordinary commercial purity and aluminium-base alloys that are suitable for conventional anodising treatments. The term aluminium article as used herein is intended to include semi-fabricated products, such as rolled aluminium sheet and aluminium extruded sections.

The present invention relates to a known two-stage process for producing a coloured coating which comprises forming an anodic oxide coating on an aluminium article in a first stage and, in a second stage, developing a colour in the anodic oxide coating by passing an alternating current between such aluminium article and a counter-electrode, while such aluminium article and electrode are immersed in a bath that contains a dissolved compound of a selected metal in an aqueous acidic medium. Under these circumstances the anodic oxide coating on the aluminium article becomes coloured. More particularly, the invention is concerned with such process wherein the acidic bath of the alternating current treatment contains a nickel, cobalt, copper, silver or lead salt or an oxide of selenium, tellurium or manganese or a salt of such oxide.

The known process is described in United [Price 25p]

States Patent No. 3,382,160 and British Patent No. 1,022,927.

In the known process the counter-electrode may be a material, such as graphite, which is inert to the electrolyte, or may be a metal, which has a solution potential more noble than aluminium and preferably is the same metal as constituted by the selected ions in solution in the electrolyte. For instance, where the bath electrolyte contains nickel dissolved therein, a nickel counter-electrode may be very effectively employed, but with most of the other baths a graphite electrode is preferred.

The known process produces in the anodic coating, a coloured deposit of an oxide or hydroxide. A variety of colours are obtainable, including gold or other yellow tones, various shades of red and brown, bronze and like deep colours, including black by selection of the salt and the intensity or duration of that treatment.

In the known process certain difficulties have been experienced especially when the treatment time or conditions are adjusted to give darker shades, associated with a relatively large or intense deposit in the anodic oxide film. In particular there is an increased tendency to spalling, i.e. local flaking of the anodic oxide film, this effect being to produce colourless or pale local spots in the coating, which may be of minute size but are nevertheless extremely objectionable.

A chief object of the present invention is to reduce the incidence of spalling and particularly to obtain the darker tones, that are achieved with higher voltages or longer times or both, with a reduction or avoidance of deterioration of the coloured coating by spalling.

With the aim of inhibiting or avoiding spalling a magnesium salt or, except in the case of a bath containing a nickel or cobalt salt, an aluminium salt is introduced into the bath employed in the alternating current

treatment step in an amount sufficient to introduce at least 100 parts per million by weight of magnesium or aluminium ions which corresponds approximately to one gram per litre of magnesium sulphate (calculated as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), or aluminium sulphate (calculated as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). Thus a typical bath may constitute the salt selected for colouring function, appropriate acidic and related constituents, and a magnesium or aluminium salt, advantageously containing an anion otherwise present in the electrolyte.

The known method of producing coloured coatings has been found of special practical value when utilising nickel-containing or copper-containing baths, and it has correspondingly been noted that such processes are markedly improved according to the invention by the maintenance of magnesium ions in solution or, in the case of a copper-containing bath, of aluminium ions in at least the amount indicated above. A special advantage of the present invention is that one electrolyte can be employed to provide a wide range of shades or tones, notably up to the darkest values, so that the process has improved flexibility in practice. Moreover it has been noted in the nickel-containing and copper-containing solutions, and others, that more intensely coloured and spall-free surfaces are obtainable under otherwise identical conditions.

As stated, the complete process of producing a coloured coating on an aluminium surface involves first anodising the surface in conventional manner to produce an anodic oxide coating, e.g. of a type customarily applied for protective or like purposes. The anodising step is preferably a conventional direct current anodising in sulphuric acid under conditions selected to provide a rather porous coating, such as anodisation for 20-60 minutes in 15% (by weight) sulphuric acid at 15°-25°C. The operating conditions of the anodising step do not appear to be very critical, however, being selected largely to suit the thickness and other characteristics of anodic coating desired; the subsequent colouring step may be applied satisfactorily through a considerable range of thicknesses of porous anodic aluminium oxide coatings.

In the bath employed in the subsequent a.c. colouring stage the selected magnesium or aluminium salt (or other compound which becomes dissolved) is preferably added in substantial excess of the amount required to introduce 100 parts per million of magnesium or aluminium ions so as to accommodate slow but continuing depletion of such ions as the bath is repeatedly used, i.e. to avoid need for frequent replenishment of the Mg content.

Numerous examples of suitable baths for

the production of coloured anodic oxide coating are set forth in the United States Patent No. 3,382,160 and British Patent No. 1,022,927. These patents show that good results have been attained in baths containing nickel or cobalt salts when the pH is adjusted to the range of 3.5-5.5, preferably 4 to 4.5, while in the case of other salts of the group named herein above the preferred pH range is 0.5 to 2.

For the purposes of this invention, magnesium or aluminium is preferably added to the electrolyte in the form of a salt, the anion of which is already present in the bath or is otherwise compatible as will be understood or may be readily determined. Thus for example a preferred nickel electrolyte contains nickel sulphate and boric acid, to which magnesium may be added as magnesium sulphate or borate. Alternatively, magnesium or aluminium can actually be supplied as a reactive form of the corresponding oxide or hydroxide, then becoming a corresponding dissolved salt in the presence of the acidic constituents of the bath.

In general the amount of magnesium or aluminium dissolved in the bath should be sufficient to provide significant inhibition of spalling, i.e. to avoid or reduce the occurrence of minute spots or flaked-off areas, or like spots or defects in the coloured product, e.g. in the darker or very dark tones, obtainable with the selected metal. Although such spalling is often represented by colourless or pale spots, it may sometimes occur otherwise, as for instance where flaking near the outset of the alternating current treatment leads to a more intense tone due to preferential flow of current to the spalled area. In general at least 100 parts per million by weight of magnesium or aluminium ions should be present for good results and indeed preferably at least 2 grams per litre of magnesium or aluminium salt, e.g. sulphate, corresponding to about 200 parts per million by weight of magnesium or aluminium ions. Most preferably the magnesium or aluminium compound is added in amount to provide at least 1000 parts per million by weight of Mg or Al ions as for example 10 to 25 grams per litre of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, especially to avoid unduly rapid depletion. Even considerably greater amounts up to 40 grams per litre of magnesium or aluminium salt (4000 parts per million by weight Mg or Al) ions have shown no adverse effect, so that the upper limit appears primarily economic.

The exact effect of adding magnesium or aluminium salts to the electrolyte is not known. However a possible explanation is that spalling is due to local differences in the resistance of the anodic aluminium

oxide coating and more particularly that spalling may be related to the evolution of hydrogen where the oxide layer at the bottom of one or more pores of the coating is thin in a local area. It is believed that the incorporation of magnesium or aluminium sulphate in the electrolyte leads to some co-deposition of magnesium or aluminium oxide with the coloured oxide or hydroxide in the pores of the anodic oxide film and that such deposition increases the thickness of electrically resistant oxide at the bottom of the pores, thus removing the postulated cause of spalling and permitting the development of darker colours therein. Stated in another way, this hypothesis is that magnesium or aluminium oxide is coprecipitated with the coloured oxide or hydroxide to provide a more electrically-resistant deposit. The relatively larger flow of current during that part of the a.c. cycle when the anodised article is the cathode is believed to result in depletion of hydrogen ions at the base of the pores, causing localised rise in pH (greater alkalinity) and consequently the desired precipitation of the metal oxide or hydroxide, and in the present process, of magnesium or aluminium oxide as well. The precipitation of aluminium hydroxide from solutions of aluminium salts commences at about pH 5, whereas nickel and cobalt hydroxides do not commence to precipitate until the pH value rises to about 7 and thus aluminium hydroxide precipitates preferentially and the colouring effect of nickel and cobalt electrolytes is masked by the presence in the electrolyte of an aluminium salt in more than trivial amount. However, the beneficial effects of this invention have been abundantly demonstrated and it is not to be understood as dependent on the above or any other theories.

Referring to the following specific examples of the method of the invention, aluminium articles were first anodised by conventional anodic treatment with direct current, e.g. for periods upwards of 20 minutes in a 15% (by weight) aqueous sulphuric acid solution at a temperature in the range of 20°C. to 25°C., conveniently 21°C. It will be understood that other strengths of acid solution, or indeed solutions of other acids and likewise other modifications of condition as to suit the protective or like requirements of the coating may be employed. Conveniently operation with a current density of about 15 amperes per square foot (1.3 amperes per square decimeter) of work surface is very satisfactory, for a time selected to yield a desired film thickness, normally from 0.4 to 1.0 mil (10-25 microns) or more. As will be understood, the anodised aluminium is then rinsed before introduction into the colouring bath. In general, the alternating current is passed between the

anodised aluminium and the counter-electrode at a voltage of 5 to 20 volts for a time from a few minutes up to 10 or 15 minutes, sometimes with intermediate increase in voltage or other suitable electrical control. Generally, the shade of colour achieved depends on the time of treatment and on electrical conditions; for instance, lighter shades are produced by relatively brief treatment with lower voltages, whereas darker or stronger or very dark colours require a longer time or greater electrical values.

EXAMPLE 1

Aluminium sheets were first anodised in 15% sulphuric acid in conventional manner and after rinsing were then subjected to the alternating current treatment, with a counter-electrode of metallic nickel in a bath (adjusted to pH 4.0 to 4.5) having the following composition:

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	25 g.p.l.	
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	20 g.p.l.	
H_3BO_3	25 g.p.l.	90
$(\text{NH}_4)_2\text{SO}_4$	15 g.p.l.	

The anodised aluminium sheets were respectively treated for different times and under different voltages in this bath, yielding a range of colours from light bronze to very dark bronze or nearly black. In these and in other examples herein, the coloured anodised sheets were preferably subjected to conventional sealing treatment, for example by immersion in very hot or boiling water, for usual purposes. Whereas the a.c. treatment of anodised aluminium sheets in the stated bath for 5 minutes produced light and medium bronze tones at voltages of 10 and 12 volts respectively, treatment for 5 minutes at 15 volts produced a dark bronze colouring. A very dark bronze colour was produced by treatment for 5 minutes at 13 volts, followed by 5 minutes more at 17 volts. For comparison, operation of such bath without the magnesium sulphate occasioned spalling difficulty in endeavours to produce the dark bronze and especially the very dark bronze colour.

EXAMPLE 2

Anodised aluminium sheets, when subjected to alternating current in baths containing copper sulphate and sulphuric acid in aqueous solution having a pH of about 1.3, and containing magnesium sulphate addition of about 20 grams per litre yielded a range of coloured coatings, including pink, light maroon, dark maroon and black, depending on voltage and treatment time. Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was used, for example, in various concentrations from 25 to 50 grams per litre, and sulphuric acid in amounts of 5 to 6 grams per litre. As one

specific instance, the electrolyte contained 25 grams per litre copper sulphate, from 1 to 3 grams per litre magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), acidified by added sulphuric acid to a pH of about 1.3. Using a graphite counter-electrode, the anodised aluminium sheets were subjected to 8 volts a.c. for 3 minutes, followed by 12 volts a.c. for 9 minutes. A uniform black colour was developed in the anodic coating, whereas comparable treatment without magnesium sulphate addition to the bath generally resulted in spalling defects in the coating.

EXAMPLE 3

An aluminium sheet anodised in 15% sulphuric acid for 40 minutes was submerged, with a nickel counter-electrode, in an aqueous bath of 2.5% boric acid containing 4.0% nickel ammonium sulphate and 3.5% magnesium sulphate at a pH of 4.5. With the bath at room temperature alternating current was passed for 10 minutes at 15 volts. The product was sealed in boiling water for about 30 minutes and had a very dark brown colour, free of coating defects.

EXAMPLE 4

An aluminium sheet, anodised as in Example 3, was treated under the same conditions, except for the use of a graphite counter-electrode and the use of 2.5% magnesium sulphate in the electrolyte. After passage of the alternating current for 13 minutes at a potential of about 16 volts, and sealing as before, the aluminium sheet was found to have an anodic oxide coating characterised by a uniform black colour.

EXAMPLE 5

Aluminium sheets were first anodised by conventional treatment as indicated in Example 3 and then subjected to the alternating current treatment, with a graphite counter-electrode, in a bath containing from 25 to 30 grams per litre of lead acetate, 20 to 25 grams per litre of acetic acid and 20 grams per litre of magnesium acetate ($\text{Mg}[\text{C}_2\text{H}_3\text{O}_2]_2 \cdot 4\text{H}_2\text{O}$) at 13 volts for about 5 minutes. A uniform black coating was produced, whereas similar treatment without the addition of a magnesium salt tended to result in some spalling or like difficulty.

EXAMPLE 6

Aluminium sheets were first anodised in the conventional 15% (by weight) sulphuric acid solution for 30 minutes to a film thickness of 0.6 mil (15 microns), and after rinsing were then subjected to the alternating current treatment, with a counter-electrode of graphite in a copper-containing bath (adjusted to pH about 1.3) having the following composition:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	15 g.p.l.
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	20 g.p.l.
H_2SO_4	6 g.p.l.

The anodised aluminium sheets were treated in this bath for 3 minutes at 10 volts followed by 9 minutes at 15 volts, resulting in a coating of black colour of good uniformity, i.e. free of spalling. The treated sheets were then sealed in conventional manner by immersion in boiling water. The treatment of anodised aluminium sheets under the same conditions but with the bath free of added magnesium or aluminium salt produced a coating which was considerably spalled.

It will be understood that, as in Example 2, treatment at lower voltages and/or shorter times result in lighter colours, e.g. ranging through pink, light maroon and dark maroon. In practice, the content of copper salt can be selected over a considerable range, e.g. up to 50 grams per litre, the acid being added as required to obtain a preferred pH and the aluminium sulphate being included in amounts, for example, from 2 to 30 grams per litre or more.

EXAMPLE 7

Aluminium sheet was first anodised and then subjected to the alternating current treatment as in Example 6, except that the bath for the latter contained a silver salt and had the following composition:

AgNO_3	1.0 g.p.l.
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	20 g.p.l.
H_2SO_4	To provide pH 0.7

Passage of alternating current for 3 minutes at 10 volts produced a coating of uniform, golden brown colour, free of defects.

EXAMPLE 8

Aluminium sheet was first anodised and then subjected to the alternating treatment as in Example 6, except that the bath contained selenium and had the following composition:

$\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$	5 g.p.l.
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	20 g.p.l.
H_2SO_4	To provide pH 1.1

Passage of alternating current for 10 minutes at 15 volts produced a coating of uniform gold colour, free of defects. The colour was significantly more intense than was obtainable by exactly the same treatment without the aluminium sulphate addition to the bath.

EXAMPLE 9

Aluminium sheet was first anodised and then subjected to the alternating treatment

as in Example 6, except that the bath contained tellurium and had the following composition:

5	Na_2TeO_3	1.0 g.p.l.
	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	20 g.p.l.
	H_2SO_4	To provide pH 1.0

10 Passage of alternating current for 10 minutes at 15 volts produced a coating of uniform green gold colour, free of defects.

EXAMPLE 10

Aluminium sheets were first anodised by 15 conventional treatment as indicated in other examples, and then subjected to the alternating current treatment under the same conditions as in Example 5 except that the magnesium acetate content of the bath was 20 replaced by $(\text{Al}[\text{C}_2\text{H}_3\text{O}_2]_3)$. A uniform black coating was produced, free from spalling defects.

The addition of magnesium salt, usually 2 to 30 grams per litre magnesium sulphate, 25 have been found beneficial in the case where the treatment baths contained respectively 2.5 grams per litre selenium oxide (SeO_2) in aqueous sulphuric acid at pH 0.8, one gram per litre sodium tellurite (Na_2TeO_3) in aqueous sulphuric acid at pH 0.6 and one gram 30 per litre silver nitrate (AgNO_3) in aqueous sulphuric acid at pH 1.2. Treatment in these baths respectively resulted in a reddish gold, dark gold and yellow-green colour in the 35 anodic oxide coating.

Useful results were also obtained when 20 grams per litre of cobalt sulphate was used to replace nickel sulphate in the treatment bath of Example 1.

40 The addition of aluminium salt or magnesium salt, e.g. sulphate in the amount of 2-30 grams per litre to a treatment bath containing potassium permanganate, acidified to about pH 1.2 is also beneficial. Treatment is carried out at about 13 volts for a 45 period of about 10 minutes.

WHAT WE CLAIM IS:—

1. A method of producing an inorganically coloured anodic oxide coating on an aluminium surface wherein said surface has been anodised to produce an anodic oxide 50 coating in a first stage and wherein in a second stage alternating current is passed between said anodised surface and a counter-electrode in an aqueous acidic bath containing a nickel, cobalt, copper, silver or 55 lead salt or an oxide of selenium, tellurium or manganese or salt of such oxide characterised in that the acidic bath includes a magnesium salt or (except where the bath includes a nickel or cobalt salt) an aluminium salt in an amount sufficient to provide at least 100 parts per million by weight of magnesium or aluminium ions in the bath.

2. A method according to Claim 1, in which a magnesium or aluminium salt is included in the bath in an amount of at least 2 grams per litre.

3. A method according to Claim 1 or 2, in which said bath contains nickel sulphate, 70 boric acid and magnesium sulphate.

4. A method according to Claim 3 in which the bath further includes ammonium sulphate.

5. A method according to Claim 3 or 4, 75 in which $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is added to the bath in an amount of at least 10 grams per litre.

6. A method according to Claim 1 or 2, in which said bath contains copper sulphate, sulphuric acid and magnesium sulphate or 80 aluminium sulphate.

7. A method according to Claim 6, which comprises adding $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or 85 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to the bath in an amount of at least 10 grams per litre.

8. A method of producing on an aluminium surface a coloured anodic oxide substantially free from spalling substantially as herein described.

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as in Example 6, except that the bath contained tellurium and had the following composition:

5	Na_2TeO_3	1.0 g.p.l.
	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	20 g.p.l.
	H_2SO_4	To provide pH 1.0

10 Passage of alternating current for 10 minutes at 15 volts produced a coating of uniform green gold colour, free of defects.

EXAMPLE 10

15 Aluminium sheets were first anodised by conventional treatment as indicated in other examples, and then subjected to the alternating current treatment under the same conditions as in Example 5 except that the magnesium acetate content of the bath was replaced by $[\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3]$. A uniform black coating was produced, free from spalling defects.

The addition of magnesium salt, usually 2 to 30 grams per litre magnesium sulphate, 25 have been found beneficial in the case where the treatment baths contained respectively 2.5 grams per litre selenium oxide (SeO_2) in aqueous sulphuric acid at pH 0.8, one gram per litre sodium tellurite (Na_2TeO_3) in aqueous sulphuric acid at pH 0.6 and one gram per litre silver nitrate (AgNO_3) in aqueous sulphuric acid at pH 1.2. Treatment in these baths respectively resulted in a reddish gold, dark gold and yellow-green colour in the 35 anodic oxide coating.

Useful results were also obtained when 20 grams per litre of cobalt sulphate was used to replace nickel sulphate in the treatment bath of Example 1.

40 The addition of aluminium salt or magnesium salt, e.g. sulphate in the amount of 2-30 grams per litre to a treatment bath containing potassium permanganate, acidified to about pH 1.2 is also beneficial. Treatment is carried out at about 13 volts for a 45 period of about 10 minutes.

WHAT WE CLAIM IS:—

1. A method of producing an inorganically coloured anodic oxide coating on an aluminium surface wherein said surface has been anodised to produce an anodic oxide coating in a first stage and wherein in a second stage alternating current is passed between said anodised surface and a counter-electrode in an aqueous acidic bath containing a nickel, cobalt, copper, silver or lead salt or an oxide of selenium, tellurium or manganese or salt of such oxide characterised in that the acidic bath includes a magnesium salt or (except where the bath includes a nickel or cobalt salt) an aluminium salt in an amount sufficient to provide at least 100 parts per million by weight of magnesium or aluminium ions in the bath. 50 55 60

2. A method according to Claim 1, in which a magnesium or aluminium salt is included in the bath in an amount of at least 2 grams per litre. 65

3. A method according to Claim 1 or 2, in which said bath contains nickel sulphate, boric acid and magnesium sulphate. 70

4. A method according to Claim 3 in which the bath further includes ammonium sulphate.

5. A method according to Claim 3 or 4, in which $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is added to the bath in an amount of at least 10 grams per litre. 75

6. A method according to Claim 1 or 2, in which said bath contains copper sulphate, sulphuric acid and magnesium sulphate or aluminium sulphate. 80

7. A method according to Claim 6, which comprises adding $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to the bath in an amount of at least 10 grams per litre. 85

8. A method of producing on an aluminium surface a coloured anodic oxide substantially free from spalling substantially as herein described.

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