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(54) **A process for producing colour variations on electrolytically pigmented anodized aluminium**

(57) A process for producing a coloured article of anodized aluminium or aluminium alloy, wherein an anodized aluminium or aluminium alloy article (A), which is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer, is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place, and sealed.

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Description

[0001] Many methods are known to colour anodized aluminium finishes. A commonly used method involves impregnation of the anodic film by a suitable dye. Another common practice is deposition of a metallic pigment within the pores of the anodic film by means of electrolysis. Although the former method can be used to achieve an almost limitless range of colours, lighter shades will fade when exposed to sunlight. The latter method can be used to produce ultraviolet (UV) light fast pastel finishes. However, the palette of colours that can be produced is somewhat limited to hues associated with the specific metal being deposited. For example, nickel, tin, and cobalt can be used to produce bronze shades, copper can be used to produce pink shades, and silver can be used to produce yellow shades.

[0002] A recent patent, U.S. Patent No. 5,587,063, describes a method where a double electrolysis step is used to codeposit metallic pigments. An article coloured by this method exhibits a colour which is a combination of the hues which are specific to each of the metallic species deposited. This technique is not practical to many aluminium finishers because of the costs associated with installing a second power supply as well as the required electrical bussing. Additionally, one of ordinary skill in the art would expect colour non-uniformity and consistency problems as a direct result of multiple electrolysis steps.

[0003] Less common colouring methods include alloy modification, interference colouration, electrophoresis of colloidal carbon, and decomposition of impregnated salts. Many of these methods are discussed in detail by Wernick, Pinner, and Sheasby in The Surface Treatment and Finishing of Aluminum and Its Alloys, Fifth Edition, ASM International Finishing Publications Ltd.

[0004] U.S. Patent No. 5,510,015 describes one of several methods used to produce an inteference colour on anodized aluminium. Colouration by interference methods requires a morphological adjustment to the aluminium oxide barrier layer prior to the electro-deposition of a thin layer of pigment. Although such methods have been in existence for over twenty years, they have not enjoyed wide commercial success due to either the cost involved in implementation and/or the difficulty in achieving colour consistency and reproducibility.

[0005] U.S. Patent No. 5,334,297 describes a relatively new technique where colloidal carbon is deposited within an aluminium anodized film via electrophoresis. This technique requires great care in the production of colloidal particles small enough to physically pass into the pores of the anodic film. Such pores are typically in the range of twenty nanometers in diameter for conventional anodizing. Extremely high, and therefore dangerous, voltages are required for the process.

[0006] Another colouring method, commonly referred to as double decomposition, requires a non-electrolysis step whereby an anionic chemical compound is simply absorbed onto the cationically charged surface of the anodic film. A subsequent immersion in a chemically reactive solution alters the chemical and therefore optical characteristics of the deposited compound.

[0007] There is a need in the aluminium anodizing industry to increase the palette of light fast colour aluminium finishes that are both economically and technically feasible. Therefore, it is a main object of the present invention to produce coloured articles of anodized aluminium or aluminium alloys in such a manner and which are in particular highly light fast. The process of the present invention is relatively simple, inexpensive, and easy to implement in particular on an existing anodizing/pigmenting/sealing line.

[0008] Another object of the present invention is to provide a process which further extends the palette of UV light fast colours or colour variations on anodized aluminium or aluminium alloys. The colours which are achieved are highly light fast and as a result are particularly suitable for outdoor applications.

[0009] It has now surprisingly been found that by treatment of an anodized aluminium or aluminium alloy surface that has been electrolytically coloured with a metal cation, with a solution comprising a metal cation different from the one employed for the electrolytical colouration, under substantially non-sealing conditions and in the absence of applied electric power, its colour can be changed (in particular shifted and/or shaded) and the process can then be completed by sealing, which sealing may be brought about sequentially or - where (C) is a treatment bath - also in part simultaneously in the same bath, or also in a different bath (optionally after intermediate rinsing), to give very light-fast coloured articles. By this method there may be produced a very broad choice of shades, even pastel shades, of surprisingly high reproducibility and light fastness. An article that is coloured by this method can e.g. be exposed to ultraviolet (UV) light for extended periods of time with the effect of little or no fading.

[0010] The invention thus relates to a process for producing in this way articles of metal-pigmented anodized aluminium or aluminium alloys of modified colour.

[0011] In particular the invention relates to a process for producing a coloured article of anodized aluminium or aluminium alloy, wherein an anodized aluminium or aluminium alloy article (A), which is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer, is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place

[0012] A particular feature of the invention is represented by a process, wherein an anodized aluminium or aluminium alloy article (A) is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer and is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place.

[0013] A further particular feature of the invention is represented by a process, wherein an aluminium or aluminium alloy article is anodized to form an oxide layer on the surface of the aluminium or aluminium alloy article, the so formed anodized aluminium or aluminium alloy article (A) is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer and is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place.

[0014] The process can then be completed by sealing, which sealing may be brought about sequentially or - where (C) is a treatment bath comprising a sealant solution (C1) - also in part simultaneously in a bath (C1) which may be the same bath, or also in a different bath, optionally after intermediate rinsing.

[0015] According to one feature of the present invention the process comprises the steps of: (a) anodizing aluminium or aluminium alloy to form an anodic oxide film on the aluminium or aluminium alloy, (b) electrolytically depositing a metallic pigment within said anodic film to produce a coloured article, and (c) converting the colour of said article by immersing said article in a solution comprising metallic ions of a species other than that of said metallic pigment. The process may then be concluded with a sealing treatment.

[0016] In each of the stages of anodization, metallic pigmentation, colour conversion and sealing, the process may be carried out in a continuous way or batchwise as desired or suitable.

[0017] The invention relates also to the coloured articles produced by the method of the invention.

[0018] The oxide layers on articles of aluminium or aluminium alloys may be produced in conventional manner by anodization. Such alloys are well-known in the art and mostly contain at least about 80% by weight of aluminium and preferably at least about 95 % by weight of aluminium. Prior to anodization, aluminium or aluminium alloy may be treated by known pretreatments such as by degreasing, cleaning, desmutting, polishing and/or etching.

[0019] The aluminium or aluminium alloy articles may be of any desired and suitable shape as employable for anodization, e.g. in the form shaped articles (e.g. of panels) or of continuous articles (e.g. bands or coils). Anodization may be performed by conventional means generally known in the art, e.g. as follows: An aluminium or aluminium alloy article (e.g. a panel) is placed in an anodizing bath which generally comprises an aqueous strong acid electrolyte. The anodizing bath preferably comprises sulfuric acid, but other acids such as chromic, phosphoric, oxalic, or combinations of two or more thereof may be used. A sulfuric acid-based electrolyte is most preferred because it provides anodized aluminium of "architectural quality", meaning having suitable hardness, thickness and corrosion resistance for outdoor use; the acid concentration in the anodizing bath is may suitably range in the scope of from 5 to 20 vol-%, preferably 8 to 12vol-%. In some cases, additives can be used in the anodizing bath. Aluminium ions may also be present dissolved in the anodizing bath.

[0020] The anodizing bath is usually maintained at a temperature in the range of 55°F (12.8°C) to 90°F (32.2°C), preferably 65°F (18.3°C) to 80°F (26.7°C). The aluminium or aluminium alloy article is the anode (positive electrode), and the counter-electrode is the cathode (negative electrode). The counter-electrode may be made of aluminium, carbon, graphite, lead, stainless steel and the like. Anodization is performed by applying electrical current under conditions suitable for formation of aluminium oxide. Typically direct current is used, however, alternating current or alternating current with intercalation of direct current can be applied. Direct anodic current, for example, is applied to the aluminium panel at a current density in the range of from 5 A/ft^2 (53.8 A/m^2) to 30 A/ft^2 (322.9 A/m^2), and preferably 10 A/ft^2 (107.6 A/m^2) to 20 A/ft^2 (215.3 A/m^2). Anodization can occur to a satisfactory degree suitably within 5 to 90 minutes, and preferably 10 minutes to 60 minutes. During anodization, the surface of the article of aluminium or aluminium alloy is consumed correspondingly to produce the oxide, which results in a microporous anodic layer of oxide on the surface of the aluminium or aluminium alloy article. The anodized article of aluminium or aluminium alloy is referred to herein as (A).

[0021] Subsequent to the anodization step is the electrolytic colouring step. The anodized article (A) is put in another bath, referred to as the electrolytic colouring bath, which is connected to another power supply. The power supply is typically alternating current. However, it may be direct current or alternating current with intercalation of direct current. The counter-electrode is typically graphite or stainless steel, but can be any suitable metal used in the electrolytic bath or any other suitable neutral metal. When alternating current is applied, at each moment in time the current is in either the anodic phase or the cathodic phase. Plating occurs during the cathodic phase. During plating, particles are deposited in the pores of the anodic microporous oxide layer. This plating or metal-pigmenting of the oxide layer may be brought about by employing a suitable counter-electrode and a dissolved metal-cation-electrolyte, as desired and suitable. For the pigmenting electrolytic baths the cations may be any metal cations other than aluminium cations, as conventionally employable for plating, e.g. as mentioned below for (C), of which the transition metals an tin are preferred for (B), especially copper, silver, nickel, cobalt or tin. They may be employed in the form of conventional salts of said cations e.g. with anions of acids as usable for the anodizing bath mentioned above, or also as chlorides, fluorides, nitrates or acetates.

[0022] This deposit of (B), which is referred to as a metallic pigment, produces a colour. For example if tin is used, bronze to black colours may result. If copper is used, pink, maroon or black colours may result. If silver is used, yellow to yellow-brown colours may result.

[0023] That (A) is pigmented with (B) "within" the oxide layer, or that (B) is deposited "within" the oxide layer, means in particular that (B) is applied to the substrate in such a density that a substantial activity of the (B)-pigmented substrate is maintained, promoted or even increased, so that it may interact with the metal cation present in (C) applied by plain immersion or even by spraying, i.e. in the absence of applied electric power and under substantially non-sealing conditions - but also in part simultaneously sealing is possible. In other words the electrolytical pigmentation with (B) is suitably carried out to such a degree, that the subsequent treatment with the other metal cation present in (C) may provoke a perceivable change of colour, in particular in hue (as perceivable there being meant visually perceivable, which would mean about such a change as in the CIELAB system of colour space co-ordinates corresponds to a $\Delta E \geq 3$, preferably ≥ 5). The suitable and in particular the preferred or optimum density of (B) on the substrate for a certain metal cation to be used in (C) may vary with the constitution of the substrate, the nature of (B) and (C) and the application parameters and may be assessed for each case by means of a few preliminary tests.

[0024] Copper has been found particularly useful as a metallic pigment (B) in the process of the present invention. For example, a copper bath employed in the process of the present invention is typically comprised in the concentration range of 2 to 30 g/l sulfuric acid and 0.1 to 20 g/l of copper sulfate (in the usual commercial form of its pentahydrate). Typically the electrolytic bath is held at room temperature (=20°C) and an AC voltage in the range of 5 to 20 V rms, preferably 8 to 12 V rms, is employed for a time of 10 seconds to 5 minutes.

[0025] Before treatment with (C), the (B)-pigmented article may be rinsed with water.

[0026] The colour conversion step with (C) subsequent to electrolytic colouring with (B) is critical to the process of the invention. It is referred to as the conversion step. During the conversion step, the electrolytically pigmented, anodized article of aluminium or aluminium alloy (e.g. a panel) is treated with a metal cation solution (C) without a power supply. The solution (C) is in particular an aqueous solution and comprises metal cations of a species other than that of the pigment (B). Metal cations useful in (C) in the process of the present invention include, but are not limited to, alkali metal cations (especially lithium or potassium cations), alkaline earth metal cations (especially magnesium or calcium cations), transition metal cations (especially chromium, molybdenum, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold or zinc cations) and other metal cations of the third or fourth group of the Periodic Table Of The Elements (especially tin cations) or mixtures of two or more thereof Among the most preferable of the metal cations are lithium, magnesium, iron, cobalt, nickel, palladium, platinum, copper, silver and gold, and mixtures of two or more thereof. They may be employed in the form of water soluble salts, e.g. of the acids mentioned above for (B). The treatment with (C) may be carried out preferably by immersing the (B)-pigmented and optionally rinsed article in (C) or even by spraying (C) on the (B)-pigmented and optionally rinsed article.

[0027] The solution (C) may also, but does not necessarily, contain other additives such as fluorides, buffers, surfactants and other organic materials. Suprisingly with the process of the present invention, the colour shifts from the original colour achieved in the electrolytic colouring step to the final desired colour during the conversion treatment. This colour shift, however, depends upon the chemical make-up of the metal cation solution. For example, an effective means of achieving a light fast gray shade can be achieved by electrolytically depositing a small amount of copper within the anodic film to give a pink shade and subsequently immersing the copper-pigmented article in a solution (C2) comprising metal cations of a species other than that of said copper, especially in a solution comprising either magnesium, lithium, nickel, cobalt or some other similarly reactive metal cation(s).

[0028] A particular aspect of the invention thus embodies a process for producing a gray colour shade on an article of anodized aluminium or aluminium alloy comprising the steps of: (a) anodizing aluminium or aluminium alloy to form an anodic oxide film or layer on the surface of the aluminium or aluminium alloy article, (b) electrolytically depositing copper within said oxide layer to produce a pink coloured article, and (c) converting the colour of said article by immersing said article in a solution (C2) comprising metal cations of a species other than that of said copper, so as to obtain a gray colour shade. The process may then be concluded with a sealing treatment.

[0029] For achieving a light fast gray, magnesium, lithium, nickel, or a combination of any two or all three thereof is preferred. A yellow hue is developed when the same article, after copper deposition is immersed in a solution comprising silver ions, and a purple hue with gold ions.

[0030] In general, a conversion solution (C) employed in the process of the present invention comprises advantageously a metal cation concentration of 0.1 g/l to 50 g/l. The temperature of the solution is usually in the range of from 50°F (10°C) to 190°F (87.8°C). The pH is advantageously in the range of 5 to 7, and the duration of the immersion is advantageously in the range of 30 seconds to 1 hour. For example, a conversion solution (C) employed in the process of the present invention to obtain a light fast gray on a pink copper-pigmented substrate typically comprises a concentration of 5 g/l to 50 g/l of magnesium acetate. The temperature of the solution is advantageously in the range of from room temperature to 180°F (82.2°C), preferably 120°F (48.9°C) to 170°F (76.7°C). The pH is preferably 5 to 7, and the duration of the immersion is usually 30 seconds to 1 hour.

[0031] After colour conversion, optionally with intermediate rinsing, the treated substrate may be sealed. Alternatively sealing may also be carried out in part simultaneously with the colour conversion and be completed after completion of the colour conversion.

[0032] By monitoring the process conditions and progress, the colour shifting and sealing may be controlled so that colour conversion and sealing are carried out separately or in part simultaneously, since, when using sealant salts (C1) for colour shifting, the colour shifting reaction and the sealing reaction are in a certain equilibrium with each other, insofar as when colour conversion is taking place or in particular prevails, no substantial or predominant sealing occurs, and when sealing is substantially promoted, practically no or no further colour shifting takes place. This equilibrium is different from cation to cation and depends also on the particular substrate (A), on the particular anodic pigmentation with (B) and on the reaction conditions. The typical equilibrium for each combination of (A), (B) and (C1) may be determined by means of some preliminary testing.

[0033] The conversion step can thus be combined with the sealing step. Although it is not necessary to do so, it does allow for easy implementation of the technology. In the sealing step, the pores in the anodic oxide film are closed to provide a significant enhancement in the corrosion resistance of the coating. In general, there are three classes of aqueous seal practices that are widely used in the industry, and can be used in the process of the present invention. They are: 1) high temperature where the seal solution is operated at or near the boil, 2) medium temperature where the temperature is generally operated between 160°F (71.1 °C) and 190°F (87.8 °C), and 3) low temperature where the seal is operated between 70°F (21.1 °C) and 100°F (37.8 °C). An advantage associated with combining the seal step with the conversion step in the process of the present invention is that the impact on an existing anodizing/pigmenting/sealing line is minimal and therefore, easily practicable.

[0034] When the conversion step is combined with the sealing step and the seal is high temperature, typically 190°F (87.8°C) to 210°F (98.9°C), the cation concentration is usually in the range of from 0.1 g/l to 50 g/l. The pH is preferably in the range of from 5 to 7, and the duration of the immersion is usually in the range of from 30 seconds to 1 hour. The bath may or may not contain organic additives to control smut and to promote seal. When the conversion step is combined with the sealing step and the seal is medium temperature, typically 160°F(71.1°C) to 190°F(87.8°C), the cation concentration is usually in the range of from 0.1 g/l to 50 g/l. The pH is preferably in the range of from 5 to 7, and the duration of the immersion is usually in the range of from 30 seconds to 1 hour. The bath may or may not contain organic additives to control smut and to promote seal. When the conversion step is combined with the sealing step and the seal is low temperature, typically 70°F (21.1°C) to 100°F (37.8°C), the cation concentration is usually in the range of from 0.1 g/l to 50 g/l. The pH is preferably in the range of from 5 to 7, and the duration of the immersion is usually in the range of from 30 seconds to 1 hour. The bath's fluoride level is generally 100 ppm to 2000 ppm.

[0035] By the process of the invention there may be achieved a very wide palette of colour variations that allow a large choice of colour combinations, e.g. for artistic or other fancy decoration or lettering of articles of anodized aluminium or aluminium alloys, and which are distinguished by a very high light and weathering fastness and by optimum reproducibility and uniformity of shade.

[0036] In the following examples the temperatures are indicated in degrees Fahrenheit, the corresponding temperature in degrees Celsius being indicated in brackets; where linear units are not indicated in metric units the corresponding value in metric units is indicated in brackets; where no temperature is indicated, the temperature is ambient temperature.

Example 1

[0037] Aluminium sheet samples of alloy AA5005 are anodized to 0.30 mil (7.62 μm) in an anodizing bath comprising 160 g/l H_2SO_4 and 8 g/l dissolved Al at 70°F (21.1°C). The treatment time was 15 minutes. These panels were subsequently rinsed and pigmented in a bath comprising 1 g/l $CuSO_4{\cdot}5H_2O$ and 10 g/l H_2SO_4 by applying an AC voltage of 11 V rms using a type 316 SS rod as the counter-electrode. The treatment time was 110 seconds. At this point the panels were withdrawn, and it was noticed that their colour was pink. After rinsing, they were immersed and sealed for 10 minutes in a solution of about 2 g/l nickel acetate and an organic compound, commercially available from Clariant Corporation as Anodal® MS-1, at a pH of 5.5 and a temperature of 163°F (72.8°C). The colour shifted to light gray with a slight pink cast.

Example 2

[0038] Aluminium sheet samples of alloy AA5005 were anodized to 0.30 mil (7.62 μm) in an anodizing bath comprising 160 g/l H_2SO_4 and 8 g/l dissolved Al at 70°F (21.1°C). The treatment time was 15 minutes. These panels were subsequently rinsed and pigmented in a bath comprising 1 g/l $CuSO_4{\cdot}5H_2O$ and 10 g/l H_2SO_4 by applying an AC voltage of 11 V rms using a type 316 SS rod as the counter-electrode. The treatment time was 110 seconds. At this point the panels were withdrawn, and it was noticed that their colour was pink. After rinsing, they were immersed and sealed for 10 minutes in a solution of about 8 g/l magnesium acetate and an organic compound, commercially available from Clariant Corporation as Anodal® ES-1, at a pH of 5.5 and a temperature of 163°F (72.8°C). The colour shifted to light gray. After 200 hours exposure to carbon arc Fade-O-meter a colour change was barely perceptible. However, no further change occurred even after a total exposure of 1000 hours.

Example 3

[0039] Aluminium sheet samples of alloy AA5005 were anodized to 0.30 mil (7.62 µm) in an anodizing bath comprising 160 g/l H_2SO_4 and 8 g/l dissolved A1 at 70°F (21.1°C). The treatment time was 15 minutes. These panels were subsequently rinsed and pigmented in a bath comprising 1 g/l $CuSO_4{\cdot}5H_2O$ and 10 g/l H_2SO_4 by applying an AC voltage of 11 V rms using a type 316 SS rod as the counter-electrode. The treatment time was 110 seconds. At this point the panels were withdrawn, and it was noticed that their colour was pink. After rinsing, they were immersed and sealed for 10 minutes in a solution of about 5 g/l nickel fluoride, commercially available from Clariant Corporation as Anodal® CS-2, at a pH of 5.5 and a temperature of 70°F (21.1°C). The colour shifted to slightly deeper gray than in Example 1 with a similar slight pink cast.

Example 4

[0040] Aluminium sheet samples of alloy AA5005 measuring 8 inches by 1.5 inches (203.2 mm by 38.1 mm) were alkaline cleaned and given a brief etch in an alkaline solution. These panels were then anodized in a room temperature bath comprising 170 g/l H_2SO_4 and 8 g/l Al at 15 A/ft^2 (161.4 A/m^2) for a period of 25 minutes to produce a film measuring 0.5 mil (12.7 µm) in thickness. They were then pigmented in a bath comprising 1 g/l $AgNO_3$ and 5 g/l H_2SO_4. With the panel as one electrode, and type 316 stainless steel as the counter electrode 11 V rms was applied for a period of 60 seconds. The result was a yellow panel. This panel was then immersed in a 10 g/l $PdSO_4$ solution for 2 minutes. The result was a shift in hue from the original yellow to an attractive brass.

Example 5

[0041] Aluminium sheet samples of alloy AA5005 measuring 8 inches by 1.5 inches (203.2 mm by 38.1 mm) were alkaline cleaned and given a brief etch in an alkaline solution. These panels were then anodized in a room temperature bath comprising 170 g/l H_2SO_4 and 8 g/l Al at 15 A/ft^2 (161.4 A/m^2) for a period of 25 minutes to produce a film measuring 0.5 mil (12.7 µm) in thickness. They were then pigmented in a bath comprising 2 g/l $CuSO_4{\cdot}5H_2O$ and 10 g/l H_2SO_4. With the panel as one electrode, and type 316 stainless steel as the counter electrode 11 V rms was applied for a period of 60 seconds. The result was a pink panel. This panel was then immersed in a 10 g/l $AuCl_2$ solution for a period of 2 minutes. The result was a shift in hue from the original pink to an attractive purple.

Example 6

[0042] Aluminium sheet samples of alloy AA5005 measuring 8 inches by 1.5 inches (203.2 mm by 38.1 mm) were alkaline cleaned and given a brief etch in an alkaline solution. These panels were then anodized in a room temperature bath comprising 170 g/l H_2SO_4 and 8 g/l Al at 15 A/ft^2 (161.4 A/m^2) for a period of 25 minutes to produce a film measuring 0.5 mil (12.7 µm) in thickness. They were then pigmented in a bath comprising 2 g/l $CuSO_4{\cdot}5H_2O$ and 10 g/l H_2SO_4. With the panel as one electrode, and type 316 stainless steel as the counter electrode 11 V rms was applied for a period of 60 seconds. The result was a pink panel. This panel was then immersed in a 17 g/l $AgNO_3$ solution for a period of 2 minutes. The result was a shift in hue from the original pink to yellow.

Example 7

[0043] Aluminium sheet samples of alloy AA5005 measuring 8 inches by 1.5 inches (203.2 mm by 38.1 mm) were alkaline cleaned and given a brief etch in an alkaline solution. These panels were then anodized in a room temperature bath comprising 170 g/l H_2SO_4 and 8 g/l Al at 15 A/ft^2 (161.4 A/m^2) for a period of 25 minutes to produce a film measuring 0.5 mil (12.7 µm) in thickness. They were then pigmented in a bath comprising 20 g/l $SnSO_4$ and 20 g/l H_2SO_4. With the panel as one electrode, and type 316 stainless steel as the counter electrode 11 V rms was applied for a period of 30 seconds. The result was a light bronze panel. This panel was then immersed in a 10 g/l $AuCl_2$ solution for a period of 2 minutes. The result was a shift in hue from the original bronze to an attractive mauve.

Comparative Example

[0044] Aluminium sheet samples of alloy AA5005 were anodized to 0.30 mil (7.62 µm) in an anodizing bath comprising 160 g/l H_2SO_4 and 8 g/l dissolved Al at 70°F (21.1°C). The treatment time was 15 minutes. These panels were subsequently rinsed and pigmented in a bath comprising 1 g/l $CuSO_4{\cdot}5H_2O$ and 10 g/l H_2SO_4 by applying an AC voltage of 11 V rms using a type 316 SS rod as the counter-electrode. The treatment time was 110 seconds. At this point the panels were withdrawn, and it was noticed that their colour was pink. After rinsing, they were immersed and sealed for 10 minutes in boiling water with 1 g/l ammonium acetate buffer pH 5.5. The colour remained pink (i.e. no metallic ion was present.)

Claims

1. A process for producing a coloured article of anodized aluminium or aluminium alloy, wherein an anodized aluminium or aluminium alloy article (A), which is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer, is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place.

2. A process according to Claim 1, wherein an anodized aluminium or aluminium alloy article (A) is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer and is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place.

3. A process according to Claim 1 or 2, wherein an aluminium or aluminium alloy article is anodized to form an oxide layer on the surface of the aluminium or aluminium alloy article, the so formed anodized aluminium or aluminium alloy article (A) is electrolytically pigmented with a metallic pigment (B) within the anodically produced oxide layer and is treated with a solution (C) comprising metal cations of a species other than that of said metallic pigment (B), until a perceivable colour conversion has taken place.

4. A process according to any one of Claims 1 to 3, wherein said colour conversion is carried out at least in part under substantially non-sealing conditions and in the absence of applied electric power.

5. A process according to any one of Claims 1 to 4, comprising sealing the article treated with (C).

6. A process according to any one of Claims 1 to 5, wherein said solution (C) comprises a sealant solution (C1) which is also employed for subsequent sealing.

7. A process according to Claim 6, wherein sealing is carried out in part simultaneously with colour conversion.

8. A process according to any one of Claims 1 to 7, wherein in (C) said metal cation of said species is selected from the group consisting of lithium, potassium, magnesium, calcium, chromium, molybdenum, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc and tin cations.

9. A process according to any one of Claims 1 to 8 for producing a gray colour shade on an article of anodized aluminium or aluminium alloy, comprising:

   (a) anodizing the aluminium or aluminium alloy article to form an oxide layer on the surface of the aluminium or aluminium alloy article,
   (b) electrolytically depositing copper within said oxide layer to produce a pink coloured article, and
   (c) converting the colour of said article by immersing said article in a solution (C2) comprising metal cations of a species other than copper cations, so as to obtain a gray shade.

10. A process according to Claim 9, wherein in (C2) said metal cation of said species is a magnesium, lithium or nickel cation or a combination of two or all three thereof.

11. A process according to any one of Claims 1 to 9, wherein the (B)-pigmented article is rinsed with water before treating it with (C).

12. A process according to any one of Claims 1 to 11, wherein the treatment with (C) is carried out by immersion of the (B)-pigmented article into (C).

13. A process according to any one of Claims 1 to 11, wherein (C) is applied by spraying.

14. A process according to any one of Claims 1 to 13, which is carried out batchwise or continuously.

15. A coloured anodized aluminium article produced by the process according to any one of Claims 1 to 14.