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Dorward et al.

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[54] **ALUMINUM SHEET**

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[52] **U.S. Cl.** **148/2,** 75/139, 75/142, 75/147, 148/11.5, 204/58

[51] **Int. Cl.** **C22f 1/04,** C22c 21/04

[58] **Field of Search**. 75/139, 142, 147; 148/2, 11.5, 148/31.5, 12.7; 204/58; 72/364, 700

[56] **References Cited**

UNITED STATES PATENTS

3,370,943	2/1968	Beatty et al.	75/142
3,265,597	8/1966	Neunzig et al.	204/58
2,853,409	9/1958	Helling et al.	148/4 X
3,104,189	9/1963	Wagner	75/142 X
3,164,494	1/1965	English	74/142 X
3,379,580	4/1968	Zeigler	148/11.5
3,475,167	10/1969	Beatty et al.	204/58 X

OTHER PUBLICATIONS

Alloy Digest, A1–42, August 1956.

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[57] **ABSTRACT**

This invention relates to an improved aluminum sheet material which, when integral color anodized, forms an anodic coating having a color from gold to black within a commercially acceptable thickness range. The alloy composition is essentially 0.05–0.20 percent silicon, 0.15–0.40 percent iron, 0.15–0.30 percent copper, 0.10–0.30 percent manganese, 0.6–1.0 percent magnesium, 0.04–0.12 percent chromium, and the balance aluminum and inconsequential amounts of other elements. In the process of forming the sheet product the alloy is cast into an ingot, homogenized at a temperature between about 1,000°F and 1,125°F and hot rolled to a desired thickness.

5 Claims, No Drawings

ALUMINUM SHEET

BACKGROUND OF THE INVENTION

This invention relates to an aluminum sheet material which, when anodized in an integral color anodizing electrolyte, will form an anodic coating having a color ranging from a light gold to black within a commercially acceptable thickness range.

It is now well-known to integrally color anodize aluminum and aluminum alloy products, such as sheets, extrusions, castings and the like for architectural and other purposes where the integrally colored coating provides a high aesthetic appeal. The basic process was first described by Deal et al. in U.S. Pat. No. Re. 25,566 assigned to the present assignee. The electrolyte described by Deal et al. is an aqueous solution of sulfosalicylic acid and small amounts of sulfuric acid and/or metal sulfates included therewith. Subsequently, it has been found that many compounds, both organic and inorganic, can be utilized with small amounts of sulfuric acid and/or metal sulfates in aqueous solutions to form integrally colored anodic oxide coatings. Examples of these compounds include sulfophthalic acid, sulforesorcinol, lignosulfophonic acid, oxalic acid, maleic acid, succinic acid, and combinations thereof, and dichromates, molybdates, tungstates and vanadates. Many other compounds could be cited.

As used herein, the expression "integral color anodizing" and words of similar import relate to the process of anodizing which forms a colored anodic oxide coating characterized by a resistance which increases at a substantial rate during the formation thereof and a color which is primarily a function of the cell voltage during anodizing.

In the commercial color anodizing processes the desired color is normally obtained by varying the electrical program employed during anodizing, such as current density, voltage and the like. The electrical programs used heretofore have been (1) a two-stage program wherein the initial stage is at a constant current density until a predetermined peak voltage is reached, and a second stage of constant voltage at that peak voltage until the desired color and coating thickness of obtained, and (2) a single-stage program wherein the current density is maintained at a constant level until the desired color and oxide thickness is obtained. The current density in the constant current density stage may range from 10 to 50 amp/ft^2 and the voltage may range from 30 to 75 volts in the constant voltage stage. At times, the bath temperature is raised or lowered from a normal operating temperature of 25°C to 15°C and 35°C for darker and lighter colors, respectively.

During the initial development of the integral color anodizing process it became evident that, although the process would produce a large spectrum of colors on many aluminum alloys, the alloys employed for commercial color anodizing would be quite limited. This was due to the fact that many aluminum alloys form mottled or streaked anodic oxide coatings and, further, that many alloys could not be anodized to give a broad spectrum of colors without rather severely modifying anodizing parameters such as bath composition, bath temperature, current density, voltage, and the like. Changing of the bath composition and large changes in bath temperatures are impractical and expensive procedures. Further, heretofore it has been extremely difficult to develop anodic coatings within a commercially acceptable thickness range for exterior architectural applications, ie. 0.5 to 1.5 mils, with a full range of colors by practical variations in voltage and current density and small variations, e.g. up to 10°C, in bath temperature. The minimum thickness for anodic oxide coatings for use in exterior architectural applications set by the Aluminum Association is 0.7 mils. There is no limitation on the maximum thickness for anodic oxide coatings, but from an economic standpoint, the thinner the oxide coating the lower the cost involved in producing the coating. Most anodic coatings for architectural coatings vary from about 0.5 to 1.5 mils in thickness.

It was early found that different lots of the same alloy, when subjected to the same anodizing program, would not produce oxide coatings which would match, ie. look the same when viewed side-by-side. The color developed would be the same, e.g. gold, amber, statuary bronze or black, but there would be sufficient differences in the shade or hue of the color that the anodized material would have a visually different appearance and thus be commercially unacceptable. This variation in the shade or hue of the color was found to be due to a large extent to the variations in composition and metallurgical structure which occur in the processing of the alloy.

E. C. Beatty et al., in U.S. Pat. No. 3,143,765, solved one aspect of this problem by developing an aluminum alloy for extrusions which would develop a full range of colored anodic oxide coatings within a commercially acceptable thickness range, and which would form colored coatings which would match when color anodized in the same manner.

In the past, it has been necessary to provide at least two separate alloys, sometimes three, to obtain the full range of colors on sheet products. A modified 5005 alloy (Aluminum Association designation) described in U.S. Pat. No. 3,379,580, assigned to the present assignee, has been used to obtain colors from gold to dark brown or statuary bronze. A 5086 alloy (Aluminum Association designation) has been used to obtain a black anodic oxide coating. The popular dark brown, or statuary bronze, colored coating was extremely difficult to obtain with the modified 5005 alloy described in the above-mentioned patent, because of the long anodizing time and the large amount of total current quantity which was necessary to generate this color. For statuary bronze coatings, typical anodizing times include up to an hour or more, and typical total current quantities range up to 14 amp hrs/ft^2, which considerably increase the cost of the anodized product.

Against this background the present invention was developed.

DESCRIPTION OF THE INVENTION

The present invention provides for a sheet product having substantially improved response to integral color anodizing and a process for forming said sheet product. The product is characterized by a metallurgical structure which allows for the formation of an anodic oxide coating having a color ranging from light gold to black within a commercially acceptable thickness range, ie. 0.5 to 1.5 mils by changing anodizing parameters. Moreover, the sheet product will consistently produce uniform coatings which will match when the material is color anodized in the same manner.

Essential to the present invention is an alloy composition consisting essentially of 0.05–0.20 percent silicon, 0.15–0.40 percent iron, 0.15–0.30 percent copper, 0.10–0.30 percent manganese, 0.6–1.0 percent magnesium and 0.04–0.12 percent chromium, and the balance aluminum and inconsequential amounts of other elements. Preferably, the composition ranges from 0.08–0.14 percent silicon, 0.15–0.25 percent iron, 0.16–0.25 percent copper, 0.16–0.25 percent manganese, 0.70–0.90 percent magnesium, 0.04–0.08 percent chromium, and the balance aluminum and inconsequential amounts of other elements. The sum of the copper and manganese contents should not exceed 0.45 percent. The other elements should not exceed 0.05 percent, preferably not more than 0.03 percent maximum each, and the total amount of other elements should not exceed 0.15 percent, preferably not more than 0.10 percent. Unless stated otherwise, all percentages described herein are on a weight basis.

In accordance with the present invention, the above alloy composition is cast into ingot, normally by the direct chill casting technique, homogenized, and then hot rolled. If desired, the resultant product can be cold rolled further. For consistent color reproducibility, the homogenizing step must be conducted at a temperature between 1,000°–1,125°F for a period of time from 4–24 hours. Preferably, the maximum homogenizing temperature variation from batch to batch should be ± 30°F within the range of 1,000°–1,125°F for more uniform color response. A relatively slow heat-up rate of less than 100°F/hr, particularly 75°F/hr, for homogenizing is preferred. After homogenizing, the ingots are allowed to cool to room temperature, preferably at a rate lower than 100°F/hr and then scalped. After scalping, the ingots are then reheated to rolling temperatures, e.g. 750°–850°F and then hot rolled. An alternate procedure after casting comprises scalping, homogenizing, cooling to hot rolling temperatures and then hot rolling. If desired, the sheet product can be cold rolled at a temperature below 250° F.

The above-described fabrication procedure in effect "locks in" the necessary metallurgical structure to provide material which, when anodized in the same manner, will produce products that match. The normal variations which occur in the above-described fabrication procedure do not create significant variances in the color response of the resultant sheet products to the same anodizing program. The sheet material, when anodized in an integral color anodizing electrolyte, will form an anodic coating from light gold to black within a commercially acceptable thickness range by merely changing the anodizing program.

Although many of the alloying elements affect the color of the resultant oxide coating, the chromium content of the present alloy is particularly critical for color reproducibility, ie. color match. Without chromium in the specified amounts, small variations in the manganese content, particularly in the lower portion of the range, create large variations in color when the workpiece is color anodized in the same manner.

The following examples are given to further illustrate the advantages of the present invention.

Example I

An ingot was DC cast having the following alloy composition: iron 0.21 percent, copper 0.18 percent, manganese 0.16 percent, chromium 0.06 percent, silicon 0.13 percent, magnesium 0.73 percent, and the balance aluminum with normal impurities. The ingot was homogenized at 1,000°F for 6 hours with a heat-up and cooling rate of 60°F per hour, scalped and hot rolled at an initial temperature of 825°F and a final temperature of 650°F and then cooled to room temperature. The specimens were cleaned in an inhibited alkaline cleaner, deoxidized in a 50 percent nitric acid solution, etched for 10 minutes in a 5 percent caustic solution at 135°F and desmutted in a 50 percent nitric acid solution. Four samples of this sheet material were anodized in an aqueous electrolyte containing 65 grams/liter sulfosalicylic acid, 5.8 grams/liter of sulfuric acid, and 1.7 grams/liter dissolved aluminum with four different electrical programs. The colors of the resultant anodic oxide coatings were gold, amber, statuary bronze and black, respectively, and the various anodizing parameters employed to produce these colors are set forth below. It should be noted that the statuary bronze and black colors were obtained in 20 and 40 minutes, respectively, with a total current quantity of 10 and 12 amp hrs/ft², respectively.

TABLE I

	Anodizing Parameters					
Color of Coating	Current Density amps/ft²	Peak Voltage Volts	Total Anodizing Time	Total Current Quantity amp-hrs/ft²	Oxide Thickness mils	Bath Temp. °C
Gold	12	40	55	9	0.8	25
Amber	20	51	30	10	0.8	25
Statuary Bronze	30	65	20	10	0.8	25
Black	30	65	40	12	0.9	15

EXAMPLE II

Three separate alloys were prepared, the compositions of which are set forth in Table II, and three ingots were cast from each alloy composition. One ingot from each alloy composition was homogenized at temperatures of 1,000°F, 1,075°F and 1,125°F, respectively. The heat-up rate and cooling rate in each case was 60°F per hour. The ingots were then scalped at room temperature, reheated to a temperature of 825°F and hot rolled to a thickness of 0.14-inch thick. Samples of each of the resultant sheet products were then prepared for anodizing by cleaning in an inhibited alkaline cleaner, deoxidizing in a 50 percent nitric acid solution, etching for 10 minutes in a 5 percent caustic solution at 135°F, and desmutting in a 50 percent nitric acid solution for 1 minute. The samples were then anodized in

an aqueous electrolyte containing 65 grams/liter sulfosalicylic acid, 5.8 grams/liter sulfuric acid, and 1.7 grams/liter of dissolved aluminum. The temperature of the electrolyte was maintained at 25° C ± 1°C. The anodizing program employed was a two-stage program in which the first stage was a constant current density of 30 amps/sq ft until a peak voltage of 65 volts was reached, and the second stage was a constant voltage period at 65 volts until a total current quantity of 10 amp hrs/sq ft had passed. The colors of all of the samples were a statuary bronze and generally matched. The photometric color determinations are given in Table II below. The instrumental evaluation of the color was obtained with a Photovolt Model 610 reflectance meter with a Model T head. The reflectance values were taken with reference to a porcelain enamel standard calibrated against MgO at 100 percent. The yellowness factor is determined from the relationship $Y = 100\ (A - B)/G$ where A is the amber reflectance, B is the blue reflectance and G is the green reflectance.

TABLE II

	Composition						
Alloy No.	Si	Fe	Mg	Cu	Mn	Cr	Al
1	.13	.21	.73	.18	.16	.06	Bal
2	.10	.20	.75	.16	.24	.05	Bal
3	.12	.22	.84	.25	.19	.06	Bal

TABLE III

	Instrumental Evaluation		
Alloy No.	Homo Temp.	Green Reflect	Yellowness Factor
1	1000	4.2	16
1	1075	5.2	21
1	1125	6.1	26
2	1000	4.0	10
2	1075	4.5	16
2	1125	5.8	24
3	1000	3.8	13
3	1075	4.7	20
3	1125	5.7	25

The green reflectance normally indicates the lightness or darkness of the sample, the lower the reflectance value the darker the color. The yellowness factor generally indicates the yellowness of the sample; the higher the factor, the more yellow appearing in the coating. A green reflectance variation of less than 4, preferably less than 3, for lighter colors and less than 2.0, preferably less than 1, for darker colors is generally acceptable for architectural applications. As indicated by the above, the sheet products of the present invention are characterized by forming an integrally colored anodic oxide coating which, when color anodized in a particular manner, has a color having a green reflectance that varies less than 4 units, usually less than 3 units, for lighter colors and less than 2 units, usually less than 1 unit, for darker colors from another sample of said sheet material which has been anodized in the same manner.

It is obvious that various modifications can be made to the present invention without departing from the spirit of the invention or the scope of the appended claims.

What is claimed is:

1. The process of forming aluminum sheet material characterized by a metallurgical structure which allows for the formation of an anodic oxide coating between about 0.5 and 1.5 mils thick having a color from light gold to black when anodized in an integral color anodizing electrolyte by varying anodizing parameters comprising preparing an aluminum alloy consisting essentially of from 0.05–0.20 percent silicon, 0.15–0.40 percent iron, 0.15–0.30 percent copper, 0.10–0.30 percent manganese, 0.6–1.0 percent magnesium, 0.04–0.12 percent chromium, and the balance aluminum and inconsequential amounts of other elements, casting said alloy into an ingot, heating said ingot at a rate of less than 100°F/hr. to homogenizing temperature, homogenizing said ingot at a temperature of from about 1,000°F to 1,125°F for a period of time of about four to 24 hours, and hot rolling said ingot to sheet gauge.

2. The method of claim **1** wherein the aluminum alloy consists essentially of 0.08–0.14 percent silicon, 0.15–0.25 percent iron, 0.16–0.25 percent copper, 0.16–0.25 percent manganese, 0.70–0.90 percent magnesium, 0.04–0.08 percent chromium, and the balance aluminum and inconsequential amounts of other elements.

3. The method of claim **1** wherein the resultant sheet product is cold rolled at a temperature below 250°F.

4. The preparation of aluminum sheet products by the method of claim **1** from a plurality of ingots which have been homogenized in separate loads wherein the homogenization temperature from load to load does not vary by more than ±30° but in no instance is the homogenizing temperature less than 1,000°F. or greater than 1,125°F.

5. An aluminum sheet material formed by

a. preparing an ingot of an aluminum alloy consisting essentially of from 0.05–0.20 percent silicon, 0.15–0.40 percent iron, 0.15–0.30 percent copper, 0.10–0.30 percent manganese, 0.6–1.0 percent magnesium, 0.04–0.12 percent chromium, and the balance aluminum and inconsequential amounts of other elements;

b. heating said ingot at a rate less than 100°F/hr. to homogenizing temperature;

c. homogenizing said ingot at a temperature from 1,000°F. to 1,125°F. for a period from 4–24 hours; and

d. hot rolling said ingot to sheet gauge, said sheet material characterized by metallurgical structure which allows for the formation of anodic oxide coating between 0.5 and 1.5 mils thick having a color from light gold to black when anodized in an integral color anodizing electrolyte.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,793,089 Dated February 19, 1974

Inventor(s) Ralph C. Dorward, Earl C. Beatty, Frank L. Howard and Jacqueline L. Thompson

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

Page 1, Inventors, add the following:

Jacqueline L. Thompson, Spokane, Washington

Signed and sealed this 2nd day of July 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER,JR.
Attesting Officer

C.MARSHALL DANN
Commissioner of Patents

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.