Oct. 20, 1964 H. MARTIN ETAL 3,153,278

METHOD OF FORMING A COMPOSITE ALUMINUM ARTICLE

Filed Aug. 28, 1959 2 Sheets-Sheet 1

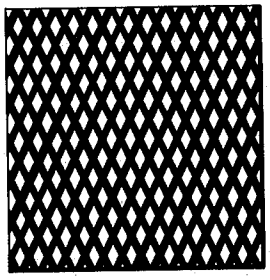


FIG. 1A.

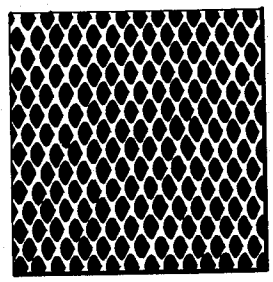


FIG. 1B.

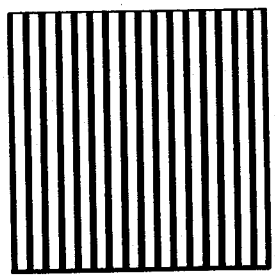


FIG. 2.

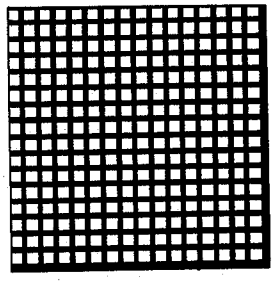


FIG. 3A.

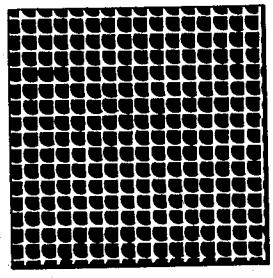


FIG. 3B.

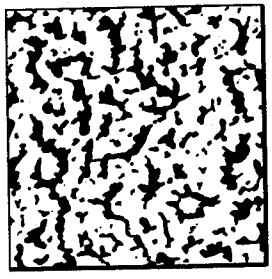


FIG. 4.

INVENTORS.
HUBERT MARTIN
BRUCE E. DEAL
LARRY SWANSON

BY James E. Toomey
ATTORNEY

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METHOD OF FORMING A COMPOSITE ALUMINUM ARTICLE

Filed Aug. 28, 1959 2 Sheets-Sheet 2

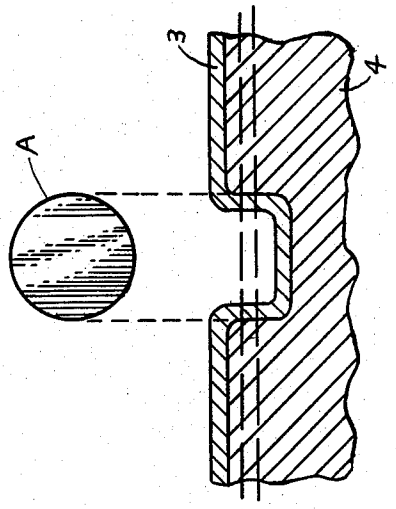


FIG. 5B.

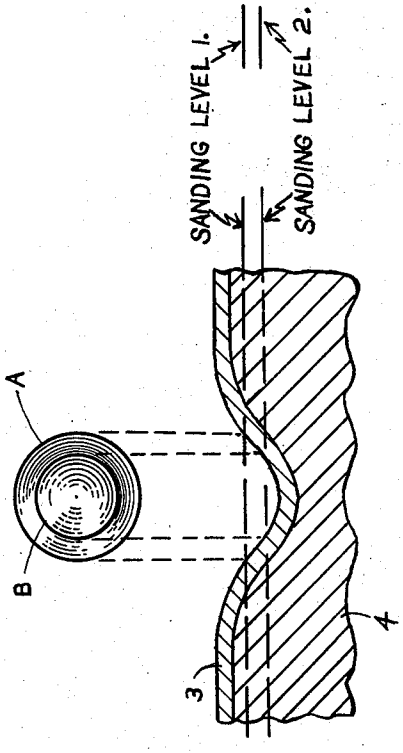


FIG. 5A.

INVENTORS
HUBERT MARTIN, BRUCE E. DEAL,
LARRY SWANSON
BY
James E. Toomey

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METHOD OF FORMING A COMPOSITE ALUMINUM ARTICLE

Hubert Martin and Bruce E. Deal, Spokane, Wash., and Larry Swanson, Coeur d'Alene, Idaho, assignors to Kaiser Aluminum and Chemical Corporation, Oakland, Calif., a corporation of Delaware

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2 Claims. (Cl. 29—424)

This invention relates in general to ornamenting the surfaces of composite metal articles. More particularly, the invention relates to a new and improved method for producing multicolored designs upon the surfaces of aluminum metal articles, said surfaces being of a plurality of aluminum metal layers, and to the articles produced thereby.

The art of coloring aluminum metal surfaces has been substantially developed. Artificial oxide films produced either chemically or electrochemically on aluminum metal may be colored by well-known procedures. The colors which can be obtained by the chemically produced oxide film do not compare in quality to those obtained on electrochemical treatment, more commonly referred to as anodizing. In anodizing, an oxide film which is minutely porous is formed by treating the aluminum metal surface in an oxidizing electrolyte, such as a dilute solution of sulfuric or oxalic acid. These films are hard and offer excellent abrasion and corrosion protection to the underlying metal. The coloring of porous oxide films obtained either by chemical means or by anodizing may involve the absorption of organic dyes into the pores of the films or the treatment of the films with an inorganic salt or pigment. A wide array of colors is possible through the use of the organic dyes; however, these colors have the disadvantage in that they fade rapidly when exposed to sunlight. Colored anodic oxide films wherein the color is substantially sunfast may be produced simultaneously with the anodizing operation by controlling various factors of the process. For example, the time, temperature, current density, electrolyte used, as well as the aluminum alloy treated, have a direct bearing on the color obtained in anodic films.

The term "aluminum" and "aluminum metal" as used herein in the specification and the appended claims include both high purity aluminum and aluminum base alloys.

Although the art of coloring aluminum metal surfaces is substantially developed, there has heretofore not been developed a method suitable for large scale production for producing multicolored designs on aluminum metal surfaces, particularly for large sheets of aluminum. There have been developed specialized finishing processes for producing multicolored patterns on aluminum metal surfaces, such as the silk screen method, which have found application in the making of name plates, small signs, etc., but have not been amenable to large scale production because of cost and the large number of manipulative steps involved.

It has now been discovered according to the instant invention that multicolored ornamental designs can be produced by a process suitable for large scale production on the surface of a composite metal article comprised of multiple layers of different metals, for example copper bonded to aluminum or of different aluminum metals or alloys. The process of the instant invention comprises generally the steps of bonding, as by cladding multiple layers of metal wherein at least one of said layers is aluminum metal, the composition of said aluminum

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metal layer being chosen so as to give a color contrast with at least one of the other metal layers upon the formation of artificial oxide coating thereon, selectively removing portions of the aluminum layer to form a desired pattern, and then forming an artificial oxide coating on the aluminum layer and the exposed portions of said other layer.

The bonding of layers of metals, such as aluminum alloys into a composite article may be done by any suitable means, such as cladding. The cladding of aluminum alloys is accomplished by bonding a metal surface member comprised of at least one layer of aluminum metal to the surface of an aluminum metal core member by hot rolling. Slabs of the cladding alloy or surface member are strapped to a scalped ingot of the core material and the assembly is heated for rolling. The straps are removed after the assembly is placed on the hot mill rolling table, and the hot rolling is then done in a manner similar to that used in rolling the usual aluminum alloy ingots. If desired, a plurality of layers of cladding metal may be used. The thickness of the cladding layer of the finished sheet is usually on the order of about 2 to 15% of the total thickness of the sheet. However, the multiple layer may be of all the same thickness or any combination of thicknesses depending upon the end use of the article or product.

Other methods of bonding layers of aluminum alloy, such as extrusion of various aluminum alloys simultaneously, are also within the scope of the invention.

The forming of the desired pattern on the surface of the composite article, such as clad sheet, may be done by any suitable method of selectively removing portions of clad surface layer or layers to give the pattern configuration. The preferred method of the invention is the embossing of the clad material to give a design in relief, that is, certain portions will be raised and certain portions sunken. Also, the relief design may be done by coining or stamping. The embossed material is then subjected to a treatment, such as sanding, wherein the clad layer or layers on the high portions are removed thereby exposing one or more bottom layers. The embossing of the material may be accomplished by any suitable apparatus, such as embossing rolls, knuckle joint presses, etc. The usual embossing apparatus, such as rolls and presses, involve male and female dies for producing the relief design on the material, however, apparatus having the pattern on only one die with the surface of the other die smooth may be employed. Embossing apparatus is well known in the art and will not be discussed in detail herein.

The removal of the clad layer or layers of the raised portions may be removed by suitable means, as above mentioned, such as by sanding. Belt type sanding machines are available on the market which can readily accommodate sheet or coil material which is of a large width, for example, on the order of up to 72 inches wide.

Also, the selective removal of the surface layer or layers by grinding, engraving, etching or chemical milling is also within the scope of the instant invention.

After the pattern has been established on the composite article, that is, the desired portions of the surface layer or layers have been removed, the article is subjected to a suitable anodizing treatment wherein, during the electrolytic forming of the oxide film, various colors are imparted to the film depending upon the alloy composition of the various exposed layers of metal. As stated previously, the colors obtainable are influenced by the anodizing electrolyte, current densities and times used in the

anodizing treatment, as well as the composition of the aluminum alloy. Examples of colors obtainable are: various shades of gold and bronze, many shades of brown and grey, black, dark blue, light blue and silver.

Any suitable anodizing process may be used in the practice of the instant invention, for example, the sulfuric anodizing process, oxalic acid anodizing process, phosphoric acid anodizing process and others which are well known and profusely disclosed in the prior art. Also, anodizing in a sulfosalicylic acid electrolyte as disclosed in pending application Serial No. 799,089, Bruce E. Deal et al., filed March 13, 1959, now abandoned, can be employed. Although the various different anodizing electrolytes have effect on the color and on the characteristics, such as thickness and hardness, of the oxide film, the procedures of anodizing are basically similar. In all of the processes the aluminum workpiece is made the anode (instead of the cathode as in electroplating) in an electrolyte capable of yielding oxygen on electrolysis. Upon passage of current, a porous absorptive aluminum oxide is formed. It is usual practice to convert the aluminum oxide in the coating into the monohydrate form which is non-absorptive. This is commonly termed "sealing" and may be done by immersing the anodized material in boiling water.

It is general procedure in the anodizing process to first clean the metal, for example, in a hot mild alkaline solution after which it is rinsed. This cleaning procedure may be used in the instant invention. A short caustic etch may be used to remove particles embedded in the metal surface during the sanding operation. Also, if desired, a chemical brightening treatment in a suitable bright dip solution for aluminum of which there are several commercially available may be used to improve the lustre and color contrast of the finished metal article.

In obtaining a multicolored surface as taught by the instant invention the anodizing electrolyte and operating conditions are controlled so that the reaction between the electrolyte and one or more constituents of the aluminum alloys gives the desired color. For example, aluminum Alloy 4343 (having a composition in percent by weight of Si—6.8% to 8.2%, Fe—0.8% max., Cu—0.25% max., Mn—0.10% max., Zn—0.20% max., others 0.05% max. each or 0.05% max. total, Al—balance) upon anodizing in a 15% H_2SO_4 solution at 70° F., at 12 amps. per square foot for 75 minutes will have a black color. Alloy 3003 (having a composition in percent by weight of Si—0.6% max., Fe—0.7% max., Cu—0.20% max., Mn—1.0–1.5%, Zn—0.20% max., others—0.5% max. each or 0.15% max. total, Al—balance), under like conditions will give a silver to gray color while on an alloy having a composition in percent by weight of Si—0.06%, Fe—0.06%, Cr—0.35%, others total—0.05% or less, balance Al, a gold color is obtained. An alloy having a composition in percent by weight Si—0.02%, Fe—0.02%, Cu—0.02%, Mg—0.50 to 0.70%, others total—.005%, balance Al, under these conditions will give a silver color. With just these few mentioned alloys and the particular anodizing electrolyte and procedure, it is possible to make many exciting color contrasts on aluminum metal surfaces as shown in FIGS. 1–4, inclusive. By employing other alloys than those mentioned and other anodizing electrolytes and procedures a myriad of color contrasts is available.

The fabricating of the multicolored aluminum metal articles according to the invention, as well as the numerous patterns or designs in contrasting colors possible, will be more apparent from the ensuing specific discussion with reference being had to the accompanying drawings wherein:

FIGURE 1, comprised of FIGURES 1A and 1B, gives views of the top side and reverse side, respectively, of aluminum clad sheet which has a diamond pattern in contrasting colors.

FIGURE 2 shows a multicolored ribbed pattern that can be obtained on aluminum clad sheet.

FIGURE 3, comprised of FIGURES 3A and 3B, gives views of the top side and reverse sides, respectively, of aluminum clad sheet which has a square pattern in contrasting colors.

FIGURE 4 shows aluminum clad sheet which has a random pattern simulating a stucco finish in contrasting colors.

FIGURE 5, comprised of FIGURES 5A and 5B, depicts diagrammatically a poor relief design and a good relief design, respectively, for embossing equipments, such as rolls, used in the practices of the invention.

The multicolored design patterns of the clad aluminum metal sheets depicted in FIGURES 1 to 4, inclusive, were prepared as follows: Clad liner sections were prepared and strapped on to aluminum metal ingots and the composite ingot-liner sections were hot and cold sandwich rolled to a gauge of 0.040 inch. After rolling, the long strips of metal were subdivided into small coils, and subsequently embossed.

The coils were then cut into 36" x 96" sheets, sanded and finally anodized.

The liner sections for the cladding were prepared according to standard procedures well known in the aluminum industry. The alloy compositions and the dimensions of the liner sections are given in Table 1 below.

Table 1

Alloy	No. of Liner Sections	Finish Dimensions
A [1]	3	33" x 102" x 1.050"
4343	2	34" x 102" x 1.050"
B [2]	1	33" x 102" x 1.050"

[1] Composition of Alloy A in percent by weight: Si—0.06%, Fe—0.06%, Cr—0.35%, others—total—0.05% or less, balance Al.
[2] Composition of Alloy B in percent by weight: Si—0.02%, Fe—0.02%, Cu—0.02%, Mg—0.50 to 0.70%, others total—.005%, balance Al.

The liner sections were placed onto aluminum metal ingots having cross-sectional dimensions of 13" x 38" and a length of approximately 110 inches. The composition of the aluminum metal core ingots and the liners clad thereon are given in Table 2.

Table 2

Ingot No.	Ingot Alloy	Alloy—Liner I	Alloy—Liner II
1	3003	A [1]	MR–14
2	4343	B [2]	T–509
3	3003	4343	4343

[1] Composition of Alloy A in percent by weight: Si—0.06%, Fe—0.06%, Cr—0.35%, others—total—0.05% or less, balance Al.
[2] Composition of Alloy B in percent by weight: Si—0.02%, Fe—0.02%, Cu—0.02%, Mg—0.50 to 0.70%, others total—.005%, balance Al.

The clad assemblies were sandwich hot and cold rolled to 0.040 gauge sheet (H–14 Temper.), said rolling being according to standard practices in the art of aluminum rolling. The three 0.040 inch gauge coils which were obtained upon rolling the clad assemblies were embossed on embossing rolls, subdivided into sheets, and the sheets were then individually sanded.

The individual sheets were embossed with various designs and sanded according to Table 3.

Table 3 identifies the compositions of the cores and the compositions of the clad liners, as well as the sheet thicknesses before and after sanding. The embossed sheets were sanded on a belt type sanding machine (Sander Serial No. 332, Hill Acme, 1205 W. 65th Street, Cleveland, Ohio) which could accommodate material up to 48 inches wide. The number of passes made and the grit index of the belts used are also indicated in Table 3.

Table 3

Master Ingot Number	Core Alloys	Liner Alloys	Emboss Pattern	Sides Sanded	Average Sheet Gauge, inches		Average Number Of Sanding Passes Per Side		
					Before Sanding	After Sanding	80 Grit	150 Grit	240 Grit
1	3003	A[1], A[1]	Stucco	1	.050	.042	17	2	2
	3000	A[1], A[1]	Diamond	2	.049	.036	17	2	2
	3003	A[1], A[1]	Square	2	.048	.0315	15	2	2
	3003	A[1], A[1]	Ribbed	2	.0495	.039	18	2	2
2	4343	A[1], B[2]	Stucco	1	.047	.040	20	2	2
	4343	A[1], B[2]	Diamond	2	.050	.036	19	2	2
	4343	A[1], B[2]	Diamond	2	.049	.033	22	2	2
	4343	A[1], B[2]	Square	2	.049	.033	22	2	2
	4343	A[1], B[2]	Square	2	.050	.032	16	2	2
	4343	A[1], B[2]	Ribbed	2	.050	.040	18	2	2
	4343	A[1], B[2]	Ribbed	2	.050	.040	18	2	2
3	3003	4343, 4343	Stucco	1	.048	.041	20	2	2
	3003	4343, 4343	Diamond	2	.049	.034	22	2	2
	3003	4343, 4343	Square	2	.049	.032	22	2	2
	3003	4343, 4343	Ribbed	2	.048	.036	14	2	2

[1] Composition of Alloy A in percent by weight: Si—0.06%, Fe—0.06%, Cr—0.35%, others—total 0.05% or less, balance Al.
[2] Composition of Alloy B in percent by weight: Si—0.02%, Fe—0.02%, Cu—0.02%, Mg—0.50 to 0.70%, others total—.005%, balance Al.

In anodizing the sheets, after embossing and sanding, the following procedure was used:

(1) Etched for 30 seconds in 3.5% aqueous NaOH solution at 160° F.
(2) Rinsed in cold water.
(3) Immersed in a chemical brightening solution having a composition of 54 ml./l. of 70% HNO_3, 6 g./l. of NH_4HF_2, 0.05 g./l. of $CuCO_3 \cdot Cu(OH)_3$, balance H_2O, (this brightening solution and method of using same is covered in one or more of the following patents: U.S. 2,593,447, Frederick H. Hesch, issued April 22, 1952; U.S. 2,593,448, Frederick H. Hesch, issued April 22, 1952; U.S. 2,593,449, Frederick H. Hesch, issued April 22, 1952; U.S. 2,614,913, Harold J. Reindl et al., issued Oct. 21, 1952; U.S. 2,620,265, Frederick H. Hesch, issued Dec. 2, 1952; U.S. 2,625,468, Stanley R. Prance et al., issued Jan. 13, 1953; U.S. 2,719,781, James F. Murphy, issued Sept. 27, 1955). The solution was maintained at 200° F., plus or minus 5° F., and the panels were immersed for four minutes.
(4) Rinsed in cold water.
(5) Anodized in 15% aqueous H_2SO_4 solution at 70° F. for 75 minutes with a current density of 12 amps./sq. ft.
(6) Rinsed in cold water.
(7) Sealed by treating in boiling water for fifteen minutes.

With reference to FIGURES 1 to 4, inclusive, the contrasting colors which are possible in the various designs are very attractive and decorative. With particular reference to the diamond pattern shown in FIGURE 1, the clad material using a core of 3003 alloy and a cladding of 4343 gives contrasting colors of gray and black, the inner part of the diamond designs being black and the outlining portions being gray on the top side of the sheet (FIGURE 1A). On the reverse side of the sheet (FIGURE 1B) the inner part of the diamond designs are gray and the outlining portions are black. In the case of Alloy A clad on to a core of Alloy 4343, the inner part of the diamond designs are gold while the outlining portions are black (FIGURE 1A showing the top side of the sheet). On the reverse side of the sheet (FIGURE 1B) the inner part of the diamond designs are black and the outlining portions are gold. In the case of Alloy B clad onto a core of Alloy 4343, the inner part of the designs (FIGURE 1A) are silver while the outlining portions are black; on the reverse side of the sheet (FIG. 1B) the inner part of the diamond designs are black while the outlining portions are silver. In the case of Alloy B clad onto a core Alloy 3003, the inner parts of the diamond designs (FIGURE 1A) are gold while the outlining portions are gray, on the reverse side of the sheet (FIGURE 1B) the inner part of the diamond designs are gray while the outlining portions are gold.

In regard to the pattern designs shown in FIGURES 2, 3 and 4, the same exciting color contrasts were obtained as discussed in relation to FIGURE 1.

FIGURES 1 to 4, inclusive, depict only a few of the multicolor designs which are possible through the practice of this invention. There are literally hundreds of designs which are possible in the embossing of clad aluminum sheet. Also, by using multiple cladding layers, it is possible to obtain a pattern with three or more contrasting colors. The sheet samples such as depicted in FIGURES 1 to 4, inclusive, could be used for automotive trim, automotive dash panels, panels and trim for appliances, architectural paneling, grills, lighting fixtures, furniture, housings for vacuum cleaners, typewriters and the like, clock faces, dial backgrounds and instrument panels and many others.

FIGURES 5A and 5B, which demonstrate the importance of having the proper relief design in the embossing equipment in practice of the instant invention, show drawings in section of clad sheet wherein **3** designates the core member and **4** designates the clad liner. In FIGURES 5A and 5B, respectively, there are shown the poor and good relief designs of embossing rolls for embossing a polka dot pattern. For proper relief design, which is important in the practice of the instant invention, the relief slopes should be as close as possible to a 90° angle to the relief bottom and peak planes, as shown in FIGURE 5B. Small diameter curves should lead from planes to slopes. The good embossed design, as shown in FIGURE 5B, allows for considerable tolerance in the sanding depths without changing the dot size. In comparing FIGURES 5A with 5B you will note that in proceeding from Sanding Level **1** to Sanding Level **2** the size of the dot in FIGURE 5A becomes considerably reduced as shown by the areas A and B in the projected drawing, in size while in the good relief design of FIGURE 5B the dot size remains the same between Sanding Level **1** and Sanding Level **2**; that is, the area A in the projected drawing is the same for Sanding Level **1** and Sanding Level **2**. Also of importance in embossing is that the emboss depth of the particular design should be uniform, otherwise, it would be impossible to produce consistently the same pattern or the pattern itself will not be clearcut in the multicolor appearance.

If desired, the color contrast obtained on anodizing (prior to sealing) can be modified by absorption of an organic dye into the anodic film.

It will also be understood that various other changes, modifications and alterations may be made in the instant invention without departing from the spirit and scope

thereof, and as such, the invention is not to be limited except by the appended claims, wherein—

What is claimed is:

1. A method of producing multicolored composite aluminum articles comprising the steps of providing bonded multiple layers of aluminum, the composition of a first one of said layers being different from that of at least one other layer and being chosen so as to give a color contrast with said other layer upon formation of an artificially produced oxide coating thereon, selectively removing portions of said first mentioned layer to expose portions of said other layer and to produce a relief design with relief slopes of about 90°, and then forming an artificial oxide coating of contrasting colors on said first aluminum layer and the exposed portions of said other layer.

2. A method of producing multicolored composite aluminum articles comprising the steps of providing composite layers of aluminum, the composition of a first one of said layers being different from that of at least one other layer and being chosen so as to give a color contrast with said other layer upon formation of an artificial oxide coating thereon, embossing a relief design on said composite aluminum layers to a substantially uniform depth and with relief slopes of about 90°, selectively removing portions of said first mentioned layer to expose portions of said other layer and then anodizing the composite layers to form an artificial oxide coating of contrasting colors on said first aluminum layer and the exposed portions of said other layer.

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