

1

2,769,265

METAL FOIL APPLIQUES AND METHOD OF MAKING SAME

Robert Nelson Page, Seattle, Wash., assignor to Boeing Airplane Company, a corporation of Delaware

No Drawing. Application June 18, 1947
Serial No. 755,493

9 Claims. (Cl. 41—26)

My invention relates to metal appliques, which may be applied easily to materials of many types, and may be of any desired design.

Decalcomanias for many years have been used to apply decorations and labels to surfaces of a wide variety of materials, but these are not very durable, particularly when exposed directly to all types of weather conditions and abrasion. It is a principal object of my invention to provide an applique of metal, which may be manufactured in a variety of shapes, designs, sizes, and colors, yet which will not be eroded by inclement weather nor defaced appreciably by accidental abrasion.

Particularly it is an object to make such an applique of a metal which does not corrode easily, for example, aluminum, which can nevertheless be extremely thin, and may be designated a foil, yet may be processed to present indicia, such as a design or legend, in a color or colors. As well as being corrosion-resistant it is desired that such a metal applique be very light.

An additional feature of my invention is the process which I have devised to produce the indicia on a metal foil applique, so that it will be permanent, and which process preferably will render the surface of the applique nonreflecting, rather than shiny.

In describing my invention reference is made to the material used for manufacturing the applique as a foil, but it will be understood that the thickness of the applique may vary within reasonable limits. Preferably metallic sheet material approximately .003 of an inch thick is suitable for my purpose, although sheet material somewhat thinner or somewhat thicker than that may be employed, all of which material is intended to be included generally within the term "foil." Also while substantially pure aluminum is the preferred metal of such foil, various aluminum alloys, and perhaps other metals, may be used for my purpose.

The primary consideration in the process of manufacturing my metal appliques is to apply to it permanent coloring, either in the form of a design or legend, or as the background of the design or legend, in the latter case the design or legend having a metallic finish, or being of a different color. Such a design or legend I have designated generally as indicia. To apply the color merely by painting on the smooth foil surface is unsatisfactory, because the paint will soon wear off. It is not feasible to make a foil which in the process of manufacture is given a rough surface, and even if this could be done, the permanency of the color applied to it would be questionable.

I have discovered that it is possible to anodize foil, such as that of aluminum base, even as thin as .001 of an inch thick, for the purpose of rendering its surface porous, so that a dye or paint applied to it will penetrate into the surface pores to produce a colored surface finish having a permanency not otherwise attainable. In order to be effective for this purpose the anodizing operation must oxidize the surface to a substantial depth, considering the thickness of the foil, yet the anodized foil must be suf-

2

ficiently strong to withstand reasonable stress which might otherwise tear it, such as might be applied to it in handling the material during steps of the process subsequent to the anodizing step, while being handled after the manufacture is completed, or while being applied to a surface to be labeled or decorated.

A primary consideration of my process, therefore, is that the foil used be as thin as practicable, while at the same time affording adequate thickness to allow the anodizing operation to produce an oxide coating to a depth sufficient to render the coloring reasonably permanent, without disintegrating the entire foil during the anodizing process or reducing its strength to the point where it will tear too easily. On the contrary, for use as an applique, the foil should not be thick enough so that a small piece will be stiff. Such a piece would be pulled off the backing surface if a corner should come loose and be caught inadvertently.

When a foil .003 of an inch thickness is employed, the anodizing operation is continued until preferably a substantial portion of the foil thickness has been converted to oxide, such as approximately .0005 of an inch on each side of the foil, leaving a layer of unanodized material only .002 of an inch thick in the center of the foil sheet between the anodized surface layers. If the layer of anodized oxide is substantially less than .0005 of an inch in thickness, an insufficient depth of porosity will be available to insure a reasonably permanent color penetration. On the other hand, if substantially less than .001 of an inch unoxidized material at the center of the sheet remains, the applique will be too fragile to be serviceable.

It will be evident, therefore, that the foil must not be less than approximately .002 of an inch in thickness to be strong enough, after being anodized, to be handled without damage, and preferably it is not substantially more than .003 of an inch in thickness, because it is desired to keep the weight as low as possible, to have minimum projection of the applique beyond the surface to which it is applied, and particularly for a small piece to be sufficiently flexible so that an applique cannot be peeled off by one corner, but rather the corner itself would be torn from the rest of the applique.

In order to color part or all of the applique surface durably, the first step of major importance is to anodize the foil. Since it is preferred to anodize the foil to produce the desired porosity without discoloring the surface of the sheet, the sulfuric acid anodizing process should be used instead of the chromic acid process, although the latter may be employed if desired. To condition the foil for the anodizing operation it should first be cleaned with a hot alkaline solution for a few minutes, to remove all grease and surface film, and then rinsed in cold water. The anodizing step is then carried out in a 20% sulfuric acid bath (13 parts of sulfuric acid to 100 parts of water by volume). Preferably the temperature of the anodizing bath is somewhat higher than usually used in anodizing thick sheet or relatively heavy material, and the time of the anodic treatment is shorter. Thus I have found that the temperature may be 93° to 97° F. and a current of 15 to 18 amperes per square foot of foil area may be passed through the bath for a period of twenty minutes, to give a satisfactory anodic film. In calculating the surface area the entire metallic surface of the anode should be figured, including that of the rack or other metallic support carrying the foil. Upon completion of the anodizing operation the foil again is rinsed thoroughly with cold water.

If the foil is anodized in the manner described, its surface will not be discolored, and will be shiny. If a non-reflecting surface or mat finish on the applique is desired, the foil may be subjected to an etching operation before the anodizing step.

The etching action may be effected by dipping the foil

in an etching bath, such as a 10% solution of ammonium bifluoride. The foil should be allowed to remain in the etching bath, warmed to approximately 75° F., for a period of about five minutes, after which it is removed, rinsed thoroughly with cold water, and then neutralized. The neutralizing bath should be weakly acidic, such as a 5% solution of sulfuric acid. The foil should be kept in the neutralizing bath until effervescence ceases, whereupon it will be removed from the bath, and again rinsed thoroughly with cold water before being anodized in the manner described above.

After completion of the anodizing operation to produce a color penetrable porous surface, the coloring technique may vary, depending upon whether the indicia on the one hand, or the background on the other hand, is to be colored, and further depending upon which constitutes the major portion of the area. If the larger area is to be colored, it will be more expedient to dye the entire surface, and then to remove the dye from the area which is to have a natural finish. On the other hand, if the larger area is to be finished naturally, it may be easier to dye initially only the area which is to be colored.

Following the former procedure mentioned, the metal foil is dipped in a hot dye bath, preferably at a temperature of 140 to 160 degrees F., where it is left for about ten minutes. Depending upon the color desired, this dye may be red, black, yellow, etc. The pH of the solution should be maintained carefully, depending upon the type of dye employed, such dyes for aluminum being available commercially and not being a part of this invention.

In the time mentioned the dye will have penetrated thoroughly into the anodized porous surface of the foil, so that it may be rinsed thoroughly in cold water without removing the dye. In order to improve the permanency of the coloring effect, the porous surface of the foil impregnated with dye is next sealed by dipping the foil in a bath of aqueous sealing solution. Various types of sealing solution may be used, one satisfactory one containing ½% of nickel acetate at a pH of 5.5 to 5.8. The sealing solution should be approximately at boiling temperature, 208° to 212° F., and the foil should be subjected to this sealing treatment for a period of three to five minutes. Even water alone of such temperature will effect a satisfactory sealing action.

Inevitably the foil will carry over into the sealing solution a small residue of dye despite the rinsing of the foil with cold water between the dyeing and sealing steps. Consequently the sealing liquid in the dip tank normally would soon become tinged with the dye. As long as the appliques are dyed only one color, such tingeing of the sealing solution is not particularly important, but if the same equipment is used alternately or successively for sealing foils dyed different colors, such as black foil and red foil, for example, as is frequently the case, the tinted sealing bath would adulterate the dye principally applied to the foil. Consequently in such cases it is very important that the sealing solution be clarified by adding to it small amounts of activated charcoal or circulating the sealing solution periodically or continuously through an activated charcoal filter. Following the sealing step the foil should be rinsed thoroughly in hot water and wiped clean with a soft cloth to remove any smut.

The next step of the process is to produce the indicia on the foil. Where the entire surface of the applique has first been colored, a protective coating is applied to that portion which is to be colored in the finished product, while the remainder is uncoated. The portion of the applique not covered by the protective coating will now be etched to remove the layer of anodic oxide film impregnated with color and to expose the unanodized central layer of the sheet.

A similar protective coating procedure may be used in the alternative process where only a desired area is colored in the first instance. In such case the portion

on which the natural finish is desired is coated with the protective coating and the foil is then subjected to a dyeing process like that described above. The part not covered by protective coating will be colored and the natural finish will be preserved on the part protected from anodization.

Whether etching part or coloring part of the applique, it will ordinarily be easier to apply the protective coating to the smaller area, in the first case leaving the larger unprotected area to be etched for removing the color, and in the second case coloring the larger area by dyeing process, although such selection of procedures is not mandatory.

The masking of the parts to be protected may be accomplished by the silk screen process, and the protective coating may be a water insoluble ink which does not dry, such as offset printing ink, although preferably it is lacquer which will be dried. The portion of the foil surface which is to undergo subsequent treatment, and therefore is not to be protected with the ink or lacquer, is covered by a stencil, so that the protective coating is applied only to selected parts. The protective coating may then be sprayed or brushed on, according to a well-understood technique in selective coloring processes.

If the masking procedure described is applied to foil already colored over its entire surface, the foil will next be placed in an etching solution, which may be a 10% solution of hydrofluoric acid, until the color has been removed from the unprotected area. This bath may be at room temperature, and it should not be necessary to leave the foil in it for more than one minute to remove the dye completely from the unprotected parts. Upon being withdrawn from this bleaching bath the protective ink or lacquer is removed by swabbing the foil with a suitable known lacquer or ink solvent, depending on the type of protective coating used. The coloring of the applique thus will have been completed, so that it is merely necessary to trim the foil to the final shape, or to blank out the individual appliques.

Following the alternative procedure, where the protective coating has been applied to the portions of a piece of uncolored foil which are to retain their natural color, the foil is dyed in the same manner as described previously, by dipping it in a dye bath of appropriate color. Because of the protective coating the dye will not impregnate those parts of the anodized surface thus coated. The foil is then removed from the dye bath and rinsed with cold water. If the anodic oxide film were sealed before removal of the masking ink or lacquer, the masked surfaces would not be sealed. Consequently it is preferred that the masking ink be removed by swabbing the foil with hydrocarbon cleaner or dipping it in a tank of such protective coating remover before sealing. The foil may then be sealed in a suitable aqueous solution, as described. Following the sealing operation the foil is rinsed in hot water, and is then wiped clean. As in the alternative process, the foil is now ready for trimming to final shape, or for cutting out the individual appliques.

As mentioned previously, where the sealing solution is reused for sealing appliques colored different colors, small pieces of activated charcoal are placed in the sealing solution or it is passed continuously or intermittently through a charcoal filter to clarify the solution. In the alternative process just described where the anodized surface is partly colored and partly uncolored when sealed, the sealing solution should be clarified with charcoal in every case because the foil remains in the solution for an appreciable length of time. If the sealing bath should become tinged with dye from the colored part it may tint somewhat those parts of the applique which are intended to remain natural in color.

Moreover, in both of the processes described, the solvent utilized to remove the masking ink or lacquer should be clarified by including in the solvent activated char-

5

coal, or passing it through a charcoal filter. If the solvent is not thus clarified of ink by charcoal, the ink or lacquer will not be removed completely from the cavities of the porous anodic film, and it will be spread over the unmasked portion of the surface, so that a clean surface will not be obtained.

By whichever process the appliques are colored, they are now ready to be affixed to the receiving surface. Different techniques may be employed, depending on the nature of the receiving surface. If it is of metal, the applique may be soldered or brazed in place. Preferably it is affixed by adhesive, whether the receiving surface is metal, glass, wood or other material. A representative procedure, which is not part of my invention, includes first cleaning thoroughly both the back of the applique and the receiving surface with aliphatic naphtha, and then applying to both surfaces a coat of adhesive, commercially available for bonding metal to metal or other materials. Although other types of adhesive may be employed, one satisfactory for this purpose is synthetic or reclaimed rubber dissolved in some suitable solvent. The surfaces are allowed to dry until they are not tacky, and when thus conditioned it is not necessary to affix the applique for several days, and possibly weeks.

When it is desired to attach the applique, one or both of the contacting surfaces should be moistened with a hydrocarbon solvent, such as toluol, and then allowed to dry until the surface is somewhat tacky. The applique is then applied to the receiving surface, one edge being put in place first, and then the body of the applique rolled down toward its opposite edge to effect an intimate contact of the entire surface of the applique with the receiving surface. Excess adhesive may be removed with high flash-point naphtha swabbed over and around the applique within a couple of hours after it has been secured to the receiving surface.

When thus applied, the applique will not project appreciably from the receiving surface, because of its very slight thickness, and it will be held firmly in place so that any object rubbing against it will not pull it off, nor, because of the manner in which it is colored, as described above, will the color be destroyed. It will be evident that such an applique is eminently satisfactory for use on the exterior of airplanes, because it is very light, does not project outward from the receiving surface sufficiently to create any appreciable air turbulence or drag, and can neither be ripped off by the considerable force exerted by air flowing over it nor deteriorated by the rain, hail, snow, wind, and sun to which it would be subjected.

I claim as my invention:

1. A labelled article bearing a metal applique comprising a piece of aluminum base foil having an aluminum oxide layer on a side thereof and of a thickness, including said aluminum oxide layer, of about .003 inch, bonded to said article sufficiently strongly with respect to the fragility of said foil to prevent said applique being peeled off the article without tearing of the applique, dye impregnating said oxide layer over a portion of the area of such side, and the remainder of such side being of color contrasting with said dye.

2. A metal applique comprising a piece of aluminum base foil having an aluminum oxide anodized layer on a side thereof and of a thickness, including said aluminum oxide layer, of about .003 inch, dye impregnating said oxide layer over a portion of the area of such side, and the remainder of such side being of color contrasting with said dye, defining thereon substantially indestructible indicia.

3. The metal applique defined in claim 2, in which the remainder of such side has an undyed mat finish.

6

4. The method of making a metal applique which comprises the step of anodizing a piece of aluminum base foil of about .003 inch in thickness in a sulfuric acid anodizing solution at a temperature of 93 degrees F. to 97 degrees F. for a period of approximately twenty minutes at a current density of 15 to 18 amperes per square foot of anode.

5. The method of making a metal applique which comprises anodizing a piece of aluminum base foil of about .003 inch in thickness in a sulfuric acid anodizing solution at a temperature of 93 degrees F. to 97 degrees F. for a period of approximately twenty minutes at a current density of 15 to 18 amperes per square foot of anode, and dyeing the anodized foil in selected areas of its surface.

6. The method of making a metal applique which comprises anodizing a piece of aluminum base foil of about .003 inch in thickness in a sulfuric acid anodizing solution at a temperature of 93 degrees F. to 97 degrees F. for a period of approximately twenty minutes at a current density of 15 to 18 amperes per square foot of anode, dyeing the anodized foil in selected areas of its surface, and sealing the dyed anodized foil.

7. The method of making a metal applique which comprises subjecting a piece of aluminum base foil of about .003 inch in thickness to the action of ammonium bifluoride solution and thereby producing a mat finish on such foil, and thereafter anodizing such foil in a sulfuric acid anodizing solution at a temperature of 93 degrees F. to 97 degrees F. for a period of approximately twenty minutes at a current density of 15 to 18 amperes per square foot of anode, and dyeing the anodized foil in selected areas of its surface.

8. The method of making a metal applique which comprises the step of subjecting a piece of aluminum base material to the action of ammonium bifluoride solution and thereby producing a mat finish on such piece.

9. The method of making a metal applique which comprises the step of anodizing a piece of aluminum base foil of about .003 inch in thickness in a sulfuric acid anodizing solution at a temperature of 93 degrees F. to 97 degrees F. for a period of approximately twenty minutes at a current density of 15 to 18 amperes per square foot of anode, dyeing the anodized foil in selected areas of its surface, and sealing the dyed anodized foil in nickel acetate solution.

References Cited in the file of this patent

UNITED STATES PATENTS

1,988,012	Mason	Jan. 15, 1935
2,018,388	Tosterud	Oct. 22, 1935
2,150,395	Nagata	Mar. 14, 1939
2,150,409	Yashoshima	Mar. 14, 1939
2,153,060	Guthrie	Apr. 4, 1939
2,237,483	Graenacher	Apr. 8, 1941
2,305,657	Aehnelt	Dec. 22, 1942
2,365,153	Stevens	Dec. 19, 1944
2,424,621	McClatchey	July 29, 1947
2,507,314	Mason	May 9, 1950

FOREIGN PATENTS

503,451	Great Britain	Apr. 6, 1939
865,902	France	Mar. 17, 1941
876,462	France	Aug. 3, 1942

OTHER REFERENCES

Metal Industry, June 18, 1943, pages 386-388 (an article by Henley).