MULTI-COLORED ALUMINUM ANODIZING PROCESS

Filed March 17, 1966

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Filed Mar. 17, 1966, Ser. No. 535,182
Int. Cl. C23b 9/00; B44c 1/04
U.S. Cl. 204—19
19 Claims

ABSTRACT OF THE DISCLOSURE
Method of producing a decorative effect on an anodizable metal surface, especially by integral color hardcoat anodizing at a high voltage utilizing resist material for preventing dielectric breakdown during such anodizing; the resist material being applied to protect selected areas while unprotected areas are being anodized.

This invention relates to a novel method for the production of multidimensional and/or multicolored designs upon anodized metal surfaces. More particularly, the invention concerns a novel method for producing three-dimensional colored and decorative effects on anodized aluminum or aluminum base alloy sheet or panels suitable for long exterior exposures and high temperature applications.

The production of designs on aluminum metal surfaces by etching methods has long been established. Customarily, etchants, such as solutions of ferric chloride, or caustic soda are used to produce designs in dyed anodized aluminum to contrast with bare etched metal, or in natural anodized aluminum to contrast with dyed re-anodized aluminum or in dyed or natural anodized aluminum in contrast to a lacquer or paint fill-in of etched aluminum areas. In these methods, conventional sulfuric acid anodizing is employed, with voltages ranging from 10 to 24 volts D.C., and current densities below about 18 amperes per square foot, generally about 12 amperes per square foot. The result is the production of relatively thin anodic films, having a thickness of the order of 0.2 mil or less, except for dyed blacks, which are usually 0.4 mil. The anodic film produced under these conditions has limited capability as a resist layer and is most often further protected by an asphaltum type resist material, as is done in the anodized name plate industry. There has not been available prior to the present invention, a feasible method which would eliminate the use of externally applied dyes to produce colors and shades, and which would provide colors or patterns stable to heat and to exterior exposure.

In accordance with the present invention, there is provided a novel method for the production of colored, multicolored, and, if desired, three-dimensional effects and designs on the surfaces of anodized metals, particularly aluminum metal.

The method of the invention differs fundamentally from prior art practices in that it dispenses with the use of auxiliary dyes, and produces desired shades by means of hard integrally colored anodic coatings on the surfaces of aluminum and aluminum base alloys. The integral colors thus produced arise from the character of the metal or of the anodizing treatment and will consequently withstand severe exposure to heat and weathering to a degree unattainable with applied dyes.

The term hard coat anodizing as employed herein is well understood by those skilled in the anodizing art and signifies an anodic coating having superior resistance to abrasion, generally applied by anodizing at low temperatures, in the range of 20° to 35° F., resulting in production of dark gray to black shades. Hard coat anodizing may however also be performed at ordinary temperature by including in the anodizing bath an organic acid, such as sulfosalicylic, sulfophthalic, or oxalic acid, and a metal salt or an organic acid, the aluminum alloy being one which will produce a desired color in the anodic film. Baths of this type are operated at room temperature, and at comparatively high voltage and current density.

Illustrative alloys of aluminum which are known to be applicable for use in connection with the present invention in the form of sheet are Nos. 1100, 3003, 3004, 5052, 5066, 5257, 5457, 6061, and 6061. It is possible to carry out this invention on easily extruded aluminum alloys such as Nos. 6061, 6063, 6351 and 6463.

The aluminum or aluminum base alloy is advantageously prepared for anodizing by degreasing and cleaning in a conventional bath of a non-silicated alkaline cleaning agent, rinsing in tap water, caustic etching if desired, and desmutting in dilute nitric acid.

The method of the invention comprises the steps of:
(a) Hard coat or natural architectural anodizing an aluminum or aluminum base alloy panel over its entire surface to produce a first anodic coat of a predetermined color or natural aluminum color thereon, and then either (1) rinsing and drying, or (2) partially sealing and drying;
(b) Applying a first layer of resist material to selected areas of the anodized surface thereby masking and retaining the color of these areas under the resist; the resist is applied by silk screening, stenciling, or by masking and spraying;
(c) Where the anodic coating has been partially sealed after the original anodizing step, the anodic coat is removed from the areas not protected by the resist by etching, for example caustic etching; the partially sealed areas remaining intact under the resist; the chemical etching exposes bare metal where it is not protected by the resist;
Where the anodic coating has been rinsed and dried without sealing, the etching step is omitted;
(d) Further hard coat or natural architectural anodizing the areas not under the resist to produce a second anodic coat of a predetermined color thereon, and either (1) rinsing and drying, or (2) partially sealing and drying;
(e) Applying a second layer of resist material to selected areas not under the first resist layer, thereby masking the areas under which the second color is to remain, while leaving the first resist layer in place;
(f) Where the second anodic coating has been partially sealed, the second anodic film is removed from areas not protected by the second resist layer, by etching, the second partially sealed areas remaining intact under the second resist; the chemical etching again exposing bare metal;
Where the second anodic coating has been rinsed and dried without partial sealing, the second etching step is omitted;
(g) Further hard coat or natural architectural anodizing the areas not under the first and second resist layers to produce a third anodic coat of a predetermined color thereon; if this is the last color desired, the panel is then completely sealed;
(h) Removing the resist material, thereby exposing the entire contrasting color design.

In the preferred practice of the invention, partial sealing of the successive anodic coatings is carried out, so that the sequence of steps omits the rinsing and drying variations in steps (a) and (d), and becomes:
(a) Hard coat or natural architectural anodizing an aluminum or aluminum base alloy panel over its entire surface to produce a first anodic coat of a predetermined color or natural aluminum color thereon and then par-
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tially sealing in distilled or deionized water at 205°-
212° F. for three minutes and drying said coat;
(b) Applying a first layer of resist material to selected
areas of the anodized surface, whereby retaining the color
of these areas under the resist;
(c) Etching to remove the anodic coat from areas
not protected by the resist, exposing bare metal in these
areas;
(d) Further hard coat or natural architectural anodizing
said exposed areas to produce a second anodic coat of a
predetermined color thereon and then partially seal-
ing in distilled or deionized water at 205°-212° F. for
three minutes and drying;
(e) Applying a resist material to a second set of selected
areas not under the first resist layer, thereby masking the
areas under which the second color is to remain, while
leaving the first resist layer in place;
(f) Etching to remove the anodic coat from areas not
protected by the second resist layer, exposing bare metal
in these areas;
(g) Further hard coat or natural architectural anodizing
said exposed areas under the first and second resist
layers to produce a third anodic coat of a predetermined
color thereon;
(h) If no further colors are desired, completely sealing
said third anodic coat; and
(i) Removing the first and second resist layers, there-
by exposing the entire contrasting color design.

The method employing partial etching is preferred be-
cause it affords protection against finger printing or ac-
cidental damage of the coating.

The resist material is preferably an organic polymeric
material, such as, for example, a heavy bodied vinyl resin.
It must be capable of withstanding the anodizing or blend-
ning of up to about 110 volts for a current density of 24 to 60
ampères per square foot, without dielectric breakdown
or pinhole penetration. Moreover, the resist material must
be capable of withstanding the repeated action of the
caustic soda bath at 140° F. maximum employed for
stripping the exposed anodic coat, and for a length of
time of 1.5-2.0 minutes times the number of different
colors in the final pattern. A suitable resist material hav-
ing these characteristics is sold commercially under
the designation "Vinyl Type 372-HM1-1. This is a vinyl
fluoride, vinyl acetate copolymer dissolved in ketone sol-
vents with a small amount of silicone resin to increase its
viscosity so that it may be applied to the metal surface either by
silk screening, by stenciling, or by mask and spray. The resist
material should be resistant to an anodizing process as
well as toward the etchant employed, but should be
readily removable when desired by a suitable organic
solvent or paint stripper, such as, for example, methyl-
isobutyl ketone, methyl ethyl ketone, or isophorone.

Silk screening is preferred in the practice of the inven-
tion for applying the resist. In carrying out silk screen-
ing, a stencil is attached to a mesh material which has
been stretched over a frame. The frame is then posi-
tioned over the metal surface and resist material is forced
through the open mesh portions of the mesh or screen by
the application of a rubber squeegee. The frames may be
made of wood or aluminum. The mesh or screen ma-
terials commonly employed are silk, nylon, or stainless
steel, the latter for long production runs. Silk is the most
versatile and least expensive of the screen materials.

The practice of silk screening is well known and need
not be described in detail. The stencils applied to the
screen may be hand-cut, made by utilizing a film of gelatin
coated onto a tin plastic support. The design is cut into
the gelatin and stripped away, and the gelatin film is
then adhered to the mesh. After drying the support is
peeled away leaving the stencil attached to the mesh.

The resist design may also be applied to the silk screen
by indirect or direct photoscreening. In indirect photo-
screening, gelatin impregnated with a dichromate is coated
on a plastic support. A photographic film positive con-
taining the design is placed against the photoscreen ma-
terial in a vacuum frame for good contact and exposed to
actinic light, as from a single-point carbon arc. The photoscreen material hardens where exposed to light. After
immersion in a pottasite developer, the material is washed
in warm water, removing unexposed gelatin and leaving
the design in the film attached to the support. This is
then attached to the mesh, and the support peeled away.
In the direct photoscreen method, the mesh is coated
with polyvinyl alcohol containing dichromate. Then the
photographic film negative is placed in close contact with
the coated mesh and exposed to actinic light. After ex-
posure, the screen is washed to remove unexposed emul-
sion, leaving the design ready to print.

In screen printing upon metal, a metal panel is placed
under the lowered screen and manipulated until the
stencil is in the correct position. The screen is then raised
and locked and register stops are attached. Printing is
conducted by pouring the resist material onto the screen,
lowering, wiping the resist material across the stencil
with a squeegee, raising the screen, removing the printed
piece, and repeating with a new piece. The second screen
is placed in register with the first and the process is
repeated.

The hard anodic coat can be applied by any suitable
method. Thus, for example, the aluminum or aluminum
base alloy panel or sheet or its exposed areas may be
anodized in a bath containing from about 5 to about
20% by weight of sulfuric acid, at a temperature be-
tween about 68° and 74° F., and at a current density from
about 10 to 24 amperes per square foot, for a period of 5 to 60
minutes, to produce an anodic film having a thickness be-
tween about 0.08 to 1 mil in various shades, dependent
upon alloy, followed by rinsing and drying, or partial
etching for three minutes in boiling water. Another known
method of hard coating which may be employed utilizes
an anodizing bath containing sulfosalicylic acid or sul-
phonic acid, together with small amounts of sulfuric
acid, a temperature of 60°-85° F., a current density of
24 to 60 amperes per square foot, and a time of 10 to
90 minutes to produce integral shades of gold to black, or
light gray to charcoal gray.

A preferred method of multicolor anodizing involves
using an electrolyte containing from about 0.05% to about
4.3% sulfuric acid, from about 0.50% to about 9.0% oxalo-
ic acid, and from about 0.50% to about 8.0 ferric oxalate,
all parts being by weight, at a current density between
about 12 and 60 amperes per square foot, and a tem-
perature of 50° to 80° F. for 10-60 minutes to form a hard
anodic coat 0.7-2.0 mil thick. The color of the anodic
coating will depend upon the alloy and its temper, the
electrolyte composition, anodizing time, applied voltage,
programming voltage, and thickness of the coat, but ranges
from gold to black and from light gray to charcoal gray.

The practice of the method of the invention will be more
readily understood by reference to the following example,
and to the accompanying drawings, which illustrate the
preparation of an aluminum panel having a three-color
(gold-bronze-black) design and exhibiting a three-dimen-
sional effect or pattern.

In the drawings:
FIGURE 1 depicts an aluminum panel hard coat anod-
ized over its entire surface in a gold color;
FIGURE 2 shows the panel with a first resist applied
in selected areas over the gold coat;
FIGURE 3 depicts the panel with the resist in place but
etched to expose metal in areas not under the resist;
FIGURE 4 shows the panel with a bronze second anodic
coat and the first resist in place;
FIGURE 5 shows the panel with a second resist ap-
plied over selected areas of the bronze anodic coat;
FIGURE 6 depicts the panel with first and second
resists in place and remaining areas etched to expose
metal;
FIGURE 7 shows the panel with a black third anodic coat and the resists still in place; FIGURE 8 shows the finished panel with resists removed and exhibiting the final pattern.

**EXAMPLE 1**

A 6" x 8" panel of 99.99% aluminum sheet was degreased in alkaline detergent, rinsed in tap water, etched with caustic soda 5 minutes at 150° F., rinsed for 2 minutes, and desmutted in 1-1 nitric acid, and rinsed in tap water. The panel was then anodized for about 15 minutes in a bath having the composition:

- Distilled water \[ \text{ml.} \times 1.000 \]
- Sulfophthalic acid \[ \text{gm.} \times 90 \]
- Aluminum radical \[ \text{gm.} \times 0.5 \]
- Sulfate radical \[ \text{gm.} \times 4.5 \]

The anodizing temperature was 80° F., and a constant current density of 48 amperes per square foot. A gold coat having a minimum thickness of 0.7 mil and a Knoop hardness of 512 was obtained. The coat was partially sealed in boiling water.

This gold first anodic coat is shown as 1 in the drawings. A silk screen stencil was prepared having the pattern designated 2 in FIGURES 2-7 inclusive. The panel was placed under the lowered screen and manipulated until the stencil was in correct position. The screen was then raised and locked, and register stops were attached so that succeeding screens could be placed in exact registry with the first screen. The resist ink, a vinyl resin, was poured into the screen, the screen was lowered, the resist ink was wiped firmly across the screen with a rubber squeegee, the screen raised, and the panel resistive. This resulted in the first resist design 3 being applied over gold first anodic coat 1, as depicted in FIGURES 2-7.

The panel was then etched for 1.5 minutes with 5% sodium hydroxide solution containing a sequestering agent, at a temperature below 140° F. to remove the first anodic coat in areas not under the first resist, leaving exposed metal areas 4, as shown in FIGURE 3.

The panel was then anodized a medium bronze color in the exposed metal areas using a bath having the composition:

- Distilled water \[ \text{ml.} \times 1.000 \]
- Sulfophthalic acid \[ \text{gm.} \times 90 \]
- Aluminum radical \[ \text{gm.} \times 0.5 \]
- Sulfate radical \[ \text{gm.} \times 4.5 \]

The time was about 15 minutes, constant current density of 48 amperes per square foot, electrolyte temperature 75° F. The resulting bronze coat is designated 5 in FIGURES 4, 5, and 8, and is darker than the original gold coat. The coat was partially sealed in boiling water.

A second resist was applied in a manner similar to the first resist to selected areas designated 6 in FIGURES 5, 6, and 7.

The panel was then etched as before to remove anodic coat 5 from areas not protected by the second resist, thus exposing metal in areas 6 in FIGURE 6.

The panel was then anodized in a brownish-black color in the exposed metal areas using a bath having the following composition:

- Distilled water \[ \text{ml.} \times 1.000 \]
- Sulfophthalic acid \[ \text{gm.} \times 90 \]
- Aluminum radical \[ \text{gm.} \times 0.5 \]
- Sulfate radical \[ \text{gm.} \times 4.5 \]

The time was about 20 minutes, constant current density of 48 amperes per square foot, and an electrolyte temperature 60° F. The resulting black coat 8 (FIGURE 7) was completely sealed.

The panel was then treated with methyl isobutyl ketone to dissolve and remove the resists 2 and 6, thereby exposing the entire pattern in contrasting colors of gold 1, bronze 5, and black 8, as shown in FIGURE 8. The particular design employed also produced a three-dimensional effect as shown.

**EXAMPLE 2**

A panel of alloy 6061-T6, dimensions 10" x 14" x 0.040", was prepared by cleaning for 3 minutes in a non-etching cleaner (Oakite NST, 5 oz./gal. at 125° F.), rinsing in water, etching for 5 minutes at 130° F. in a sodium hydroxide etchant (Alumix), rinsing in water, desmutting in nitric acid at room temperature for 3 minutes and double rinsing in water.

The panel was then anodized for 10 minutes at 17.5 volts and 320 amperes in 15% sulfuric acid at 70° F., double water rinsed, and sealed for 5 minutes in deionized water at 210° F., air-dried and cooled. A silver anodized shade was produced.

The areas intended to retain their silver shade were printed with a resist through a patterned stencil, air dried, and then etched 1.5 minutes with 130° F. caustic soda, and rinsed, deoxidized and rinsed again. A gold anodized hard coat was then applied to the areas not under the resist, using a bath whose composition is as follows:

- Distilled water \[ \text{ml.} \times 1.000 \]
- Ferric oxalate \[ \text{gms.} \times 80 \]
- Oxalic acid \[ \text{gms.} \times 20 \]
- Sulfuric acid \[ \text{gms.} \times 99 \]

The temperature of the bath was 70° F., the panel was pre-anodized for 5 minutes at 5-15 volts, gradually increasing the voltage to 40 volts and 220 amperes or approximately 12 amperes per square foot, followed by rinsing, sealing for 3 minutes as in Example 1, drying and cooling.

The silver and gold patterned areas were then printed with a resist through a silk screen and air dried. After etching and desmutting as before, the panel was anodized using the hard coat bath above, increasing the voltage from 5-15 to 38-42, and the amperage from 40-60 to 160-220 amperes, or approximately 12 amperes per square foot, for a total of 23 minutes at 70° F. After rinsing and sealing for 3 minutes, the panel was air dried and cooled. The resulting shade was dark gold.

Proceeding as before, a light bronze colored area was produced, anodizing in the same bath at a voltage to 47 volts, and a current of 320 amperes, approximately 24 amperes per square foot, rinsing, sealing and drying, a light bronze colored area was produced.

Similarly, a bronze colored area was produced by masking the previously colored areas, etching, desmutting and anodizing at approximately 36 amperes per square foot, current of 460 amperes and 52 volts.

Continuing, the previously produced colored areas were masked, and a dark bronze area was obtained by anodizing first at 5 volts for 3 minutes and 30 amperes, and then for 20 minutes at 45-56 volts and 520 amperes, approximately 48 amperes per square foot.

A black anodized area was produced by masking the previously obtained colored areas, removing unmasked areas with 4-30 second etches, and rinse, followed by anodizing at 50° F., first for 30 seconds at 5 volts, then for 30 minutes, by raising the voltage from 5 to 50 volts during 1 minute, and the amperage from 20 to 520, and holding at the latter value for 10 minutes (67 volts). At the end of 10 minutes, the voltage was raised to 69 volts and 560 amperes, approximately 48 amperes per square foot, and the work held at 80 volts for 20 minutes, and then for an additional 10 minutes, with amperage dropping from 560 to 450.

Finally the work was water rinsed twice, sealed in deionized water at 210° F. for 15 minutes, air dried and cooled. All masking material was then removed with methyl isobutyl ketone.

In all instances, it is necessary to apply an anodic film, either partially sealed or unsealed, before applying the
resist material in order to insure that the resist material will stay in place for the addition of other colors.

What is claimed is:

1. Method for the production of a decorative pattern on the surface of an aluminum or an aluminum base alloy workpiece, comprising the steps of:
   (a) anodizing said surface to produce a first anodic coat thereon;
   (b) applying a first layer of resist material to selected areas of said first anodic coat masking and retaining such areas under said first layer of resist;
   (c) anodizing the unprotected areas on the surface subsequent to the production of said first anodic coat thereon, leaving said first layer of resist in place;
   (d) applying a second layer of resist material to selected areas of said second anodic coat thereby masking and retaining said areas of the second anodic coat under said second layer of resist;
   (e) anodizing the unprotected areas on the surface not under said first and second resist layers to produce a third anodic coat thereon;
   (f) thoroughly sealing said last anodic coat, said sealing being effective to thoroughly seal said first and second anodic coats through the covering layers of resist material, and sealing the entire resist material, thereby exposing the pattern thereon.

2. The method of claim 1 in which the resist material is applied by silk screening.

3. The method of claim 1 in which the first and each succeeding anodic coat is rinsed and dried prior to applying the resist material.

4. The method of claim 3 in which each successive coat is darker in color than any previous coat.

5. The method of claim 1 in which the first and each succeeding anodic coat is partially sealed and dried prior to applying the resist material.

6. The method of claim 1 in which said aluminum or aluminum base metal alloy is in sheet form.

7. The method of claim 1 in which said aluminum or aluminum base metal alloy is in the form of an extrusion and said decorative pattern is applied to a flat area thereon.

8. The method of claim 1 in which the anodizing employed is hard coat anodizing.

9. Method for the production of a decorative pattern on the surface of an aluminum or an aluminum base alloy workpiece, comprising the steps of:
   (a) anodizing said surface to produce a first anodic coat thereon and then partially sealing and drying said coat thereon;
   (b) applying a first layer of resist material to selected areas of said first anodic coat thereby masking and retaining such areas under said first layer of resist;
   (c) etching to remove said first anodic coat from areas not protected by said first layer of resist to produce first unprotected areas of exposed metal;
   (d) anodizing said first unprotected areas not under said first layer of resist to produce a second anodic coat thereon and then partially sealing and drying said second coat, leaving said first layer of resist in place;
   (e) applying a second layer of resist material to selected areas of said second anodic coat thereby masking and retaining said areas of the second anodic coat under said second layer of resist;
   (f) etching to remove said second anodic coat from areas not protected by said first and second layers of resist to produce second unprotected areas of exposed metal;
   (g) anodizing said second unprotected areas not under said second layer of resist material to produce a third anodic coat thereon, and completely sealing said third coat;
(d) anodizing the unprotected areas not under the layer of resist to produce a second anodic coat thereon, leaving said layer of resist in place;
(e) thoroughly sealing both of said anodic coats; and
(f) removing the resist material from the metal surface.

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U.S. Cl. X.R.

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