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[54] **METHOD FOR CREATING A POLYCHROME MOTIF ON AN OBJECT MADE OF ALUMINUM OR ALUMINUM ALLOY**

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[52] **U.S. Cl.** .... **204/18 R;** 204/35 N

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[58] **Field of Search** .... 204/35 N, 58, 18, 18 R, 204/18 PC, 27, 30, 31, 33

[56] **References Cited**

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[57] **ABSTRACT**

This method is characterized by applying to the surface of the object a bichromated colloid, exposing the surface to light through a positive cut of the motif to be reproduced, developing the image obtained, treating the object by electrolysis in a bath containing at least one metal salt, eliminating the residual colloid and by plugging or sealing the aluminum layer.

3 Claims, No Drawings

METHOD FOR CREATING A POLYCHROME MOTIF ON AN OBJECT MADE OF ALUMINUM OR ALUMINUM ALLOY

The present invention relates to the creation of a polychrome motif on an object made of aluminum or aluminum alloy.

In the following text the word "aluminum" is to be understood to include "aluminum and its alloys". "Polychrome motif" shall mean a motif comprising several colors, for example brown and black or red and black or several hues of the same color, for example grey or black or lighter or darker shades of brown. The effect of coloration results from a continuous coloration of the colored zones and not from the effect produced by a series of colored dots.

Polychrome motifs already have been produced on aluminum objects by forming on these objects a porous oxide layer, then immersing them in successive baths of mineral or organic dyes, after having produced screened parts for example in fatty ink or with a varnish, on the parts of the surface which should not be colored in the bath in which the object is going to be immersed. Such a method does not make it possible to obtain degraded hues. It also has been suggested to paint the oxidized surface anodically, but even after sealing, the motifs so obtained deteriorate rather rapidly, even under ordinary atmospheric conditions.

The method according to the invention combines numerous advantages: very good preservation even under conditions of severe exposure; possibility of reproducing designs or motifs prepared by lines, dots or weaving, as well as of motifs in degraded, perfectly continuous hues; and finally, there is a considerable ease of reproduction.

According to the method of thc invention, a porous alumina layer is formed on the surface to be colored, by well known conventional means. A layer of bichromated colloid is applied to this surface. The object is exposed to light across a cut of the motif to be reproduced. The image obtained is developed, the object is washed and then treated in a manner known per se, as by electrolysis in a bath containing at least one metal salt selected from among those known as being usable for the coloration of aluminum, and the residual colloid is eliminated. If desired, the alumina aluminum layer thus colored may be sealed, for example by immersing the object in boiling water or by any other method.

In the areas protected against light by the cut, where the insolubilization of the colloid is zero or weak, the development causes the colloid to be removed completely or partly on the surface of the object, which enables the metal cations of the electrolysis bath to be fixed in the pores of the stripped portions of the aluminum layer. The thickness of the sensitive layer may be slight; a few microns, for example, about 2 microns. A cut prepared by lines or dots leads to a composite motif or lines or dots. A cut resulting from a dummy in degraded hues leads to a motif in continuous degraded hues in function of the degree of insolubilization of the colloid in each dot. The diversity of the insolubilization of the colloid also permits, in the same electrolysis bath, the obtaining of not only varied hues of the same color, but also different colors generally with the progressive passage from one color to another. Finally, by repeating the process, the zones which remained unexposed can be colored in a different color during one or several preceding passes.

For the state of coloration, different baths may be used which are known for dying aluminum, each of them leading to one color, which frequently depends on the tension applied and/or on the time of application of the current. Generally, these baths are slightly acid baths with a pH ranging from 1 to 5 and containing at least one cation originating from a Fe, Co, Ni, Mn, Cr, Bi, Ag, Sb, Sn, Cu, Cd, Mo, Ti, Ca, Mg, V, Pb, Zn salt. For example, brown colors generally are obtained with Ni, Sn, Co; pink or red colors with Cu; yellow colors with Ag or Cd; certain blue colors with Mo. Certain colors are obtained by using certain special salts. Baths containing two cations, for example Ag, Cu, make it possible to obtain from the same bath, different colors in function of the time of application of the current and/or of the voltage applied. It is possible to operate with AC or DC. In the latter case the object is mounted as the cathode.

The nature of the anodization bath also may have an influence on the color obtained. Thus, a surface anodized in sulfuric medium is colored pink, red or black when subjected to the coloring process in a bath containing copper salts and silver salts. In the same coloring bath, a deep green is obtained by effecting the anodization in an oxalic-chrome bath. Likewise a coloring treatment in a bath containing copper sulfate, silver sulfate and gold hydroxide leads to pink or red colors if the anodization has been carried out in sulfuric medium, or to dark green, pink or mauve colors if the anodization was carried out in chrome-oxalic medium.

It can be readily understood that, by suitably selecting the coloring baths, their conditions of use, and the conditions of pre-anodization, the method according to the invention offers very broad possibility for industrially obtaining very diversely decorated surfaces, which are prefectly reproducible and highly resistant against the usual conditions of exposure such as the exposure of a part of an architectural ensemble.

A general embodiment of the method of the invention will hereinafter be described, without excluding from the domain of this invention, variations of the described embodiment.

After having deposited on the aluminum surface of the object, placed anodically into a bath, a porous layer of alumina having a thickness generally ranging between about 5 and about 15 microns, this object is rinsed carefully, for example with distilled water, then the surface is dried, for example with hot air or in a moderately heated oven. Subsequently, a thin layer, in the order of 2 microns of a bichromated colloid is applied to the surface to be colored; gelatin sensitized by a bichromate, such as ammonium, potassium or pyridine bichromate, may be used. This coating may be carried out by any conventional coating means, for example by immersion, with a spray gun or by centrifuge. The surface thus sensitized is dried; a drying of 15 minutes at about 40°C may be suitable. Then the surface is exposed through a cut to the action of luminous radiation capable of insolubilizing the points or zones of the colloid engaged by the radiations. This insolubilization is proportional with the quantity of light received. For example, an arc lamp of 70 amperes, placed at 80 cm from the surface, may be used for an exposure time of 10 minutes. Following this exposure, the image obtained is developed. If the object can be dipped into a bath, it is immersed in a bath for about one minute. Then it is rinsed carefully, for instance with a water jet, under slight pressure. The object then is mounted as an electrode in a coloring bath.

If the colored motif should be protected, it may be subjected to a fill or seal, for example by subjecting it for about 10 minutes or more to the action of boiling water. However, the filling action of this kind must be preceded by the elimination of the colloid which had been insolubilized. For this purpose the object may be immersed for one minute into a concentrated potassium permanganate solution, then be rinsed with water, dipped in an acid solution of hydrogen peroxide for one minute, finally it again is rinsed with water.

The particular examples given below show the diversity of the coloration effects the method of the invention makes possible.

EXAMPLE 1

A 99.5% aluminum plate was used. This plate was anodized in a sulfuric acid bath to a thickness of 8 microns. Following washing and drying, a bichromated gelatin layer (ammonium bichromate), about 2 microns thick, was deposited thereon. There also was a cut resulting from the photography of a design in degraded hues. The surface to be colored was exposed to the radiation from an arc lamp through said cut. The sensitive layer, thus exposed, was developed, rinsed and then the plate was used as electrode in a coloring bath having a pH of 1.5, containing 15 grams/liter of copper sulfate. The previously insolubilized colloid is dissolved, and the plate is washed. A coloring is obtained which ranges from pink to dark red, the color in each dot depends on the opacity of the cut at the corresponding point.

EXAMPLE 2

A plate of the same metal, prepared as in Example 1, is used. A cut was used which comprises opaque and transparent parts. With this cut, the plate is provided with a print, forming thus completely insolubilixed zones besides soluble colloid zones; this latter colloid is dissolved and the plate is rinsed. Then the plate was mounted as an electrode in a coloring bath having a pH 4, containing 100 grams/liter of nickel sulfate, for 5 minutes at a tension of 13 volts, and then the plate was rinsed. Dark brown areas were obtained. Then the previously insolubilized colloid was dissolved, and the plate was washed and dried. The latter then was covered with a new layer of the same bichromated colloid and it was printed on by a reverse cut in comparison with the first to insolubilize the colloid of the areas which had to be printed during the first exposure. Following development of this new layer and rinsing of the plate, it was mounted as an electrode in a coloring bath having a pH 1 and containing 15 grams/liter of copper sulfate. This was done for 5 minutes at a tension of 14 volts. The previously insolubilized colloid was dissolved and the plate was washed. The areas which had not been colored brown previously were colored in red. This produced a colored plate with one part brown and one part red.

EXAMPLE 3

An aluminum panel was anodized in a sulfuric acid bath to a thickness of 8 microns. Following washing and drying, it was coated with a layer of about 2 microns of bichromated gelatin. Use was made of a cut resulting from the photograph of a design in degraded hues, thus a cut comprising grey zones adajcent to light zones and black zones. The surface to be colored was exposed to the radiation of an arc lamp through this cut. The sensitive layer, thus exposed, was developed, thus removing the parts not insolubilized of the sensitive layer. The plate was then mounted as an electrode in a bath containing 5 grams/liter of sulfuric acid, 15 grams/liter of copper sulfate and 0.15 gram/liter of silver sulfate, for 3 minutes with an intensity of 0.4 A eff/-square decimeter, at a voltage increased progressively to 11 volts. Following this coloration treatment, the previously insolubilized colloid was eliminated and the plate was washed. Next to the colorless zones, corresponding with the light zones of the cut, zones were obtained whose coloration varied continuously and progressively from yellow to pink, to brick red, in function of the degree of opacity of the corresponding points of the cut used.

EXAMPLE 4

A plate anodized in a sulfuric bath was used as in the preceding examples and this plate was covered with a layer of about 2 microns of bichromated colloid. A printing was applied to this plate by a cut originating from a photograph of a design in degraded hues. Following development and rinsing, this plate was used as electrode in a bath containing 1 gram/liter of copper sulfate, 0.25 gram/liter of silver sulfate, 0.25 gram of gold hydroxide and 6 grams/liter of sulfuric acid, for 10 minutes with a current density of 0.5 A eff/square decimeter.

Pink colors were obtained from pale pink to "flesh" pink in function of the degree of lighting of each point during exposure to light.

EXAMPLE 5

An anodized plate was prepared in chromic-oxalic bath, and this plate was covered with a layer of about 2 microns of a bichromated colloid. This plate was provided with a print through a cut from a photograph of a design in degraded hues. Following the development and rinsing, this plate was mounted as an electrode in the same bath as in Example 4 with an electrical current at the terminals of 10.2 volts. Shades were obtained from mauve to purple in function of the degree of lighting of each point during the exposure to light.

We claim:

1. A method for producing a polychrome motif on an object made of aluminum or aluminum alloy having an anodized surface, comprising applying a bichromated colloid to the surface of the object, exposing the surface to light through a cut of the motif to be reproduced, developing the image thus obtained to effect removal of colloid from the unexposed portions and reduce the cover over the underlying oxidized surface of the object, mounting the object as an electrode in an electrolysis bath containing at least one metal salt selected from those used for the electrochemical coloring of aluminum, passing an alternating current between the electrodes whereupon a coloring effect is produced in the anodized surface of the object corresponding to the unexposed portions of the colloid coating, and removing the remaining colloid, wherein the cut formed in degraded hues provides a progressively variable insolubilization of the colloid with the removal of colloid

varying inversely to the amount of insolubilization to provide a variable amount of coloring corresponding inversely to the amount of insolubilization.

2. The method as claimed in claim **1** which includes the step of sealing the colored surface layer after removal of the remaining colloid.

3. Aluminum or aluminum alloy objects produced by the method of claim **1.**

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