# United States Patent [19]

**Patrick**

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[54] **COLORING OF ANODIZED ALUMINUM**


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**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 54,842, July 14, 1970, abandoned.

[52] **U.S. Cl.** ..... **96/36,** 96/35.1, 96/27 R, 96/86 P, 148/6.1, 117/5.5, 106/22

[51] **Int. Cl.** ..... **G03c 5/00**

[58] **Field of Search** ..... 148/6.1; 117/5.5; 204/38.1; 96/27 R, 36, 35 N, 115 R; 209/35.1; 260/37; 106/22



[56] **References Cited**

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[57] **ABSTRACT**

Coloring of anodized aluminum using a resist which includes a dye which can be absorbed by the anodized layer.


**4 Claims, No Drawings**

# COLORING OF ANODIZED ALUMINUM

This application is a continuation-in-part of Application Ser. No. 54,842, filed July 14, 1970, now abandoned.

This invention relates to a procedure for selectively dyeing anodized aluminum.

The dyeing of anodized aluminum by dipping the same into liquid dye baths to produce a uniform coloring of the aluminum is old and well known. Dyes useful in this art are also well known and include those noted in Wainer U.S. Pat. No. 3,264,142, and in a book by S. Wernick and R. Pinner entitled *Surface Treatment and Finishing of Aluminum and Its Alloys* published in 1964 by Robert Draper, Ltd., Teddington, England, and in numerous other texts in this field.

The non-uniform coloring of anodized aluminum is a highly developed art in which a variety of techniques have been utilized. One way in which non-uniform dyeing is achieved is by blocking off or masking the article to be dyed so that the dye is accessible only to the unmasked area, e.g., as described in Fromson U.S. Pat. No. 3,092,523. Another technique described in Wainer U.S. Pat. No. 3,264,142 involves the use of a fulling agent to control the amount of dye taken into the pores of the substrate.

The present invention resides in the discovery that if the dye is incorporated in a photosensitive resist which is then applied to an unsealed anodized aluminum plate, the dye will be absorbed by the unsealed anodic layer so as to uniformly color the aluminum. Thereafter the plate is dried and is then exposed in accordance with the known properties of the photosensitive resist. The resist is then developed, i.e., the resist is selectively removed in the usual way e.g., by wash off with suitable developer compositions leaving some areas of the unsealed anodized aluminum plate bare of resist while other areas remain covered by the resist.

By selection of suitable developer compositions, the wash off step may be accomplished concurrently with a bleaching or leaching of the dye from the pores of the unsealed aluminum areas so that the resist-covered areas remain dyed and the washed off areas are now bleached free of dye. Where the developer or wash off liquid does not remove the dye from the pores of the anodized aluminum, a further dip in a suitable bleach may be utilized to accomplish this, before the remaining portions of the resist have been removed.

Thereafter the remainder of the resist is stripped from the aluminum base and the entire plate is then sealed by immersion in a heated nickel acetate solution or by any other sealing technique commonly practiced in this art.

The dyes which are particularly preferred in the practice of this invention are water soluble azo dyes, commonly used in the dyeing of anodized aluminum, these being readily absorbed from the resist into the pores of the oxide layer.

When more than a single color is to be applied, it is applied before the sealing step, described above. Application of such color, or colors, to the areas which have been stripped of color is achieved by applying a dye to the unsealed, uncolored anodized area e.g., by spraying or swabbing through a stencil or mask to the areas from which the original dye has been leached and then sealing the entire surface, in the usual way, after the last dye has been applied.



The following examples will serve to further illustrate the practice of my invention and are not intended to limit the invention in any way.

## Example 1

1. A commercial polyvinylcinnamate photoresist is prepared in the liquid form in the usual way e.g., as described in Example 1 of U.S. Pat. No. 2,670,286 and an anodizing dye compatible with the resist is added in an amount sufficient to produce the desired amount of color. One suitable composition consists of the proposed resist into which 0.05 to 25 parts by weight of Sandoz Origal Red B1 Solvent Soluble are added for each 100 parts by weight of resist.

2. An anodized aluminum plate is coated with the photoresist containing the anodizing dye prepared as in the previous paragraph, using any of the common coating methods, for example by simply pouring the dye-resist mixture onto the plate.

3. The plate is then dried. During the drying process the unsealed anodized aluminum absorbs at least some of the dye present in the photoresist which is taken into the pores of the anodized layer.

4. After drying, using a negative having opaque and clear areas, the plate is exposed to radiation of the kind normally used in exposing photoresist systems.

5. After exposure, the resist is developed in a suitable photoresist solvent, such as trichlorethylene. During this development stage, in areas which are being developed, the dye also is leached from the unsealed anodized aluminum.

6. After development of the resist, the resist is removed by any method which is applicable to the resist being used, for the resist of this example methylene chloride-methanol mixture (1:1 by volume) removes the resist.

7. The plate is then sealed in any of the commonly used sealing techniques practiced in this art, for example, by dipping in a solution consisting of 1 to 5 grams of nickel acetate in 1 liter of pure water, heated to 95° to 100° C, or in boiling water.

## Example 2

It is sometimes necessary to leach the area where the photoresist has been developed away, as the photoresist developer may not remove all the dye. This can be done by immersing the plate in an anodizing dye leach, comprising an aqueous solution containing 50–100 grams of 85 percent $H_3PO_4$ and 50 grams of sodium bichromate in 1 liter of solution. The balance of the resist is then stripped away and the plate sealed, in the usual way.

## Example 3

After the dye has been removed, whether during developing the resist or by a subsequent leaching, some areas of the plate remain masked and other areas unmasked. The areas which have been developed and/or leached may now be redyed with a second color, by spraying, swabbing or immersing the plate in an anodizing dye, such as Sandoz Bordeaux RL Red Anodizing Dye. The plate is then rinsed, the balance of the resist removed, and the plate is then sealed by dipping in a boiling aqueous solution of nickel acetate, as in Example 1.

Example 4

It is also possible to remove the first applied resist and apply a second layer of photoresist with a second dye in the photoresist before the plate is sealed. The procedures described above may then be repeated as often as necessary. Multiple coatings of photoresist and dye may be applied as many times as desired to produce any number of colors, after which the colored plate is sealed as described above.

Other photoresists have been used in place of the polyvinylcinnamate including those based on Minsk U.S. Pat. No. 2,670,286, Minsk U.S. Pat. No. 2,690,966, and others, it merely being necessary that the coloring material which is to be impregnated into the pores is compatible with the resist composition while it is being applied to the anodized plate.

As will be readily understood by those skilled in the art, substantially without exceptions, all commercial photoresists exhibit the characteristics of being insoluble or unattacked, in water solutions of etching or dyeing agents after exposure and development.

Suitable anodizing procedures are those described in Wernick and Pinner, noted above, and are known in the art.

I claim:

**1.** A process for selectively dyeing an anodized aluminum article which comprises:

applying a dye-containing photosensitive resist to an unsealed anodized surface on said article, whereby dye in said resist is absorbed in the anodized surface of said article;

thereafter photographically exposing said photosensitive resist;

then selectively removing the resist by applying a wash off composition thereto, while bleaching the areas from which the resist is stripped;

then removing the remainder of the resist;

and then sealing the pores in the dyed anodized article.

**2.** The process of claim **1** wherein the bleaching is carried out as a separate step after wash off of the resist.

**3.** The process of claim **1** wherein prior to sealing the pores in the dyed anodized article at least one additional dye is applied to the undyed areas through a mask, after which the article is sealed, whereby a multicolor article is produced.

**4.** The process of claim **1** wherein prior to sealing the pores in the dyed anodized article, a second dye-containing photosensitive resist is applied to the dyed anodized article and then exposed, developed and removed whereby the article is dyed with a second color and then sealing the double dyed anodized article.

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