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C. B. BLAKE ET AL

3,484,342

PRINTING ON ANODIZED ALUMINUM

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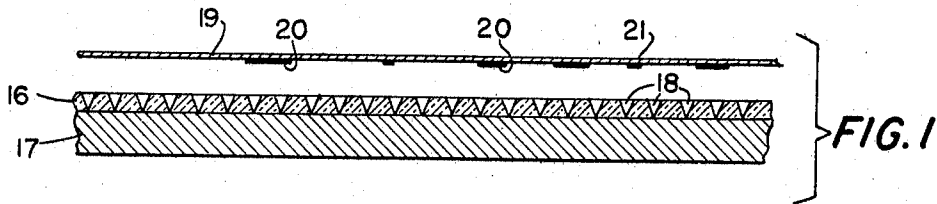


FIG. 2

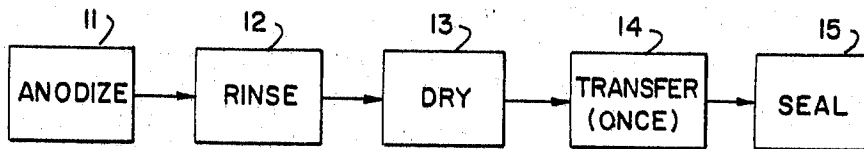
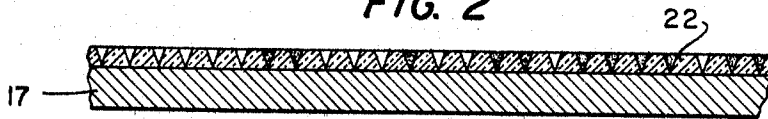


FIG. 3

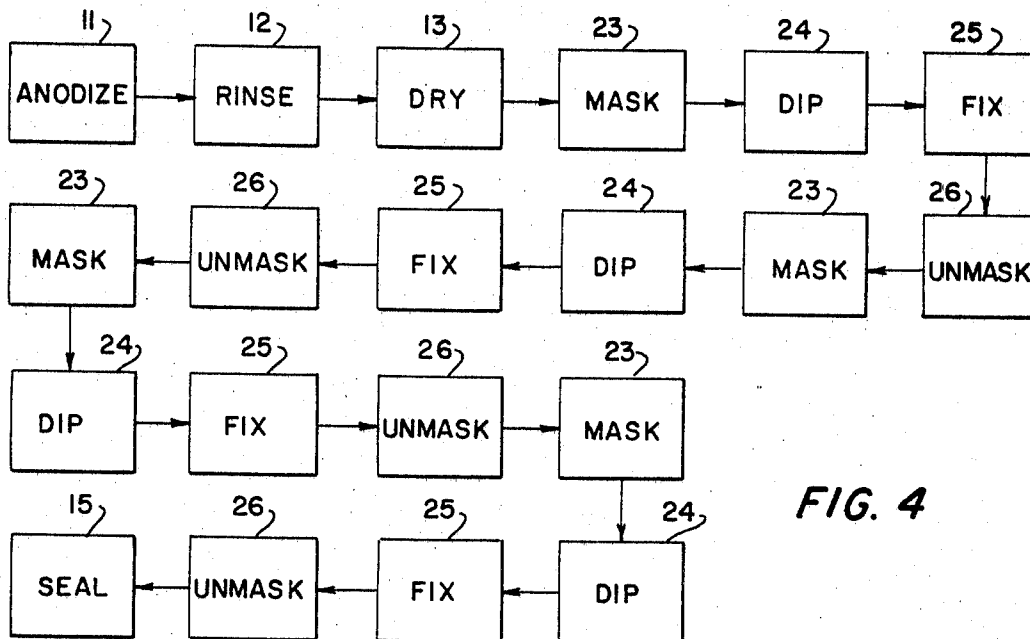


FIG. 4

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PRINTING ON ANODIZED ALUMINUM

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Continuation-in-part of application Ser. No. 252,311, Jan. 18, 1963. This application Aug. 5, 1966, Ser. No. 570,593
Int. Cl. C23b 9/02; C23f 17/00; B44c 1/04
U.S. Cl. 204—18

7 Claims

ABSTRACT OF THE DISCLOSURE

A process for decorating aluminum comprising anodizing said aluminum to provide a porous anodic surface. The porous anodic surface is then contacted with a sheet having printed matter thereon, said printed matter comprising a heat volatile coloring agent. The assembled anodic surface and sheet is then heated to cause transfer of the printed matter. Thereafter the anodized surface is sealed.

This application is a continuation-in-part of application Ser. No. 252,311, filed Jan. 18, 1963, now abandoned.

The present invention relates to a process for decorating anodized aluminum surfaces and, more particularly, to a process wherein heat transfer of ink impressions onto anodized aluminum surfaces is employed as one step thereof. The invention is especially directed to the application of complex patterns, particularly those in which numerous colors are included to the anodized aluminum surface. Subsequent to decoration the colored anodized aluminum surface is sealed as by prolonged immersion in boiling water, the colored pattern upon the aluminum surface being resistant to such boiling and preferably also to prolonged exposure to light to provide reasonable resistance to fading.

The present invention employs the dye heat transfer process disclosed in the application of Carl B. Blake, Ser. No. 115,152, filed June 6, 1961, now abandoned, the disclosure of said application being incorporated herein by reference.

In accordance with the present invention, a surface of material, preferably paper, which has been printed in mirror image of the design to be produced with an ink comprising a partially sublimable coloring agent is placed in close proximity with, and preferably in direct contact with, an anodized aluminum surface and heat is applied to cause progressive gasification or sublimation of the coloring agent to produce a distinct image by condensation of the gases generated on the anodized aluminum surface within a short period of time, desirably within 15 seconds. Heat is applied at a temperature of from 140–500° F., especially from 250–450° F.

The invention is illustrated by the drawing in which:

FIG. 1 is a view in cross section of the color stage of the present invention;

FIG. 2 is a cross-sectional view of the product of the present invention;

FIG. 3 is a schematic outline of the steps employed in connection with the present invention; and

FIG. 4 is a schematic outline of steps employed in prior art processes.

A feature of the invention is the finding that sulfuric acid anodized aluminum surfaces (including the anodized surfaces of alloys containing at least about 80% aluminum) are unusually receptive of the sublimation dyes in accordance with the invention. It has further been found that certain dyes are unusually substantive toward the anodized aluminum surface so as to provide a degree of light fastness which is unusual for dyes which sublime at moderate temperature. Indeed, it is clear that a chemical

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association is formed between preferred sublimed dyes in accordance with the invention and the anodized aluminum surface because, and even prior to sealing, organic soluble dyes are not significantly dissolved away from the aluminum surface by the very organic solvents in which they are highly soluble.

As an unusual facet of the present invention, transfer of dye to the anodized aluminum receiving surface is achieved through the use of heat. Nevertheless, and despite transfer to the anodized aluminum surface by sublimation and condensation, it has been found that the dye is sufficiently retained, especially by sulfuric acid anodized aluminum surfaces, to resist prolonged exposure to boiling water, except where the dye per se is hydrolyzable by contact with water.

Referring more particularly to the coloring of anodized aluminum surfaces by prior art methods, the conventional surface coatings which sit on top of the anodized aluminum surface, are subject to film deterioration, they can be removed by abrasion, and are often opaque, or, even when transparent, the conventional coatings detract somewhat from the beauty of the aluminum surface itself. Because of the extremely minute nature of the pores in anodized aluminum surfaces, most lacquers, varnishes or the like applied to an anodized surface do not penetrate into the pores. Such lacquers, varnishes, etc., merely form, for the most part, a surface layer which, as mentioned before, can be abraded or washed away.

Anodized aluminum surfaces have also been colored by dyeing, usually by dipping the aluminum surface in the dye to provide a single overall color. It is also possible to apply a resist to predetermined areas of the aluminum surface followed by dipping in the dye and one, or possibly two colors can be applied in this manner. However, it is necessary to remove the resist and, as a result of the difficulty of this step, the application of several colors becomes extremely cumbersome and uneconomical. If sufficient colors are to be applied in a pattern which is very intricately related, as in the multi-color printing of photographs using half-tone technique, the required registration makes the sequential application of resist and dye dip in a repetitive manner substantially impossible.

One method for the multi-color printing of aluminum surfaces which has achieved some overall success is disclosed in United States Patent 2,614,912 in which dyes are applied by direct printing upon the aluminum surface. However, those familiar with anodizing and sealing of aluminum surfaces tend to shy away from printing operations. Also, it is necessary in the process of said patent to remove the ink by a washing operation which would tend to slow a fast production line. Accordingly, there is a very real need for improved processes enabling the efficient, economical and attractive multi-color finishing of aluminum.

Part of the problem solved by the present invention is the production of high quality multi-color prints on surfaces which are not readily adapted to pass through printing machinery. If one skilled in the arts of printing and anodizing were faced with the problem of producing high quality printing on an anodized surface of a massive object, for example, an aluminum sphere, even the highest skill in the known arts would be of little one. The skilled artisan would be forced to use crude methods, e.g. silk screens, to stencil his design. While they are very useful, silk screens produce a low quality print when compared to the quality of prints produced by lithography, gravure, letterpress and like methods. By means of the present invention a relatively unskilled person can transfer a highly sophisticated quality print to any anodized aluminum surface upon which he can temporarily fasten a sheet, strip or patch of transfer substrate, e.g. paper, plastic or the like. The skilled artisan would have to provide a stencil for each

color applied and provide some means for registering each of the stencils to provide a clear total image. By means of the present invention all colors are applied to the anodized surface at one time. Registration is provided for on a cheap paper substrate in the manner normal to the printing art. Printed transfer sheets can be stored for substantial periods of time enabling both the most efficient use of valuable press time and adaptability in metal decoration. The transfer of the already registered, high quality design from the transfer sheet to the anodized aluminum surface is practically foolproof. Thus the present invention provides not only a process for accomplishing what could not be done before, but also provides, at the same time, a process which practically eliminates decoration rejects on valuable, anodized surfaces.

In accordance with the present invention, a printable surface, e.g. a sheet of material, is printed, preferably by offset printing, in mirror image of the desired design (including letters, pictorial matter, abstracts, etc.) with an ink which comprises a coloring agent constituted by a non-hydrolyzable, water insoluble dye having the following sublimation characteristics:

(A) No noticeable sublimation below 120° F.;

(B) A sublimation half-life at 500° F. of less than 75 seconds; and

(C) A sublimation half-life at a temperature in the range of from 140° F. to 500° F. of from 0.5-75 seconds. Preferably, the desired sublimation half-life of the coloring agent exists at a temperature in the range of from 180° F. to 450° F., and most preferably in the range of from 250° F. to 425° F. to provide a print in mirror image of the design to be produced.

The term "sublimation half-life" designates the time required for a 50% weight loss through elimination of part of the coloring agent as a result of its conversion to the gaseous state.

Since the ink impression to be formed is a thin film (usually 3-5 microns in thickness), the surface area per unit weight is very large and the characteristics of the coloring agent referred to are measured with the coloring agent in any convenient form with a similar very large surface area to weight ratio.

In accordance with the invention, it has been found that certain dyes are unusually substantive, especially to sulfuric acid-anodized aluminum substrates, these dyes falling within the following categories:

(1) Anthraquinone dyes having in the 1, 4, 5 or 8 position a hydrogen substituent, or an hydroxyl substituent, or a nitrogen atom carrying an active hydrogen atom, said nitrogen atom being present in the form of an amine or an amide. The other substituent on the nitrogen atom may be any hydrocarbon.

(2) Azo dyes having a hydrogen atom in the position ortho to the azo group; and

(3) Dyes containing the 1,3 indandione group.

It should be understood that the specific types of dyes referred to above are still required, in accordance with the invention, to possess the required sublimation characteristics and to be non-hydrolyzable in order that they may be applied to the anodized aluminum surface by sublimation and resistance to the boiling water treatment required in connection with the sealing of the anodized aluminum surface.

It is desired to emphasize that the inks which are employed should not include wax or other meltable component since this would cause the heat transfer process to include mechanical transfer of the meltable component which would interfere with the process of the invention.

Preferred dyes which have been found to be substantive to the anodized aluminum surface in accordance with the present invention, and reasonably resistant to destruction by boiling water, are illustrated by the following dyes.

A suitable anthraquinone dye is Quinizarine Green Base described in the Colour Index as C. I. Solvent Green

3 and identified by C. I. No. 61565. This dye contains an hydroxyl group in the 1 position and an amino group on the 4 position. Similar anthraquinone dyes in which either the amino or the hydroxyl substituent is present are also useful. The amino group may be a primary amino group in which the two reactive positions on the nitrogen atom are occupied by a hydrogen or one of the hydrogen groups may be reacted with an organic carboxylic acid to form an amide such as by reaction with acetic acid or benzoic acid or one of the hydrogens can be substituted by any monofunctional hydrocarbon radical such as lower alkyl and aryl groups so long as the substituent forming the secondary amine is not so long as to interfere with the desired sublimation characteristics of the dye which have been defined.

Suitable disazo dyes are illustrated by Sudan Yellow GRA conc. described in the Colour Index as C. I. Solvent Yellow 30 and identified by Colour Index No. 21240. This dye contains an hydroxyl group ortho to each of the two azo groups in the dye.

Dyes containing the 1,3 indandione group and which are sublimable in accordance with the invention are illustrated by Quinoline Yellow Base described in the Colour Index as C. I. Solvent Yellow 33 and identified by Colour Index No. 47000.

As pointed out in the application of Blake referred to hereinbefore, the ink containing the sublimable dye in accordance with the invention comprises an organic resinous binder which, when deposited either with or without the use of moderate heat, supplies a dry solid film which remains solid and dry upon exposure to the elevated temperature transfer conditions which are employed.

The invention will be illustrated by the following example.

EXAMPLE

Each of the dyes specifically referred to hereinbefore was formulated into a printing ink as follows:

	Parts by weight
Long oil linseed-isophthalic alkyd ¹	12.50
Medium viscosity linseed oil	25.00
Heavy viscosity linseed oil	12.50
Calcium carbonate extender pigment	30.00
Dye	20.00

¹ An alkyd of equimolar proportions of glycerin and isophthalic acid containing 65% by weight of linseed oil.

These components are stirred together and then milled on a 3 roll mill until the mixture has a grind gauge of 3. The ink so-produced was printed on thin paper on an offset press and is dry to the touch in a very few minutes and thoroughly dry in about 4-8 hours. The dry print is placed over a sulfuric acid anodized aluminum surface and pressed slightly with a heated hand iron set at 400° F. for a period of 6 seconds. In each instance, and using each of the dyes referred to hereinbefore, a true, clear and clean image was produced on the anodized aluminum surface. Despite the fact that these inks are soluble in organic solvents such as methyl ethyl ketone, immersion of the printed anodized aluminum surface in methyl ethyl ketone for a period of two hours does not significantly affect the quality of the image. When the freshly printed anodized aluminum surface is placed in boiling water for ½ hour, the quality and clarity of the dye remained acceptable and the anodized aluminum surface was effectively sealed by the boiling water procedure. Moreover, the dye image produced by the invention remains clearly visible through the glass-like sealed surface provided by the conventional boiling water treatment.

The printed and sealed surfaces produced as described above can be exposed to light in a Fadeometer and are found to provide a degree of light fastness which one would not normally associate with a dye having sublimable characteristics. In this manner, the product of the invention is unexpectedly adapted for prolonged use

in exposure to light as well as adverse weather conditions.

The process steps associated with the present invention in printing a four color design on anodized aluminum are illustrated in FIG. 3 of the drawing. Referring now thereto, metal, such as aluminum, after being cleaned is anodized in step 11 to produce a surface having a porous anodic film. Surface 16 on base alloy 17 having pores 18 (greatly enlarged) is shown in FIG. 1. Surface 16 is then rinsed with water in step 12 and dried in step 13. In step 14 substrate 19 having imprinted thereon areas 20 (all as shown in FIG. 1) is positioned face down on anodized surface 16. Printed areas 20 are in mirror image of the desired design and are imprinted with inks containing dyes with sublimation characteristics as set forth hereinbefore. Heat is applied to the non-face side 21 of substrate 19 to transfer dye to anodized porous surface 16. The printed substrate is removed and the anodized surface is sealed resulting in a sealed and decorated anodized surface 22 as shown in FIG. 2. In contrast to the simple five-step procedure of the present invention is the complex operation, illustrated in FIG. 4, which is typical of dip-dyeing processes of the prior art. The operations of masking 23, dipping 24, fixing 25, and unmasking 26 must be carried out for each color. Each time these operations are done, care must be taken in registration so as to maintain the integrity of the image. Each time these operations are performed, one must also carefully select materials and processes so as not to disturb what has gone before. As a matter of fact, in some commercial practices, fixing constitutes sealing the anodized surface, which step is followed by the steps of etching of selected areas and reanodizing. By means of the present invention all registration is taken care of by the printer, the expert in this art. All colors go on simultaneously. The process operations of the present invention are the same whether one, two, four or twenty colors are used. No care need be exercised to protect prior deposits. Thus the present invention provides a novel process eliminating substantially all need for skilled labor in decorating anodized aluminum. From the point of view of metal treatment, the present invention provides a simple process essentially involving only anodizing to provide a porous surface, heat transfer of an image and sealing by means of hot water, boiling water or the like to close the pores of the anodized surface and seal the design therein.

The invention is defined in the claims which follow.

We claim:

1. A process for decorating aluminum with a design having at least one color, which comprises anodizing said aluminum to provide a porous anodic layer thereon, contacting said porous, anodic layer, after drying, with a substrate, face down, having imprinted on the face thereof a mirror image of said design in at least one ink containing a coloring agent having the following sublimation characteristics:

- (A) no noticeable sublimation below 120° F.;
- (B) a sublimation half-life at 500° F. of less than 75 seconds; and
- (C) a sublimation half-life at a temperature in the range of from 140° F. to 500° F. of from 0.5-75 seconds;

only once while in contact with said dry porous anodic layer, subjecting said substrate and its ink impression to a temperature in excess of 140° F. for a period of time sufficient to cause said coloring agent to sublime and condense within said anodized aluminum surface in design configuration and thereafter sealing said anodized aluminum surface.

2. A process as in claim 1 wherein the design is in a plurality of colors, the substrate paper and the anodized aluminum is sealed in boiling water.

3. A process as in claim 1 wherein the coloring agent is substantive to an anodized aluminum surface.

4. A process as in claim 1 wherein the aluminum is anodized in an aqueous sulfuric acid electrolyte.

5. A process for decorating aluminum with a design having a plurality of colors, which comprises anodizing said aluminum in an aqueous sulfuric acid electrolyte to provide a porous anodic layer thereon, contacting said porous, anodic layer, after drying, with a substrate, face down, having imprinted on the face thereof a mirror image of said design in a plurality of inks each containing a coloring agent having the following sublimation characteristics:

- (A) no noticeable sublimation below 120° F.;
- (B) a sublimation half-life at 500° F. of less than 75 seconds; and
- (C) a sublimation half-life at a temperature in the range of from 140° F. to 500° F. of from 0.5-75 seconds;

only once while in contact with said dry porous anodic layer, subjecting said substrate and its ink impressions to a temperature in excess of 140° F. for a period of time sufficient to cause said coloring agents to sublime and condense within said anodized aluminum surface in design configuration and thereafter sealing said anodized aluminum surface.

6. A process as in claim 4 wherein the substrate is paper and the anodized aluminum is sealed in boiling water.

7. A process as in claim 4 wherein the coloring agents are substantive to an anodized aluminum surface.

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