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COLORING OXIDE-COATED ALUMINUM WITH DYE

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This invention relates to a process for coloring oxide-coated aluminum with dye, and more particularly to an improved aqueous-organic solvent process for coloring oxide-coated aluminum wherein dyes are applied to the surface of the oxide-coated aluminum from an aqueous-organic solvent solution. As used herein, "aluminum" includes pure aluminum, aluminum of various commercial grades, and aluminum base alloys. The term "oxide-coated" means in relation to aluminum, artificially oxide coated, by anodizing or chemical conversion processes.

It is well established that dyeings possessing some acceptable light-fastness are achieved on oxide-coated aluminum when the aluminum is properly anodized and the surface sealed after dyeing by treating it with hot water, hot aqueous solutions or steam. Heretofore oxide-coated aluminum has usually been dyed with acid dyes in water solution. Some current practices of dyeing anodized aluminum with water soluble dyes are described in "Dyestuffs," vol. 41, No. 8, December 1956. When utilizing the water-solution dyeing technique it has been found that the depth of shade obtained is often limited, especially on thin polished anodized surfaces, and also the colored coating often does not exhibit sufficient light-fastness to make it useful for exterior applications under weathering conditions. Another shortcoming of the conventional dyeing procedures arises in the use of extended periods of dyeing in order to obtain a deep penetration of dye into the oxide coating on the aluminum.

Completely non-aqueous organic solvents have long been considered for dyeing anodized aluminum. These solvents include alcohols, benzene, acetone, pyridine, oil varnish, fat and mineral spirits. However, when using these organic solvents it has not been possible to obtain concentrated solutions of the high molecular weight light-fast dyes, and the organic solvent procedure does not avoid many problems such as poor light-fastness, slow dyeing and lack of depth of shade. It is quite apparent that it would be highly desirable to provide an improved process for dyeing oxide-coated aluminum whereby the problems and disadvantages of the prior art procedures are overcome.

It is an object of the present invention to provide an improved process for coloring oxide-coated aluminum. A further object is to provide a process for rapidly coloring anodized aluminum in level shades at ambient temperatures. A still further object is to provide a process for coloring anodized aluminum in either light or heavy shades having excellent fastness to light. Other objects will appear hereinafter.

These and other objects of this invention are accomplished by the improvement in the process for coloring oxide-coated aluminum with a dye, normally followed by sealing of the dye in the aluminum oxide coating by means of a hot aqueous sealing medium, which improvement comprises employing as a solvent for the dye a minor portion of an organic compound selected from the group consisting of dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide and dimethylsulfoxide, together with a major portion of water. The process of the present invention is otherwise generally similar to the prior art procedures in that the oxide-coated aluminum is colored by means of a dye and the

dye may be sealed in the aluminum oxide coating. Although the dye may be one that is soluble in water, or of limited solubility in water, it has been found, quite unexpectedly, that the use of an organic solvent together with water markedly affects the dyeing of oxide-coated aluminum and leads to exceptionally light fast colored coatings. Further, although the dyeing may be made from an organic solvent solution, substantial economies and surprisingly good dyeing may, nevertheless be made when a dye-organic solvent solution is flushed into water as the major solvent.

The essence of this invention, consequently, consists in the use of a particular organic solvent-water system for the dye. By means of the present invention it is now possible to dye oxide-coated aluminum with a wide variety of dyes, including both the water-soluble and water-insoluble species, in a rapid manner and in a wide variety of strengths. This process is devoid of the numerous problems associated with the prior art procedures, particularly in regard to light-fastness, in that the colored oxide-coated aluminum displays unexpected light-fastness of at least 500 Fade-O-Meter hours.

In carrying out the process of this invention any use of the dyes which have been employed heretofore for coloring anodized aluminum may be used, as well as others not practical to use in bath having water as the only solvent. The process is particularly applicable with the chromium or cobalt complexes of the o,o'-dihydroxy or o-hydroxy-o'-carboxy azo dyes. If desired, these dyes may contain water solubilizing groups; however, it is to be understood that the improved results from the process of the present invention are obtained when either water-insoluble or water-soluble dyes are employed. As noted above, any of the dyes normally used in coloring anodized aluminum may be employed. These include the chromium or cobalt complexes of mono- or poly-azo dyestuffs as well as the complexes of anthraquinone derivatives, triarylmethane dyestuffs, azines, thiazines or oxazines. Specific dyes which may be employed include those used in the examples; those which are listed in Colour Index, second edition, under C.I. Nos. 14006, 13900A (Solvent Yellow 19), 18745 (Solvent Orange 5), 19351, 18736, 15685, 19115, 16055, 16260, 13425, 15711, 62105, 62085, 63010, 17045, 34220, 74220, and 74005; 3'-hydroxy quinophthalone, 1-hydroxy-4-anilino anthraquinone and 2,2',4,4'-tetrahydroxybenzophenone.

In accordance with the present invention the dyes are best applied to the oxide-coated aluminum by employing, as the initial solvent for the dye, an organic compound which is either dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide or dimethylsulfoxide. Mixtures of these compounds may be used. These solvents should constitute the minor portion of the liquid vehicle and may be reduced to as little as 5 percent of the vehicle by flushing into water. Of course, other organic solvents may also be present, together with thickeners if desired for particular modes of application. The solution of the dye should contain a minor portion, at least 5 percent by weight (and preferably less than 30 percent) of the liquid portion of an organic solvent, which is either dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide or dimethylsulfoxide, together with a major portion (above 50 and up to 95 percent) of water into which the initial organic solvent is flushed. Suitable other solvents which may be present, but are not required, include alcohols, such as methanol, ethanol and butanol; ketones, such as acetone and methyl ethyl ketone; hydrocarbons, such as benzene, toluene and heptane; ethers, such as dioxane; glycols, such as ethylene glycol; polyglycols and their ethers, such as 2-ethoxyethanol and carbitol; basic compounds, such as pyridine and quinoline; and chlorohydro-

carbons, such as carbon tetrachloride and chlorobenzene.

The mechanism of obtaining greater light-fastness with the above system is not well understood. It may be the system permits greater dye absorption, or the physical manner in which dye is deposited in the coating may be such as to yield greater resistance to light-fading. An alternative explanation is that solvation of the dye by the organic solvent prevents polymer "olation" of the dye and therefore allows it to be absorbed as a much more discrete entity than from water alone. It should be pointed out that the desired effects are obtained, in most cases, only when the dye is first dissolved in the organic solvent and then flushed into the water. Simply dissolving dye in a water-organic solvent bath, or in water and then adding the organic solvent, apparently does not produce the best results. Hence, it appears that solvation of the dye by the organic solvent is an important factor in the process.

The process of the present invention permits great flexibility in the application of the dye to oxide-coated aluminum. Painting, printing, spraying or dipping procedures may be employed. In general it is preferred to carry out the dyeing procedure at moderate temperatures; however, the oxide-coated aluminum may be treated at temperatures of room temperature up to the boiling point of the solvent system used.

The concentration of the dye in the solution which is used is not critical. High concentrations of the dyes make possible the production of deep shades, particularly when water-insoluble dyes are employed. However, it is to be understood that concentrations below saturated solutions may be used. The concentration depends on the dye and depth of shade desired. Concentration up to and including saturation may be used.

When coloring oxide-coated aluminum in accordance with the present invention the time factor involved is not critical. For example, conventionally anodized aluminum may be immersed in the dye solution for a period of time ranging from about 5 seconds to 30 minutes depending on the depth of shade desired. The longer time periods may be used to advantage in the exceptional cases where the dyes have low solubility or in the case of dyeing very thin oxide coatings.

The process of the present invention overcomes the numerous problems associated with the prior art procedures. By using the solvent systems of this invention a wider variety of dyes can be used to color anodized aluminum since one is no longer limited to the water-soluble species. The acid dyes themselves are frequently more soluble in the solvent systems employed in this invention than they are in water alone. Thus the dyeing rate of the acid dyes and their penetration into the pores of the anodized coating are improved. Since the process of this invention permits the use of more concentrated, or more effective even if not more concentrated, dye solutions, it is now possible to utilize smaller dye tanks, shorter dyeing periods and more flexible dyeing methods, such as spraying and brushing. The process of this invention makes it possible to apply water-insoluble colors successfully, rapidly and in a variety of strengths. This means an extension of shade range and fastness qualities. Thus a greater range of dyes is now available, a distinct advantage in the selection of dyes for use in dye mixtures. The use of mixtures for color matching is now more feasible since the various color components remain in solution and can be applied evenly in deep shades.

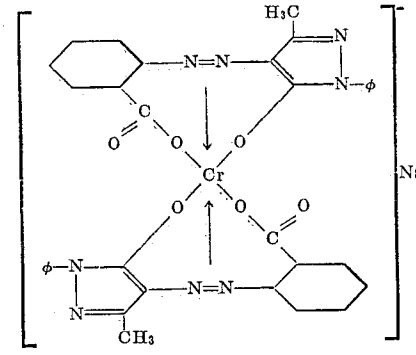
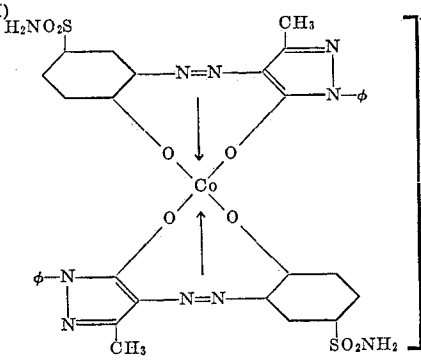
A significant advance achieved by the process of the present invention is that the colored oxide-coated aluminum exhibits extremely good light-fastness which, in terms of Fade-O-Meter hours, often exceeds 1000 hours. This superior light fastness means that the colored anodized aluminum may be employed more reliably in exterior construction in a wider variety of colors.

The following examples will better illustrate the nature of the present invention; however, the invention is not intended to be limited to these examples. Parts are by weight unless otherwise indicated.

Examples

A saturated (or less concentrated) solution of dye (see Table below) is made up in dimethylformamide, e.g. 10 grams per 100 milliliters. This organic solvent solution is then flushed into sufficient volume of water to make ten volumes of solution, e.g. one liter. Anodized aluminum (1.0 mil oxide coating) is immersed in this organic solvent-aqueous dye solution at room or elevated temperature for 15 minutes. The pH of the solution is desirably controlled between 5.5 and 7 with acid or base such as caustic soda or nitric acid. The oxide coating may be rinsed in water and then sealed by immersion in boiling water (pH 5.6 to 6.4) for 15 minutes. Alternatively a hot aqueous nickel acetate sealing solution may be employed. Deep, level shades are obtained.

TABLE I

Dye Structure	Color
(A)  The 1:2 Cr complex of the azo dye; anthranilic acid → 3-methyl-1-phenyl-5-pyrazolone.	Yellow.
(B) The 1:2 Cr complex of the azo dye; 2-amino-1-phenol-4-sulfonamide → 3-methyl-1-phenyl-5-pyrazolone.	Orange.
(C) The 1:2 Cr complex of equal mole ratios of the two azo dyes; 4-chloro-2-aminoanisole → 3-methyl-1-phenyl-5-pyrazolone and 4-chloro-2-aminoanisole → 3-methyl-1-(p-sulfophenyl)-5-pyrazolone. Similar results are obtained when the coupling component in the second azo dye is the isomeric 3-methyl-1-(m-sulfophenyl)-5-pyrazolone.	Red
(D) The 1:2 Cr complex of the azo dye; 4-choloro-2-aminoanisole → 2-naphthol-6-sulfonamide.	Violet.
(E) The 1:2 Cr complex of the azo dye; 2,5-dimethoxyaniline → 2-naphthol.	Blue.
(F) The 1:2 Cr complex of the azo dye; 2-amino-4-nitrophenol → 2-naphthol.	Brown.
(G) The 1:2 Cr complex of the azo dye; 1-amino-6-nitro-2-naphthol-4-sulfonic acid → 2-naphthol.	Black.
(H)  The 1:2 Co complex of the azo dye; 2-amino-1-phenol-4-sulfonamide → 3-methyl-1-phenyl-5-pyrazolone.	Yellow.
(I) The 1:2 Co complex of the azo dye; 2-amino-1-phenol-4-sulfonamide → acetoacetanilide.	Yellow.
(J) The 1:2 Co complex of the azo dye; 2-amino-1-phenol-4-sulfonamide → 2-naphthol.	Red.
(K) Tetrasulfonated copper phthalocyanine	Blue.
(L) Sulfonated quinoline yellow	Yellow.

Similar results have been obtained with many other dye concentrations and conditions of use, e.g. 4 grams of dye in 250 milliliters of organic solvent, flushed in

water to make one liter. Or 4 grams dye, 40 milliliters dimethylformamide, and 60 milliliters of Cellosolve (2-ethoxyethanol), flushed into water to make one liter.

The variations in the process of the examples such as the following, may be employed: (*a*) The anodized aluminum may be immersed in the dye solution at room temperature for various periods of time, e.g. from 5 seconds to 30 minutes, depending on the depth of shade desired. Relatively little dye builds up on the aluminum oxide coating beyond that which is achieved after an immersion of about 5 to 10 minutes. (*b*) Dimethylformamide may be replaced by diethylformamide, dimethylacetamide, diethylacetamide or dimethylsulfoxide. (*c*) These organic solvents may be used in mixtures with other organic solvents, such as methanol, ethanol, butanol, acetone, methyl ethyl ketone, benzene, toluene, heptane, dioxane, ethylene glycol, carbitol, 2-ethoxy ethanol, pyridine, quinoline, carbontetrachloride, chlorobenzene and linseed oil. This allows the use of lower concentrations of dye and of organic solvent, to limit depth of shade or to take advantage of properties of other solvents, such as fast drying and viscosity. (*d*) The amount of water employed may be reduced or increased, but it is a particularly important aspect of the invention that large amounts of water may be employed thus reducing the need to use large amounts of expensive, and otherwise objectionable organic solvent.

What is claimed is:

1. In the process of coloring oxide-coated aluminum which comprises treating the oxide-coated aluminum with a solution of a dye, the improvement which comprises employing as a solvent for the dye a minor portion, at least 5 percent by weight of the liquid portion of the solution, of an organic compound selected from the group consisting of dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide, and dimethylsulfoxide, together with a major portion of water.

2. A process for coloring oxide-coated aluminum which

comprises treating the oxide-coated aluminum with a solution of a metal complex of an azo dye, said metal being selected from the group consisting of chromium and cobalt and said azo dye being selected from the group consisting of o,o'-dihydroxy azo dyes and o-hydroxy-o'-carboxy azo dyes, said solution comprising a minor portion, at least 5 percent by weight of the liquid portion thereof, of an organic solvent selected from the group consisting of dimethylformamide, diethylformamide, dimethylacetamide, diethylacetamide, and dimethylsulfoxide, together with a major portion of water, and sealing the color in the oxide-coated aluminum by treating with a hot aqueous medium.

3. A process according to claim 1 wherein the organic compound is dimethylformamide and the dye is first dissolved therein and then flushed into the water.

4. A process according to claim 3 wherein the dye is the 1:2 chromium complex of the azo dye obtained by coupling the diazo of 1-amino-6-nitro-2-naphthol-4-sulfonic acid with 2-naphthol.

5. A process according to claim 3 wherein the dye is the 1:2 chromium complex of the azo dye obtained by coupling the diazo of 2-amino-4-nitrophenol with 2-naphthol.

6. A process according to claim 3 wherein the dye is tetrasulfonated copper phthalocyanine.

7. A process according to claim 3 wherein the dye is sulfonated quinoline yellow.

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