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3,071,494

SEALING OF DYED ANODIZED ALUMINUM
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No Drawing. Filed Sept. 27, 1961, Ser. No. 141,021
5 Claims. (Cl. 117-127)

This invention relates to the sealing of the anodic pores of dyed anodized aluminum. In one specific aspect, it relates to novel, storage-stable sealing solutions which, when used to seal the pores of dyed anodized aluminum, impart improved light fastness to the sealed dyed surfaces irrespective of the particular dyestuff used. In another aspect, it relates to a method of improving, by a new sealing technique, the light fastness of anodized aluminum dyed with water soluble dyestuffs or with water-insoluble, solvent-soluble dyestuffs according to the method described and claimed in U.S. 2,975,081 of Ben H. Kirby et al.

A dyed anodic coating on aluminum must be sealed in order to prevent bleeding of the dyestuff through the anodic pores and possible loss of color by sublimation of the dye. Although sealing can be accomplished by the use of boiling water alone, the majority of the useful dyes bleed extensively into the sealing bath unless hydrolyzable metallic salts are present. Conventionally, anodized aluminum that has been dyed with organic dyestuffs is sealed by immersion in a dilute aqueous solution of nickel acetate or its equivalent using a temperature at or near the boiling point of the solution. This treatment is believed to effect a rapid sealing of the anodic pores, possibly by the precipitation of an insoluble metallic hydroxide on the surface of the dye or by reaction with the dyestuff to form an insoluble complex within the anodic pores.

The sealing of anodized aluminum in the manner described hereabove was first disclosed by Tosterud in U.S. Patent 2,008,733. Tosterud found that the most useful metallic salts were the metallic acetates, e.g. the nickel, cobalt, cadmium, zinc, barium, copper, aluminum or lead acetates, the metallic sulfates, oxalates, chlorides, nitrates, citrates, tartrates and fluorides. Tosterud also noted that the pH of an unbuffered sealing solution or metallic salt tended to rise during use and, accordingly, he proposed to control the pH by using a buffering agent, such as boric acid or various borates and acetates.

Several workers in the art have developed improvements on the basic process of Tosterud. For example, Glauser et al. in U.S. Patent 2,755,239 proposed a method for overcoming the dullness of the dyed aluminum surface occasioned by the film of metallic hydroxide formed on the surface after the sealing operation. This was accomplished by the presence, in the sealing solution, of a water-soluble condensation product of formaldehyde and an aromatic sulfonic acid. Stiller, in U.S. Patent 2,888,388, proposed to control the film formation resulting from the sealing operation by the presence, during the sealing operation, of at least 0.1% by weight of a lignosulfonate.

It is known that the light fastness of dyed anodized aluminum is influenced by the particular dyestuff used and also by the sealing technique. While it was recognized that the light fastness obtained using a particular color could be greatly enhanced by the use of a carefully selected sealing formulation designed for that particular color, the control of the light fastness of dyed panels in this manner is commercially impractical, since it necessitates maintenance of a large number of separate sealing baths by the anodizer. Although it has been the practice in the past to use more than one salt in a sealing bath; for example, nickel and cobalt acetates are commonly used together, no one has been able to develop a sealing bath which provides substantially optimum light fastness with all classes of dyestuffs.

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I have discovered a novel sealing solution containing a new ingredient, and in a preferred embodiment a balanced formulation of ingredients, which, quite surprisingly, is capable of imparting improved light fastness to sealed anodized aluminum dyed with substantially all classes of water-soluble and solvent-soluble dyestuffs.

It is, therefore, an object of the present invention to provide a new storage-stable sealing solution for sealing of the anodic pores of dyed anodized aluminum. It is a further object to provide a sealing solution which is effective in imparting optimum light fastness to anodized aluminum dyed with water-soluble and solvent-soluble organic dyestuffs, regardless of the particular dyestuff used for the dyeing operation.

In accordance with the invention, I have discovered a novel storage-stable sealing solution which comprises a minor portion of the ammonium salt or complex of a hydrolyzable copper salt in a major portion of water. The pH of the solution is maintained in the range of 5.5-6.0. For all purpose use the ammonium complex of the hydrolyzable copper salt can be augmented with an ammonium complex of a hydrolyzable salt of nickel or cobalt.

Although it is known from the teachings of Tosterud in U.S. Patent 2,008,733 that the hydrolyzable salts, preferably the acetates, of nickel, cobalt and copper can be used as individual components of a sealing solution, the use of copper salts has never enjoyed commercial success and the combination of the three ingredients has never been reported. I have discovered that modified copper salts, augmented, if desired, with modified nickel or cobalt salts, unexpectedly impart superior light fastness to sealed anodized aluminum dyed with water-soluble or solvent-soluble organic dyestuffs, irrespective of the particular dyestuff used. In practice, I have found that a copper salt cannot be used effectively at a pH above 3.5 because of precipitation of the copper from solution in the form of copper oxide. As a practical matter, the use of a sealing solution having a pH below about 3.5 is not possible, since the high acidity of such a solution causes pitting and degradation of the anodic coating. The desired pH range for sealing purposes is between 5.5 and 6.0.

Surprisingly, I have found that stable solutions containing copper ions can be prepared by treating an aqueous solution of a hydrolyzable salt of copper with sufficient ammonia to convert the salt to its ammonia complex. Thus, according to a preferred embodiment of invention, an aqueous solution containing between about 0.3-1.5% by weight of copper acetate or a combination of copper and nickel acetate, copper and cobalt acetate or nickel, cobalt and copper acetate is treated with ammonia in an amount sufficient to convert the acetates to the corresponding complex ammonium acetates. The sealing solution of the invention is prepared therefrom by adding sufficient acid to bring the pH within the range of 5.5-6.0 which, as I have previously noted, is the most desirable pH range for the sealing of dyed anodized aluminum. The resulting solution is stable for long periods of time, even when heated at 100° C.

It is essential to my invention to have present a hydrolyzable copper salt and often desirable to use a combination of the hydrolyzable salts of copper and nickel, copper and cobalt or copper, nickel and cobalt. While I have found that the acetates are the preferred salts, as I have noted hereabove, it is possible to use other water-soluble hydrolyzable salts, such as sulfates, oxalates, chlorides, nitrates, citrates, tartrates and fluorides. The acetates are preferred because certain of the other salts tend to lessen the corrosion resistance of the anodized surface.

If a combination of hydrolyzable salts is used, it is necessary, in order to effectively impart light fastness to

dyed anodized aluminum colored using any water-soluble or solvent-soluble dyestuff, that the copper salt be present in an amount of at least 25% by weight based on the weight of the total salts.

The sealing solution of the invention comprises of about 0.3–1.5% by weight of the ammonium salt or complex of copper or one of the copper-nickel, copper-cobalt or copper-nickel-cobalt combinations described hereabove and about 98.5–99.7% water. If a combination is used, the solution is easily prepared by dry blending the desired salts, which must comprise at least 25% by weight of a copper salt, and dissolving them in water. Care should be taken to avoid melting the metal salts during the blending operation. The salts are then converted to their ammonia complexes by adding to the solution at least a stoichiometric quantity of ammonia based on the number of moles of combined salts that is present.

The metal salts may be added to the solution separately and then converted to their ammonia complex, or the ammonia complex of the metal salts may be separately prepared and added to the solution. No particular advantage is seen in this latter technique, since it is considerably more cumbersome than simply dissolving the required amount of salts in water and forming their ammonia complex by adding to the resulting solution at least a stoichiometric quantity of ammonia based upon the combined weight of the salts.

The sealing solution must contain at least about 0.3% by weight of the copper salt or of the combined salts in order to effectively seal the anodic pores. No advantage is seen in using the salt or salts in an amount greater than 1.5% by weight, since such usage is obviously wasteful, and there is some danger of enhancing the formation of undesirable film or scum on the aluminum surface, and pitting of the anodic surface by electrochemical attack.

In addition to the ammonium complex present in my novel sealing solution, the solution preferably contains a buffering agent to combat the tendency of the pH of the solution to rise during long periods of use. While any of the common buffering agents, such as boric acid, the borates and the like, can be used, I prefer to use sodium acetate. If used, the buffering agent should be present in an amount ranging between 0.1 and 0.2% based on the total weight of the solution.

In addition to the buffering agent, I have found it helpful to add to the sealing solution between about 0.5–2.5% by weight of a wetting agent in order to minimize scum formation or water spotting of the sealed dyed anodized aluminum.

As I have noted hereabove, after the solution comprising the ammonium salt or complex of a hydrolyzable copper salt (augmented, if desired, with the ammonium complex of nickel or cobalt salts) is formed, the pH of the solution is adjusted to between 5.5 and 6.0 for use by the anodizer. If the ammonia complexes of the salts are formed in situ by the addition of ammonium hydroxide according to the preferred embodiment of my invention, the resulting pH is approximately 9.5–10.0. The pH is easily adjusted to the desired range of 5.5–6.0 by the addition of glacial acetic acid. Other acids such as sulfuric and hydrochloric acid cannot be used, since their presence causes the precipitation of insoluble compounds even at room temperature. The solution is then ready for use by the anodizer at the conventional temperature of about 98° C., and it is stable at this temperature for only periods of time.

My invention is further illustrated by the following examples:

Example I

Nickel acetate, 10 g., cobalt acetate, 10 g., copper acetate, 10 g., and a buffering agent, sodium acetate, 5 g., were dissolved in 4000 ml. of distilled water at 25–30°

C. The pH of the solution was approximately 6.0. To this solution was added approximately 100 ml. of 28° Bé. ammonium hydroxide to convert the metallic acetates to their respective ammonia complexes. The pH of the resulting solution was approximately 10.0. The pH was adjusted to the desired range of 5.5–6.0 by the addition of approximately 90 ml. of glacial acetic acid. The resulting solution was a clear green color. It was found to be storage-stable under ambient conditions and also stable at a temperature between 90 and 100° C., the operating conditions generally used for sealing anodized aluminum.

Example II

Nickel acetate, 10 g., cobalt acetate 10 g., copper acetate 10 g., and a buffering agent, sodium acetate, 5 g., were dissolved in 4000 ml. of distilled water at 25–30° C. The pH of this solution was approximately 6.0. The pH was adjusted to the 5.5 with the addition of approximately 2 to 3 ml. of glacial acetic acid. The resulting solution was a clear light green in color. On heating a portion of the solution to 70° C. a dark brown precipitate started to form on the bottom of the beaker. At a temperature of approximately 90° C. considerable cloudiness was observed, and on further heating to 95–100° C. a heavy dark brown to black precipitation of copper oxide occurred. This would effect removal of the copper salt from the sealing solution in actual use, and prevent any sealing or complexing of this component with the dyed anodic surface.

Example III

An 800 ml. quantity of the original solution obtained in Example II above (taken before heating occurred) was treated with 20 ml. of glacial acetic acid to obtain a pH of approximately 3.5. On heating this solution no precipitation or decomposition of any kind occurred, even after prolonged periods at the boiling temperature. However, when attempts were made to seal dyed anodized aluminum with the solution, the metal surface invariably became roughened and pitted even after an immersion of only a few minutes, often with complete or nearly complete stripping of the color from the aluminum surface.

Example IV

Nickel chloride, 10 g., cobalt chloride, 10 g., copper chloride, 10 g., and a buffering agent, sodium acetate, 5 g., were dissolved in 4000 ml. of distilled water at 25–30° C. The pH of this solution was approximately 4.4. To this solution was added approximately 100 ml. of 28° Bé ammonium hydroxide to convert the metallic chlorides to their respective ammonia complexes. The pH of the resulting solution was approximately 10.0. The pH was adjusted to the desired range of 5.5–6.0 by addition of approximately 90 ml. of glacial acetic acid. The resulting solution was a clear deep bluish-green color. It was found to be storage-stable under ambient conditions and also stable at a temperature between 90 and 100° C., the operating conditions used for sealing anodized aluminum.

Example V

A sealing solution made up as in Example I, but omitting the nickel and cobalt acetates. Such a solution was a clear deep blue in color and was found to be completely stable at both ambient and operating temperatures.

Example VI

A sealing solution made up as in Example I, but omitting the nickel acetate. Such a solution was a clear greenish-blue in color and was found to be completely stable at both ambient and operating temperatures.

Example VII

A sealing solution made up as in Example I, but omitting the cobalt acetate. Such a solution was a clear

bluish-green in color and was found to be completely stable at both ambient and operating temperatures.

Example VIII

Sealing solutions were made up as in Examples I, IV, V, VI and VII but with the addition of boric acid as the buffering agent. Such solutions were found to be completely stable at both ambient and operating temperatures.

Example IX

Sealing solutions such as described in Examples I, IV, V, VI, and VII, being made up with the addition of the requisite amount of ammonium hydroxide to form the ammonia complexes, but having the pH then adjusted downward to the desired range of 5.5-6.0 with acids other than acetic, i.e. dilute sulfuric or hydrochloric acids, were found to be unstable at both ambient and consequently operating temperatures.

Example X

A 1" x 6" panel of aluminum suitable for anodizing and subsequent dyeing was cleaned, degreased, deoxidized and anodized in the conventional manner. The panel was then dyed a golden yellow color by immersing it in an aqueous solution containing 0.2% by weight of the product obtained by coupling m-nitroaniline with salicylic acid, C.I. Mordant Yellow 1; C.I. 14025, at a dyeing temperature of between 50 to 60° C. After a period of five to ten minutes the panel was removed from the dye bath and rinsed with water at room temperature to remove excess dye solution.

The dyed panel was then placed in a sealing solution prepared as described above in Example I, at a temperature of 98-100° C. for a period of from 5 to 10 minutes. After this the panel was removed, rinsed with cold water and subsequently immersed in a bath of boiling distilled water for a further 10 to 15 minutes to ensure complete sealing, then removed, buffed lightly with pumice powder and dried.

The finished panel was a deep golden yellow in color. It showed no appreciable change after 1000 hours of exposure in a "Fade-O-Meter" (a laboratory testing device for the accelerated exposure of a panel to ultraviolet light), which indicated that the color was exceptionally light fast.

Example XI

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of the chromium complex of 6-amino-4-nitro-1-phenol-2-sulfonic acid coupled with 3-methyl-1-phenyl-5-pyrazalone; C.I. Acid Orange 74, C.I. 16745. A bright golden orange color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XII

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of the coupling product of p-nitroaniline with salicylic acid, C.I. Mordant Orange 1, C.I. 14030. A deep reddish-orange color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XIII

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of 1,2-dihydroxy-3-sulfo anthraquinone, C.I. Mordant Red 3, C.I. 58005. A bright yellowish-red color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XIV

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of the coupling product of 2-amino-1-phenol-4-sulfonic acid with 2-naphthol, C.I. Mordant Vio-

let 5, C.I. 15670. A bright red color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XV

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of 1,4-dihydroxy-2-sulfo anthraquinone, C.I. Pigment Violet 5 (sulfonated), C.I. 58055. A strong reddish-violet color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XVI

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of copper phthalocyanine disulfonic acid, C.I. Direct Blue 86, C.I. 74180. A strong bright blue color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XVII

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed from an aqueous solution of the coupling product of 2-amino-4-nitrophenol with H Acid, C.I. 17230 (isomer). A deep black color was obtained. The light fastness obtained was comparable to that of the panel of Example X.

Example XVIII

The sealing procedure of Example X was repeated using an aluminum panel dyed with a 0.5% by weight solution of 1,4-dihydroxyanthraquinone in 1,2,4-trichlorobenzene according to the procedure described in U.S. Patent 2,975,081 of Ben H. Kirby et al. The finished panel had a very deep crimson color. It showed no appreciable change in shade after 1000 hours' exposure in the "Fade-O-Meter," which indicated that the color was especially light fast.

Example XIX

The sealing procedure of Example X was repeated using an anodized aluminum panel dyed with a 0.5% by weight solution of 1,4-di(2-hydroxyethylamino)-5,8-dihydroxyanthraquinone in 1,2,4-trichlorobenzene as described in Example XVIII above. The finished panel had a very deep blue color. It showed no appreciable change after 1000 hours' exposure in the "Fade-O-Meter," which indicated that the color was especially fast to light.

Example XX

A sealing solution was prepared by dissolving 10 g. of nickel acetate and 10 g. of cobalt acetate in 2500 ml. of distilled water, .5 g. of sodium acetate was added as a buffering agent and the pH adjusted to 5.5 by the addition of 5-10 ml. of glacial acetic acid. The resulting solution was stable at ambient temperature and also stable at the required temperature for the sealing of dyed anodized aluminum.

Aluminum panels dyed with the dyes used in Examples X to XIX above were sealed by immersion in this solution for 10 minutes at a temperature of 98-100° C., followed by a water rinse and subsequent immersion in boiling distilled water for a further 10 to 15 minutes. The finished panels appeared to have same shade and strength as those sealed with the sealing solution described in Example I, but on exposure in a "Fade-O-Meter" all showed considerable fading after 1000 hours' exposure, many fading badly after only 500 hours' exposure. This clearly shows the use of the sealing solution of this invention gives greatly improved light fastness, regardless of the dyestuff used.

Example XXI

Aluminum panels dyed with dyes used in Examples X to XIX above and sealed by immersing in sealing solutions prepared as described in Examples IV, V, VI,

VII and VIII all gave superior light fastness over that obtained by using a sealing solution prepared as in Example XX.

I claim:

1. A storage stable sealing solution for sealing the anodic pores of dyed anodized aluminum, capable of imparting improved light fastness to sealed dyed anodized aluminum surfaces, comprising 0.3–1.5% by weight of the metal ammonium complexes of hydrolyzable salts of nickel, cobalt and copper, said copper salt being present in an amount of at least 25% by weight based on the total weight of said salts, and 98.5–99.7% by weight water, the pH of said solution being in the range of 5.5–6.0.

2. A storage stable sealing solution for sealing the anodic pores of dyed anodized aluminum, capable of imparting improved light fastness to sealed dyed anodized aluminum surfaces, comprising 0.3–1.5% by weight of the metal ammonium complexes of the acetates of nickel, cobalt and copper, said copper acetate being present in an amount of at least 25% by weight based on the total weight of said acetates, and 98.5–99.7% by weight water, the pH of said solution being in the range of 5.5–6.0.

3. A method of preparing a stable sealing solution for sealing the anodic pores of dyed anodized aluminum, capable of imparting improved light fastness to sealed dyed anodized aluminum surfaces, comprising dissolving in water substantially equal parts by weight of nickel acetate, cobalt acetate and copper acetate, treating the resulting solution with sufficient ammonium hydroxide to

convert said acetates to metal ammonium complexes, and thereafter adjusting the pH of the solution by adding sufficient glacial acetic acid to bring the pH within the range of 5.5–6.0.

4. A method of preparing a stable sealing solution for sealing the anodic pores of dyed anodized aluminum, capable of imparting improved light fastness to sealed dyed anodized aluminum surfaces, comprising dissolving in water substantially equal parts by weight of hydrolyzable salts of nickel, cobalt and copper, treating the resulting solution with sufficient ammonium hydroxide to convert said salts to metal ammonium complexes, and thereafter adjusting the pH of the solution by adding sufficient glacial acetic acid to bring the pH within the range of 5.5–6.0.

5. In the sealing of dyed anodized aluminum by means of a hydrolyzable metallic salt in aqueous solution, the improvement comprising carrying out the sealing operation in a solution comprising 0.3–1.5% by weight of the metal ammonium complexes of the acetates of nickel, cobalt and copper, said copper acetate being present in an amount of at least 25% by weight based on the total weight of the acetates and 98.5–99.7% by weight water, the pH of said solution being in the range of 5.5–6.0, whereby improved light fastness is imparted to the sealed dyed anodized aluminum surface.

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