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TREATMENT OF OXIDE COATED ALUMINUM ARTICLES

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This invention relates to a method of improving the coloring characteristics of oxide coated aluminum surfaces. The term "aluminum," as herein employed, embraces aluminum and aluminum base alloys, as well.

Aluminum articles which have been provided with an adsorptive oxide coating can be colored or dyed with a variety of materials. The term "oxide coating," as used herein, is descriptive of an adsorptive layer of aluminum oxide artificially produced on aluminum surfaces by chemical treatment, with or without the use of externally applied electrical energy, but the term does not include the thin film of aluminum oxide which is naturally formed on the metal by contact with the air. In the customary coloring procedure, the oxide-coated article is rinsed to remove in so far as practical all of the electrolyte, or the solution employed in the production of the coating, following which the article is dipped into one or more coloring solutions. Considerable difficulty has been experienced, however, in obtaining surfaces which will color evenly, or which will permanently retain an even color over the entire surface. For example, a condition known as spotting may occur, wherein numerous small areas develop which are not colored at all, or are somewhat lighter in color than the remaining portions of the surface. This difficulty is one which is perhaps most frequently encountered in connection with the coating produced when the article is made anode in an electrolyte of a relatively strong acid, such, for example, as sulfuric acid, oxalic acid, or chromic acid. However, the condition may develop with coatings produced by non-electrolytic means. Again, spotting is much more likely to arise when dealing with surfaces which have been colored with dyes, as distinguished from mineral pigments. Aluminum castings which have been anodically treated in a strong acid electrolyte and thereafter dyed are particularly subject to spotting.

It may also be noted that irregular coloration is encountered in connection with aluminum articles which have been provided with a rolled bead or with other shape which acts to entrap the electrolyte and prevent its complete removal by washing. Articles of this nature exhibit uneven coloring in the vicinity of the entrapped electrolyte, as along the surfaces marginal to the open edge of the bead.

It is accordingly an object of this invention to provide an oxide-coated aluminum surface which will color evenly and thereafter retain a uniformly colored appearance. A more particular object

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is to effect this result in connection with aluminum articles which have been provided with an oxide coating by anodic treatment in a strong acid electrolyte, and which thereafter are to be dyed. Still another object is to provide a method of eliminating spotting and irregular coloration in connection with the coloring of oxide-coated aluminum.

It is my discovery that these and other objects may be attained by immersing an oxide-coated aluminum article, prior to any coloring or dyeing step, in a bath containing a suitable quantity of alkali metal oxalate. The bath should be maintained within suitable temperature and pH ranges.

The bath should contain a total of about 1 to 20 per cent by weight in solution of at least one alkali metal oxalate. In the term "alkali metal oxalate" I include ammonium oxalate. Of the alkali metal oxalates, sodium oxalate, potassium oxalate, and ammonium oxalate are preferred. In general, a total concentration in solution in the bath of about 2 to 5 per cent by weight of one or more of the alkali metal oxalate salts is preferred. In case sodium oxalate is used, its relatively low solubility will not permit more than about 5.5 per cent by weight to be dissolved at the temperature at which the bath is ordinarily maintained, though potassium oxalate or ammonium oxalate can be added if desired to bring the total concentration of alkali metal oxalate above this figure.

The bath is prepared by dissolving the alkali metal oxalate in water. The resulting solution is alkaline in character and its pH should be adjusted to between about 4.5 and 8, though a preferred pH range is about 6 to 6.5. While this adjustment is usually made by adding oxalic acid, any other acidic substance may be used which will not otherwise modify the action of the bath.

The alkali metal oxalate bath should be maintained at a temperature of about 100 to 200° F. when in use, though a range of about 120 to 150° F. is preferred. The time of treatment in the bath may vary from about 1 to 30 minutes, or even longer. When the bath is maintained at temperatures approximating 200° F., it is preferred that the immersion period be not longer than about 10 minutes. In general, good results are obtained when the articles are left in the bath between 5 and 10 minutes.

It has been found that the action of the alkali metal oxalate bath may in some instances be improved by incorporating therein a quantity of an aluminum oxalate salt, in which case the alu-

minum content of the aluminum oxalate salt should not exceed about 40 per cent by weight of the dissolved alkali metal oxalate. The term "aluminum oxalate salt," as employed herein and in the appended claims, is intended to embrace not only the salt normally referred to as aluminum oxalate and having the composition $\text{Al}_2(\text{C}_2\text{O}_4)_3$, but also the various complex salts which may be formed between aluminum ions and oxalic acid, or between oxalic acid and alkali metal and aluminum ions. I have found it convenient to form the aluminum oxalate salt and at least part of the necessary alkali metal oxalate by using an alkali metal aluminate, such as sodium or potassium aluminate. The oxalate salts are formed by adding oxalic acid in quantity at least sufficient to clear up any precipitate of aluminum hydroxide which may form on the initial addition of the acid to the alkali metal aluminate solution. The alkali metal aluminates have the added advantage that they do not introduce undesired acid radicals into the solution in which the oxide-coated aluminum is treated. Under proper conditions the amount of alkali metal oxalate formed in this fashion may lie within the desired range of 1 to 20 per cent by weight mentioned above for the solution used in treating the oxide-coated aluminum. However, if the desired amount of alkali metal oxalate for use of the solution in accordance with this invention is not present, further additions of alkali metal oxalate are made, as will be noted in Examples 2 and 3 below, in an amount sufficient to provide the amount of alkali metal oxalate desired and the proper pH for the solution. Sodium or potassium hydroxide may also be used in adjusting the pH of the solution to the proper range. In any case the aluminum content of the aluminum oxalate salt in solution in the bath should not exceed about 40 per cent by weight of the dissolved alkali metal oxalate which has been formed in, or added to, the bath.

It may be desirable in some instances to immerse briefly in a dilute sulfuric acid bath those articles which have been treated in the oxalate bath and which thereafter are to be colored in a dye bath having a pH greater than about 6.5. The concentration of sulfuric acid in this solution may vary from about 5 to 25 per cent, though a bath containing about 15 per cent sulfuric acid is generally employed. This bath is maintained at room temperature. The aluminum articles, on coming from the oxalate bath, are rinsed in water, immersed in the sulfuric acid bath, again rinsed, and thereafter dyed. The effect of this immersion in the sulfuric acid is to reduce the time it is necessary to leave the article in the dye solution to obtain a given intensity of color.

The introduction of the alkali metal oxalate immersion step does not interfere with the beneficial results obtained by sealing dyed surfaces in any of the various ways known in the art.

To illustrate the manner in which this invention finds application, the following examples will be given.

Example 1

The bath was prepared by dissolving 25 grams of potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) in warm water. Oxalic acid was added until the pH of the solution was reduced to about 6.2. The volume of the solution was then made up to 1 liter by the addition of water. The bath was maintained at a temperature of about 130° F. Several of a group of aluminum sand castings which had been provided with an oxide coating by anodic

treatment in a sulfuric acid electrolyte containing about 15 per cent sulfuric acid, and which thereafter had been thoroughly washed in water, were then immersed in the oxalate bath for a period of about 8 minutes. They were then removed from the bath and again thoroughly washed in water, following which they were immersed for a period of 2 or 3 seconds in an aqueous bath containing about 15 per cent sulfuric acid. After removal from the sulfuric acid bath, the articles were washed and immersed in an organic, lake-forming dye solution. For comparative purposes another portion of the same group of castings was dyed in the same dye solution, but without intermediate treatment in the alkali metal oxalate bath or in the sulfuric acid solution. Inspection following the dyeing step disclosed that those castings which had not been treated in the alkali metal oxalate bath exhibited considerable spotting, which increased with time, while those castings which were treated in the oxalate bath never exhibited any spotting.

Example 2

A test similar to that described in Example 1 was run on another group of anodically coated aluminum sand castings, but in this case a bath containing alkali metal oxalate and an aluminum oxalate salt was employed. The bath was prepared by first dissolving 5 grams sodium aluminate (commercial grade), and then adding about 12 grams of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). This resulted in a clear solution free of any visible precipitate. Potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) to the amount of 11.2 grams was then dissolved in the bath, which resulted in a solution having a pH of about 6.2. The total volume of the solution was then made up to 1 liter by the addition of water. When sodium aluminate of reagent quality is employed in preparing the solution, about 14 grams potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) are required in order to attain this pH. This quantity of potassium oxalate corresponds to about 12.6 grams of the anhydrous salt. The employment of this bath in the fashion described in Example 1 resulted in the complete elimination of all spotting and uneven coloring of the dyed aluminum surfaces.

Other baths were prepared containing the same weight of the various solute components, but variously containing from 100 to 1500 cc. of water. These baths all proved as successful for the purposes of this invention as did that described in the preceding paragraph.

Example 3

The first bath described in Example 2 was employed in the treatment of a group of anodically coated wrought aluminum articles which had been provided about their periphery with a tightly rolled bead. The immersion procedure outlined in Example 1 was again followed in making this test. Similar articles were also treated in this same fashion but omitting the steps of immersion in the oxalate and sulfuric acid baths. Those articles which had not been immersed in the oxalate bath were unevenly colored along the surfaces adjacent the open end of the bead, whereas those articles which had been immersed in the alkali metal bath exhibited a uniform color over the entire surface.

The weights and percentages employed herein and in the appended claims are expressed in terms of the anhydrous salt unless otherwise indicated.

I claim:

1. The method of uniformly coloring an aluminum article having an oxide coating anodically produced in strong acid electrolyte, said coating containing entrapped acid electrolyte, comprising immersing said article in an aqueous bath containing as a predominant component about 1 to 20 per cent by weight of dissolved alkali metal oxalate, said bath being at a pH of about 4.5 to 8, and at a temperature of about 100 to 200° F., whereby irregular coloring and spotting of the coating by the subsequent coloring step is prevented, and thereafter immersing said article in a coloring solution.

2. The method of uniformly coloring an aluminum article having an oxide coating anodically produced in strong acid electrolyte, said coating containing entrapped acid electrolyte, comprising immersing said article in an aqueous bath containing in solution as a predominant component a total of about 2.0 to 5.0 per cent by weight of at least one salt selected from the group consisting of ammonium oxalate, sodium oxalate, and potassium oxalate, said bath being at a pH of about 6 to 6.5, and at a temperature of about 120 to 150° F., whereby irregular coloring and spotting of the coating by the subsequent coloring step is prevented, and thereafter immersing said article in a coloring solution.

3. The method of uniformly coloring an aluminum article having an oxide coating anodically

produced in strong acid electrolyte, said coating containing entrapped acid electrolyte, comprising immersing said article in an aqueous bath containing as a predominant component about 1 to 20 per cent by weight of dissolved alkali metal oxalate, together with an aluminum oxalate salt, the aluminum content of which does not exceed about 40 per cent by weight of the alkali metal oxalate dissolved in the bath, said bath being at a pH of about 4.5 to 8, and at a temperature of about 100 to 200° F., whereby irregular coloring and spotting of the coating by the subsequent coloring step is prevented, and thereafter immersing said article in a coloring solution.

4. The method of uniformly coloring an aluminum article having an oxide coating anodically produced in strong acid electrolyte, said coating containing entrapped acid electrolyte, comprising immersing said article in an aqueous bath containing by weight in solution as predominant components about 5 parts alkali metal aluminate of commercial grade, about 12 parts oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), about 11.2 parts potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$), and about 100 to 1500 parts water, said bath being at a pH of about 6 to 6.5 and at a temperature of about 120 to 150° F., whereby irregular coloring and spotting of the coating by the subsequent coloring step is prevented, and thereafter immersing said article in a coloring solution.

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