A solution for imparting tarnish resistance on aluminium surfaces and method for applying it.

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References cited:
CORROSION, vol. 18, no. 4, April 1962, pages 143—153 D.G. ALTENPOHL: "Use of Boehmite Films for Corrosion Protection of Aluminium"
A solution for imparting tarnish resistance on aluminium surfaces and method for applying it.

This invention relates to a solution for imparting tarnish resistance on aluminium surfaces during exposure to hot water baths. This invention relates further to a method of treating an aluminium surface to impart tarnish resistance thereto.

As is known, when metal surfaces are exposed to hot aqueous solutions, especially aluminium surfaces, for extended periods of time there is a marked tendency for such surfaces to tarnish to a brown or black coloration. Apparently, this coloration is a refractive effect of the light as it passes through amorphous platelets of generally hydrated aluminium oxides that deposit and build up on the surface of the metal. This problem becomes acute in certain industries. For example, it has been the general practice in breweries to pasteurize alcoholic beverages such as ale, stout and beer in metal containers and this is generally done by subjecting the cans to hot water baths or sprays in the range of 60 to 77°C (140°F to 170°F). In subjecting metal containers to hot water there is a marked tendency for the metal surface, especially aluminium, to stain upon exposure and this is especially noted on the bottom portions of the containers. In practice, the severest problem of staining or discoloration is encountered during pasteurizing of the package as no organic coating is applied to the container bottom to protect it from corrosion and if left untreated, it will discolor during pasteurization, turning brownish. While seemingly this effect does not harm the contents thereof, it makes the product unappealing in its appearance to the consumer. Heretofore it has been a practice in the art to apply a so-called conversion coating to metal containers in order to suppress or passivate such metal and to prevent tarnishing as well as to promote the adhesion of inner lacquers and outer coatings of ink, paints and the like.

Various corrosion inhibitors have been used commercially such as inorganic ions including chromates and phosphates and are referred to as conversion coatings. Generally, the surface to be treated is subjected to an aqueous solution containing such ions. It is believed that these inorganic ions or heavy metal ions have the ability to bond or adhere in the form of insoluble oxides which resist tarnishing and corrosion of the metal surface. In general, the conversion coating solution is prepared and sprayed at some elevated temperature for a short period of time. After treating the metal surface with the solution, the surface is thoroughly rinsed with water to remove unreacted coating solution. However, in spite of the advantages of these corrosion inhibiting solutions, these inorganic ions have come under increasing scrutiny by environmental groups and governmental agencies with the result that there has been an increasing demand for compositions that do not have these detrimental heavy metal ions.

It is accordingly the object of the present invention to provide a solution and method that offers stain and tarnish resistance to aluminium surfaces, the solution having absent therefrom any heavy metal ions.

This solution should be free of toxic materials and be capable of forming on an aluminium surface a uniformly clear and colorless coating. Moreover, this solution should be in the position to protect surfaces of aluminium from blackening or other discoloration when exposed to hot or boiling water, especially during pasteurization processes associated with aluminium containers.

This object of the present invention is achieved by a solution for imparting tarnish resistance on aluminium surfaces during exposure to hot water baths which is characterized by containing 0.01 to 10 weight percent of a water-soluble portion containing 10 to 95 weight percent of an alkali metal silicate and 5 to 90 weight percent of an organic polymer selected from the group consisting of copolymers of acrylic acid and acrylonitrile-acrylic acid copolymer, suitable for use as a binder for paints, tarnishes and the like. However, the composition of this reference is formed by heating a solution of the alkali silicate with a particular copolymer to form a reaction product, the product being referred to as an acrylic-silicate binder. In contrast to this, the copolymer and alkali silicates constituents of the inventive solution are separate components and exist independently from one another.

"TENSIDE-TEXTILHILFSMITTEL-WASCHROHSTOFFE", K. Linder, Vol. III, 1971 — Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart — comprises a general information on anti-corrosion agents for aluminium surfaces. Aside from this general information, no clear teaching as to the specific tarnishing problems contemplated by the present invention and the specific composition of a treating solution to render aluminium surfaces tarnish and corrosion resistant can be taken from this reference.
The inventive solution for surface treating a metal to render the surface thereof tarnish and corrosion resistant contains an alkali metal silicate and a water-soluble organic polymer having displacable hydrogens or displaced hydrogens.

Metal surfaces treated by the solution and the process of this invention remain stain and corrosion resistant over a long period of time and do not have to be further treated or coated. Furthermore, the solutions do not present toxic materials and do not have any disposal problems. Thus, the solutions are free of chromium ions and of the chromium subgroup of the Periodic Table and also materials such as ferricyanide and ferrocyanide.

The particular group of silicates that have been found to be effective herein are those aqueous silicates such as sodium, potassium or lithium, or mixtures of such silicates. These silicates are known generally as water glasses and are usually aqueous solutions containing numerous varieties of alkali metal silicates, e.g.,

\[
\begin{align*}
&\text{M}_2\text{O-SiO}_2; \quad \text{M}_2\text{O-2SiO}_2; \quad \text{M}_2\text{O-3SiO}_2; \quad \text{M}_2\text{O-4SiO}_2; \quad \text{M}_2\text{O-5SiO}_2
\end{align*}
\]

and may be represented generally as

\[
\begin{array}{c}
\text{O}^{-M^+} \\
\text{Si} \\
\text{O}^{-M^+}
\end{array}
\]

where \( M \) is sodium, potassium or lithium and \( x \) is an integer, generally between 1 and 10.

In general these aqueous silicate solutions have a specific gravity range from about 1.3 to about 1.6 and comprise about 23 to about 48 percent by weight of the alkali metal silicate. Effective silico to metal oxide weight ratios range from about 1.87 to about 10.0.

The useful organic polymers of the inventive solutions are organic, polymeric substances having displacable or displaced hydrogens and are generally derived by polymerization of at least one monoolefinic compound through an aliphatic unsaturated group to yield a water-soluble synthetic polymer having a structure substantially free of cross-linkage. In general, the polymers herein are those water-soluble polymers having a linear polymeric structure of carbon or carbon with some other atom such as oxygen and contain in a pendant side chain a hydrophilic group from the class consisting of hydroxyl, carboxylic acids, carboxylic acid amides, sulfonic acids and phosphoric acids. It will be appreciated that in its broadest aspect the aforementioned polymers fall into two classes, (1) those consisting of polymeric organic substances which in an aqueous medium will form organic anions having a substantial number of negative charges distributed at a multiplicity of positions on the polymer, and (2) those consisting of polymeric organic substances which in an aqueous medium will not form ions but nonetheless contain a sufficient number of hydrophilic groups to be water-soluble.

The first class of polymers may be referred to as anionic organic polymers and the second class may be called non-ionic organic polymers.

Very small concentrations of the ingredients herein defined have been found effective for improving the corrosion resistance. The synthetic organic polymers containing only carboxylic acid, sulfonic acid, phosphoric acid, as well as the salts thereof in a side chain are anionic and those that contain hydroxy and carboxylic acid amide in the side chain are non-ionic. Natural carbohydrates have been found effective herein and included the highly branched polymers of acacia gum. The invention herein contemplates polymers that contain either the anionic or non-ionic groups as well as mixtures thereof.

The inventive solutions may be readily formulated in an aqueous media. The organic and inorganic ingredients may be mixed in any order into water. Preferably, the solutions are prepared by mixing the components in a given amount of water with constant stirring within ambient temperatures until the ingredients go fully into solution.

The preferred range for both the alkali metal silicates and soluble polymers is 0.05 to 5 weight percent. At its most preferred embodiment a mixture of the alkali metal silicate and soluble polymer is present at about 3 weight percent based on the total weight of the solution. Lower concentrations do not produce an appreciable improvement in corrosion characteristics, and higher concentrations do not increase these characteristics, generally, any further. To the inventive solutions may be readily added other various ingredients that are compatible with the system. Such ingredients include wetting agents, dyes, pigments and germicides. The inventive solutions may be readily applied by various conventional means known to the art and including dipping, spraying, immersion, and roll-on techniques. It is believed that the compositions herein can be readily applied most economically and effectively by spraying.

The following tabulation gives Examples comprising compositions as defined herein that were prepared with the amount indicated in grams per liter for the ingredients. To each of Examples 8—20
were added about 0.01 grams of a commercial wetting agent, Triton X—100*. Each formulation was placed in contact with an aluminum coupon for about two (2) minutes, at the temperature indicated and thereafter rinsed and dried. The thus-treated coupons were thereafter submerged for fifteen (15) minutes at about 75°C, in a standard solution comprising an aqueous solution of 220 ppm NaHCO₃ and 83 ppm NaCl. The processing conditions of temperature, contact time, and contact method are interdependent. In general, application of the inventive solutions is conventionally by spray technique and, considering normal plant operations, the temperature of the solution will normally be from 30 to 90°C, preferably about 35 to about 60°C, and the contact time will be between about 15 and 90 seconds and usually less than 70 seconds. Two commercial formulations were also tested as indicated in the table. The ratings in the respective columns represent the amount of discoloration for each example.

It will be appreciated that it has been found in accordance with the present invention that aqueous coating solutions containing an alkali metal silicate and a water-soluble organic polymer of the anionic, non-ionic type or mixtures thereof are effective in protecting aluminum surfaces. The corrosion resistant properties of the coating formed by applications of such solutions include the ability of the coating to withstand blackening or other discoloration when subjected to boiling water for a period of time of at least two minutes or longer.

The particular solutions of the present invention can be used to protect pure aluminum or alloys of aluminum, for example, aluminum alloys containing minor amounts of metals such as, for example, magnesium, manganese, copper and silicon. Presently, two of the most common alloys used in the aluminum container industry are aluminum alloys 3003 and 3004.

After the coating compositions are applied the surfaces may be dried by conventional means such as an oven having forced circulation of hot air. After the coating has dried it can be readily subjected to lacquering or to decorative operations which can include applying to the surfaces inks, paints or other resin coating. With the methods and compositions of this invention very excellent adhesion of these decorative finishes is realized.

A large number of water-soluble polymers of both the anionic and non-ionic type may be readily employed. Illustrative of the non-ionic polymers are poly(vinyl alcohol), poly(acrylamide) and a number of organic polymeric coagulants of vegetable and cellulosic origin including Gum Arabic. Illustrative of the anionic types are copolymers of acrylic acid, methacrylic acid, methyl methacrylate, methacrylic acid and derivatives thereof, poly(acrylic acid), copolymers of maleic anhydride and methylvinyl ether, poly(styrene sulfonic acid), sodium poly(acrylate), sodium poly(methacrylate), poly(itaconicco-vinyl acetate) and the like.

*Triton X—100 is acknowledged as trademark
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Rating:  
A: Bright  
B: Loss of lustre  
C: Light brown  
D: Distinct brown
Claims

1. A solution for imparting tarnish resistance on aluminum surfaces during exposure to hot water baths, characterized by containing 0.01 to 10 weight percent of a water-soluble portion containing 10 to 95 weight percent of an alkali metal silicate and 5 to 90 weight percent of an organic polymer selected from the group consisting of copolymers of acrylic acid and acrylic acid derivatives, poly(vinyl alcohol), poly(acrylic acid), poly(acrylamide), copolymers of maleic anhydride and methylvinyl ether, and poly(styrene sulfonic acid), and 90 to 99.99 weight percent water.

2. The solution of Claim 1 wherein the alkali metal silicate is sodium silicate.

3. The solution of Claim 1 wherein the solution comprises 0.01 to 5 weight percent of the water-soluble portion and 95 to 99.99 weight percent water.

4. The solution of Claim 1 wherein the alkali metal silicate is present in an amount between 60 and 70 weight percent and the organic polymer is in the amount between 30 and 40 weight percent of the water-soluble portion.

5. The solution of Claim 1 wherein the organic polymer is a copolymer of acrylic acid and acrylic acid derivatives.

6. A method of treating an aluminum surface to impart tarnish resistance thereto, characterized by the steps of contacting said surface with a solution comprising 0.01 to 10 weight percent of a water-soluble portion containing 10 to 95 weight percent of an alkali metal silicate and 5 to 90 weight percent of an organic polymer selected from the group consisting of copolymers of acrylic acid and acrylic acid derivatives, poly(vinyl alcohol), poly(acrylic acid), poly(acrylamide), copolymers of maleic anhydride and methylvinyl ether, and poly(styrene sulfonic acid), and 90 to 99.99 weight percent water.

7. The method as recited in Claim 6 wherein the aluminum surface is contacted with the solution for at least 10 seconds at a temperature of at least 40°C.

8. The method as recited in Claim 6 wherein the surface is exposed to the solution of a temperature greater than 60°C.

9. The method as recited in Claim 6 wherein the alkali metal is present in an amount between 60 and 70 weight percent and the organic polymer is present in an amount between 30 and 40 weight percent of the water-soluble portion.

10. The method of Claim 6 wherein the solution comprises 0.01 to 5 weight percent of the water-soluble portion and 95 to 99.99 weight percent water.

11. The method of Claim 6 wherein the solution contacts the surface for about one minute.

12. The method of Claim 6 wherein the contacted aluminum surface is thereafter rinsed.

Patentansprüche


2. Lösung nach Anspruch 1, dadurch gekennzeichnet, daß das Alkalimetallsilicat Natriumsilicat ist.

3. Lösung nach Anspruch 1, dadurch gekennzeichnet, daß die Lösung 0.01 bis 5 Gew.-% wasserlöslichen Teils und 95 bis 99,99 Gew.-% Wasser enthält.

4. Lösung nach Anspruch 1, dadurch gekennzeichnet, daß das Alkalimetallsilicat in einer Menge zwischen 60 und 70 Gew.-% vorhanden ist und daß das organische Polymer in einer Menge zwischen 30 und 40 Gew.-% des wasserlöslichen Teils vorhanden ist.

5. Lösung nach Anspruch 1, dadurch gekennzeichnet, daß das organische Polymer ein Copolymere von Acrylsäure und Acrylsäurederivaten ist.


8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß man die Oberfläche der Lösung mit einer Temperatur von mehr als 60°C aussetzt.

10. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die Lösung 0,01 bis 5 Gew.-% wasserlöslichen Teil und 95 bis 99,99 Gew.-% Wasser enthält.

11. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die Lösung die Oberfläche etwa 1 Minute lang berührt.

12. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß man die in Berührung gebrachte Aluminiumoberfläche danach spüht.

Revendications

1. Solution propre à conférer de la résistance au ternissage à des surfaces d'aluminium alors qu'elles sont exposées à des bains d'eau chaude, caractérisée en ce qu'elle contient 0,01 à 10% en poids d'une fraction soluble dans l'eau contenant 10 à 95% en poids d'un silicate de métal alcalin et 5 à 90% en poids d'un polymère organique choisi dans le groupe qui comprend copolymères d'acide acrylique et de dérivés d'acide acrylique, l'alcool polynylacrylique, l'alcool polynyléthylène, l'acide polynyléthylène, le polyacrylamide, des copolymères d'anhydride maléique et d'éther méthyléthyléthylène et l'acide poly styriène sulfonique, et 90 à 99,99% en poids d'eau.

2. Solution selon la revendication 1, caractérisée en ce que le silicate de métal alcalin est du silicate de sodium.

3. Solution selon la revendication 1, caractérisée en ce qu'elle comprend 0,01 à 5% en poids de la fraction soluble dans l'eau et 95 à 99,99% en poids d'eau.

4. Solution selon la revendication 1, caractérisée en ce que le silicate de métal alcalin est présent à raison d'une quantité comprise entre 60 et 70% en poids et le polymère organique est présent à raison d'une quantité comprise entre 30 et 40% en poids de la fraction soluble dans l'eau.

5. Solution selon la revendication 1, caractérisée en ce que le polymère organique est un copolymère d'acide acrylique et le dérivé d'acide acrylique.

6. Procédé de traitement d'une surface d'aluminium pour conférer à celle-ci de la résistance au ternissage, caractérisé par les étapes de mise en contact de cette surface avec une solution comprenant 0,01 à 10% en poids d'une fraction soluble dans l'eau contenant 10 à 95% en poids d'un silicate de métal alcalin et 5 à 90% en poids d'un polymère organique choisi dans le groupe qui comprend des polymères d'acide acrylique et des dérivés d'acide acrylique, l'alcool polynyléthylène, l'acide polynyléthylène, le polyacrylamide, des copolymères d'anhydride maléique et d'éther méthyléthyléthylène et l'acide poly styriène sulfonique, et 90 à 99,99% en poids d'eau.

7. Procédé selon la revendication 6, caractérisé en ce que la surface d'aluminium est mise en contact avec la solution pendant au moins 10 secondes à une température d'eau moins 40°C.

8. Procédé selon la revendication 6, caractérisé en ce que la surface est exposée à la solution à une température supérieure à 60°C.

9. Procédé selon la revendication 6, caractérisé en ce que le silicate de métal alcalin est présent à raison d'une quantité comprise entre 60 et 70% en poids et le polymère organique est présent à raison d'une quantité comprise entre 30 et 40% en poids de la fraction soluble dans l'eau.

10. Procédé selon la revendication 6, caractérisé en ce que la solution comprend 0,01 à 5% en poids de la fraction soluble dans l'eau et 95 à 99,99% en poids d'eau.

11. Procédé selon la revendication 6, caractérisé en ce que la solution est en contact avec la surface pendant environ une minute.

12. Procédé selon la revendication 6, caractérisé en ce qu'après avoir été mise en contact avec la solution, la surface d'aluminium est rincée.