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METHOD FOR COATING ALUMINUM

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This invention relates to an improved method for coating aluminum and more particularly relates to a continuous 4-step process which employs an improved aqueous acidic cleaner as its first stage for conditioning the surface of the aluminum to receive an integral chemical conversion coating.

Heretofore, in commercial installations for cleaning and providing aluminum with chemical conversion coatings such as chromates, chromate-phosphates, chromate-oxides, or mixed chromate-phosphate oxides or the like, it has been customary to employ a 5-stage or 6-stage process. Such a process includes an alkali cleaner stage, a water rinse, a de-smutter stage followed by a water rinse, a chemical conversion coating stage and a final rinse. The final rinse may be either water or dilute chromic acid and when chromic acid is used, it is sometimes preceded by an intermediate water rinse following the conversion coating stage. In such processes, it has been found that the conventional alkali cleaners are incapable of removing surface oxide films or other films resulting from preliminary deformation of the aluminum in for example, extrusions or rolling operations, to satisfactorily prepare the surface for receiving the chemical conversion coating. Such difficulties have been encountered, particularly with aluminum alloy compositions such as the 3,000 series and 6,000 series where the aluminum alloy has been extruded into final form for use as windows, door jambs and the like.

In accordance with this invention, it has been found that the 4 stages prior to the chemical conversion coating stage can be satisfactorily replaced by two stages when the cleaning is accomplished by an aqueous acidic solution, rather than an alkaline cleaning solution. In a preferred form, the aqueous acidic cleaning solution is one which is capable of etching the contaminated aluminum surface sufficiently to make it receptive to the chemical conversion coating, and simultaneously is capable of forming a protective coating on the surfaces of a mild steel tank to enable continuous processing of aluminum therethrough. Briefly stated, therefore, the improved process of this invention comprises the steps of contacting the aluminum surface to be coated with an aqueous acidic cleaning solution, rinsing, forming on the cleaned and rinsed surface the desired chemical conversion coating and thereafter rinsing the chemical conversion coated surface, with water or dilute chromic acid solution or the like.

In accordance with this invention it has been found that satisfactory cleaning and surface preparation of aluminum for receiving a chemical conversion coating is obtained by the use of an aqueous acidic phosphate solution containing controlled quantities of the fluoride ion and the hydrogen ion. The controlled quantities of fluoride and hydrogen ion function jointly to maintain the ability of the cleaning solution to etch the aluminum surface at a controllable and substantially constant rate and concurrently permit the use of a mild steel tank surface. The aqueous acidic solutions of this invention appropriately may be characterized as buffered solutions, which buffering resists change in acidity of the solution during its continuous use. In those installations in which the aqueous acidic cleaning solution tank is mild steel, the preferred solution is one which contains the phosphate of zinc, iron

or manganese, and preferably is zinc phosphate, the solution having a pH within the range of about 1.8 to about 3.2. It has been found in the use of such zinc phosphate solutions that the steel tank lining receives an adherent phosphate coating which becomes sufficiently continuous to substantially stop any further reaction between the steel lining and the aqueous acidic cleaning composition and thus enables the continuous use of the cleaning solution for aluminum surface cleaning without destroying the tank lining or losing its necessary hydrogen ion concentration to enable satisfactory aluminum surface cleaning. In those installations in which the alkali metal phosphate are employed, the pH should be maintained in the same range as that above stated, namely about 1.8 to about 3.2, but in this case, it is necessary to employ a stainless steel tank for the alkali metal cleaning solution. In this case, the cleaning solution is buffered by the simultaneous presence of a mixture of alkali metal phosphates and phosphoric acid.

The fluoride ion should be present in the aqueous acidic cleaning solutions of this invention in an amount sufficient to form AlF_x, where x equals at least about 1.1–1.2, and preferably is present in an amount of at least about 0.02% in excess of AlF (1.1–1.2). When these ratio quantities are present, the cleaning solution exhibits a satisfactory and controllable rate of aluminum surface etching, but as the concentration of fluoride increases, the rate of etching both increases and becomes less controllable. Moreover, with increasing fluoride ion concentrations, introduced as HF, the cleaning solution achieves an ability to attack the tank lining and in the case of a mild steel tank quantites of fluoride in excess of AlF (1.1–1.2) in amounts above about 0.05%–0.1% cause difficulty, whereas with stainless steel tank linings concentrations of active fluoride in excess of AlF (1.1–1.2) of about 0.2%–0.3% are similarly undesirable.

The fluoride ion may be provided in the aqueous acidic cleaning solutions of this invention as HF, fluoboric acid, or fluosilicic acid and since equal quantities of fluoboric and fluosilicic acids provide less fluoride ion activity in the solution than HF supplies, the concentration of fluoboric and fluosilic may be substantially greater than that given above for HF, e.g. fluoboric may be present in concentrations of 2–3 times that of HF, while fluosilicic may be present in concentrations of 2–2½ times that of HF.

The phosphate ion may be provided at least partially as phosphoric acid and partially as the salt of one of the metal ions zinc, iron or manganese, or one of the alkali metal ions, sodium, potassium or ammonium. The PO_4 ion concentration may satisfactorily extend upwardly from about 0.10% as a minimum. There is nothing critical about the upper concentration to which the PO_4 ion may extend, but for practical purposes concentrations in excess of 2%–3% PO_4 provide no additional benefit. The concentration of the selected metal ion, or the metallic phosphate salt is preferably such as to provide sufficient metallic ion to form a phosphate salt with all of the PO_4 ion which is present, to thus produce a solution having a pH within the above stated range. The zinc, iron or manganese ions may be used in any installation which employs a mild steel tank for the aqueous acidic cleaning solution and in this case zinc is the preferred metal ion for this purpose.

It has been found that the rate of cleaning is improved, in certain instances, and that in other instances difficult to remove surface coatings on the aluminum to be cleaned are more effectively removed when the cleaning solution includes an oxidizing agent. For this purpose, the nitrate ion represents the preferred oxidizing agent, but it is satisfactory to employ other conventional oxidizing agents such as chlorate, bromate, peroxide, sulfite and the like. For this purpose, quantities of oxidizing agents in the

range of about 0.01% to 1% nitrate, or its equivalent is satisfactory. It is understood that the cleaning solutions of this invention operate satisfactorily on the wide variety of aluminum materials without the presence in the solution of an oxidizing agent and that such solutions containing zinc as the metal ion and an oxidizing agent constitute a preferred form of this invention which have been found to be particularly advantageous for use with certain aluminum alloys such as 6061, 6062, etc.

For cleaning aluminum surfaces which are greasy, oily, or have other hydrocarbon deposits on their surfaces, it is advantageous to incorporate in the cleaning solution a compatible surface active agent. For this purpose, suitable surface active agents include the non-ionic types such as polyethylene or polypropylene glycols, polyether alcohols, and substituted polyglycol esters, and the anionic types such as sulfonated hydrocarbons and fatty alcohol sulfates. The preferred wetting agents for this purpose are the substituted polyglycol esters and derivatives of polyethylene glycols and polyether alcohols sold under the trade name of "Igepal" (Allied Chemical and Dye Corporation), particularly Igepal CA 630 or Igepal CA 630 and those sold under the trade name "Triton" (Rohm & Haas Co.) and particularly Triton X–100.

Cleaning solutions of this invention may be applied to the aluminum surface to be cleaned by spraying or dipping the aluminum part into the tank containing the cleaning solution. The cleaning solution may be suitably maintained at a temperature in the range of about 90° F. to the boiling point of the solution in the absence of a surface active agent in the solution. In those solutions which contain a non-ionic surface active agent and which are to be applied by spraying, the temperature of the solution should be slightly above the cloud point temperature for the particular surface active agent which is present. In these cases, it has been found that the maintenance of a temperature which as a minimum is the cloud point temperature, causes a small quantity of the surface active agent to be precipitated during spraying and this precipitate functions as an anti-foaming agent to thereby permit spray application without excess foaming. Where the surface active agent is an anionic type and the cleaning solution is to be applied by spraying, it may be necessary to add an anti-foaming agent of conventional type.

The chemical conversion coating which may be formed on the aluminum surface cleaned with the above described aqueous acidic cleaning solution is any of the conversion coatings which are now conventional and well understood by those skilled in this art. Such conversion coatings include those which result from the application of hexavalent chromium-containing aqueous solutions which may include a reducing agent in the solution as applied or function to reduce the hexavalent chromium compound in situ on the surface, chromate phosphate solutions, chromate-fluoride, chromate-film forming resin solutions and the like. Typically suitable solutions for the formation of such conversion coatings are disclosed in Bell U.S. Patent 2,902,390, issued Sept. 1, 1959, Schuster et al. U.S. Patents 2,768,103 and 2,768,104, issued Oct. 23, 1956, and Schuster U.S. Patents 2,911,332, issued Nov. 3, 1959, and 3,094,435, issued June 18, 1963. Such conversion coating forming solutions are typically applied by spraying or dipping the part to be coated in the solution at room to elevated temperatures as high as about 180° F., preferably room to 130° F. The applied solution may be dried on the surface with air or the application of heat in the form of infra-red rays, hot air or the like, and the coating is then in condition for rinsing in water or dilute hexavalent chromium-containing aqueous solutions of conventional type. For certain applications, it is desirable to employ deionized water or to employ a water rinse and thereafter a final dilute aqueous chromic acid rinse of conventional strength such as about 0.2 to 2 grams per liter of CrO_3.

The below given examples are intended to illustrate the process of this invention in somewhat greater detail but it is to be understood that the specific materials, concentrations thereof, and application conditions contained therein are given for illustrative purposes only and do not define the limits of this invention which have been set forth hereinabove.

EXAMPLE I

A solution was prepared containing 0.02% zinc, 0.28% PO_4 and 0.02% fluoride as HF. This solution gave a free acid based on 10 ml. sample titrated against 0.1 normal sodium hydroxide of 0.6 point, using bromcresol green as the indicator, and a total acid of 4.6 points, using phenolphthalein as the indicator. The pH was 2.90.

The above solution was installed in a continuous monorail line 4-stage installation for cleaning and coating aluminum extrusions for use as window stock. The extrusions were 6061 aluminum and after extrusion had soil on their surface comprising dirt, grease, fingerprints and varying quantities of aluminum oxides of unidentified constituency. The extrusions were spray-cleaned with the above described cleaning solution maintained at a temperature of about 140° F.–160° F. in a contact time of about 45 seconds-1 minute.

After cleaning, the surfaces were hot water rinsed and thereafter spray coated with a chemical conversion coating solution having the following analysis:

	Percent
CrO_3	0.35
F ion (as HF)	.26
Al	0.12
Cr^{3+}	0.06
Fe^{3+}	0.03
$Fe(CN)_6^{+++}$	0.05

This solution was applied at a temperature of about 100° F. by spraying with an average contact time of about 30 seconds.

Prior to cleaning the aluminum extrusions, they had a grayish to irridescent film containing fingerprints and spaced grease spots thereover and subsequent to the cleaning were changed to a normal appearing uniform gray aluminum surface color. After the chromate conversion coating and subsequent rinsing step, the extrusions had a light brown film of substantial uniformity over their entire surface. The coated extrusions were then dried in an oven at a temperature of about 225° F. for about one minute and withdrawn, at which time the coatings had changed to a darker brown color.

The same extrusions would not coat satisfactorily in the above chemical conversion coating solution when cleaned by standard methods, alkali cleaners based on one or more of the following materials—caustic soda, soda ash, polyphosphates, phosphates, and silicates. Any coating obtained was loose and smudgy. When the pH of the acid cleaner was increased above 3.2, the conversion coatings became irregular and at a pH of about 3.4 very little conversion coating with poor adhesion was obtained. In the fringe area of higher pH, the cleaner was definitely improved by addition of NO_3 ion. Surface active agents aid in the removal of soils in the form of oils or loose insoluble smut.

When the fluoride was increased to 0.15%, the mild steel housing and spray risers were severely etched in the direct path of the forced stream of cleaner solution. The mild steel pump impeller and shaft were also pickled.

What is claimed is:

1. A process for coating aluminum which consists essentially of the steps of contacting a surface of aluminum with an aqueous acidic cleaning solution consisting essentially of the phosphate ion, the fluoride ion and a metal ion selected from the group consisting of zinc, manganese, and iron, said solution having a pH in the range of about 1.8 to about 3.2, the phosphate ions being present in an amount of at least 0.1% by weight, the metal ion being present in an amount at least sufficient to form the phos-

phate salt with the phosphate ions present and the fluoride ions being equivalent to an amount, which when added as HF is from about 0.02 to 0.3% by weight in excess of that required to form AlF_x, where x is 1.1 to 1.2, with the aluminum introduced into the solution by the work being treated, maintaining said solution in contact with the aluminum surface for a time sufficient to effect cleaning thereof, water rinsing the surface, thereafter forming a chromate chemical conversion coating on said rinsed surface.

2. The process as claimed in claim 1 wherein the cleaning solution also contains an oxidizing agent and wherein after the formation of the chromate chemical conversion coating on the water-rinsed surface, the coated surface is rinsed with a solution selected from the group consisting of water and dilute aqueous hexavalent chromium-containing solutions.

3. A process in accordance with claim 2 wherein said oxidizing agent is nitrate.

4. The process as claimed in claim 2 wherein the cleaning solution also contains a surface active agent which is compatible with the cleaning solution.

5. A process in accordance with claim 4 wherein said surface active agent is iso-octyl phenoxy polyoxyethylene ethanol in which the polyoxyethylene represents 8–10 oxyethylene groups in the molecule.

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