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(54) **Method for inhibiting stains on aluminum product surfaces**

(57) A method for inhibiting the formation of stains,
especially water stains, on the exterior surfaces of alu-
minum alloy products. The method entails contacting
the exterior surfaces of these products, particularly
sheet or plate products, extrusions and/or forgings
made from 5000 or 6000 Series aluminum alloys, with
an organophosphonic or organophosphinic acid-de-

rived material. Preferably, liquid forms of this material
are added to an alcohol or water-based carrier solution,
then sprayed, dipped, painted or rolled onto the surfaces
of flat sheet or plate products to enhance their bright-
ness. Other more complex shapes may be dipped into
material baths.

Description

[0001] Water stains do not generally present problems for the structural properties and/or corrosion performance of an aluminum product. Aluminum surface discolorations that accompany water staining may discomfort some customers who are unfamiliar with the surface and corrosion properties of aluminum. Customers already aware of the properties of cold rolled steel may mistakenly believe that water stains on aluminum are the onset of "rusting", similar to that found on steel. For bright aluminum products, such as buffed trailer plate, rail cars, tool boxes, running boards, and tread plate on fire trucks, stain inhibition would preserve the buffed finish and enhance customer satisfaction. A simple, low-cost solution to inhibit water stain on aluminum could result in a higher degree of customer confidence in replacing steel with aluminum for their products. In addition, aesthetics of these products is important to the end customer. Water stains are aesthetically unattractive and their elimination or reduction would be valuable to the owner whether it be an aluminum trailer, rail car, tool box or other aluminum product.

[0002] Numerous uses for organophosphonic acids in conjunction with aluminum are known. These include U.S. Patent Nos. 4,957,890, 5,032,237, 5,059,258, 5,103,550, 5,124,022, 5,124,289, 5,126,210, 5,132,181, 5,238,715, 5,277,788 and 5,463,804. None of these, however, mention organophosphonic acids for the inhibition of stains, especially water stains, on aluminum surfaces. Most of the aforementioned patents describe aluminum surface pretreatments that enhance the durability of organic coatings or adhesively bonded joints. They do not describe the use of organophosphonics without a topcoat.

[0003] Other methods for inhibiting corrosion with respect to aluminum and other metals are disclosed in U.S. Patent Nos. 3,433,577, 3,672,822 and 4,427,448.

[0004] This invention addresses a low cost method for inhibiting water staining on 5000 Series, or 5XXX, aluminum alloys, most notably 5083-H321 and 5454-H32 aluminum (Aluminum Association designations). Such alloys are used to make rail hopper cars and buffed trailer tanks. Similar surprising and unexpected results have been observed when this method was practiced on 6000 Series aluminum alloys, like the 6061-T6 alloys used to make various products including vehicle wheels. According to this method, it was determined that spraying a solution consisting of about 0.25 wt% octadecylphosphonic acid (or "ODPA") in an isopropanol solvent (or other medium) onto these aluminum alloy products, then allowing the alcohol to evaporate, is effective for inhibiting water staining. Similar effects were subsequently observed with a carrier composition containing octylphosphonic acid (or "OPA"). Suitable liquid carriers include alcohols, ketones, ethers, aldehydes, alkanes, and other organic solvents with sufficient solubility for the organophosphonic acids. These organophosphonic acid-derived solutions can be applied to the metal surface by spraying, dipping, painting, or roll coating. It is also recognized that the stain inhibitor component can be delivered to the aluminum surfaces from various compositions used in the manufacture of aluminum parts, including but not limited to: aqueous suspensions or solutions; metal forming lubricants, and metal cleaning and/or rinsing formulations; a buffing compound or wax that incorporates the stain inhibitor, metal heat treatment quench waters, and/or post-rinsing polishers/sealants or the like. For certain stain inhibitor compounds, it is possible to buff a paste-like stain inhibitor directly onto the aluminum product surface.

[0005] Further features, objectives and advantages of the present invention will be made clearer from the following detailed description made with reference to the drawing in which:

[0006] The FIGURE shows the schematic formation and orientation of hydrolytically stable Al-O-P bonds of the stain inhibitor, octylphosphonic acid (OPA), as a reaction product with an oxidized aluminum surface for effecting the stain inhibition observed according to this invention.

[0007] Preliminary indications of the effectiveness of this invention, for inhibiting stains, were observed in an accelerated corrosion test that involved outgassing products of ethylvinylacetate plastic pellets (obtained from Millennium Petrochemicals), high humidity and temperature cycling. After 12 temperature cycles, no water stains were observed on 5000 Series alloy samples initially etched in caustic, then sprayed with an ODPA-containing solution. Water staining was also inhibited for "mill finish" metal sprayed with ODPA; though some spots were interspersed with unstained surface in the latter case. By contrast, mill-finish and etched-only samples were completely covered with water stains. It is believed that the difference in performance as a result of pre-etching were most likely due to the removal of residual rolling lubricants via etching. In that manner, the stain inhibiting molecules of this invention would be allowed to chemically bond with surface aluminum oxides.

[0008] Chemical reaction of the inhibitor to the surface can also be achieved by changing the means of application or using a different solvent. The surface ODPA inhibits access of water to the aluminum oxide and forms hydrolytically stable bonds with the oxide, thus inhibiting water staining. ODPA is a commercial compound manufactured and sold by Albright & Wilson Ltd. Working solution concentrations and surface coverages of this invention are relatively low, which results in low treatment costs of cents per square foot of Al plate or sheet product. The same would be true for other aluminum product forms, including castings, forgings and extrusions.

[0009] Another potential stain inhibitor, octylphosphonic acid (OPA), was evaluated. It showed even better performance results than the ODPA samplings above. OPA has the following chemical structure: $\text{CH}_3(\text{CH}_2)_7\text{P}(\text{O})(\text{OH})_2$. It can

be applied with a water and surfactant carrier as effectively as with an isopropanol carrier. OPA is more soluble than ODPa in isopropanol thus allowing for increased solution concentrations. And while OPA is not water soluble, it forms a suspension of solids with water. In either case, no volatile organic carbons (or VOC's) result therefrom.

[0010] Preliminary humidity test results show that OPA is highly effective for inhibiting stains on mill finish or buffed aluminum products without cleaning, pickling or pre-etching. After three hours at 50°C (125°F) and 100% relative humidity, the OPA treated surface was unstained, whereas "as-buffed", untreated surfaces were considerably stained.

[0011] It may also be possible to apply certain formulations by the methods of this invention with no carrier solution. For example, one may directly buff a more solid form of OPA onto an aluminum product surface. It is also possible, actually even more practical depending on the aluminum surface to be treated, to incorporate the stain inhibiting compounds of this invention into mill lubricants for providing an *in situ* type of stain inhibition and eliminating subsequent processing steps. It may also be possible to similarly add such stain inhibitors to buffing, sealing and/or polishing compound formulations.

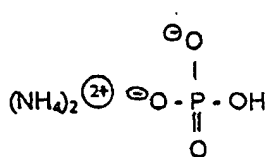
[0012] When the aluminum to be treated is mill finish or "as-buffed", a preferred carrier/solvent is an alcohol, more preferably 2-propanol or isopropanol. Isopropanol is also beneficial in that its solvent action is believed to displace residual mill lubricants or buffing compounds and wet the surface aluminum resulting in the formation of Al-O-P bonds with the oxidized aluminum surface. Isopropanol is also non-toxic. When the aluminum surface has been pre-cleaned or etched, the choice of solvent is not as critical. In many instances, water may be used to transport (or apply) such stain inhibitors.

[0013] In addition to forming hydrolytically stable Al-O-P bonds, organophosphonic acids may provide yet another mechanism for stain inhibition. For example, when OPA or ODPa reacts on the Al surface, the reaction end product is believed to orient or align so that its hydrocarbon chains extend away from said surface. A schematic representation of the bonding that is believed to take place is shown in the accompanying FIGURE. The latter surface takes on a "hydrophobic" or non-wetting quality thereby further inhibiting the conversion of oxides to hydroxides (or effecting a water stain thereon). Under the latter scenario, longer chained organophosphonic acids become the preferred stain inhibitors for this invention.

[0014] In some embodiments of this invention, a full (and not partial or non-uniform) haze on the aluminum product surface may form. It is preferred that such haze be wiped away with a dry cloth to further enhance stain inhibition. On a less preferred basis, this haze may be removed by rinsing the aluminum product's outer surface.

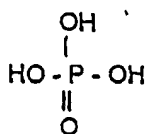
[0015] Certain classes of phosphorus oxo acids, acid esters, and acid salts are effective to various degrees in preventing water stains according to this invention. Phosphate salts, phosphate esters, and phosphonic acids each impart some stain inhibition. In comparative tests, however, octadecylphosphonic (C-18) acid (ODPA) and several fluorophosphonic acids were not as effective as OPA (C-8) in inhibiting stains. Poly(vinylphosphonic acid), and copolymers thereof, may work even better than OPA, but it is currently cost prohibitive to use in commercial quantities. Some of the representative stain inhibitors can be grouped by the following "families":

a) acidic aluminum phosphate salts

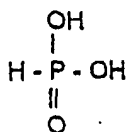


dibasic ammonium phosphate

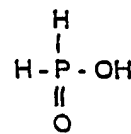
b) inorganic phosphorus oxo acids



phosphoric acid

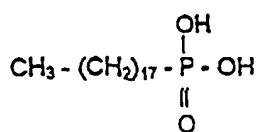


phosphorous acid

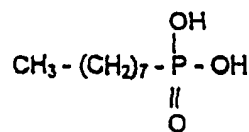


hypophosphorous acid

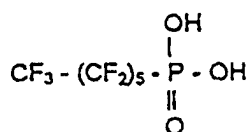
c) organophosphonic and organophosphinic acids



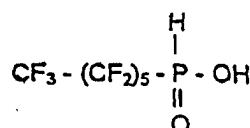
octadecylphosphonic acid (ODPA)



octylphosphonic acid (OPA)



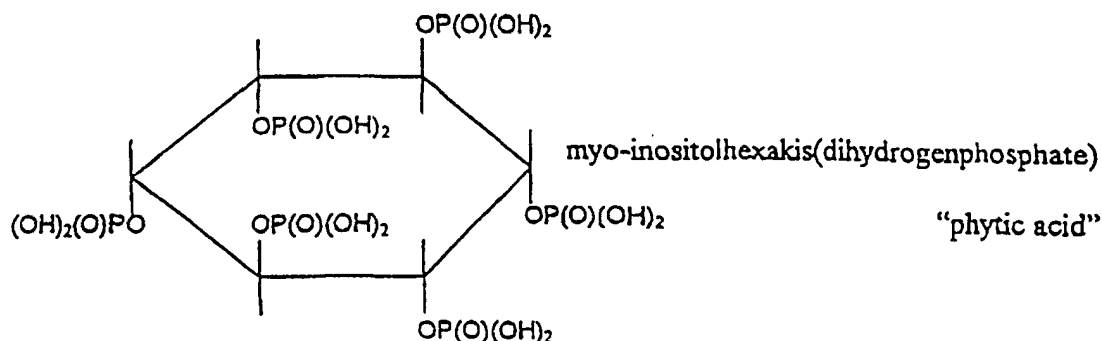
perfluorohexylphosphonic acid



perfluorohexylphosphinic acid

(a component of the FluowetPP® product sold by Hoechst-Celanese)

d) phosphate acid esters



e) organo phosphonic acid polymers and copolymers; and

for example, poly(vinyl phosphonic-co-acrylic acid)

f) phosphate ester polymers

for example, poly(vinyl phosphoric acid)

[0016] This invention can be used to improve the stain inhibition of numerous aluminum alloy surfaces, including various sheet or plate products, extrusions and forgings, regardless of whether such products have welded joints or other connections. It is best suited for any aluminum product that its purchaser, the end user/consumer, would prefer that said product "look good" (i.e. brighter, less stained, etc.) longer! This includes a whole family of building/architectural products, appliances, lighting supplies, and other household cosmetics like vertical blind stock. On a preferred basis, the method of this invention works well with 5000 and 6000 Series alloys (Aluminum Association designation). It should also enhance the stain inhibiting performance of products made from other aluminum alloys, including but not limited to 1000 and 3000 Series alloys.

EXAMPLES:First Study -

[0017] Several sections of buffed trailer tank plate product (made from 5454 aluminum alloy) were sprayed with two comparative stain inhibiting compositions:

Set 1: 0.2 wt% octylphosphonic acid (OPA) in isopropanol; and
Set 2: 0.2 wt% octadecylphosphonic acid (ODPA) in isopropanol.

Haze on both sets of sprayed plates was rinsed away with water, then gently buffed with dry cheesecloth. These treated plates, along with an "as-buffed" control, were then placed in a humidity cabinet at 50°C (125°F) with 100% relative humidity for 3 hours. After exposure, the plates were removed from the cabinet, dried with a towel, and visually examined for staining.

[0018] No noticeable loss of specularly was observed with either of the above stain inhibition treatments. All surfaces had the same visual appearance as the "as-buffed" sample. After humidity exposure, however, brownish colored, water stains were evident over a majority of the "as-buffed" and ODPA-treated surfaces. The OPA treated surface did not exhibit any water stains and appeared the same as unexposed specimens. While ODPA specimens did not fare as well as OPA in this particular study, as compared with its earlier positive results, different application techniques are believed to have caused its reduced stain inhibiting performance here.

Second Study - Tanker Trial results

[0019] A covered hopper trailer, made from 5454 aluminum Bulk Transportation Sheet ("BTS") was treated with various applications according to the invention before being exposed to harsh, in-service conditions: from an aggressive environment of salt air due to seacoast proximity; and harsh winter conditions with numerous road salt applications. Subsections of this hopper/tanker were treated as follows: (a) 1 wt.% solution of OPA, in isopropanol, was sprayed on the first section of tanker, dried to a film, water rinsed and air dried thereafter; (b) the same solution as above was sprayed onto another adjoining section of the same hopper/tanker, then dried to a film and wiped to an initial shine using cheesecloth; (c) for this section of hopper/tanker, the treatment material was 1 wt% OPA, suspended in water. After spraying, this water-based solution was allowed to sit on the product surface for about 10 minutes before being dried and wiped to a shine with cheesecloth. The last comparative section of hopper/tanker was sprayed with a 5 wt. % solution of OPA, in water, before being allowed to sit for 10 minutes, then water rinsed and air dried.

[0020] After three months of service along the U.S. East Coast, this hopper/trailer was brought back for inspection. While OPA treatments were observed to provide a substantial degree of water stain inhibition over that 3 month trial period, one of the first conclusions drawn from that inspection was that monthly reapplications could ensure a pristine, polished surface on such trailer stock.

[0021] Following a wash with non-etching alkaline cleaner, various sides and subsections of this hopper/tanker were photographed and closely compared by visual inspection. From that inspection, it was noted that the water-based sections of treated hopper fared better than their alcohol-based counterparts (in terms of water staining inhibition). In addition, wiping to a shine after application of the OPA, as per example (a) above, was most effective, even more than merely applying, rinsing and air drying, the latter treatment resulting in a noticeable, residual haze at first

Third Study - Coil Line Trial

[0022] A coil of 5182-H19 aluminum sheet was roll coated with a 5% aqueous suspension of OPA. Phosphorus surface concentrations were measured on the treated surface using X-ray fluorescence spectroscopy (XRF). From previous bench scale tests, it was observed that phosphorus surface levels of about 2 Kcps were sufficient for inhibiting water staining. Phosphorus surface levels on the aforementioned sheet product were measured at about 10 Kcps, however.

Fourth Study - Forged Truck Wheels

[0023] Forged and polished truck wheels made from aluminum alloy 6061-T6 were treated with comparative solutions of 0.5 and 1 wt.% OPA in isopropanol. For testing, the treated wheels were placed into a cabinet with condensing humidity set at 100°F. The wheels were examined every hour for water stains. The tests were stopped after 120 hours of humidity exposure. Untreated wheels (as-polished) were substantially stained within 11 hours of humidity exposure. The wheels that were treated with OPA, then buffed to shine lasted the longest without substantial water staining. On

certain OPA-treated wheels, only a few small, widely dispersed spots were observed after 120 hours of exposure testing, but that level of staining was insignificant compared to the gross quantities of water staining observed on the untreated wheels after only 11 hours of humidity exposure.

5 Fifth Study - Lighting Sheet

10 **[0024]** Aluminum alloy 5657-H18, used for making bright lighting sheet, was treated with a 5 wt.% solution of OPA stain inhibitor in isopropanol. Specular reflectance measurements showed that after buffing the resultant haze from said sheet surfaces, the OPA treatment did not reduce reflectivity. Furthermore, such OPA-treated panels lasted up to 13 days in condensing humidity at 100°F without staining, as compared to their untreated sheet equivalents that were significantly stained within 24 hours of such humidity exposure.

Sixth Study - Quench Water Additions

15 **[0025]** Phosphorus compounds, like those described above, were added to the quench waters used for making extruded tubes and rolled sheet from 6061-T6 alloy. In this comparison, the aluminum product forms were heated to about 1000°F before being cold water quenched, said quenching solution containing various phosphorus compounds. Thereafter, these products were allowed to remain in the quench water for 24 hours. By visually examining these aluminum product forms, and by further measuring the amount of hydroxides formed thereon using Fourier-transform
20 infrared spectroscopy (FT-IR), it was determined separately that 10 g/L solutions of dibasic ammonium phosphate - $(\text{NH}_4)_2\text{HPO}_4$ - and 10 g/L phytic acid best prevented the formation of water stains on these products. They also prevented the formation of bayerite powders on the interior aluminum surfaces of these extruded tubes.

25 **Claims**

1. A method for inhibiting formation of stains on an exposed exterior of an aluminum alloy product, said method comprising:
30 contacting the exposed exterior with a material that is capable of forming a hydrolytically stable Al-O-P bond therewith, said material selected from an organophosphonic acid or organophosphonic acid polymer, or copolymer; an acidic aluminum phosphate salt; and inorganic phosphorus oxo acid; an organophosphinic acid; a phosphate acid ester; and an organophosphate acid ester polymer or copolymer, or mixtures thereof.
- 35 2. The method of claim 1, wherein the material consists essentially of an organophosphonic or organophosphinic acid.
3. The method of claim 2, wherein the material is a solid or semi-solid at room temperature and manually applied to the exposed exterior of the aluminum alloy product.
- 40 4. The method of claim 2, wherein the material is a liquid at room temperature and combined with a carrier selected from the group consisting of: an alcohol, a ketone, an ether, an aldehyde, an alkane, water and mixtures thereof.
5. The method of claim 4, wherein the, material consists essentially of octadecylphosphonic acid and the carrier includes isopropanol.
- 45 6. The method of claim 4, wherein the material consists essentially of octylphosphonic acid and the carrier is isopropanol, water or mixtures thereof.
7. The method of claim 4, wherein said exposed exterior is contacted with an aqueous solution containing up to 10
50 wt.% octadecylphosphonic acid or octylphosphonic acid, 5-90 wt.% isopropanol, a balance of water and impurities.
8. The method of claim 4, wherein said exposed exterior is contacted with an aqueous solution containing 0.5-10 wt.% octylphosphonic acid, a balance of water and impurities.
- 55 9. The method of claim 4, wherein said contacting includes: spraying, dipping, painting or rolling material on said exposed exterior of said alloy product.
10. The method of claim 9, wherein said material is incorporated into a composition for surface treating said alloy

product.

11. The method of claim 10, wherein said composition is a mill lubricant, a quenching solution, an intermediate rinse, an etching solution, a solvent, a surfactant, a cleaner, a polish, a post-rinse, a sealant or mixtures thereof.

12. The method of claim 2, wherein said alloy product is sheet product, plate product, an extrusion or a forging.

13. The method of claim 12, wherein said alloy product is:

(a) a sheet or plate product having at least one bright exterior surface and is suitable for making transportation goods therefrom, said goods consisting of trailer plate, rail car skin, tool boxes, vehicle running boards or tread plate;

(b) a sheet product used to make reflective lighting sheet;

(c) an extrusion used to make transportation or household goods therefrom, said goods consisting of: truckbed rails, hydraulic tubing, window frames, tub and shower frames, and greenhouse structural supports; or

(d) a vehicle wheel.

14. The method of claim 1, which further includes rinsing said material from the exposed exterior, and/or wiping said exposed exterior.

15. The method of claim 1, wherein said alloy product is made from a 1000, 3000, 5000 or 6000 Series aluminum alloy (Aluminum Association designations).

16. The method of claim 15, wherein said 5000 Series aluminum alloy is: 5083, 5086, 5454, 5657, 5182, or 5454 aluminum (Aluminum Association designations).

17. The method of claim 15, wherein said 6000 Series aluminum alloy is 6061, 6111 or 6022 aluminum (Aluminum Association designations).

FIG. 1

