

PROCESS FOR SEALING PHOSPHORIC ACID ANODIZED ALUMINUMS

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ORIGIN OF INVENTION

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10 governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

15 This invention relates to a process for depositing a film or coating onto aluminum and its alloys that have been phosphoric acid anodized. The coating system comprises phosphoric acid anodize aluminums, a supplemental post-treatment or seal coating, optimally, an adhesive bond primer or other supplemental coatings. Phosphoric acid anodized aluminum coatings are very porous and therefore have poor inherent corrosion
20 resistance. These coatings do, however, have excellent adhesive properties. Accordingly these anodized coatings would benefit from a post-treatment or seal coating that enhances corrosion protection without adversely affecting the adhesion properties. The performance characteristics of this invention allows the phosphoric acid anodized coatings to be used in unpainted applications which are currently unfeasible; to replace
25 chromic acid anodize aluminum and FPL Etch, both of which contain chromates for corrosion-prone fatigue-sensitive applications; in all adhesive bonding applications where

the transition to non-chromated bond primers is made; and, in general use applications to reduce fatigue debit and coating weight compared to other general use anodize coatings.

This invention relates to a process for treating phosphoric acid anodized aluminum(s) to maintain and improve the corrosion-resistant properties. More specifically, this invention relates to the process of sealing phosphoric acid anodized aluminum and anodized aluminum alloys. The trivalent chromium post-treatment (TCP) process comprises an acidic aqueous solution containing effective amounts of at least one water-soluble trivalent chromium compound, an alkali metal hexafluorozirconate, at least one alkali metal tetrafluoroborate and/or hexafluorosilicate, at least one divalent zinc compound, and effective amounts of water-soluble thickeners and/or water-soluble surfactants.

Anodized aluminum(s) are generally sealed or post-treated after anodizing by processes employing a variety of sealing processes and compositions. Current high-performance post treatments or sealers for anodized aluminum are based on hexavalent chromium chemistry. Hexavalent chromium is highly toxic and a known carcinogen. As a result, the solutions used to deposit these protective coatings and the coating per se are toxic. These films or coatings do, however, yield good adhesion and improved corrosion resistance to the anodized aluminum. Typically, seal coatings are deposited onto the anodized coating at elevated temperatures and are usually applied by immersion or spray processes. Post treatments can be required by the military and by commercial specifications that govern each coating being treated. As such, there is not a unique "post treatment" specification for all anodize aluminums like there is for "conversion coating" aluminum.

Further, environmental laws, executive orders, and local occupational, safety, and health (OSH) regulations are driving the military and commercial users in the search for hexavalent chromium-free treatments. In the case of anodized aluminum, the anodize film and base metal are relatively non-toxic. With the addition of the required hexavalent chromium-treatment, these coatings become toxic. While some other compositions used for coating anodized aluminum may not contain hexavalent chromium, their technical performance is inferior to the hexavalent chromium-based coatings. In addition, the use of hexavalent chromium-treatments is becoming more expensive as regulations tighten. Costs may become prohibitive with future restrictions imposed by the EPA. Thus, while existing hexavalent chromium-treatments are outstanding in their technical performance in that they provide enhanced corrosion protection and adhesion bonding e.g. with coatings such as paint at a low application cost, from a life-cycle cost, environmental, and OSH perspective, hexavalent chromium coatings are detrimental to both people and the environment.

In regard to adhesive bonding, phosphoric acid anodize is being implemented as an alternative to chromic acid anodize. Phosphoric acid anodize coatings provide excellent adhesive bonding performance, but fail to adequately protect the base aluminum from corrosion. While anodize sealers are typically applied to various other anodize coatings to boost corrosion performance, they are generally not applied to phosphoric acid anodize coatings because the adhesive bonding performance is significantly reduced. As a result, the corrosion protection of a phosphoric acid anodized coating is provided by chromated bond primers or general use primers. Phosphoric acid anodize coatings are characteristically columnar and porous, thus promoting excellent adhesive bonding performance. However, the columnar, porous structure also promotes corrosion making

phosphoric acid anodize coatings particularly difficult to protect against corrosion. For example, phosphoric acid anodized "honeycomb" core, commonly used in military aircraft, corrodes quickly in service when its protective coating is damaged and would greatly benefit from a corrosion protective sealer that does not adversely impact the adhesive bonding characteristics of the anodize coating.

SUMMARY OF THE INVENTION

This invention relates to a process of post-treating or sealing phosphoric acid anodized aluminum and its alloys at ambient temperatures or higher e.g. ranging up to about 200°F. More specifically, this invention relates to post-treating phosphoric acid anodized aluminum and its alloys to improve the corrosion-resistance and maintain adhesion bonding properties e.g. paint adhesion and the like. The trivalent chromium post-treatment (TCP) composition of this invention comprises an acidic aqueous solution having a pH ranging from about 2.5 to 5.5 and preferably 2.5 to 4.5 or 3.7 to 4.0, and per liter of said acidic solution, from about 0.01 to 22 grams of a water-soluble trivalent chromium compound, about 0.01 to 12 grams of an alkali metal hexafluorozirconate, about 0.0 to 12 or 0.001 to 12 grams of at least one fluorocompound selected from the group consisting of an alkali metal tetrafluoroborate, an alkali metal hexafluorosilicate and various combinations or mixtures thereof in any ratio, 0.001 to 10 grams of a water soluble divalent zinc compound, from about 0 to 10 grams and preferable 0 to 2.0 grams of at least one water-soluble thickener, and from 0 to 10 and preferably 0 to 2.0 grams of at least one water-soluble non-ionic, cationic or anionic surfactant or wetting agent.

It is therefore an object of this invention to provide an acidic aqueous solution comprising a trivalent chromium compound, an alkali metal hexafluorozirconate, and a tetrafluoroborate and/or hexafluorosilicate for treating phosphoric acid anodized aluminum and its alloys to maintain its adhesion and improve its corrosion-resistance characteristics.

It is another object of this invention to provide a stable acidic aqueous solution having a pH ranging from about 2.5 to 5.5 which contains effective amounts of a trivalent chromium salt and a hexafluorozirconate for sealing phosphoric acid anodized aluminum and its anodized alloys.

It is a further object of this invention to provide a stable acidic aqueous solution having a pH ranging from about 3.7 to 4.0 containing a trivalent chromium salt and a hexafluorozirconate for treating or sealing phosphoric acid anodized aluminum and its alloys at about room temperature and higher wherein said acidic solution contains substantially no hexavalent chromium.

These and other objects of the invention will become apparent by reference to the detailed description when considered in conjunction with the accompanying Figs. 1-9 (photos).

DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photo of phosphoric acid anodized aluminum, 2024-T3 with no post treatment after exposure to 24 hours (1 day) of ASTM-B 117 neutral salt fog test.

Fig. 2 is a photo of phosphoric acid anodized 2024-T3 post treated with the composition of Example 5 (10 minute immersion at about 75°F) after exposure to 96 hours (4 days) of ASTM-B 117 neutral salt fog test.

Fig. 3 is a photo of a phosphoric acid anodized 2024-T3 post treated with the composition of Example 6 (10 minute immersion at about 75°F) after exposure to 96 hours (4 days) of ASTM-B 117 neutral salt fog test.

Fig. 4 is a photo of phosphoric acid anodized 2024-T3 post treated with the composition of Example 5 (10 minutes at 100°F) after exposure to 1000 hours (42 days) of ASTM-B 117 neutral salt fog test.

Fig. 5 is a photo of a phosphoric acid anodized 2024-T3 post treated with the composition of Example 7 (10 minutes at 100°F) after exposure to 1000 hours (42 days) of ASTM-B 117 neutral salt fog test.

Fig. 6 is a photo of a phosphoric acid anodized 2024-T3 post treated with the composition of Example 5 (40 minutes at ambient (75°F)) after exposure to 1000 hours (42 days) of ASTM-B 117 neutral salt fog test.

Fig. 7 is a photo of a phosphoric acid anodized 2024-T3 post treated with the composition of Example 7 (40 minutes at ambient (75°F)) after exposure to 1000 hours (42 days) of ASTM-B 117 neutral salt fog test.

Fig. 8 is a photo of a phosphoric acid anodized 2024-T3 post treated with the composition of Example 5 (5 minutes at 150°F) after exposure to 1000 hours (42 days) of ASTM-B 117 neutral salt fog test.

Fig. 9 is a photo of a phosphoric acid anodized 2024-T3 post treated with the composition of Example 6 (5 minutes at 150°F) after exposure to 1000 hours (42 days) of ASTM-B 117 neutral salt fog test.

DETAILED DESCRIPTION OF THE INVENTION

More specifically, this invention relates to the process of using an acidic aqueous solution having a pH ranging from about 2.5 to 5.5, and preferably from about 2.5 to 4.5 or 3.7 to 4.0 for sealing phosphoric acid anodized aluminum and its alloys to maintain its adhesion bonding and to substantially improve the corrosion-resistance properties of the anodized aluminum(s). The process preferably comprises the use of an acidic solution comprising from about 0.01 to 22 grams and preferably from about 4.0 to 8.0 grams e.g. 6.0 grams of at least one water soluble trivalent chromium compound e.g. chromium sulfate, about 0.01 to 12 grams and preferably about 6.0 to 10 grams e.g. 8.0 grams of at least one alkali metal hexafluorozirconate, about 0.0 to 12 or about 0.001 to 12 grams and preferably about 0.12 to 1.2 grams e.g. 0.24 to 0.36 grams of at least one fluorocompound selected from the group consisting of alkali metal tetrafluoroborates, alkali metal hexafluorosilicates and various mixtures or combinations thereof in any ratio, and from about 0.001 to 10 grams and preferably 0.1 to 5.0 or 1.0 to 2.0 grams of at least one divalent zinc compound such as zinc sulfate.

In some processes, depending on the physical characteristics of the anodized aluminum e.g. the physical size of the anodized substrate, a feature is the addition of a thickener to the solution that aids in optimum film formation during spray and wipe-on applications by slowing down solution evaporation. This also mitigates the formation of powdery deposits that degrade paint adhesion. Moreover, the addition of thickeners, aids in proper film formation during large area applications and mitigates the diluent effect of rinse water remaining on the substrate during processing from previous steps. This additive yields films that have no streaks and have better coloration and corrosion

protection. The water-soluble thickeners such as the cellulose compounds are known and can be present in the acidic aqueous solution in amounts ranging from about 0.0 to 10 grams and preferably from 0.0 to 2.0 grams and more preferably from 0.5 to 1.5 e.g., about 1.0 gram per liter of the aqueous solution. Depending on the characteristics of the anodized aluminum, an effective but small amount of at least one water-soluble surfactant or wetting agent can be added to the acidic solution in amounts ranging from about 0.0 to 10 grams and preferably from 0.0 to 2.0 grams and more preferably from 0.5 to 1.5 grams e.g. 1.0 grams per liter of the acidic solution. These water soluble surfactants or wetting agents are known in the prior art and are selected from the group consisting of non-ionic, cationic and anionic surfactants.

The trivalent chromium is added as a water-soluble trivalent chromium compound, preferably as a trivalent chromium salt. Specifically, in formulating the acidic aqueous solutions of this invention, the chromium salt can be added, conveniently, to the solution in its water soluble form wherein the valence of the chromium is plus 3. For example, some of the preferred chromium compounds can be prepared in solution in the form of $\text{Cr}_2(\text{SO}_4)_3$, $(\text{NH}_4)\text{Cr}(\text{SO}_4)_2$ or $\text{KCr}_2(\text{SO}_4)_2$ and any mixtures or combination of these compounds. The aluminum substrates are either phosphoric acid anodized aluminum or anodized aluminum alloys containing about 60% or more by weight of aluminum. A preferred example of trivalent chromium concentration is within the range of about 4.0 to 8.0 grams or 6.0 grams per liter of the aqueous solution. It has been found that particularly good results are obtained when the trivalent chromium compound is present in solution in these preferred ranges. The preferred metal fluorozirconate addition to the acidic solution ranges from about 6.0 to 10 grams or 8.0 grams per liter of solution.

The treatment or sealing of the phosphoric acid anodized aluminum can be carried out at low temperatures e.g. about ambient or room temperature or at temperatures ranging up to about 200°F. Room temperature treatment is preferred in that this eliminates the necessity for heating equipment. The seal coating may be air dried by any of the methods known in the art, for example, oven drying, forced air drying, exposure to infra-red lamps, and the like. For purposes of this invention, the terms phosphoric acid anodized aluminum and anodized aluminum alloys include aluminum and its alloys phosphoric acid anodized by methods known in the art.

In some treatments, the alkali metal tetrafluoroborates and/or hexafluorosilicates can be added to the acidic solution in amounts as low as 0.001 grams per liter up to the solubility limits of the compounds. For example, about 50% weight percent of the fluorosilicate is added based on the weight of the fluorozirconate. In other words, for 8.0 grams per liter of the fluorozirconate salt, about 4.0 grams per liter of fluorosilicate is added to the solution. For example, an alternative is to add about 0.01 to 100 weight percent of the fluoroborate salt based on the weight of the fluorozirconate salt.

Preferably, about 1 to 10 weight percent e.g. about 3% of the fluoroborate salt can be added based on the weight of the fluorozirconate salt. A specific example comprises about 8.0 grams per liter of potassium hexafluorozirconate, about 6.0 grams per liter of chromium III sulfate basic, about 0.1 to 5.0 grams per liter of divalent zinc sulfate and about 0.12 to 1.2 grams per liter of potassium tetrafluoroborate and/or hexafluorosilicate.

An important result of the addition of the stabilizing additives i.e. fluoroborates and/or fluorosilicates is that the solution is stable while the pH is maintained between about 2.5 and 5.5. However, in some cases the pretreatment solutions may require small

adjustments to the pH by the addition of effective amounts of a dilute acid or base to maintain the pH in the range of about 2.5 to 5.5 or lower e.g. from about 3.25 to 3.5..

The composition or acid solution can also contain zinc compounds to further improve the corrosion protection of the phosphoric acid anodized coatings compared to compositions that do not contain divalent zinc compounds. The components of the solution are mixed together in water and can be used with no further chemical manipulation. The divalent zinc can be supplied by any chemical compound that dissolves in water at the required concentrations ranging from 0.001 to 10 grams and is compatible with the other components in the solution. Compounds that are particularly preferred include, for example, zinc acetate, zinc telluride, zinc tetrafluoroborate, zinc molybdate, zinc hexafluorosilicate, zinc sulfate and the like or any combination thereof in any ratio.

The following Examples illustrate the stable seal-coating solutions of this invention, and the method of using the solutions in maintaining the adhesion properties while improving the corrosion-resistance of phosphoric acid anodized aluminum and its alloys.

EXAMPLE 1

TCP5PZ2

A stable acidic aqueous solution having a pH ranging from about 3.45 to 4.0 for post-treating phosphoric acid anodized aluminum and aluminum alloys to provide a corrosion-resistant and a color recognized coating thereon which comprises, per liter of solution, about 3.0 grams of trivalent chromium sulfate basic, about 4.0 grams of potassium hexafluorozirconate and about 1.0 gram zinc sulfate.

EXAMPLE 2TCP5B3

A stable acidic aqueous solution for post-treating phosphoric acid anodized
5 aluminum and aluminum alloys to form a corrosion-resistant coating thereon which
comprises, per liter of solution, about 3.0 grams of trivalent chromium sulfate basic,
about 4.0 grams of potassium hexafluorozirconate, and about 0.12 grams of potassium
tetrafluoroborate.

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EXAMPLE 3TCP5B3Z4

A stable acidic aqueous solution for post-treating phosphoric acid anodized
aluminum and aluminum alloys to provide a corrosion-resistant and a color recognized
15 coating thereon which comprises, per liter of solution, about 3.0 grams of trivalent
chromium sulfate basic, about 4.0 grams of potassium hexafluorozirconate, about 0.12
grams of potassium tetrafluoroborate and about 2.0 grams of divalent zinc sulfate.

Table 1 shows the corrosion ratings of three Examples for post-treating
phosphoric acid anodized aluminum alloys of this invention in comparison to the
20 composition of Example 2 coatings. Example 3 (TCP5B3Z4) and Example 1 (TCP5PZ2)
on average had higher ratings.

TABLE 1**Corrosion Resistance of Phosphoric Acid Anodize with Sealer on 2024-T3 Aluminum****Alloy After 1,000 Hours of Exposure to ASTM B 117 Neutral Salt Spray**

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<i>Applicable Patents</i>	<i>TCP Sealer composition</i>	<i>Immersion conditions</i>			
		<i>Ambient/10 minute</i>	<i>Ambient/40 minute</i>	<i>100F/10-minute</i>	<i>150F/5-minute</i>
USP 6,500,532	Example 2				
	5B3	0	6.7	5.7	3
This Invention, USP 6,663,700, USP 6,669,764	Example 3				
	5B3Z4	0	1	0	8
This Invention, USP 6,663,700, USP 6,669,764	Example 1				
	5PZ2	0	7.7	7.7	6

Note: Each rating is the average of 3 identically coated and exposed panels

Corrosion ratings per ASTM D 1654

EXAMPLE 4

Add 3.0 grams per liter of chromium III sulfate basic and 4.0 grams per liter of potassium hexafluorozirconate to specific volume of deionized water. Maintain pH between 3.25 and 3.60 for 14 days using dilute potassium hydroxide or dilute sulfuric acid. After 14 days, adjust pH to 3.90 +/-0.05 and let sit overnight. Solution is ready to use.

EXAMPLE 5

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Add 3.0 grams per liter of chromium III sulfate basic, 4.0 grams per liter of potassium hexafluorozirconate, and 0.12 grams per liter potassium tetrafluoroborate to

specific volume of deionized water. Let solution stand for approximately 10 days, or until pH rises to between 3.75 and 4.00. Solution is ready to use.

EXAMPLE 6

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To Example 4, add 1.0 grams per liter of zinc sulfate during initial mixing. Solution is ready to use.

EXAMPLE 7

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To Example 5, add 2.0 grams per liter of zinc sulfate during initial mixing. Solution is ready to use.

EXAMPLE 8

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Post treatment coatings were applied to anodized aluminum as follows. The phosphoric acid anodize process per ASTM D 3933, "Standard Practice for Preparation of Aluminum Surfaces for Structural Adhesives Bonding (Phosphoric Acid Anodizing)," was followed throughout. Immediately after anodizing 3" by 10" by 0.32" aluminum panels of 2024-T3 aluminum alloys by the Phosphoric Acid Anodize process, the panels were rinsed thoroughly two times in deionized water. Immediately after rinsing, the panels were immersed into a solution of either Example 6 or 7 for 10 minutes at ambient conditions. The immersion was immediately followed by two deionized water rinses. The panels were air-dried at ambient conditions before being subjected to neutral salt fog per ASTM B 117. The coupons were held in a rack at 15 degrees for the duration of the

test. Control coupons of phosphoric acid anodized (PAA) not sealed were tested alongside the subject coatings.

Fig's.2 and 3 (photos) show the performance of post treatments from the compositions of Examples 5 and 6. Fig. 1 (photo) shows an unsealed PAA panel after exposure to ASTM B 117 neutral salt fog. The post treatments of Fig's. 2 and 3 provide improved corrosion resistance compared to the no post-treatment coating of Fig. 1.

EXAMPLE 9

10 Test specimens were anodized as in Example 8. In this example, the compositions (solutions) from Examples 5 and 7 were heated to 100° Fahrenheit and the panels were immersed for a total of 10 minutes. Fig's. 4 and 5 (photos) show corrosion performance of these coatings after 1000 hours of neutral salt fog per ASTM B 117. It is evident that the composition of example 7 is an improvement compared to the
15 composition of Example 5.

EXAMPLE 10

Test specimens were anodized as in Example 8. In this example, the
20 compositions (solutions) from Examples 5 and 7 were kept at ambient conditions, about 75° Fahrenheit, and the panels were immersed for a total of 40 minutes. Fig's. 6 and 7 (photos) show the improved corrosion resistance of these coating after 1000 hours of neutral salt fog per ASTM B 117.

EXAMPLE 11

Test specimens were anodized as in Example 8. In this example, the compositions (solutions) from Examples 5 and 6 were heated to 150° Fahrenheit, and the panels were immersed for a total of 5 minutes. Fig's. 7 and 8 (photos) show the corrosion resistance of these coatings after 1000 hours of neutral salt fog per ASTM B 117.

Table 2 compares the corrosion resistance results of the Examples based on numerical ratings from ASTM D 1654. In the ASTM rating method, the best possible score is 10, meaning substantially no corrosion is evident on the test panel. Ratings decrease to 1, which represents substantially 100% corrosion of the panel surface. From the data in Table 2, it is evident that the process of this invention is an improvement over previous processes used for post treating or sealing phosphoric acid anodized aluminum and its alloys.

TABLE 2

Numerical corrosion ratings of the panels treated with the compositions (solutions) and the process of this invention, based on ASTM D 1654, had ratings as high as 10 (no corrosion) to a low of 1 (fully corroded) where there was no post-treatments.

The ratings comprise an average of three rated panels for each condition.

Compositions in Aqueous Acidic Solution	PROCESS CONDITIONS			
	Ambient temperature (75°F) and 10 minute immersion (Example 8)	Ambient temperature (75°F) and 40 minute immersion (Example 10)	100°F and 10 minute immersion (Example 9)	150°F and 5 minute immersion (Example 11)
Control (no post treatment)	0 after 24 hours	NA	NA	NA
Example 5	NA	6.7 after 1000 hours NSF	5.7 after 1000 hours NSF	3 after 1000 hours NSF
Example 6	0 after 96 hours NSF	7.7 after 1000 hours NSF	7.7 after 1000 hours NSF	6 after 1000 hours NSF
Example 7	0 after 96 hours NSF	1 after 1000 hours NSF	0 after 1000 hours NSF	8 after 1000 hours NSF

For purposes of this invention, the water soluble surfactants or wetting agents can be added to the trivalent chromium solutions in amounts ranging from about 0 to 10 grams per liter and preferably 0.5 to about 1.5 grams per liter of the trivalent chromium solution. The surfactants are added to the aqueous solution to provide better wetting properties by lowering the surface tension thereby insuring complete coverage, and a more uniform film on the coated substrate. The surfactants include at least one water soluble compound selected from the group consisting of the non-ionic, anionic, and cationic surfactants. Some known water soluble surfactants having the solubility at the required concentrations include the monocarboxyl imidoazoline, alkyl sulfate sodium salts (DUPONOL®), tridecyloxy poly(alkyleneoxy ethanol) ethoxylated or propoxylated alkyl phenol (IGEPAL®), alkyl sulfonamides, alkaryl sulfonates, palmitic alkanol amides (CENTROL®), octylphenyl polyethoxy ethanol (TRITON®), sorbitan monopalmitate (SPAN®), dodecylphenyl polyethylene glycol ether e.g. TERGITROL®, alkyl pyrrolidone, polyalkoxylated fatty acid esters, alkylbenzene sulfonates and mixtures thereof. Other known water soluble surfactants include the alkyl phenol alkyloxylates,

preferably the nonylphenol ethyloxylates, and the various anionic surfactants, having at least one sulfonate substituent in the phenyl ring, and the adducts of ethylene oxide with fatty amines. Other known water soluble compounds are found in "Surfactants and Detersive Systems", published by John Wiley & Sons in Kirk-Othmer's Encyclopedia of Chemical Technology, 3rd Ed.

When large surfaces do not permit immersion or where vertical surfaces are to be sprayed, thickening agents are added to retain the aqueous solution on the surface for sufficient contact time. The thickeners employed are known inorganic and organic water soluble thickeners which can be added to the trivalent chromium solutions in effective amounts e.g. a sufficient concentration ranging from about 0 to 10 grams per liter and preferably 0.5 to 1.5 grams per liter of the acidic solution. Specific examples of some preferred thickeners include the cellulose compounds, e.g. hydroxypropyl cellulose (e.g. Klucel), ethyl cellulose, hydroxyethyl cellulose, hydroxymethyl cellulose, methyl cellulose and mixtures thereof. Some of the less preferred thickeners include the water soluble inorganic thickeners such as colloidal silica, clays such as bentonite, starches, gum arabic, tragacanth, agar and various combinations.

After preparing the surface to be treated via conventional phosphoric acid anodizing techniques, the solution can be applied by immersion, spray or wipe-on techniques. The solution also can be used at elevated temperatures up to 65°C and optimally applied by immersion to further improve the corrosion resistance of phosphoric acid anodize coatings. Solution dwell time is about 1 to 60 minutes, depending on the solution temperature and concentration of the solution. After dwelling, the remaining solution is then thoroughly rinsed from the substrate with tap or deionized water. No additional chemical manipulations of the deposited film are necessary for excellent

performance. However, an application of a strong oxidizing solution can yield a film with improved corrosion resistance. The additional corrosion resistance is presumed to be due to the hexavalent chromium formed in the film from the trivalent chromium. The aqueous sealer composition may be sprayed from a spray tank apparatus designed to replace immersion tanks. This concept also reduces active chemical volume from about 1,000 gallons to about 30 to 50 gallons.

Another feature of this invention is the ability of this protective seal coating to provide the phosphoric acid anodized coatings with corrosion resistance better or at least equivalent to other known sealed anodic coatings produced with sulfuric, chromic, boric-sulfuric, or other known compositions. This capability has not been available before and offers new potential applications for phosphoric acid anodized in corrosive environments that were not previously possible. Phosphoric acid anodized aluminums have a major advantage over these other coatings in that its coating weights are typically 10 to 50 times lower. This yields significant weight savings and lower fatigue debit to structural aluminum alloys. In addition, this invention has the ability to enhance the performance of phosphoric acid anodize coatings currently being implemented as an adhesive bonding alternative to chromic acid anodizing. Phosphoric acid anodize coatings that have not been post treated are known to have inferior corrosion resistance, but are known also to have excellent bonding characteristics. This invention increases the corrosion performance of the anodized aluminums, while maintaining the adhesive bonding strength of the coatings. The terms, for purposes of this invention, "solubility" and "water soluble" mean water solubility of the chemical compounds used in the solutions of this invention at least at the concentrations set-forth herein.

While this invention has been described by a number of specific examples, it is obvious that there are other variations and modifications which can be made without departing from the spirit and scope of the invention as particularly set forth in the appended claims.

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THE INVENTION CLAIMED

1. Process for sealing phosphoric acid anodized aluminum and aluminum alloys to improve the corrosion resistance and maintain the adhesive bonding strength which comprises treating the anodized aluminum and its alloys with an acidic aqueous solution having a pH ranging from about 2.5 to 5.5; said acidic aqueous solution comprising, per liter of solution, from about 0.01 to 22 grams of a trivalent chromium compound, about 0.01 to 12 grams of an alkali metal hexafluorozirconate, about 0.0 to 12 grams of at least one fluorocompound selected from the group consisting of an alkali metal tetrafluoroborate, an alkali metal hexafluorosilicate and mixtures thereof, from about 0.001 to 10 grams of at least one divalent zinc compound, from 0.0 to about 10 grams of at least one water soluble thickener and from 0.0 to about 10 grams of at least one water-soluble surfactant.
2. The process of Claim 1 wherein the pH of the aqueous solution ranges from about 3.7 to 4.0 and the temperature of the aqueous solution ranges from about ambient to 200°F.
3. The process of Claim 2 wherein the trivalent chromium is a water soluble compound ranging from about 4.0 to 8.0 grams, the hexafluorozirconate is a water soluble compound ranging from about 6.0 to 10 grams, and the fluorocompounds are water soluble compounds ranging from about 0.12 to about 1.2 grams.
4. The process of Claim 3 wherein the thickener ranges from about 0.5 to 1.5 grams and the surfactant ranges from about 0.5 to 1.5 grams.

5. **Process for sealing phosphoric acid anodized aluminum and aluminum alloys to improve the corrosion resistance and maintain the adhesive bonding strength which comprises treating the anodized aluminum and its alloys with an acidic aqueous solution having a pH ranging from about 3.7 to 4.0; said acidic aqueous solution comprising, per liter of solution, from about 4.0 to 8.0 grams of a trivalent chromium salt, about 6.0 to 10 grams of an alkali metal hexafluorozirconate, about 0.001 to 12 grams of at least one fluorocompound selected from the group consisting of an alkali metal tetrafluoroborate, an alkali metal hexafluorosilicate and mixtures thereof, from about 0.001 to 10 grams of at least one divalent zinc compound, from 0.0 to about 10 grams of at least one water soluble thickener and from 0.0 to about 10 grams of at least one water soluble surfactant.**
6. The process of Claim 5 wherein the fluorocompound is present in the solution in an amount ranging from about 0.24 to 0.36 grams and the treated anodized aluminum is subsequently washed with water at temperatures ranging up to 200°F.
7. The process of Claim 5 wherein the thickener is a cellulose compound present in the acidic solution in amounts ranging from about 0.5 to 1.5 grams per liter.
8. The process of Claim 5 wherein the chromium salt is trivalent chromium sulfate.
9. The process of Claim 5 wherein the alkali metal zirconate is potassium hexafluorozirconate.

10. The process of Claim 5 wherein the trivalent chromium salt is chromium sulfate ranging from about 4.0 to 8.0 grams, the hexafluorozirconate is potassium hexafluorozirconate ranging from about 6.0 to 10 grams, and the tetrafluoroborate or hexafluorosilicate ranges from about 0.24 to 0.36 grams.
11. The process of Claim 10 wherein the thickener is a cellulose compound ranging from about 0.5 to 1.5 grams.
12. The process of Claim 5 wherein the zinc compound is zinc acetate.
13. The process of Claim 11 wherein the chromium salt is trivalent chromium sulfate and the divalent zinc compound is zinc sulfate.
14. The process of Claim 11 wherein the water soluble surfactant is selected from the group consisting of water soluble non-ionic, anionic and cationic surfactants.
15. The process of Claim 14 wherein the zinc compound is a divalent zinc sulfate.
16. The process of Claim 15 wherein the zinc sulfate is present in the aqueous solution in an amount ranging from about 0.1 to 5.0 grams.
17. The process of Claim 5 wherein the chromium salt is chromium sulfate present in the aqueous solution in an amount ranging from 4.0 to 8.0 grams, the mixture of alkali

metal tetrafluoroborate and hexafluorosilicate are present in the aqueous solution in an amount ranging from about 0.001 to 12 grams.

18. The process of Claim 17 wherein the zinc compound is zinc sulfate present in the aqueous solution in an amount ranging from about 0.1 to 5.0 grams.

19. The seal-coated phosphoric acid anodized aluminum and aluminum alloys of Claim 1.

20. The seal-coated phosphoric acid anodized aluminum and aluminum alloys of Claim 5.