



(51) International Patent Classification:
B05D 7/00 (2006.01) **C23C 22/68** (2006.01)

(21) International Application Number:
PCT/US2011/045295

(22) International Filing Date:
26 July 2011 (26.07.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/367,899 27 July 2010 (27.07.2010) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: PRETREATMENT OF ALUMINUM ALLOYS BY HYDRATION OF THE ALUMINUM SURFACE

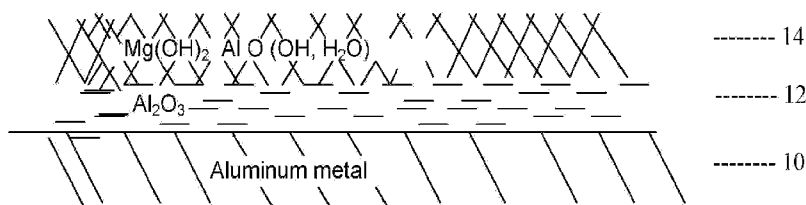


Fig. 1

(57) Abstract: A treated aluminum alloy substrate comprising: an aluminum alloy substrate; a layer of aluminum oxide on the aluminum alloy substrate; and a layer of hydrated oxide on the layer of aluminum oxide wherein the layers of hydrated oxide and aluminum oxide have a combined thickness of less than about 40 nm. The treated aluminum alloy substrate exhibits corrosion resistance and provides a surface adequate for adhesive bonding. In some embodiments, a polymer coating is applied to the substrate wherein the polymer coating resists delamination upon deformation of the substrate.

PRETREATMENT OF ALUMINUM ALLOYS BY HYDRATION OF THE ALUMINUM SURFACE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This patent application claims priority to U.S. Provisional Patent Application No. 61/367,899 filed July 27, 2010; which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] The natural oxide on aluminum can be reinforced or altered by several treatment methods to serve as a substrate suitable for bonding to a coating and to give better protection against corrosion.

SUMMARY

[0003] A process for treating an aluminum alloy substrate comprises: exposing an untreated and uncoated aluminum alloy substrate having a layer of aluminum oxide to an aqueous environment for a period of time in the range of about 1 second to about 20 seconds, wherein the aqueous environment has a temperature of at least 170°F. and wherein the environment is substantially free of deleterious ions. In some embodiments, exposing the aluminum alloy substrate to an aqueous environment comprises submerging the aluminum alloy substrate in an aqueous liquid. In some embodiments, exposing the aluminum alloy substrate to an aqueous environment comprises spraying an aqueous solution on the substrate. In some embodiments, before exposing the aluminum alloy substrate to an aqueous environment, the substrate is cleaned with a cleaning agent substantially free of deleterious ions. In some embodiments, the aqueous environment contains 5 parts per million or less of phosphates, 5 parts per million or less of fluoride, and 10 parts per million or less of silicates. In some embodiments, the aqueous environment has a temperature of about 205° F. to about 210° F. In some embodiments, the substrate is exposed to the aqueous environment for about 5 seconds to about 10 seconds. In some embodiments, the process further comprises cooling the substrate. In some embodiments, the process further comprises drying the substrate. In some embodiments, the process further comprising coating the substrate with an organic coating. In some embodiments, the substrate is a sheet in a coil. In some embodiments, the sheet is suitable for use in food or beverage packages.

[0004] A treated aluminum alloy substrate comprises: an aluminum alloy substrate; a layer of aluminum oxide on the substrate; and a layer of hydrated oxide on the layer of aluminum oxide, wherein the combined thickness of the layer of aluminum oxide and the layer of hydrated oxide is less than about 40 nm. In some embodiments, the layer of hydrated oxide appears substantially clear and colorless. In some embodiments, the substrate comprises a coil of aluminum sheet. In some embodiments, the sheet is suitable for use in food or beverage packages.

[0005] In some embodiments, the substrate may also have a polymeric coating on the layer of hydrated oxide. The polymeric coating may be organic or inorganic. In some embodiments, the polymeric coating comprises one of a vinyl, polyester, epoxy or poly-fluorinated coating. In some embodiments, the polymeric coating remains substantially intact upon deformation of the substrate.

[0006] In some embodiments, the treated aluminum substrate comprises at least 0.6% Mg, at least 3% Mg, or at least 4% Mg.

[0007] The layer of hydrated oxide is formed by exposing the layer of aluminum oxide to one of a heated aqueous solution, steam, or a combination of a heated aqueous-solution and steam. In some embodiments, a layer of hydrated oxide is formed by exposing the layer of aluminum oxide to one of a heated aqueous solution, steam, or a combination of an aqueous solution-and steam, for about 3 seconds to about 4 seconds. In other embodiments, the exposure time is about 10 seconds. In yet other embodiments, the exposure time is about 1 second to about 20 seconds. In further embodiments, the exposure time is about 5 seconds to about 10 seconds.

[0008] A method of treating an aluminum alloy substrate comprises: exposing an aluminum alloy substrate having a layer of aluminum oxide to one of heated water, steam or a combination of heated water and steam to form a hydrated oxide layer wherein the aluminum oxide layer and hydrated oxide layer have a combined thickness of about 11-40. In some embodiments, the combined thickness is about 15-35 nm. In other embodiments, the combined thickness is about 20-30 nm.

[0009] In some embodiments, the aluminum alloy substrate is exposed to one of heated water, steam or a combination of heated water and steam for about 10 seconds.

[0010] In some embodiments, the method of treating an aluminum alloy substrate further comprises applying a polymeric coating to the hydrated oxide layer.

[0011] In some embodiments, the polymeric coating remains substantially intact upon deformation of the aluminum alloy substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] These and other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings where:

[0013] Figure 1 is a magnified cross-section view of an aluminum alloy substrate having a layer of aluminum oxide and a layer of hydrated oxide according to one embodiment of the present invention.

[0014] Figure 2 is a graph illustrating temperature of metal versus the time in seconds the metal was submerged in heated water.

[0015] Figure 3 is a chart showing the results of various tests performed on three different polyester coated 5182 aluminum alloy sheets, each having undergone a different or no surface treatment prior to coating.

[0016] Figure 4 is a chart showing the results of various tests performed on three different vinyl coated 5042 aluminum alloy cans, each having undergone a different or no surface treatment prior to coating.

[0017] Figure 5 is a graph showing the enamel rating of as fabricated cans verses the thickness of the combined layer of aluminum oxide and hydrated oxide.

[0018] Figure 6 is a graph showing the enamel rating before and after HCl test verses the thickness of the combined layer of aluminum oxide and hydrated oxide.

Figure 7 shows, on the left, a can treated according to an embodiment of the invention and, on the right, a can treated with chromium phosphate according to the prior art.

[0019] Figure 8 shows the results of a test in which 610 scotch tape was applied and removed from an area where the coating had been sliced in a cross hatched pattern after the samples were exposed to boiling water per American Architectural Manufacturers Association 2605-05, Section 7.4.1.3.

[0020] Figure 9 shows the results of a test in which coating on the samples was sliced and the samples were exposed to steam per General Motors 9525P (Thermal Shock for Paint Adhesion).

[0021] Figure 10 shows the results of a test in which coating on the samples was sliced and the samples were immersed in 3.1% HCl at 35 C for 2 minutes; exposed to 85% relative humidity and 45 C for 144 hours; and dried at room temperature for 24 hours.

[0022] Figure 11 shows the results of a test in which coating on the samples was sliced and the samples were exposed sample to an alternating wet and dry acidified salt spray for twenty-one days per ASTM G85-A2.

[0023] Figure 12 is a graph that shows the rate of growth of the combined aluminum oxide and hydrated oxide layer as a function of the magnesium concentration in the aluminum alloy substrate.

[0024] Figure 13 is a graph that shows the rate of growth of the combined aluminum oxide and hydrate oxide layer as a function of the temper of the aluminum alloy substrate.

[0025] Figure 14 is a chart showing the elemental composition by X-ray photoelectron spectroscopy of the F and T43 tempered 6111 surfaces.

[0026] Figure 15 is a graph showing a comparison of the infrared spectra of F and T43 tempered 6111 surfaces.

[0027] Figure 16 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer as a function of water temperature.

[0028] Figure 17 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on various F temper aluminum alloy substrates having no surface preparation.

[0029] Figure 18 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were Elf Autochem A31K alkaline cleaned at 60 C for 5 seconds, borate, phosphate, sulfate based, pH 9.1.

[0030] Figure 19 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were sodium carbonate cleaned at 60 C for 5 seconds, pH 10.2-10.8.

[0031] Figure 20 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were cleaned with Parco 305 (available from Henkle Technologies) alkaline at 54 C for 5 seconds, potassium phosphate/potassium hydroxide based, pH 11.0-11.6.

[0032] Figure 21 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were acid cleaned with Parco 202 (available from Henkle Technologies) at 77 C for 5 seconds, phosphoric acid/sulfuric acid based, pH <1.

[0033] Figure 22 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on aluminum alloy substrates that experienced various surface treatments before the formation of the layer of aluminum hydrated oxide.

[0034] Figure 23 is a chart showing the elemental analysis by X-ray photoelectron spectroscopy of the substrates which were tested to obtain the results shown in the graph of Figure 22.

[0035] Figure 24 is a graph showing the rate of growth of the combined aluminum oxide and hydrated oxide layer on an aluminum alloy substrate sodium carbonate cleaned, exposed to 100% relative humidity for 21 days, and exposed in a laboratory atmosphere for 21 days (15-25% relative humidity).

DESCRIPTION

[0036] One embodiment of the invention, shown in Fig. 1, comprises an aluminum alloy substrate 10 having a layer of aluminum oxide 12 and a layer of hydrated oxide 14 on the layer of aluminum oxide. In some embodiments, the combination of the layer of aluminum oxide and the hydrated oxide is thick enough to have a sufficient number of bonding sites so that a coating on the hydrated oxide layer will have good adhesion. In some embodiments, the combined thickness of the layer of aluminum oxide and the layer of hydrated oxide is less than 40 nm. In other embodiments the combined thickness is less than 136 nm. In some embodiments, the combined thickness is about 15-35 nm. In other embodiments, the combined thickness is about 20-30 nm. In yet other embodiments, the combined thickness is about 7 nm to about 40 nm. These thicknesses provide a sufficiently high surface tension (> 60 dynes/cm) for good wetting of the surface by the coating. In some embodiments, a combined layer of aluminum oxide and the hydrated oxide having a thickness in the ranges listed above is substantially amorphous and provides adhesion to a coating that can undergo deformation along with the aluminum alloy substrate without delamination of the coating. In some embodiments, the adhesion of the substrate with the hydrated oxide to which the coating has been applied provides corrosion protection that is at least equal to a chromium phosphate pretreatment. In addition, in some embodiments a combined thickness of the layer of aluminum oxide and the layer of hydrated oxide of about 40 nm or less appears clear and colorless to the naked eye.

[0037] In some embodiments, the aluminum alloy substrate further comprises a polymeric coating on the layer of hydrated oxide. The polymeric coating is organic in some embodiments. In some embodiments, the polymeric coating may comprise a vinyl, polyester, epoxy or poly-fluorinated coating.

[0038] Hydrated oxide as used herein is meant to include aluminum hydroxide and aluminum hydroxide in combination with aluminum oxides. Aluminum hydroxide as used herein is meant to include the reaction product of aluminum oxides, which may be naturally occurring, and water and/or steam. In some embodiments, the reaction products may include AlOOH (H_2O) and/or $\text{Al}(\text{OH})_3$. In some embodiments, the hydrated oxide as used herein may also include reaction products of the other elements in the aluminum alloy substrate, such as magnesium hydroxide or other elements, which may be in the water. Molecules of water may be included into the hydrated oxide.

[0039] The aluminum alloy substrate may be in the form of foil, sheet, plate, extrusion, tube, foam, rod or bar, for example. It will, therefore, be understood that the use of the term aluminum alloy substrate herein is intended to include all such aluminum materials and shapes.

[0040] In some embodiments, the layer of aluminum oxide may be formed on the aluminum alloy substrate simply by exposing the aluminum alloy substrate to the atmosphere. The aluminum oxide coating may be naturally occurring. When a metal or metal alloy is exposed to the atmosphere, an oxide coating generally forms. The thickness of this coating depends on factors such as the composition of the alloy, the temper of the metal, humidity, and temperature. A typical thickness for the initial layer of aluminum oxide is about 7 nm to about 10 nm. The layer of aluminum oxide may, however, be thicker or thinner.

[0041] In some embodiments, the layer of hydrated oxide is formed on the layer of aluminum oxide by exposing the untreated and uncoated aluminum alloy substrate with the layer of aluminum oxide to an aqueous environment. Untreated and uncoated means that the substrate has not undergone any process or does not have any coatings that would prevent the aluminum oxide from reacting with heated water. An example of a process that is not considered a treatment for the purpose of this patent application is cleaning the aluminum alloy substrate. An aqueous environment can include water, steam or a combination of water and steam. The water may be substantially pure or contain additives or contaminants, such as an additive that

increases pH. In some embodiments the water is substantially free of deleterious anions. In some embodiments, substantially free of deleterious anions means water containing 5 parts per million or less of phosphates, 5 parts per million or less of fluoride, and 10 parts per million or less of silicates. It is envisioned that it would be possible that water containing greater amounts of fluoride, silicates, and/or phosphates, may still be substantially free of deleterious ions depending on what other substances are in the water. In some embodiments, substantially free of deleterious ions means substantially free of substances that inhibit growth of the hydrated oxide layer under the particular conditions in which growth is desired, e.g. for the particular alloy, temperature of liquid, chemical composition of the liquid, exposure time. In some embodiments, the aqueous environment is deionized water.

[0042] In some embodiments, the temperature of the liquid in the aqueous environment is about 170 degrees F. to about 212 degrees F. In other embodiments, the liquid temperature may be about 200 degrees F. to about 212 degrees F. In further embodiments, the liquid temperature of about 205 degrees F. to about 210 degrees F. In some embodiments, the liquid temperatures are at least 170 degrees F. and may be as high as the boiling point of the liquid.

[0043] The length of time the aluminum alloy substrate is exposed to the aqueous environment may vary. Time of exposure can be as short as one second. In some embodiments, exposure times can range from about 1 to about 20 seconds. In other embodiments, exposure times may be in the range of about 3 seconds to about 10 seconds, about 5 seconds to about 10 seconds or about 5 seconds to about 8 seconds. In some embodiments, longer exposures are possible but may not be necessary to achieve the layer of hydrated oxide or a combined layer of aluminum oxide or hydrated oxide having a desired thickness. In general, the lower the temperature of the liquid in the aqueous environment, the longer the exposure time needed to achieve a specific thickness of the combined layer of aluminum oxide and hydrated oxide. Conversely, the higher the temperature of the liquid in the aqueous environment, the shorter the exposure time needed to achieve a specific thickness of the combined layer of aluminum oxide and hydrated oxide. For example, if an aluminum alloy having a layer of aluminum oxide is submerged in 170 degrees F. water for 20 seconds, a combined layer of aluminum oxide and hydrated oxide having a thickness of almost 30 nm may result. If the same alloy under the same conditions

is submerged in 205 degrees F. water, it may develop a combined layer of aluminum oxide and hydrated oxide having a thickness of 30 nm in about 5 seconds.

[0044] In some embodiments, during at least a portion of the time period when the aluminum alloy substrate is exposed to the aqueous environment, the temperature of the aluminum alloy substrate is at least about 150 degrees F., in some embodiments about 150 degrees F. to about the boiling point of the liquid in the aqueous environment, in some embodiments, about 150 degrees F. to about 212 degrees F., in some embodiments, about 180 degrees F. to about 210 degrees F., in other embodiments, about 190 degrees F. to about 210 degrees F. Figure 2 shows average temperature of an aluminum alloy substrate verses the time the substrate was immersed in heated water.

[0045] In some embodiments, the aluminum alloy substrate is cleaned before exposing the substrate to the aqueous environment. In some embodiments, the substrate is cleaned with a cleaning agent that is substantially free of deleterious anions. In some embodiments, the substrate is cleaned by being immersed in or sprayed with a cleaning agent for about 5 seconds to about 8 seconds or about 3 seconds to about 10 seconds. In some embodiments, the temperature of the cleaning agent may be 130-150 degrees F. In some embodiments, only the surface of the substrate upon which growth of a hydrated oxide layer is desired is cleaned. In some embodiments, after cleaning, the cleaning agent is rinsed from the substrate. In some embodiments, rinsing is accomplished by rinsing the substrate in substantially deionized water for about 5 seconds to about 10 seconds.

[0046] In some embodiments, after the aluminum alloy substrate is exposed to the aqueous environment, the substrate is cooled. In some embodiments, cooling is accomplished by quenching the substrate in room temperature deionized water.

[0047] In some embodiments, the substrate is dried after cooling or after exposure to the aqueous environment. In some embodiments, drying can be accomplished via exposure to the atmosphere or by applying filtered, compressed air.

[0048] When the aluminum alloy substrate having a layer of aluminum oxide is exposed to a heated aqueous environment, a hydrated oxide layer is formed. It is unknown whether the hydrated oxide layer grows on top of the aluminum oxide layer as an entirely new layer, or if the aluminum oxide layer is hydrated in part or in full. It is thought, but not known for sure, that when the combination of the layer of aluminum oxide and the layer of hydrated oxide is about 11 nm to about 40 nm that

the layer of hydrated oxide may be about 4 nm to about 30 nm. Similarly, it is thought that when the combination of the layer of aluminum oxide and the layer of hydrated oxide is about 7nm to about 40 nm that the layer of hydrated oxide may be about 1 nm to about 30 nm.

[0049] The thickness of the aluminum oxide layer, the hydrated oxide layer and the combination of the layer of aluminum oxide and hydrated oxide is determined by several factors including, the time the aluminum alloy substrate having the layer of aluminum oxide layer is exposed to the aqueous environment; the method of exposure to the aqueous environment, e.g. spray or immersion; the composition of the aqueous environment, e.g. steam, liquid or a combination, the temperature of the aqueous environment, the pH of the aqueous environment; the composition of the aluminum alloy, the temperature of the aluminum substrate and whether the aluminum alloy was heat treated, surface treated, cleaned, and, in some cases, the composition of any cleaner used.

[0050] In some embodiments, exposing an aluminum alloy substrate having a 7-10 nm layer of aluminum oxide to substantially pure boiling water (having a pH of approximately 6-7 for about 10 seconds produces a layer of hydrated oxide on the layer of aluminum oxide wherein the combined thickness of the layer of aluminum oxide and the layer of hydrated oxide is about 11 nm to about 30 nm. The same combined thickness could be achieved in a shorter amount of time and/or a lower water temperature by raising the pH of the water. In some embodiments, forming a combined thickness of about 11 nm to about 30 nm via exposure of the aluminum alloy substrate having a 7-10 nm layer of aluminum oxide to steam requires exposure to the steam for more than 20 seconds. However, unexpectedly, in some embodiments, a combined thickness of the aluminum oxide layer and the layer of hydrated oxide of about 11 nm to about 30 nm can be formed via exposure of the aluminum alloy substrate having a 7-10 nm layer of aluminum oxide to a combination of 99 C water and steam having a pH of approximately 8 to approximately 9 for about 3 to about 4 seconds. In some embodiments, the water-steam mixture is approximately 90% water and 10% steam. The above parameters and results are accurate regardless of the alloy, heat treatment and temper.

[0051] In one example of how one embodiment of the invention could be made, an aluminum alloy substrate having a layer of aluminum oxide is exposed to an aqueous environment by spraying the aluminum alloy substrate with heated water,

steam or combination of water and steam. The water, steam or combination of water and steam is sprayed using spray nozzles. The water, steam or combination thereof can be forced through the nozzles by force generated by a pumping system, or in the case of steam, by its own vapor pressure. One approach to generating the water/steam combination is the commercial Steam Jenny cleaning process. In one example of this process, water is heated to 163 C in a closed tank. As the water exits the nozzle, typically at 150 psi, the water partially vaporizes, producing a spray consisting of approximately 90% 99 C water and 10% steam at pH 8 to 9. During contact, the aluminum alloy substrate may be stationary or moving. The direction of contact is irrelevant. The contact time may be about 3 seconds to about 20 seconds.

[0052] In one example, aluminum substrates were cleaned with a phosphate silicate and fluoride-free cleaner for a 5 second immersion time at 140 degrees F. The substrates were then rinsed in deionized water for 5 seconds at room temperature. Following this rinse the substrates were then immersed in contaminant free 205-210 degrees F pure deionized water for 5-10 seconds. A room temperature deionized water quench was applied to the substrates followed by a filtered in-house compressed air dry cycle. Substrates comprised of various aluminum alloys were treating using the process described in this paragraph and various coatings were applied on top of the hydrated oxide layer. These substrates were put through a battery of tests, the results of which are shown in Figures 3-14.

[0053] Referring to Figure 3, the substrate tested was comprised of a 5182 aluminum alloy sheet, treated using the process in the immediately preceding paragraph and coated with polyester. A 5182 aluminum alloy substrate treated with chromium phosphate (A272 chromium treatment) according to the prior art and coated with polyester and a 5182 aluminum alloy substrate cleaned only (untreated) and coated with polyester were also tested. The following tests were performed: dry adhesion, pasteurization blush, pasteurize adhesion, process blush, process adhesion and T-bends. The dry adhesion test measured percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced in a cross hatched pattern. The pasteurization blush test measured color change after heating the substrate in water at 82 C for 30 minutes. The pasteurization adhesion test measured percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced in a cross hatched pattern and after the substrate was heated in water at 82 C for 30 minutes. The process blush test

measured color change after heating the substrate in water at 121 C for 90 minutes. The process adhesion test measured percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced in a cross hatched pattern and after heating the substrate in water at 121 C for 90 minutes. The T-bend test measured coating loss after 610 scotch tape was applied and removed from the edge of a substrate folded over on itself 1, 2, 3, 4, 5 times.

[0054] The percentages listed indicate the percent of the coating that remained adhered to the substrate, or more specifically, the hydrated oxide layer on the substrate, after completion of the test. Pass indicates that the substrate and the coatings thereon exhibited no color change visible to the naked eye after completion of the test. With respect to the T-bend test, 1-T is the best result possible and indicates no coating loss on the folded edge of the substrate folded once over itself.

[0055] Figure 4 shows the results of the following tests performed on a substrates comprising 5042 aluminum alloy beverage cans coated with vinyl: dry sidewall adhesion, dry cross hatch adhesion, process sidewall adhesion, process cross hatch adhesion and exposure to HCl at 66 degrees C for 24 hours.

[0056] The dry sidewall adhesion measured percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced on the top lip of the can. The dry cross hatch adhesion test measured the percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced in a cross hatched pattern on the sidewall of the can. The process sidewall adhesion test measured the percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced on the top lip of the can and after heating the can in water at 121 C for 90 minutes. The process cross hatch adhesion test measured the percent of coating remaining after measured percent of coating remaining after 610 scotch tape was applied and removed from an area where the coating had been sliced on the top lip of the can and after heating the sample in water at 121 C for 90 minutes.

[0057] The can was exposed to HCl at 66 degrees C for 24 hours then enamel and blister ratings were taken. The HCl solution had a concentration of 0.5% and a pH of .9 to 1.1. The enamel rating indicates milliamps of current in distilled water containing 1% sodium chloride and 0.023% aerosol OT surfactant. The blister rating was a visual rating of blisters from none to severe.

[0058] Figure 5 shows how the thickness of the combined layer of aluminum oxide and hydrated oxide affects the enamel rating of a beverage can.

[0059] Figure 6 shows how the thickness of the combined layer of aluminum oxide and hydrated oxide affects the enamel rating of beverage cans after the cans were exposed to an HCl solution having a concentration of 0.5% and a pH of .9 to 1.1 for 24 hours at 66 degrees C.

[0060] Figure 7 shows, on the left, a can treated according to the embodiment of the invention described in the example above and a can treated with chromium phosphate (A272 chromium treatment) according to the prior art on the right, at 66 degrees C for 24 hours. The inside of both cans was coated with vinyl after being treated and before HCl exposure, at 66 degrees C for 24 hours. It can be observed that the can treated according to one embodiment of the invention has substantially less blistering than the can that received the chromium phosphate treatment.

[0061] Figure 8 shows the results of a test in which 610 scotch tape was applied and removed from an area where the coating had been sliced in a cross hatched pattern after the samples were exposed to boiling water per American Architectural Manufacturers Association 2605-05, Section 7.4.1.3.

[0062] Figure 9 shows the results of a test in which coating on the samples was sliced and the samples were exposed to steam per General Motors 9525P (Thermal Shock for Paint Adhesion).

[0063] Figure 10 shows the results of a test in which coating on the samples was sliced and the samples were immersed in 3.1% HCl at 35 C for 2 minutes; exposed to 85% relative humidity and 45 C for 144 hours; and dried at room temperature for 24 hours. The cycle was repeated 8 times (8 weeks).

[0064] Figure 11 shows the results of a test in which coating on the samples was sliced and the samples were exposed sample to an alternating wet and dry acidified salt spray for twenty-one days per ASTM G85-A2.

[0065] Figure 12 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer as a function of the magnesium concentration in the aluminum alloy substrate. From the graph, it can be seen that the rate of growth of the combined aluminum oxide and hydrated oxide layer correlates with the magnesium concentration in the aluminum alloy. The growth rate of the combined layer on a low Mg alloy is approximately four times the growth rate on pure

aluminum. The growth rate of the combined layer on a high Mg alloy is approximately nine times the growth rate on pure aluminum.

[0066] The graph in Figure 13 shows the rate of growth of the combined aluminum oxide and hydrate oxide layer as a function of the temper of the aluminum alloy substrate. It can be seen that the rate of growth of the combined aluminum oxide and hydrated oxide layer approximately doubles between F temper (cold rolled) and T43 temper aluminum alloy substrates.

[0067] The chart in Figure 14 shows the elemental composition by X-ray photoelectron spectroscopy of the F and T43 tempered 6111 surfaces. The XPS chart shows the oxide thickens and the magnesium migrates to the surface during the tempering process, which results in the increase in hydration rate from F to T43 tempers in the 6XXX chart above.

[0068] The graph in Figure 15 shows a comparison of the infrared spectra of F and T43 tempered 6111 surfaces. The T43 spectrum shows an increase of hydroxyl (O-H), water (H-O-H), aluminum oxide (Al-O), and magnesium oxide (Mg-O) compared with the F temper sample.

[0069] The graph in Figure 16 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer as a function of water temperature. It can be seen that hydration is a function of water temperature. Infrared analysis indicated that the type of oxide/hydroxide formed at all of the above temperatures was similar. The infrared spectrum showed that the combined layer with a thickness less than 30 nm was a mixture of aluminum and magnesium oxide and hydroxide, while the combined layer having a thickness greater than 30 nm also contained some boehmite (AlOOH).

[0070] The graph in Figure 17 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on various F temper aluminum alloy substrates having no surface preparation. This graph shows that while cleaning the surface before hydration may be preferred in some embodiments, hydration can also be accomplished on a mill finished surface.

[0071] The graph in Figure 18 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were Elf Autochem A31K alkaline cleaned at 60 C for 5 seconds, borate, phosphate, sulfate based, pH 9.1. This cleaning process had no effect on the growth rate of the combined layer on aluminum alloys having a high Mg concentration as compared

with the uncleaned F temper aluminum alloy substrate in the previous chart. However, this cleaning process appeared to inhibit the growth rate of the combined layer on aluminum alloy substrates having a low Mg concentration.

[0072] The graph in Figure 19 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were sodium carbonate cleaned at 60 C for 5 seconds, pH 10.2-10.8. This cleaning process had no effect on the growth rate of the combined layer on aluminum alloys having a high Mg concentration as compared with the uncleaned F temper aluminum alloy substrate. However, this cleaning process appeared to increase the rate of growth rate of the combined layer on aluminum alloy substrates having a low Mg concentration.

[0073] The graph in Figure 20 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were cleaned with Parco 305 (available from Henkle Technologies) alkaline at 54 C for 5 seconds, potassium phosphate/potassium hydroxide based, pH 11.0-11.6. On the Parco 305 cleaned aluminum alloy substrates, the combined layer exhibited a growth rate similar to the growth rate of the combined layer on the sodium carbonate cleaned aluminum alloy substrates with respect to the 6111, 5042 and 5182 alloys. With respect to the 3004 alloy, the growth rate of the combined layer increased relative to the sodium carbonate cleaned substrate.

[0074] The graph in Figure 21 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on various aluminum alloy substrates that were acid cleaned with Parco 202 (available from Henkle Technologies) at 77 C for 5 seconds, phosphoric acid/sulfuric acid based, pH <1. This cleaning process inhibited the growth of the combined layer on all of the alloys tested.

[0075] The graph in Figure 22 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on aluminum alloy substrates that experienced various surface treatments before the formation of the layer of aluminum hydrated oxide. The substrates were cleaned with a sodium carbonate based cleaner before the surface treatment. One substrate was treated with a 50% nitric acid solution at room temperature for 1 minute. One substrate was treated with Deox 31 (available from Henkle Technologies) at for 1 minute. One substrate was treated with a 10% phosphoric acid solution at room temperature for 1 minute. One substrate was treated with Nova bd (available from PCS Phosphates, Inc.) at 102 C for 2 minutes,

followed by a treatment with a 50% nitric acid solution at room temperature for 20 seconds. One substrate was treated with a 10% sodium silicate solution at room temperature for 1 minute. After surface treatment, each substrate was rinsed with deionized water, and then hydrated at 99 C. The nitric acid treatment had no effect on the growth rate of the combined aluminum oxide and hydrated oxide layer. The Deox 31 treatment decreased the growth rate of the combined layer by approximately 3 times. The phosphoric acid, Nova bright dip/nitric acid and sodium silicate treatments all inhibited the growth of the combined layer.

[0076] The elemental analysis by X-ray photoelectron spectroscopy in the chart in Figure 23 shows the elements that inhibited hydration shown in the graph of Figure 22. The rate of growth of the combined aluminum oxide and hydrated oxide layer correlates with the magnesium concentration on the surface of the aluminum alloy substrate; the higher the magnesium concentration, the higher the growth rate, except when ions such as phosphate, silicate or fluoride have reacted with surface hydroxyls.

[0077] The graph in Figure 24 shows the rate of growth of the combined aluminum oxide and hydrated oxide layer on an aluminum alloy substrate sodium carbonate cleaned, as detailed above, exposed to 100% relative humidity for 21 days, and exposed in a laboratory atmosphere for 21 days (15-25% relative humidity). Exposure to 100% relative humidity for 21 days had only a slight effect on the combined aluminum oxide and hydrated oxide layer growth rate relative to the carbonate cleaned aluminum alloy substrate. Exposure to a laboratory atmosphere for 21 days had a larger effect on the growth rate of the combined layer than exposure to 100% relative humidity for 21 days. An XPS analysis identified fluoride and sulfur contaminate species on the lab exposed aluminum alloy substrate. Infrared analysis identified the sulfur contaminate as sulfate. These results suggest the fluoride and/or sulfate surface contaminants inhibited hydration to a small extent.

[0078] It has been observed that the rate of growth of the combined aluminum oxide and hydrated oxide on an aluminum alloy substrate is a function of the alloy and is correlated with the magnesium concentration in the alloy. The combined growth rate is also affected by the temper of the metal as heat treatments increase the magnesium oxide/hydroxide on the surface of the substrate. The combined growth rate is also a function of the temperature of the water contacting the substrate. The chemistry of the combined layer formed via contact with water, steam or a

combination thereof, having a temperature from about 71 C to about 99 C is similar. Cleaning of the aluminum alloy substrate before the layer of aluminum oxide and hydrated oxide is formed can have a major effect on the growth rate of the combined layers depending on the type of cleaner. The effect of surface treatments of the aluminum alloy substrates on the growth rate of the combined layer can range from no effect to complete inhibition of growth. The growth rate is affected by compounds absorbed from the atmosphere onto a freshly cleaned surface.

[0079] In another example, an aluminum alloy sheet was conveyed down a coil line through a spray section where it was cleaned with a phosphate silicate and fluoride-free cleaner. Cleaner contact time was 5-8 second at 140 degrees F. Following the cleaning stage the sheet passed through 3 contaminant free room temperature deionized water spray rinses. After rinsing, the sheet was immersed via a submerged pass line in a contaminant free deionized water tank at 205-210 degree F for 5-8 seconds. The sheet left the submerged pass line tank and was immediately quenched with a contaminant free room temperature deionized water spray. The final step was to dry the sheet by passing it through a room temperature air blow-off drying zone. The combined thickness range of the layer of aluminum oxide and hydrated oxide obtained was between 14 and 25 nm.

[0080] Figures 25 - 31 show test results performed on substrates having a hydrated oxide layer produced in a coil line. Figures 29 and 30 also show test results from substrates treated using prior art methods for comparison purposes.

[0081] In some embodiments, the hydrated oxide layer can provide an excellent surface for adhesion of: paints, primers, architectural paints such as organic solvent thinned paints, shellacs, cellulose derivatives, acrylic resins, vinyl resins, bitumens, and water thinned paints (latexes) such as copolymers of butadiene and styrene, polyvinyl acetate, acrylic resin; commercial finishes such as air-drying finishes such as epoxies, urethanes, polyester resins, alkyds, modified rubbers, and baking finishes such as acrylic resins, phenolic resins; industrial coatings such as corrosion resistant coatings, phenolic resins, chlorinated rubber, coal tar, epoxies, epoxies cured from a solvent solution with polyfunctional amines, polyamide resins, vinyl resin, elastomers, polyesters, and polyurethanes, and high temperature coatings such as silicone rubber, silicone resins, polyamides, TFE polymers; and immersion service coatings such as asphalt, thermoplastic coal tar, epoxy-furans, amine-cured epoxies, fluorocarbons, furfuryl alcohol resins, neoprene, bake unmodified phenolics,

unsaturated polyesters, polyether resins, low-density polyethylene, chlorosulfonated polyethylene, polyvinyl chloride plastisols, resinous cements, rubber, urethanes.

[0082] Sheet stock coated with a polymeric material produced in accordance with some embodiments of the present invention is suitable for use in can bodies or as end stock for easy open ends. The polymer coatings can be applied, for example, by spraying, dipping, roll coating, laminating, powder coating and then formed into containers.

[0083] Although the present invention has been described in considerable detail with reference to certain versions thereof, other versions are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the embodiments contained herein.

[0084] All features disclosed in the specification, including the claims, abstracts, and drawings, and all the steps in any method or process disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. Each feature disclosed in the specification, including the claims, abstract, and drawings, can be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

[0085] Any element in a claim that does not explicitly state "means" for performing a specified function or "step" for performing a specified function should not be interpreted as a "means or step for" clause as specified in 35 U.S.C. § 112.

CLAIMS

1. A process for treating an aluminum alloy substrate comprising:
exposing an untreated and uncoated aluminum alloy substrate having a layer of aluminum oxide to an aqueous environment for a period of time in the range of about 1 second to about 20 seconds, wherein the aqueous environment has a temperature of at least 170°F, and wherein the environment is substantially free of deleterious ions.
2. The process of Claim 1 further comprising, before exposing the aluminum alloy substrate to an aqueous environment, cleaning the substrate with a cleaning agent substantially free of deleterious ions.
3. The process of Claim 1 wherein the aqueous environment contains 5 parts per million or less of phosphates, 5 parts per million or less of fluoride, and 10 parts per million or less of silicates.
4. The process of Claim 1 wherein the aqueous environment has a temperature of about 205° F. to about 210° F.
5. The process of Claim 1 wherein the substrate is exposed to the aqueous environment for about 5 seconds to about 10 seconds.
6. The process of Claim 1 further comprising cooling the substrate.
7. The process of Claim 1 further comprising drying the substrate.
8. The process of Claim 1 wherein the substrate is a sheet in a coil.
9. The process of Claim 1 wherein exposing the aluminum alloy substrate to an aqueous environment comprises submerging the aluminum alloy substrate in an aqueous liquid.

10. The process of Claim 1 wherein exposing the aluminum alloy substrate to an aqueous environment comprises spraying an aqueous solution on the substrate.

11. The process of Claim 1 further comprising coating the substrate with an organic coating.

12. The process of Claim 8 wherein the sheet is suitable for use in food or beverage packages.

13. A treated aluminum alloy substrate comprising:
an aluminum alloy substrate;
a layer of aluminum oxide on the substrate; and
a layer of hydrated oxide on the layer of aluminum oxide, wherein the combined thickness of the layer of aluminum oxide and the layer of hydrated oxide is less than about 40 nm.

14. The substrate of Claim 13 wherein the layer of hydrated oxide appears substantially clear and colorless.

15. The substrate of Claim 13 wherein the substrate comprises a coil of aluminum sheet.

16. The substrate of Claim 15 wherein the sheet is suitable for use in food or beverage packages.

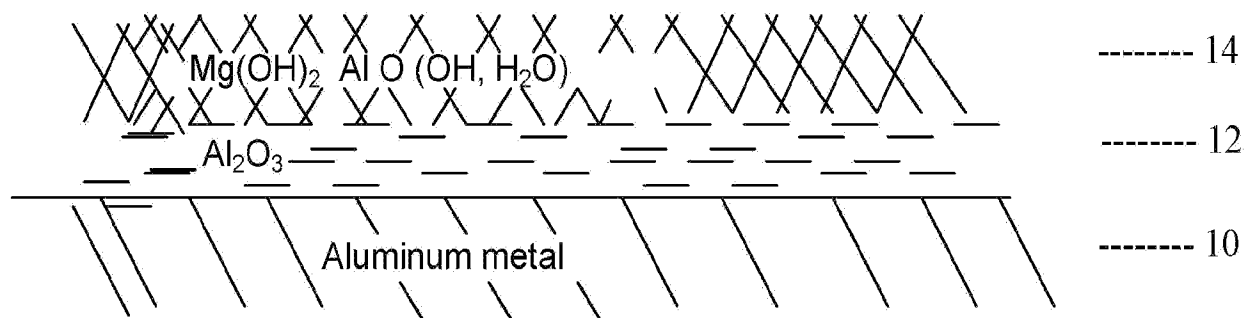


Fig. 1

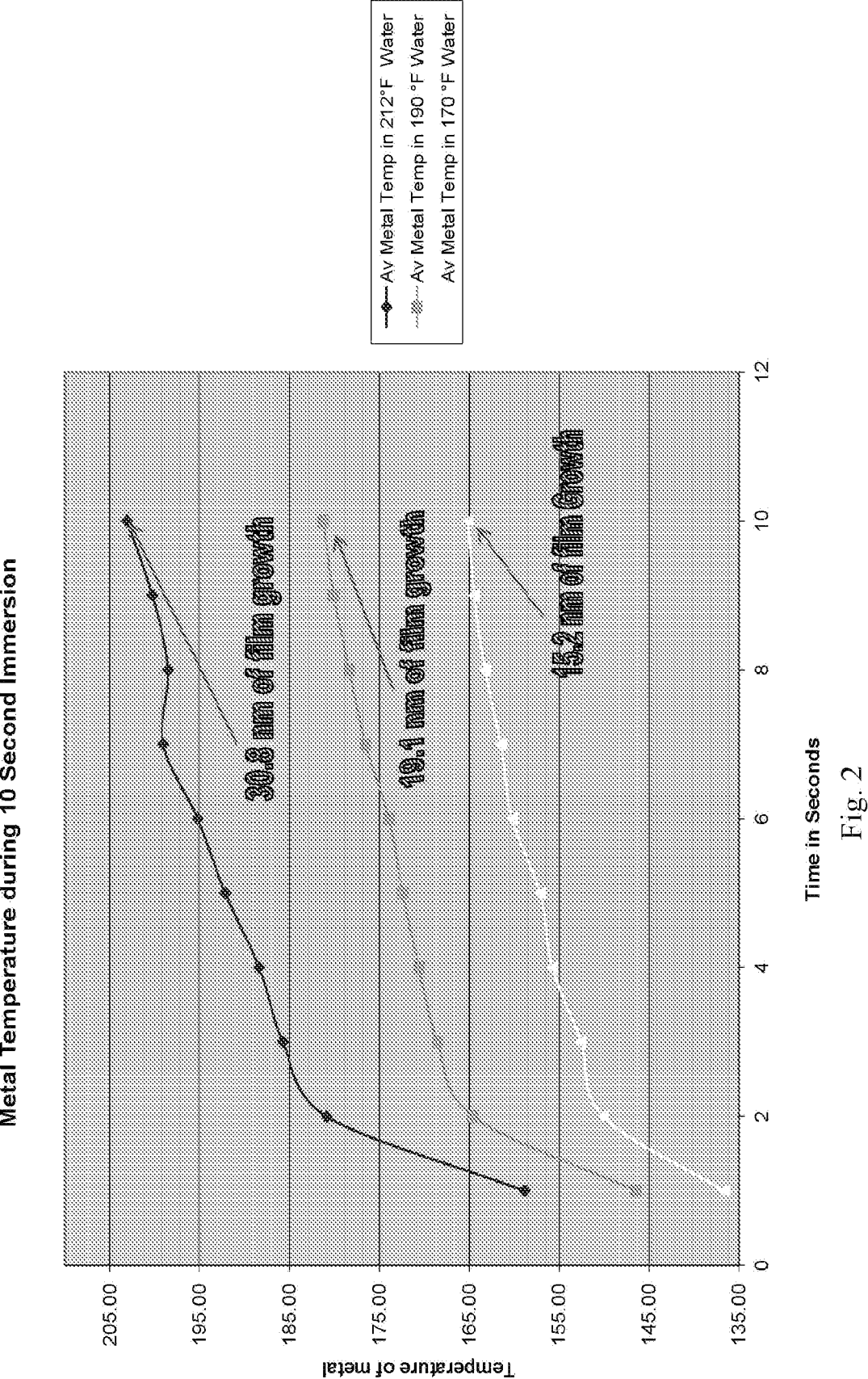


Fig. 2

Flat Sheet Performance Results

Polyester Over 5182

	Dry Adhesion	Pasteurize Blush	Pasteurize Adhesion	Process Blush	Process Adhesion	T-bends
Chromium Phosphate	Pass	Pass	Pass	Pass	Pass	1-T
Cleaned Only	Pass	Spots	Pass	Spots	Fail	1-T
Oxide/ hydroxide	Pass	Spots	Pass	Pass	Pass	1-T

Fig. 3

Can Performance Results Vinyl Over 5042-H2E72

	Dry Sidewall Adhesion	Dry Crosshatch Adhesion	Process Sidewall Adhesion	Process Crosshatch Adhesion	Enamel rating after HCl	Blister Rating
Chromium phosphate	100%	100%	100%	100%	31	Slight
Cleaned only	0%	10%	40%	80%	178	Severe
Oxide/ hydroxide	97% 100%	100%	100%	100%	18	Slight

Fig. 4

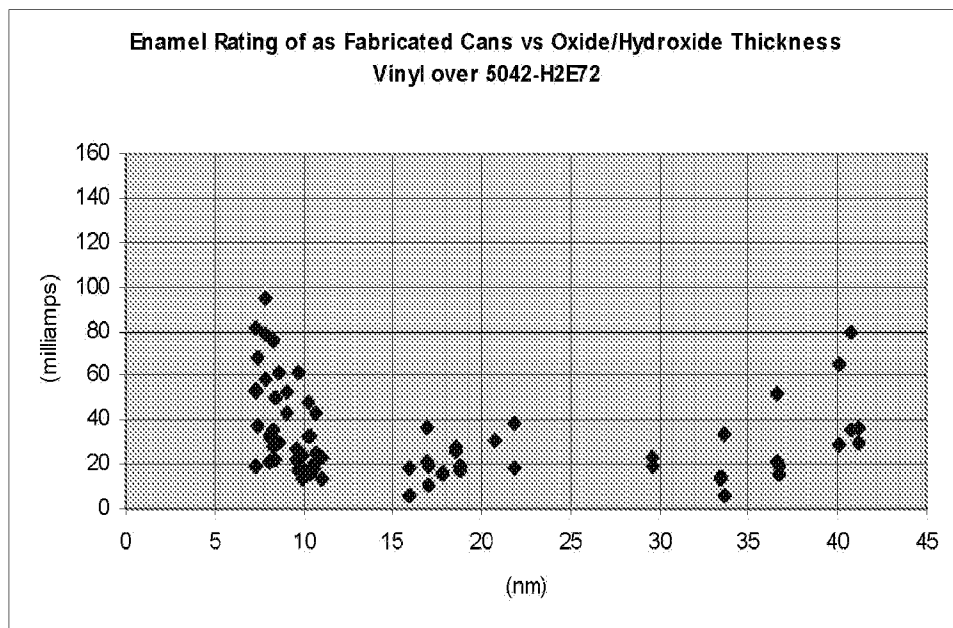


Fig. 5

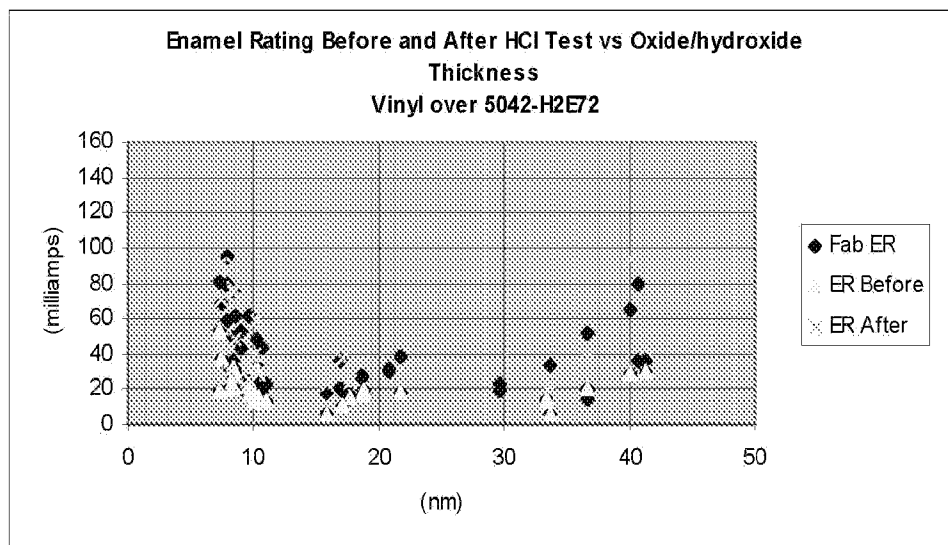


Fig. 6

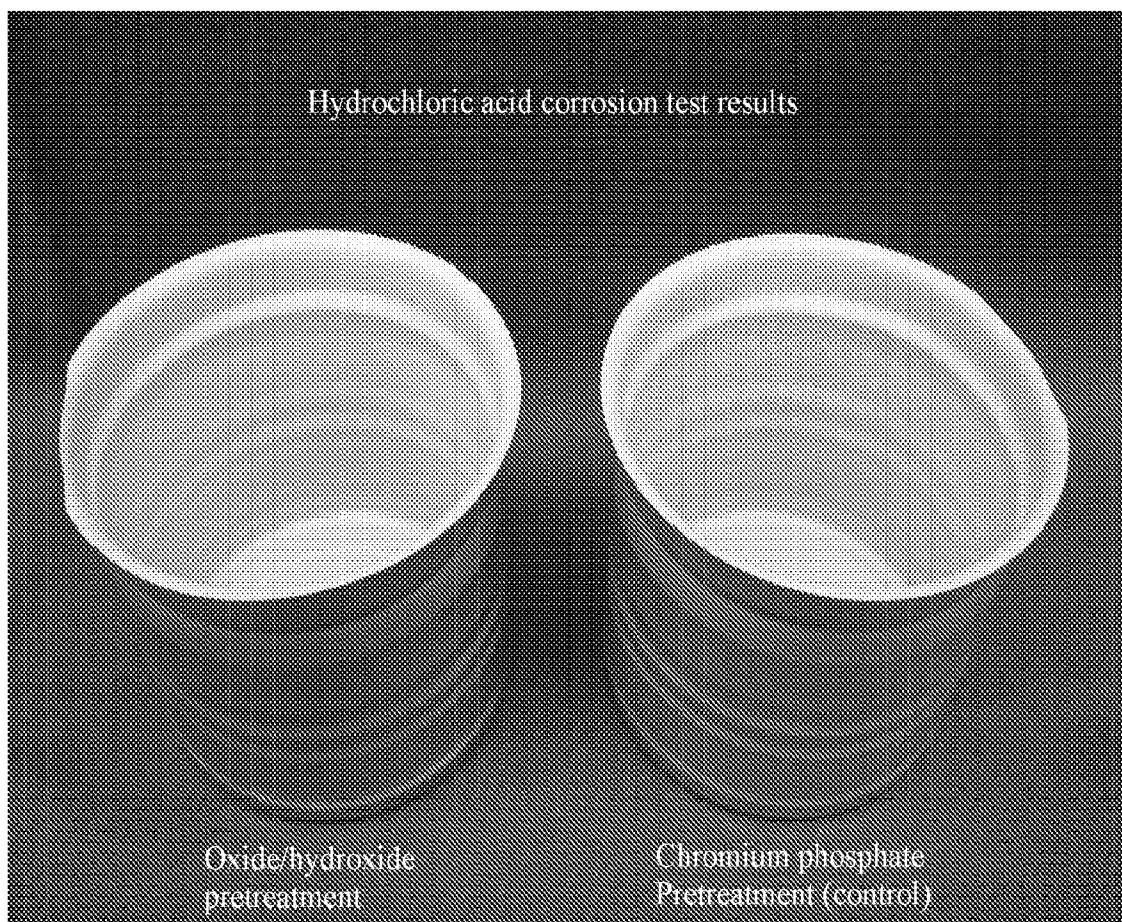


Fig. 7

Flat Panel Results
Fluoropolymer Over 6063 T4
Boiling Water Test

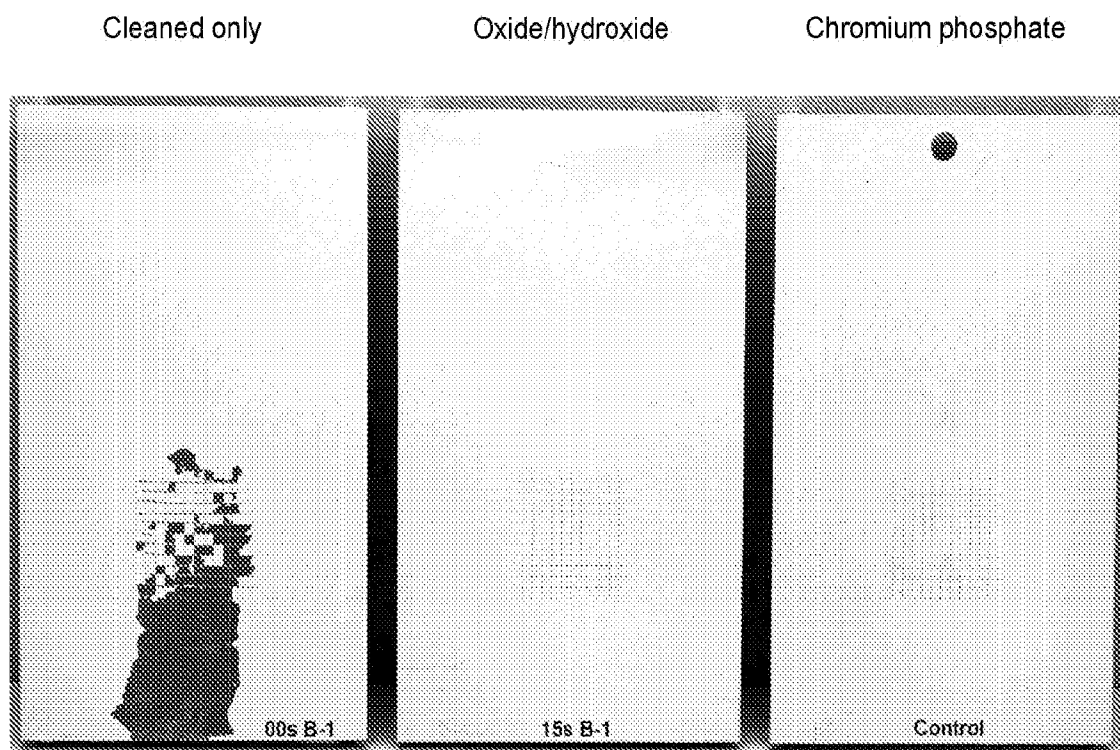


Fig. 8

Flat Panel Results
Fluoropolymer Over 6063 T4
Thermal Shock Test

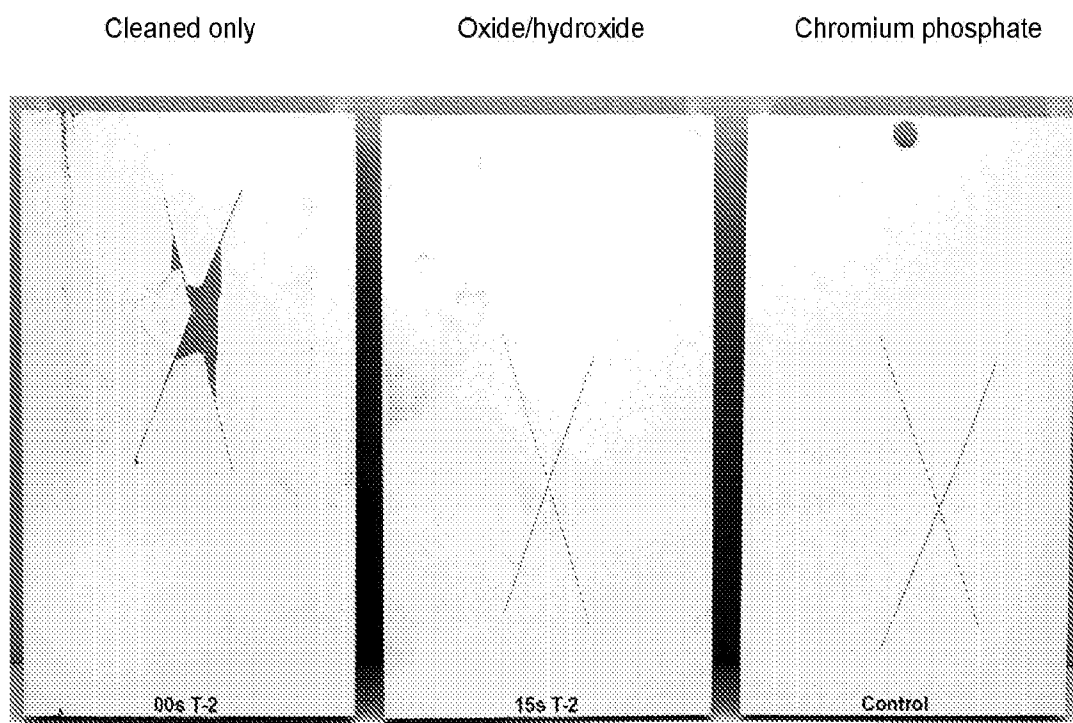


Fig. 9

Flat Panel Results
Fluoropolymer Over 6063 T4
Hydrochloric Acid Test

Cleaned only

Oxide/hydroxide

Chromium phosphate

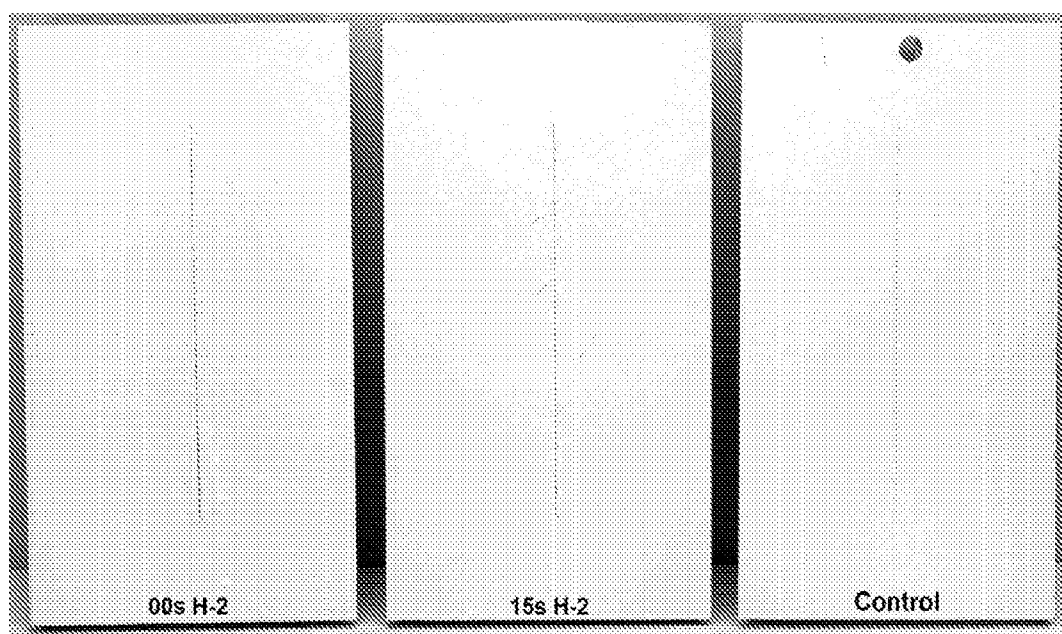


Fig. 10

Flat Panel Results
Fluoropolymer Over 6063 T4
MASTMAASIS Test

Cleaned only

Oxide/hydroxide

Chromium phosphate

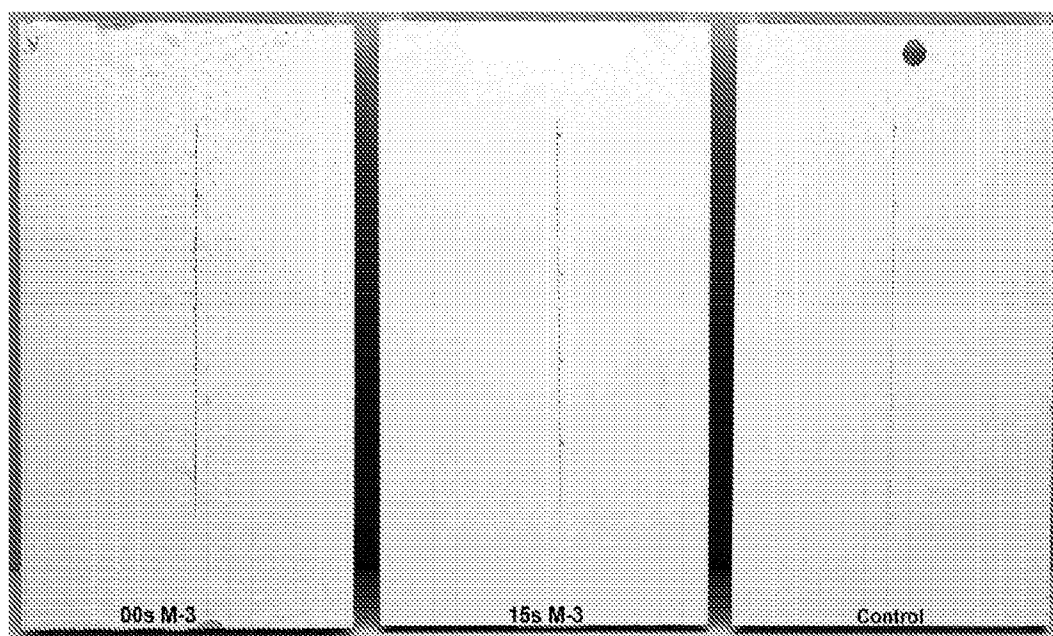


Fig. 11

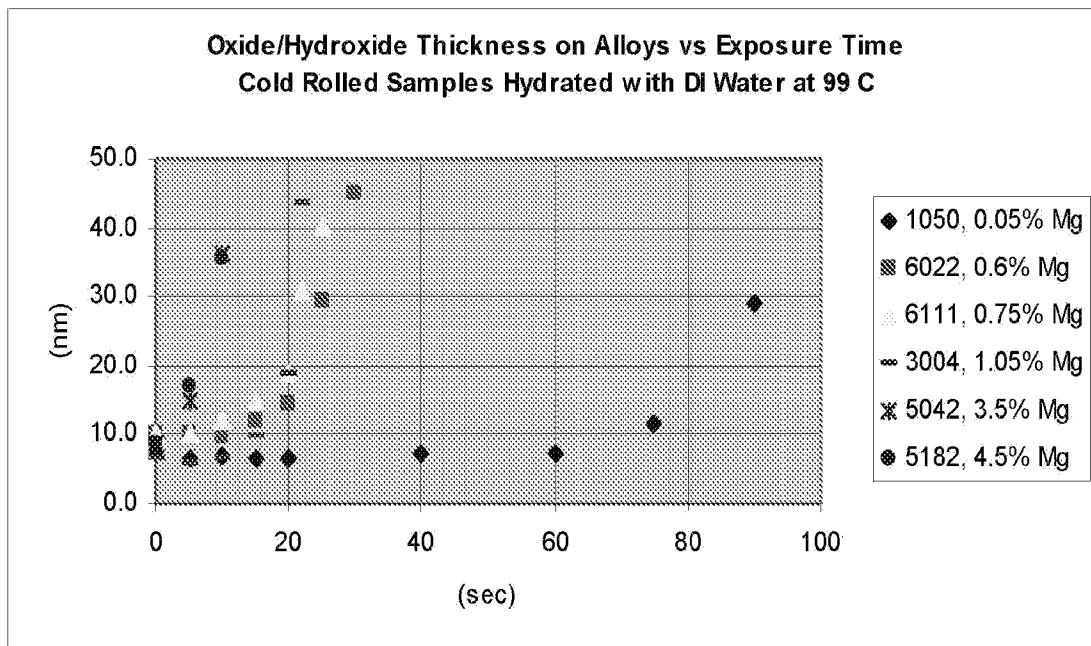


Fig. 12

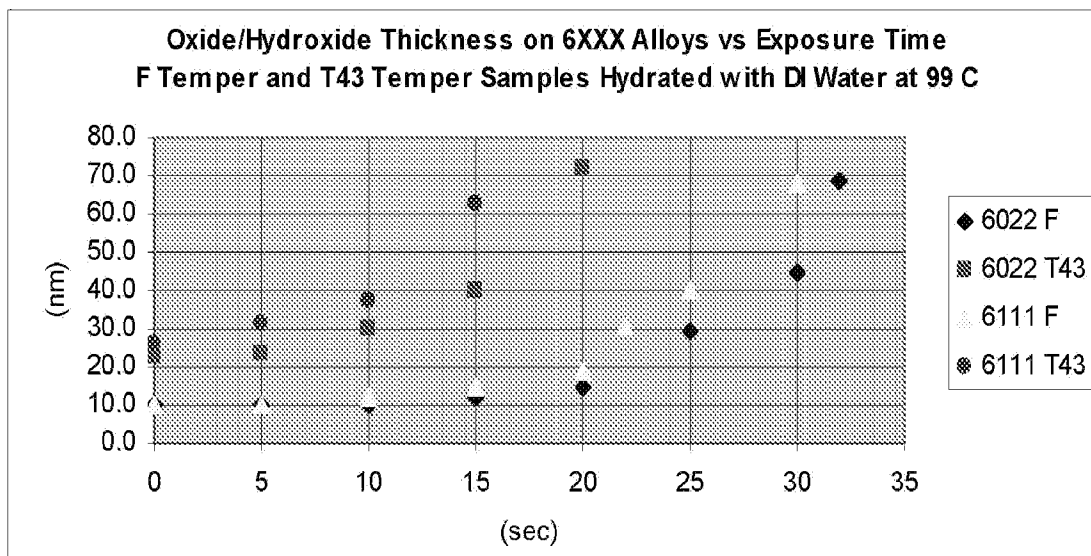


Fig. 13

XPS of 6111 F and T43 Tempers

Elemental Atomic Percent

	C	O	F	Na	Mg	Al	Si	S	Cl	Mg/Al	Al oxide thickness (nm)
F Temper, Labeled Side	49.1	32.9	0.0	0.0	1.9	14.8	1.1	0.1	0.1	0.13	5.0
F Temper, Unlabeled Side	52.3	29.6	0.1	0.0	1.9	14.7	1.3	0.1	0.0		4.5
T43 Temper, Labeled Side	51.0	32.3	0.0	0.3	9.0	5.7	0.2	1.3	0.2	1.58	>7.0
T43 Temper, Unlabeled Side	52.9	30.8	0.0	0.0	10.4	4.6	0.2	0.9	0.2	2.26	>7.0

Fig. 14

FT-IR of 6111, F and T43Temper

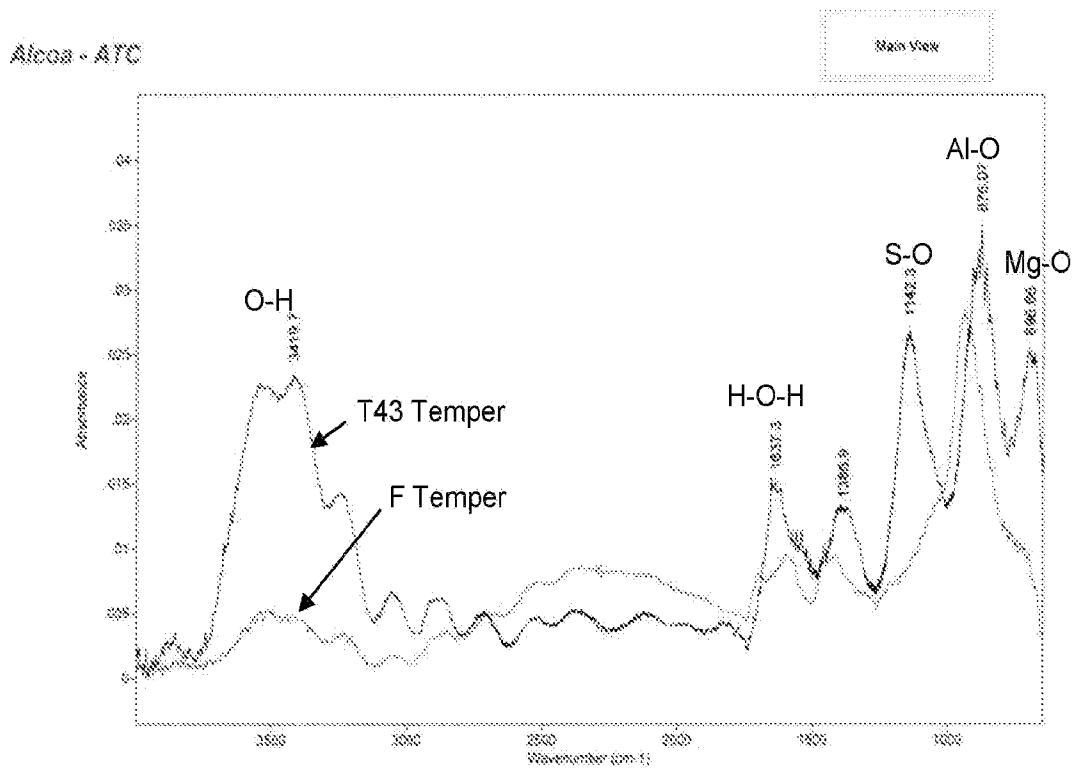


Fig. 15

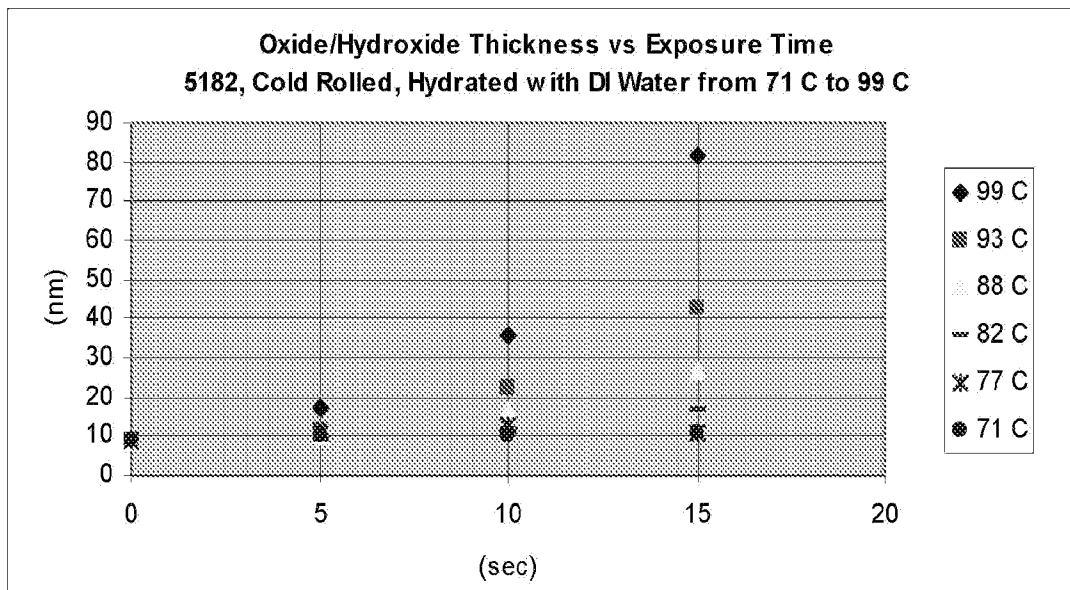


Fig. 16

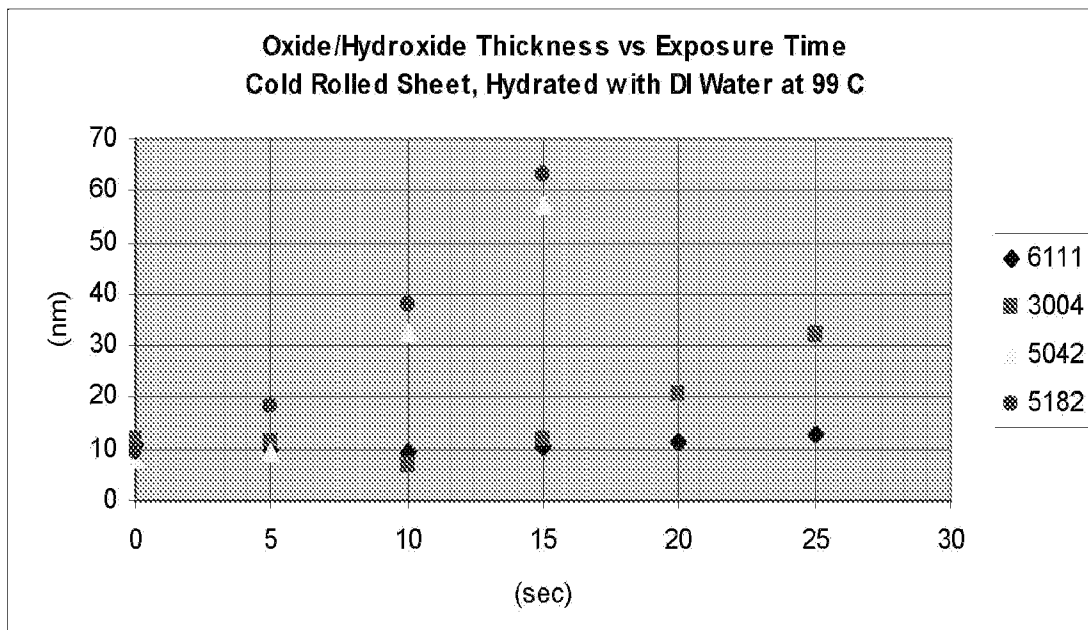


Fig. 17

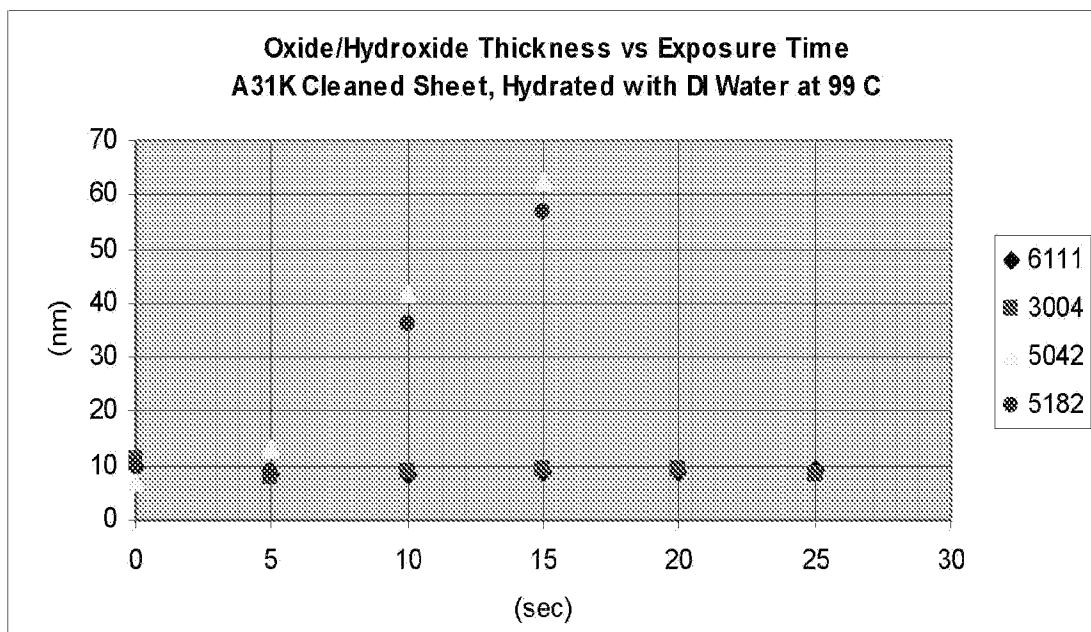


Fig. 18

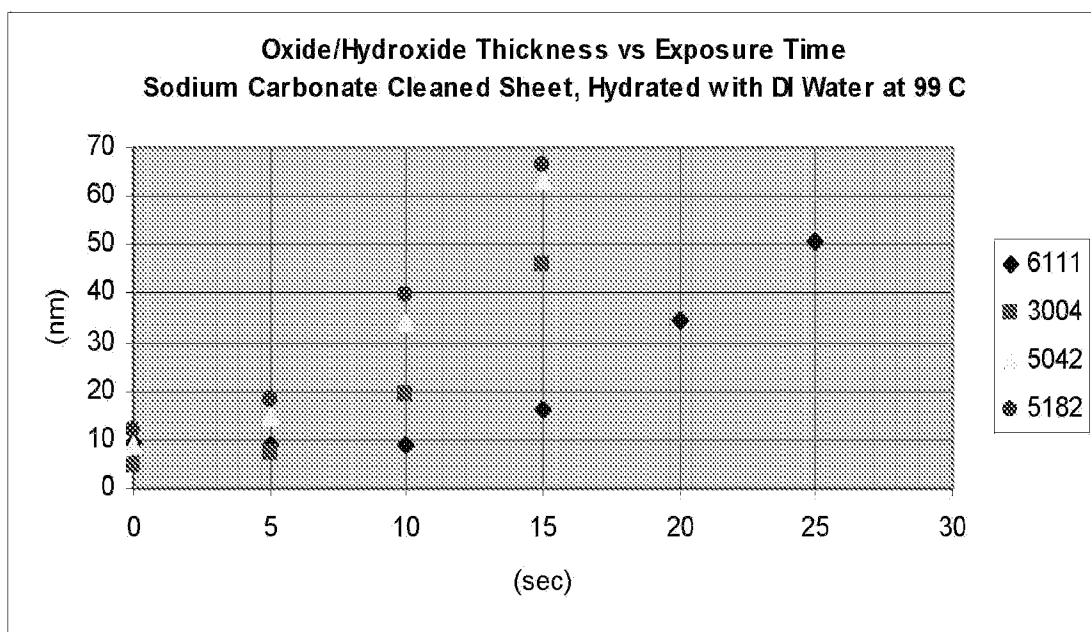


Fig. 19

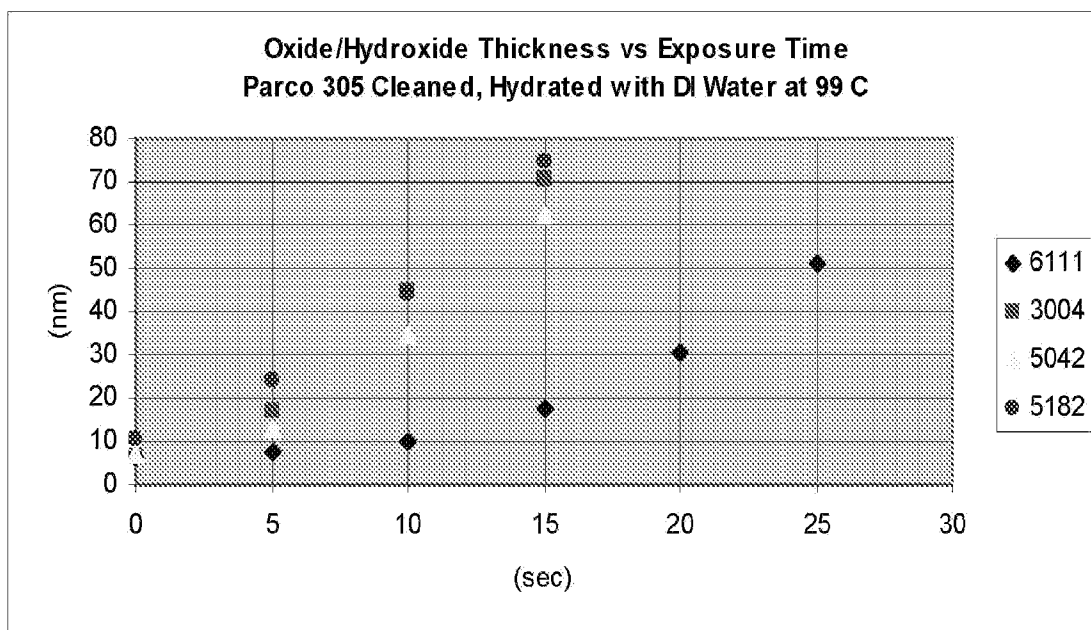


Fig. 20

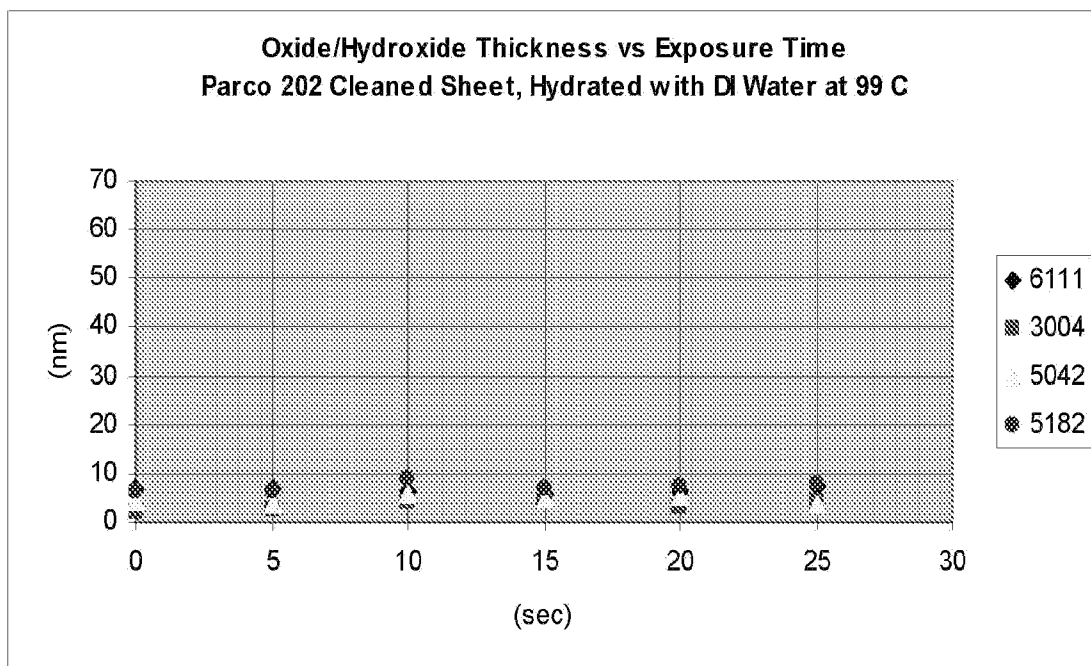


Fig. 21

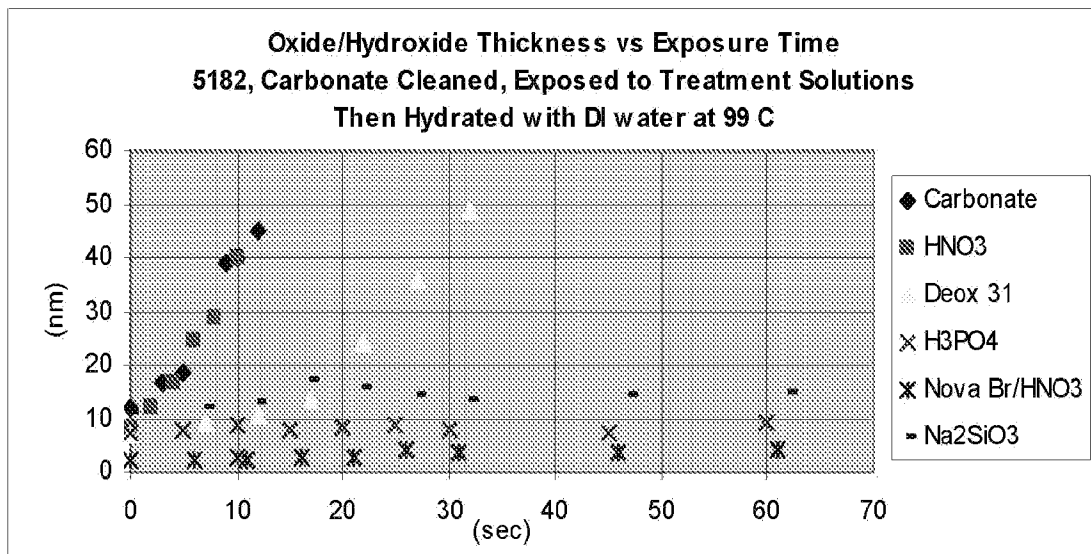


Fig. 22

XPS of Treated Surfaces
Elemental Atomic Percent

	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	Cu	Mg/Al	Oxide Thickness (nm)
Carbonate Cleaned	47.5	0.1	33.9	0.2	0.0	3.2	15.0	0.1	0.0	0.0	0.0	0.0	0.21	4.5
Nitric Acid	45.2	0.1	34.3	0.1	0.0	2.8	16.3	1.1	0.0	0.1	0.0	0.0	0.17	4.5
Deox 31	47.0	0.1	25.8	7.6	0.2	1.4	16.6	1.1	0.0	0.2	0.0	0.0	0.08	3.5
Phosphoric Acid	51.7	0.1	28.8	0.0	0.0	2.1	15.2	1.0	1.0	0.1	0.0	0.0	0.14	4.5
Nova bright dip/HNO₃	39.3	0.0	33.1	0.1	0.0	3.7	19.5	1.7	1.1	0.0	0.0	1.5	0.19	4.5
Sodium Silicate	47.4	0.0	31.9	0.0	0.2	4.4	13.0	2.9	0.0	0.2	0.0	0.0	0.34	5.0

Fig. 23

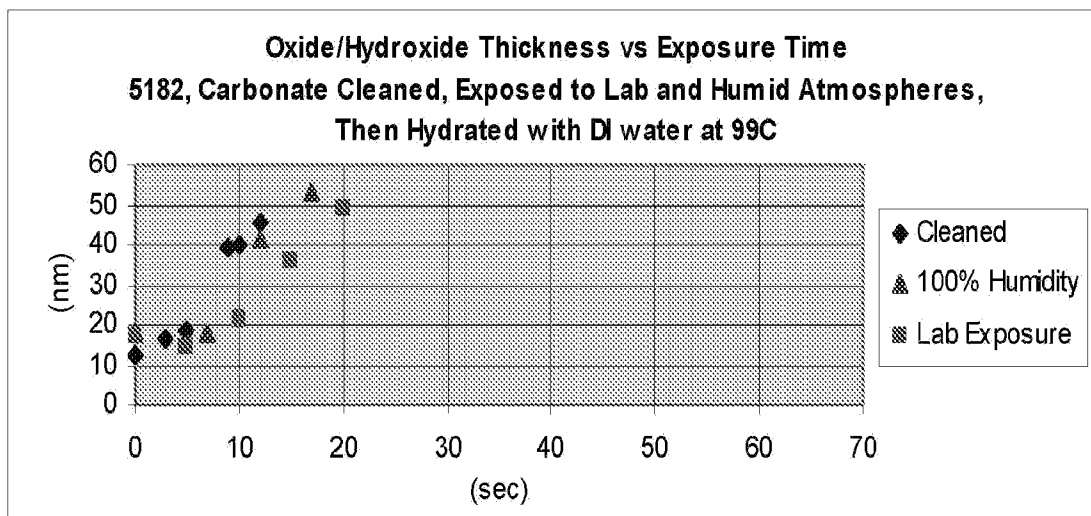


Fig. 24

6-Jul-09

Color ratings vs. R-985 thickness

Unable to obtain meaningful numbers from the color instrument.

Samples were rated visually on a 0-10 scale, 0=clear & 10=gold

These samples did not exhibit a mottling appearance just a uniform gold color

Fig. 25

Dip time seconds	thickness nm	Bare sheet Alloy			Dav-138 coated sheet Alloy		
		5182	5042	3004	5182	5042	3004
0	8.5	10.7	6.34	0	0	0	0
5	25.6	19.8	14.7	0	0	0	0
10	47.3	45.6	38.5	4	4	4	4
15	79.1	74.3	61.3	6	6	6	6
20	102	100.5	91.8	8	8	8	8
30	136.4	135.3	127.3	10	10	10	10
Current commercial sheet (A272 treated)			3.5			3.5	

Time seconds	thickness	thickness	a value	a value
	nm	nm	5182	5042
	5182	5042		
0	8.5	10.7	0.12	0.225
5	25.6	19.8	0.275	0.34
7		33.49		0.43
10	47.3	45.6	1.005	0.625
12		59.13		1.29
15	79.1	74.3	1.665	1.745
20	102	100.5	1.72	2.125
30	136.4	135.3	2.285	2.37

Fig. 26

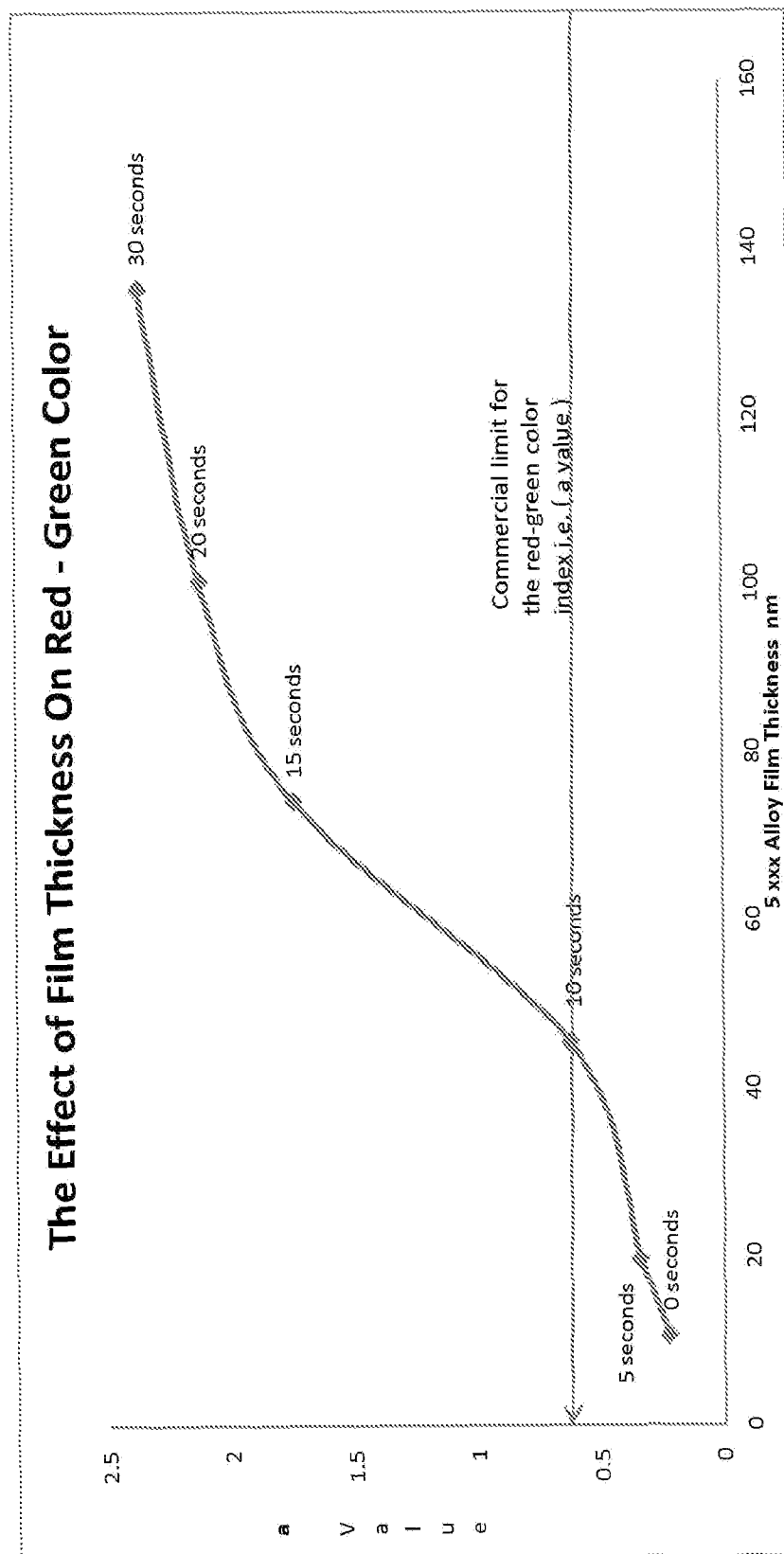


Fig. 27

Jun-09

Oxide / Hydroxide thickness ladder

All samples prepared in the lab are 5042 alloy, cleaned in A685 for 5 seconds @ 140 F

Exterior of panel coated with DAV-138, air dried. Interior coated with DAV-205 & cured in a box oven to a PMT of 450 F

As the oxide thickness increased the white coating appeared pinker in color.

Upon aging in the lab the pink color begins to fade.

Accelerated HCl pack test (208 X 207 Food Cans)

Immersion Time	Oxide Thickness nm	Enamel Ratings (milliamps)		Blister Rating 0-10, 0=Best
		Before HCl	After HCl	
212 F DI Water				
5 seconds	30.3	21.6	41.1	2.5
10 seconds	47.5	15.3	51.0	2.5
15 seconds	78.4	39.8	54.2	2.5
20 seconds	106.7	18.1	54.5	2.0
30 seconds	133.1	22.9	59.9	2.0

Flat sheet Testing

Immersion		
Time	% crosshatch	T-Bend
212 F DI Water	Adhesion	Adhesion
5 seconds	100	Pass T-0
10 seconds	100	Pass T-0
15 seconds	100	Pass T-0
20 seconds	100	Pass T-0
30 seconds	100	Pass T-0

Fig. 28

Coating & Pretreatment Variable	Adhesion Results For Fully Converted 202 Ends n= 10 ends										
	Blush after WP Public side		% Dry Adhesion Public side		% WP Adhesion Prod. side		ERs Before 10X Prod side		ERs after 10X Prod side		Visual rating after 10X Product
	Blush after WP Public side	Blush after WP Public side	% Dry Adhesion Public side	% WP Adhesion Prod. side	% WP Adhesion Public side	% WP Adhesion Prod. side	ERs Before 10X Prod side	ERs Before 10X Prod side	ERs after 10X Prod side	ERs after 10X Prod side	
ALC 156 / ALC 160 for 202 converted ends											
A272 Control	0	1	100	100	100	100	0.66 (0.20)	6.0 (4.2)	0.21 (0.16)	13.6	
R-985	0	0	100	100	100	100	0.77 (0.40)	10.1 (7.5)	0.60 (0.45)	19.6	
R-985 w/ Alkaline	0	0	100	100	100	100	0.96 (0.85)	12.2 (6.0)	0.78 (0.46)	23.8	
Cleaned only control	0	0	100	100	100	100	1.99 (1.99)	20.8 (12.8)	1.57 (1.22)	30.8	
ALC 103 / ALC 103 for 202 converted ends											
A272 Control	0	0	100	100	100	100	1.34 (1.26)	5.1 (4.8)	0.76 (0.41)	10	
R-985	0	0	100	100	100	100	1.07 (0.83)	5.2 (3.4)	0.66 (0.48)	15.2	
R-985 w/ Alkaline	0	0	100	100	100	100	0.47 (0.16)	2.1 (1.5)	0.27 (0.08)	13.4	
Cleaned only control	0	0	100	100	100	100	1.99 (1.41)	8.2 (5.4)	0.68 (0.47)	12.6	
ALC 432 / ALC 729 for 202 converted ends											
A272 Control	1	0	100	100	100	100	NA	NA	90	NA	
R-985	1	0	100	100	100	100	NA	NA	90	NA	
R-985 w/ Alkaline	1	0	100	100	100	100	NA	NA	90	NA	
Cleaned only control	1	0	100	100	100	100	NA	NA	90	NA	
ALC 729 / ALC 432 for 202 converted ends											
A272 Control	0	1	100	100	100	100	NA	NA	95	NA	
R-985	0	1	100	100	100	100	NA	NA	100	NA	
R-985 w/ Alkaline	0	1	100	100	100	100	NA	NA	100	NA	
Cleaned only control	0	1	100	100	100	100	NA	NA	100	NA	
ALC 103 Ends from Warrick CCL2											
A272 Control							0.49 (0.07)	1.4 (1.0)	0.11 (0.04)	2.8	

Fig. 29

Coating & Pretreatment Variable	Adhesion Results For 208 x 207 Deep Drawn Cans n=10 cans												
	ALC 106/DAV205 on 208 x 207 Cans	Blush Product side Water	Blush Public side Water	% Dry		% WP		% WP		ERs after HCL		Blister Rating Product side 0=NB, 4= severe	Comments Ranking (1= best)
				Adhesion	Cut Edge	Side Wall	Cut Edge	Adhesion	Cut Edge	Milliamps	HCL		
A272 Control	0	0	0	100/100	99.8/100	100/100	100/100	100/100	100/100	71.1 (22.9)	114.64 (50.0)	4.0	2
R-985	0	0	0	100/100	99.8/100	100/100	100/100	100/100	100/100	72.1 (48.8)	186.05 (107.6)	4.0	1
R-985 w/ Alkaline	0	0	0	96.4/100	74/100	100/100	100/100	100/100	100/100	107.0 (44.60)	164.53 (49.0)	4.0	4
Cleaned only control	0	0	0	100/100	98.5/100	100/100	100/100	100/100	100/100	88.2 (44.6)	129.31(65.1)	4.0	3
ALC 106/ALC 201 on 208 x 207 Cans				Product side	Product side								Ranking (1= best)
A272 Control	0	NA	NA	100	99.5 (0.53)	100	100	100	100	4.2 (2.2)	4.0 (1.9)	1.4 (0.5)	3
R-985	0	NA	NA	100	98.9 (0.88)	100	100	100	100	5.7 (3.2)	5.7 (2.5)	1.0 (0.0)	1
R-985 w/ Alkaline	0	NA	NA	97.5	46 (5.2)	100	100	100	100	10.2 (10.9)	9.9 (12.8)	1.1 (0.3)	2
Cleaned only control	0	NA	NA	100	98.1(1.29)	100	100	100	100	14.9 (12.0)	21.9 (17.4)	1.3 (0.5)	4

Fig. 30

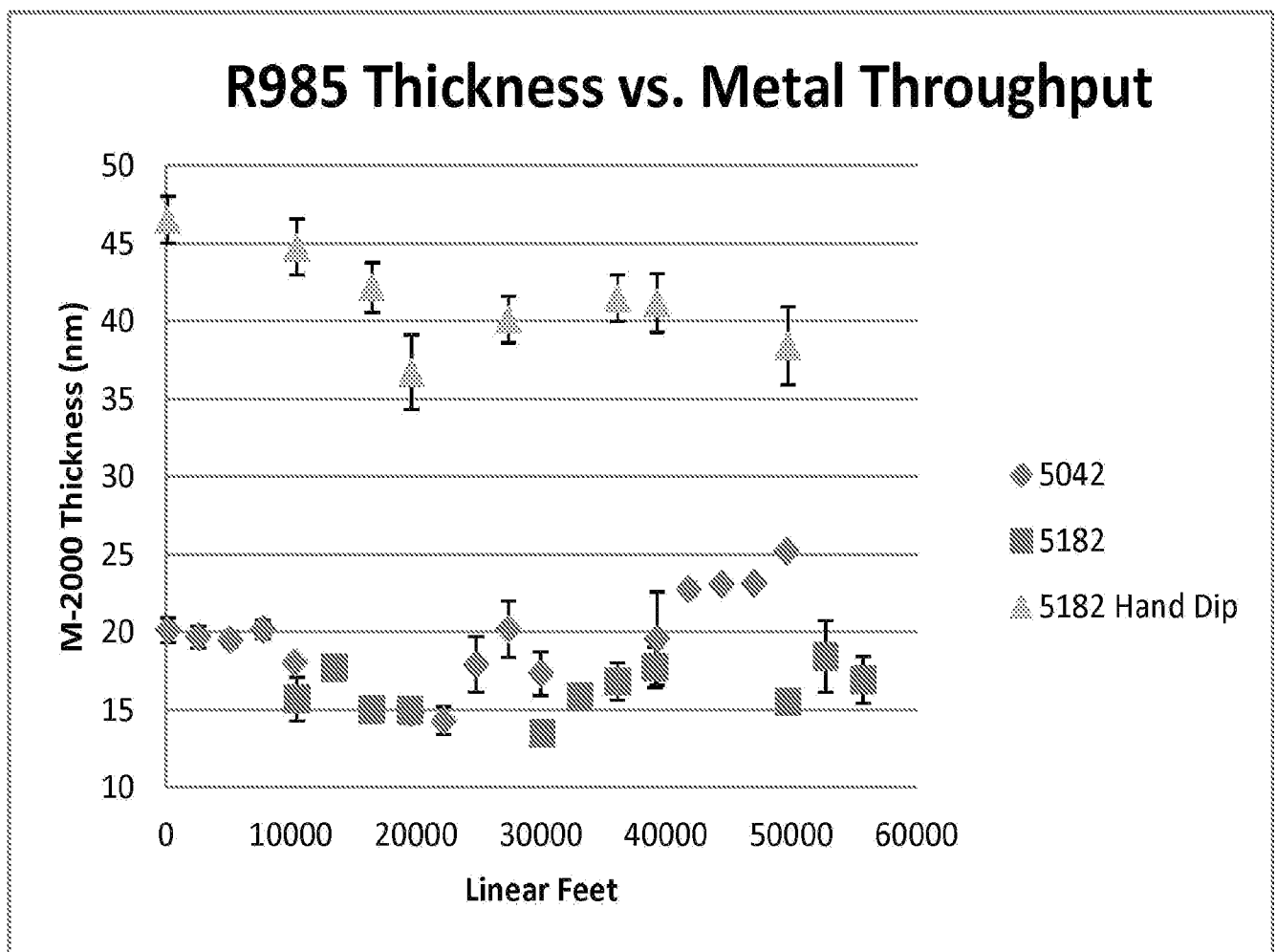


Fig. 31

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/045295

A. CLASSIFICATION OF SUBJECT MATTER
INV. B05D7/00 C23C22/68
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 103 550 A (WEFERS KARL [US] ET AL) 14 April 1992 (1992-04-14) column 2, line 50 - column 5, line 61; claims; example 1 -----	1-16
X	STRALIN A ET AL: "IMPROVED ADHESION STRENGTH BETWEEN ALUMINUM AND ETHYLENE COPOLYMERS BY HYDRATION OF THE ALUMINUM SURFACE", JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY & SONS, INC, US, vol. 49, no. 3, 15 July 1994 (1994-07-15), pages 511-521, XP000460832, ISSN: 0021-8995, DOI: 10.1002/APP.1993.070490315 "Experimental" "Discussion" figures 1,4 ----- -/--	1-16

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

17 October 2011

Date of mailing of the international search report

27/10/2011

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/048539 A1 (UCHIDA HIDETOSHI [JP] ET AL) 1 March 2007 (2007-03-01) claims; example 1; table 1 -----	13, 14
A	JP 6 322513 A (MITSUBISHI MATERIALS CORP) 22 November 1994 (1994-11-22) abstract; figures -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/045295

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			JP 4768363 B2	07-09-2011
			JP 2007063600 A	15-03-2007

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