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(54) **COATING AN ALUMINUM ALLOY SUBSTRATE**

BESCHICHTUNG VON ALUMINIUMLEGIERUNGSSUBSTRATEN

REVETEMENT D'UN SUBSTRAT EN ALLIAGE D'ALUMINIUM

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- **PATENT ABSTRACTS OF JAPAN vol. 003, no. 003 (C-033), 16 January 1979 (1979-01-16) -& JP 53 125238 A (NIPPON PAINT CO LTD), 1 November 1978 (1978-11-01)**

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Description

[0001] The present invention relates to a process for coating an aluminum alloy substrate with a polymer. More particularly, the invention relates to a process for pretreating an aluminum alloy substrate with a vinyl phosphonic acid-acrylic acid copolymer before polymer coating the substrate.

[0002] Although aluminum protects itself against corrosion by forming a natural oxide coating, the protection is not complete. In the presence of moisture and electrolytes, aluminum alloys corrode much more rapidly than pure aluminum.

[0003] Accordingly, there is a need to treat aluminum alloy substrates with pretreatments or other chemicals that provide improved corrosion resistance as well as good adhesion for polymers.

[0004] In the prior art, chemical conversion coatings have been formed on aluminum alloys by "converting" a surface of the metal into a tightly adherent coating, part of which consists of an oxidized form of aluminum. Chemical conversion coatings provide high corrosion resistance and improved adhesion for polymer coatings. A chromium-phosphate conversion coating is typically provided by contacting aluminum with an aqueous solution containing hexavalent chromium ions, phosphate ions and fluoride ions. In recent years, concerns have arisen regarding the pollution effects of chromates and phosphates discharged into waterways by such processes. Because of the high solubility and strongly oxidizing character of hexavalent chromium ions, expensive waste treatment procedures must be employed to reduce the hexavalent chromium ions to trivalent chromium ions for waste disposal.

[0005] Attempts have been made in the prior art to produce acceptable chromate-free conversion coatings for aluminum. For example, some chromate-free conversion coatings contain zirconium, titanium, hafnium and/or silicon, sometimes combined with fluorides, surfactants and polymers such as polyacrylic acid. In spite of the extensive efforts that have been made previously, there is still no entirely satisfactory non-chromate conversion coating or primer for improving the adhesion and corrosion resistance of polymer coated aluminum alloy substrates. Polymer adhesion and corrosion resistance are important characteristics in aluminum alloy sheet used for making food container bodies and ends and beverage container ends.

[0006] Attempts have also been made in the prior art to pretreat substrates with various organophosphorus compounds before coating them with a polymer. As used herein, the term "organophosphorus compounds" includes organophosphoric acids, organophosphinic acids, organophosphonic acids, as well as various salts, esters, partial salts, and partial esters of such acids. For example, Dutch Patent Application No. 263,668, filed April 14, 1961, discloses a process wherein steel sheets are treated with a vinylphosphonic acid/acrylic acid copolymer before coating with an alkyd resin enamel. Although some organophosphorus pretreatments may perform adequately, they are expensive to implement. Accordingly, there still remains a need to provide an efficient and economical process for pretreating an aluminum alloy substrate with an organophosphorus compound before applying a polymer coating.

[0007] A principal objective of the present invention is to provide an efficient and economical process for pretreating an aluminum alloy substrate with an organophosphorus compound before applying a polymer coating.

[0008] To accomplish this principal objective our process provides for removing aluminum and other cations from pretreatment solutions, thereby avoiding costly disposal of such solutions.

[0009] Additional objectives and advantages of our invention will become apparent to persons skilled in the art from the following detailed description.

[0010] The sole Figure is a flowsheet diagram of the process of the present invention.

[0011] In accordance with our invention there is provided a process for coating an aluminum alloy substrate with an organic polymer. The aluminum alloy substrate may be provided in the form of a sheet plate, extrusion or casting and is preferably a sheet.

[0012] Various aluminum alloys available in sheet form are suitable for practice of the present invention, including alloys belonging to the AA2000, 3000, 5000, 6000 and 7000 series. Aluminum-magnesium alloys of the AA5000 series and particularly the AA5042 and AA5182 alloys are preferred. Sheet made from these alloys is useful for shaping into polymer coated food container bodies or ends, and beverage container ends.

[0013] Aluminum alloys suitable for container end panels such as AA5182 are provided as an ingot or billet or slab by casting techniques known in the art. Before working, the ingot or billet is subjected to elevated temperature homogenization. The alloy stock is then hot rolled to provide an intermediate gauge sheet. For example, the material may be hot rolled at a metal entry temperature of about 371°-524°C (700°-975°F) to provide an intermediate product having a thickness of about 0.254 cm to 0.381 cm (0.100 inch to 0.150 inch). This material is cold rolled to provide a sheet ranging in thickness from about 0.0152 to 0.0381 cm (0.006 to 0.015 inch). We prefer AA5182 aluminum alloy sheet in the H19 temper. Aluminum alloy 5042 sheet for end panels is preferably in the H 19 temper.

[0014] Aluminum alloys such as AA5042 are provided as an ingot that is homogenized. This is followed by hot rolling to an intermediate gauge of about 0.254 to 0.381 cm (0.100 inch to 0.150 inch). Typically, the intermediate gauge product is annealed, followed by hot rolling and then cold rolling to a final gauge product having a thickness of about 0.0152 to 0.0381 cm (0.006 to 0.015 inch). The sheet is coated with a polymer and then drawn and redrawn into food container bodies. We prefer AA5042

aluminum alloy sheet in the H2x temper.

[0015] The natural oxide coating on an aluminum alloy sheet surface is generally sufficient for practice of our invention. The natural oxide coating ordinarily has a thickness of approximately 3-5 nm (30-50 angstroms). For better protection against corrosion, the oxide coating can be grown by treatments such as anodic oxidation or hydrothermal treatment in water, water vapor or aqueous solutions.

[0016] Aluminum alloy sheet of the invention is generally cleaned with an alkaline surface cleaner to remove any residual lubricant adhering to the surface, and then rinsed with water. Cleaning can be avoided if the residual lubricant content is negligible.

[0017] The cleaned sheet surface is then pretreated in a first container with a composition comprising an aqueous solution of an organophosphorus compound. The solution preferably contains about 1-20 g/L of a vinyl phosphonic acid-acrylic acid copolymer (VPA-AA copolymer). Solutions containing about 4-10 g/L of the copolymer are preferred. The copolymer usually comprises about 5-50 mole % vinylphosphonic acid, preferably about 20-40 mole %. The VPA-AA copolymer may have a molecular weight of about 20,000 to 100,000, preferably about 50,000 to 80,000. A particularly preferred VPA-AA copolymer contains about 30 mole % VPA and about 70 mole % AA. The solution has a temperature of about 38°-93°C (100°-200°F), more preferably about 49°-82°C (120°-180°F). A particularly preferred solution has a temperature of about 77°C (170°F).

[0018] The sheet surface may be dipped into the composition or the composition may be roll coated or sprayed onto the sheet surface. A preferred continuous cleaning and pretreating line is operated at about 152-457 meters per minute (500-1500 feet per minute). A contact time of about 6 seconds between the sheet surface and the composition is sufficient when the line is operated at 1000 feet per minute (305 meters per minute). The VPA-AA copolymer reacts with the oxide or hydroxide coating to form a layer on the sheet surface.

[0019] Aluminum alloy sheet passing through the pretreatment solution contaminates the solution with ions of various elements, including aluminum, magnesium, iron, chromium and manganese. The pretreatment solution loses effectiveness when the aluminum concentration rises above about 150-200 ppm. Accordingly, we provide a process for removing ions of aluminum and other metals from the pretreatment solution.

[0020] At least a portion of the pretreatment solution is transferred to a second container containing a cation exchange resin. The resin may be provided as pellets, beads, fibers, or particles and preferably is a hard, spherical gel type bead. The resin has a minimum total capacity in the hydrogen form, wet, of 1.9 meq/m.L. A preferred resin has an average particle size of about 650 μm (microns), a specific gravity of about 1.22-1.23, and a bulk density of about 0.7999 kg/L (49.9 lb/ft^3).

[0021] The resin is preferably a gel comprising a styrene-divinylbenzene copolymer functionalized with acid groups, preferably suifonate groups. Alternatively, the copolymer may be functionalized with phosphonic acid or arsonic acid groups. A particularly preferred cation exchange resin is sold by The Dow Chemical Company of Midland, Michigan under the trademark DOWER G-26(H).

[0022] Less preferably, the cation exchange resin may comprise ethylene, copolymerized with an unsaturated carboxylic acid such as acrylic acid.

[0023] After the pretreatment solution passes through the second container, it contains a reduced concentration of aluminum. The aluminum concentration in the treated solution is less than about 75 ppm, more preferably less than about 25 ppm, and optimally about 10 ppm or less. The treated solution, containing the organophosphorus compound and a reduced concentration of aluminum, is returned to the first container.

[0024] Optionally, the pretreated sheet may be rinsed with water to remove excess VPA-AA copolymer. The rinse water preferably has a temperature of about 77°-82°C (170°-180°F). The rinse water is concentrated by removing excess water so that the VPA-AA copolymer can be recycled. Some preferred concentrating techniques include reverse osmosis and membrane filtration. After concentration, the rinse water may be transferred to the first container in order to recover VPA-AA copolymer values.

[0025] The primed sheet is coated with a polymer composition that preferably includes an organic polymer dispersed in an organic solvent. Three preferred coating polymers are the epoxies, polyvinyl chloride and polyesters. The suitable epoxies include phenolic-modified epoxies, polyester-modified epoxies, epoxy-modified polyvinyl chloride, and cross linkable epoxies. The polymer composition may be clear or it may contain pigment particles. The pigment particles are preferably titanium dioxide, alumina or silica. We prefer titanium dioxide particles in the 0.5 to 10 μm (microns) median particle size range.

[0026] Alternatively, the primed sheet may be coated by electrocoating, slot coating, extrusion coating, flow coating, spray coating, or other continuous coating processes.

[0027] The polymer coated sheet is dried, coiled, and then finally shaped into container bodies or container end panels.

[0028] As shown schematically in the Figure, there is provided a coil of AA5182-H 19 aluminum-magnesium alloy sheet 10 having a thickness of about (8.8 mils) 224 μm (microns). The sheet 10 is cleaned with an alkaline surface cleaner in a vat 20 to remove any residual lubricant on the sheet surface. The cleaned sheet is then rinsed in a deionized water bath 30.

[0029] The cleaned and rinsed sheet is pretreated in a first container 40 with a solution comprising about 10 g/L of a VPA-AA copolymer containing about 30 mole

percent VPA and about 70 mole percent AA units, dissolved in water. The solution has a temperature of about 77°C (170°F) and it initially contains about 10 ppm aluminum. The VPA-AA copolymer reacts with an aluminum oxide or hydroxide coating on the sheet surface to form a layer comprising a reaction product of the copolymer and the oxide or hydroxide.

[0030] The pretreated sheet is then rinsed with water 50 to remove excess VPA-AA copolymer. The rinse water 50 preferably has a temperature of about 77°-82°C (170°-180°F).

[0031] The rinsed sheet is roll coated with a polymer composition 60 that preferably includes an organic polymer and pigment particles dispersed in an organic solvent. The organic polymer is preferably an epoxy resin. Some suitable epoxies include phenolic-modified epoxies, polyester-modified epoxies, epoxy-modified polyvinyl chloride, and cross linkable epoxies.

[0032] The polymer coated sheet is dried in a hot air dryer 70 and then recoiled.as a coated sheet product 80.

[0033] In order to maintain a low concentration of metal ions in the pretreatment solution, portions of the solution are periodically transferred from the first container 40 to a second container 100 holding a cation exchange resin. A particularly preferred resin is sold by Dow Chemical Company of Midland, Michigan under the trademark DOWEX G-26 (H) strong cation exchange resin. The strong cation exchange resin is sold as hard spherical beads with a 650 μm (micron) dry mesh size. The strong cation exchange resin is a gel comprised of a styrene-divinyl benzene copolymer functionalized with sulfonate groups. Treatment with the resin produces a treated solution having an aluminum concentration that is optimally less than about 10 ppm. The treated solution is returned through a pipe 110 from the second container 100 to the first container 40.

[0034] The cation exchange resin eventually becomes saturated with metal salts. The resin is regenerated by washing with a strong acid solution 120, such as 6-10 vol.% HCl or 6-12 vol.% sulfuric acid in water. Metal salts 130 washed from the second container 100 are discarded.

[0035] Used rinse water from the water rinse 50 is also recycled to recover VPA-AA copolymer values. The used rinse water is first sent to a concentrator 140 where water is removed, for example by reverse osmosis or membrane ultrafiltration. The concentrated rinse water is then returned to the first container 40.

[0036] The cation exchange process of our invention maintains aluminum concentrations at acceptable levels in the pretreatment solution. A 200 mL aliquot of the pretreatment solution at 60°C (140°F) containing 10 g/L VPA-AA copolymer, 350 ppm aluminum, and other metals was placed in a 250 mL Ehrlenmeyer flask containing 40 mL wet volume of the DOWEX G-26(H) resin in the hydrogen form. The flask was placed in a water bath and held at 60°C (140°F) for 16-20 hours. The resin was prepared by washing with 400-600 mL of 6 vol.% HCl, followed by rinsing with 600-800 mL of deionized water.

[0037] After 16 to 20 hours of contact time, the pretreatment solution was filtered and the resin was rinsed with 25 mL of deionized water. The solution was analyzed and the results are presented below in the Table. All concentrations were corrected to reflect a volume of 200 mL, for comparison.

Table-Analysis of Pretreatment Solution

Element	Initial Concentration (ppm)	After G-26(H) (ppm)
Al	350	5.3
Na	14	0.5
Si	11	12
Fe	22	18
Ca	4.1	0.8
Mg	100	0.3
Mn	1.5	n.d
Ni	0.6	n.d
Zn	0.3	n.d
Cr	11	10
K	1.8	0.5
P	820	777

n.d. = non detectable

Claims

1. A process for pretreating an aluminum alloy sheet having a surface portion in order to improve adhesion of a polymer coating to said surface portion, comprising:

   (a) in a first container, pretreating an aluminum alloy sheet having a surface portion comprising aluminum oxide or aluminum hydroxide with a pretreatment solution consisting essentially of water and an organophosphorus compound, thereby forming a layer comprising a reaction product of said compound and said oxide or hydroxide, and contaminating said solution with aluminum ions;
   (b) transferring at least a portion of said solution to a second container containing a cation exchange resin comprising a polymer and therein adsorbing aluminum ions onto said resin, thereby producing a treated solution containing said compound and having a reduced concentration of aluminum ions; and
   (c) returning said treated solution to said first container.

2. The process of claim 1, wherein said sheet compris-

es an aluminum alloy of the AA2000, 3000, 5000, 6000, or 7000 series, and further comprising:

(d) coating said layer with a coating composition comprising a polymer selected from the group consisting of polyvinyl chloride, epoxies and polyesters.

3. The process of claim 1, wherein said resin comprises a styrenedivinylbenzene copolymer functionalized with sulfonate groups.

4. The process of claim 1, wherein the treated solution contains less than about 75 ppm aluminum ions.

5. The process of claim 1, wherein the treated solution contain less than about 25 ppm aluminum ions.

6. The process of claim 1, further comprising:

(e) after step (a), rinsing said substrate with water, thereby to produce rinse water containing said organophosphorus compound and aluminum ions,
(f) concentrating said rinse water by removing water therefrom, and
(g) returning to the first container at least a portion of the rinse water treated in step (f).

7. The process of claim 1, wherein said organophosphorus compound comprises a vinylphosphonic acid-acrylic acid copolymer.

8. The process of claim 7, wherein said copolymer has a molecular weight of about 20,000 to 100,000.

9. The process of claim 7, wherein said pretreatment solution comprises about 1-20 g/L of said copolymer.

10. The process of claim 7, wherein said pretreatment solution has a temperature of about 120-200°F (49-93°C) in step (a).

Revendications

1. Procédé pour pré-traiter une plaque en alliage d'aluminium ayant une partie de surface afin d'améliorer l'adhésion d'un revêtement de polymère à ladite partie de surface, comprenant les étapes consistant à :

(a) pré-traiter, dans un premier récipient, une plaque en alliage d'aluminium ayant une partie de surface comprenant un oxyde d'aluminium ou un hydroxyde d'aluminium avec une solution de pré-traitement comprenant essentiellement de l'eau et un composé organo-phosphoré, formant de cette façon une couche comprenant un produit réactionnel dudit composé et dudit oxyde ou hydroxyde, et contaminant ladite solution avec des ions d'aluminium ;
(b) transférer au moins une partie de ladite solution dans un second récipient contenant une résine d'échange cationique comprenant un polymère et absorbant les ions d'aluminium dans ladite résine, produisant de cette façon une solution traitée contenant ledit composé et ayant une concentration réduite en ions d'aluminium ; et
(c) verser à nouveau ladite solution traitée dans ledit premier récipient.

2. Procédé selon la revendication 1, dans lequel ladite plaque comprend un alliage d'aluminium des séries AA2000, 3000, 5000, 6000 et 7000, et comprenant en outre l'étape consistant à :

(d) recouvrir ladite couche à l'aide d'une composition de revêtement comprenant un polymère choisi dans le groupe comprenant un chlorure de polyvinyle, des époxydes et des polyesters.

3. Procédé de la revendication 1, dans lequel ladite résine comprend un copolymère de divinylbenzène styrolénique fonctionnalisé avec des groupes sulfonate.

4. Procédé selon la revendication 1, dans lequel la solution traitée contient moins de 75 ppm environ d'ions d'aluminium.

5. Procédé selon la revendication 1, dans lequel la solution traitée contient moins de 25 ppm environ d'ions d'aluminium.

6. Procédé selon la revendication 1, comprenant en outre les étapes consistant à :

(e) rincer, après l'étape (a), ledit substrat avec de l'eau, afin de produire de cette façon de l'eau destinée au rinçage contenant ledit composé organo-phosphoré et lesdits ions d'aluminium,
(f) concentrer ladite eau destinée au rinçage en en retirant l'eau, et
(g) verser à nouveau dans le premier récipient au moins une partie de l'eau destinée au rinçage et traitée dans l'étape (f).

7. Procédé selon la revendication 1, dans lequel ledit composé organo-phosphoré comprend un copolymère d'acide acrylique et d'acide vinylphosphonique.

8. Procédé selon la revendication 7, dans lequel ledit copolymère a un poids moléculaire compris entre environ 20 000 et 100 000.

9. Procédé selon la revendication 7, dans lequel ladite solution de pré-traitement comprend environ 1 à 20 g/L dudit copolymère.

10. Procédé selon la revendication 7, dans lequel ladite solution de pré-traitement a une température d'environ 120 à 200°F (49 à 90°C) dans l'étape (a).

Patentansprüche

1. Verfahren zum Vorbehandeln eines Aluminiumlegierungsbleches das einen Oberflächenabschnitt aufweist, um die Haftung einer Polymerbeschichtung auf dem Oberflächenabschnitt zu verbessern, welches Verfahren umfasst:

a) in einem ersten Behälter Vorbehandeln eines Aluminiumlegierungsbleches, das einen Aluminiumoxid- oder Aluminiumhydroxid aufweisenden Oberflächenabschnitt aufweist, mit einer Vorbehandlungslösung, im Wesentlichen bestehend aus Wasser und einer phosphororganischen Verbindung, wodurch eine Lage erzeugt wird, die ein Reaktionsprodukt der Verbindung und des Oxids oder Hydroxids aufweist; und Kontaminieren der Lösung mit Aluminium-Ionen;
b) Überführen mindestens eines Teils der Lösung in einen zweiten Behälter, der ein Kationen-Austauschharz enthält, das ein Polymer aufweist; und darin auf dem Harz Aluminium-Ionen adsorbieren, wodurch eine Behandlungslösung erzeugt wird, die die Verbindung enthält und eine verringerte Konzentration an Aluminium-Ionen hat; und
c) Zurückführen der behandelten Lösung in den ersten Behälter.

2. Verfahren nach Anspruch 1, bei welchem das Blech eine Aluminiumlegierung der Reihe AA2000, 3000, 5000, 6000 oder 7000 umfasst, und ferner umfassend:

d) Beschichten der Lage mit einer Beschichtungszusammensetzung, die ein Polymer aufweist, das ausgewählt ist aus der Gruppe, bestehend aus Polyvinylchlorid, Epoxiden und Polyestern.

3. Verfahren nach Anspruch 1, bei welchem das Harz ein mit SulfonatGruppen funktionalisiertes Styrol/Divinylbenzol-Copolymer aufweist.

4. Verfahren nach Anspruch 1, bei welchem die behandelte Lösung weniger als etwa 75 ppm Aluminium-Ionen enthält.

5. Verfahren nach Anspruch 1, bei welchem die behandelte Lösung weniger als etwa 25 ppm Aluminium-Ionen enthält.

6. Verfahren nach Anspruch 1, ferner umfassend:

e) nach Schritt a) Spülen des Substrats mit Wasser, wodurch ein Spülwasser erzeugt wird, das die phosphororganische Verbindung und Aluminium-Ionen enthält,

f) Einengen des Spülwassers, indem das Wasser daraus entfernt wird, und

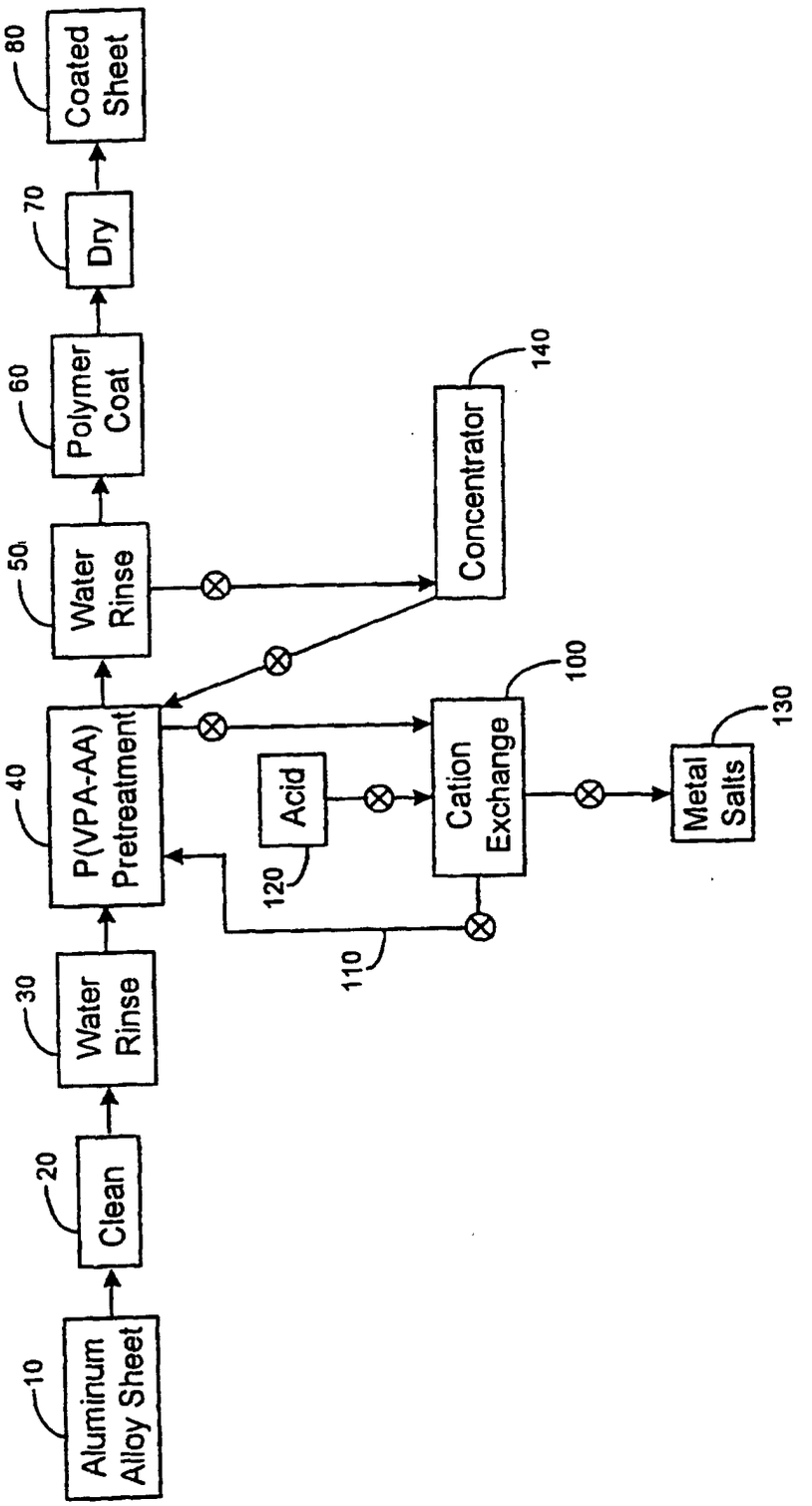
g) Zurückführen mindestens eines Teils des in Schritt f) behandelten Spülwassers in den ersten Behälter.

7. Verfahren nach Anspruch 1, bei welchem die phosphororganische Verbindung ein Vinylphosphonsäure/Acrylsäure-Copolymer aufweist.

8. Verfahren nach Anspruch 7, bei welchem das Copolymer eine relative Molekülmasse von etwa 20.000 bis 100.000 hat.

9. Verfahren nach Anspruch 7, bei welchem die Vorbehandlungslösung etwa 1 bis 20 g/l des Copolymers aufweist.

10. Verfahren nach Anspruch 7, bei welchem die Vorbehandlungslösung in Schritt a) eine Temperatur von etwa 49° bis 93°C (120° bis 200°F) hat.


10
Aluminum Alloy Sheet
20
Clean
30
Water Rinse
40
P(VPA-AA) Pretreatment
50
Water Rinse
60
Polymer Coat
70
Dry
80
Coated Sheet
100
Cation Exchange
110
120
Acid
130
Metal Salts
140
Concentrator

FIGURE