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(54) **Method of producing a chromium-free conversion coating on a surface of an aluminium or aluminium alloy strip**

(57) In a method of producing an aluminium or aluminium alloy strip with a heat-seal lacquer on a first surface and an epoxide based stove lacquer on the second surface, a chromium-free conversion coating is produced on the first and second surface of the aluminium or aluminium alloy strip in a continuous production line before applying the hot seal lacquer and the stove lacquer, the chromium-free conversion coating is produced by
(A) a no-rinse process by treatment with a solution of

silanes in a polar organic solvent, or
a no-rinse process by treatment with an aqueous solution of 5 to 10 wt.-% hexafluorotitanic acid (H_2TiF_6) and 2.5 to 5 wt.-% hexafluorozirconic acid (H_2ZrF_6), or
(B) a rinse process by treatment with an aqueous solution of < 1 wt.-% diammonium dimolybdate ($(NH_4)_2Mo_2O_7$) and 5 to 10 wt.-% hexafluorozirconic acid (H_2ZrF_6).

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Description

[0001] The invention relates to a method of producing an aluminium or aluminium alloy strip with a heat-seal lacquer on a first surface and an epoxide based stove lacquer on the second surface.

[0002] In particular, the invention relates to the preparation of cleaned surfaces with good adhesion properties of the aforementioned organic coatings on aluminium or aluminium alloy strips intended for the manufacturing of lacquered and deep-drawn capsules closed with a heat-sealed membrane lid for packaging portions of coffee.

[0003] So-called "rinse" and "no-rinse" processes are generally known in the chemical treatment of metal surfaces, for example for the subsequent application of paints, adhesives and/or plastics. In rinse and no-rinse processes, the metal surfaces are freed from oil, dirt and other residues in a first stage. Any residues of chemicals from this first stage are removed by rinsing with water. In the next stage of the rinse process, the clean metal surface is wetted with an aqueous bath solution which is rinsed off. In the non-rinse process the clean metal surface is wetted with an aqueous bath solution which is not rinsed off, but instead is dried in situ on the metal surface and, in the process, is converted into a solid film of the bath ingredients. Coatings such as these can significantly improve the surface quality of covering layers subsequently applied, particularly with respect to corrosion control and adhesion. Originally, treatment solutions containing hexavalent chromium ("yellow chromating") were often proposed in the extensive relevant prior art literature. On account of the toxic character of Cr(VI), these processes or rather the rinsing waters accumulating therein require expensive wastewater treatment. Even processes which only use trivalent chromium were not entirely satisfactory on account of increasing demands for the complete absence of chromium.

[0004] The chromium-free conversion treatment of aluminum surfaces with fluorides of boron, silicon, titanium zirconium or molybdenum alone or in conjunction with organic polymers for obtaining permanent protection against corrosion and for producing a base for subsequent painting is known in principle:

[0005] US-A-5,129,967 and US-A-4,921,552 disclose treatment baths for the no-rinse treatment (described there as "dried in place conversion coating") of aluminum containing:

- a) 10 to 16 g/l of polyacrylic acid or homopolymers thereof,
- b) 12 to 19 g/l of hexafluoro zirconic acid,
- c) 0.17 to 0.3 g/l of hydrofluoric acid and
- d) up to 0.6 g/l of hexafluoro titanate acid.

[0006] EP-A-0 008 942 discloses treatment solutions, preferably for aluminum cans, containing:

- a) 0.5 to 10 g/l of polyacrylic acid or an ester thereof and
- b) 0.2 to 8 g/l of at least one of the compounds H_2ZrF_6 , H_2TiF_6 and H_2SiF_6 , the pH value of the solution being below 3.5, and an aqueous concentrate for regenerating the treatment solution containing:

- a) 25 to 100 g/l of polyacrylic acid or an ester thereof,
- b) 25 to 100 g/l of at least one of the compounds H_2ZrF_6 , H_2TiF_6 and H_2SiF_6 and
- c) a source of free fluoride ions supplying 17 to 120 g/l of free fluoride.

[0007] DE-C-24 33 704 describes treatment baths for increasing paint adhesion and permanent protection against corrosion inter alia on aluminum which may contain from 0.1 to 5 g/l of polyacrylic acid or salts or esters thereof and 0.1 to 3.5 g/l of ammonium fluorozirconate, expressed as ZrO_2 .

[0008] US-A-4,992,116 describes treatment baths for the conversion treatment of aluminum with pH values of around 2.5 to 5 which contain at least three components, namely:

- a) phosphate ions in a concentration of 1.1×10^{-5} to 5.3×10^{-3} moles/l, corresponding to 1 to 500 mg/l,
- b) 1.1×10^{-5} to 1.3×10^{-3} moles/l of a fluoroacid of an element of the group consisting of Zr, Ti, Hf and Si (corresponding to 1.6 to 380 mg/l, depending on the element) and
- c) 0.26 to 20 g/l of a polyphenol compound obtainable by reacting poly(vinylphenol) with aldehydes and organic amines.

[0009] WO-A-92/07973 describes a chromium-free treatment process for aluminum which uses 0.01 to around 18% by weight of H_2ZrF_6 and 0.01 to around 10% by weight of a 3-(N-C₁₋₄-alkyl-N-2-hydroxyethylaminomethyl)-4-hydroxystyrene polymer as essential components in the form of an acidic aqueous solution.

[0010] DE-A-43 17 217 describes a process for the pretreatment of surfaces of aluminum or its alloys before a second conversion treatment for permanent corrosion control, in which the surfaces are contacted with acidic aqueous treatment

solutions which contain complex fluorides of the elements boron, silicon, titanium, zirconium or hafnium either individually or in admixture with one another in concentrations of the fluoroanions of, in total, 100 to 4,000 and preferably 200 to 2,000 mg/l and which have a pH value of 0.3 to 3.5 and preferably in the range from 1 to 3. The treatment solutions may additionally contain polymers of the polyacrylate type and/or in the form of reaction products of poly(vinylphenol) with aldehydes and organic hydroxyfunctional amines in concentrations below 500 mg/l and preferably below 200 mg/l. Phosphoric acid is another optional constituent of these baths.

[0011] US-A-4,136,073 claims a chromium-free treatment process for aluminum surfaces, in which the surfaces are contacted with acidic (pH 1.2 to 5.5) aqueous solutions containing an organic film former and a soluble titanium compound in a ratio by weight of polymer to titanium of 100:1 to 1:10. The preferred titanium concentration is between 0.01 and 5% by weight.

[0012] US-A-5,868,872 discloses a chromium-free process for the no-rinse treatment of aluminium and its alloys and aqueous bath solutions suitable for this process. The surfaces are contacted with solutions containing:

- a) 2.2 to 22.0 g/l of Zr(IV) and/or 1.4 to 14.0 g/l of Ti(IV),
- b) 2.4 to 24.0 g/l of orthophosphate,
- c) 3.0 to 30.0 g/l of fluoride,
- d) 0.15 to 1.5 g/l of a water-soluble or homogeneously water-dispersible organic film former, and the solutions are dried on the surface without rinsing after a contact time of 1 to 40 seconds at temperatures of 50°C to 125°C.

[0013] An object of the present invention is to provide a method of the type mentioned at the beginning with a good adhesion of the aluminium or aluminium alloy strip with a heat-seal lacquer on a first surface and an epoxide based stove lacquer on the second surface and the epoxide based stove lacquer without the need of a Cr(III) conversion coating. In particular, the aluminium or aluminium alloy strip manufactured with the method according to the present invention shall be qualified for the manufacture of deep-drawn capsules for packaging portions of coffee, the capsules having a heat-seal lacquer on the inner surface of the capsule and an epoxide based coloured stove lacquer on the outer surface of the capsule.

[0014] A further object is to provide a method of producing a chromium-free conversion coating on a surface of an aluminium or aluminium alloy strip in a continuous production line, the chromium-free conversion coating having good adhesion properties of a heat-seal lacquer on a first surface and an epoxide based stove lacquer on the second surface of the aluminium or aluminium alloy strip intended for the manufacturing of lacquered and deep-drawn capsules closed with a heat-sealed membrane lid for packaging portions of coffee.

[0015] The first of the aforementioned objectives is achieved by way of the invention in that a chromium-free conversion coating is produced on the first and second surface of the aluminium or aluminium alloy strip in a continuous production line before applying the heat-seal lacquer and the stove lacquer, the chromium-free conversion coating is produced by

(A) a no-rinse process by treatment with a solution of silanes in a polar organic solvent, or
a no-rinse process by treatment with an aqueous solution of 5 to 10 wt.-% hexafluorotitanic acid (H_2TiF_6) and 2.5 to 5 wt.-% hexafluorozirconic acid (H_2ZrF_6), or

(B) a rinse process by treatment with an aqueous solution of < 1 wt.-% diammonium dimolybdate ($(\text{NH}_4)_2\text{Mo}_2\text{O}_7$) and 5 to 10 wt.-% hexafluorozirconic acid (H_2ZrF_6).

[0016] The second of the aforementioned objectives is achieved by way of the invention in that the method comprises the steps of

continuous uncoiling of a rolled aluminium or aluminium alloy strip from a first coil;
continuous annealing of the uncoiled strip;
continuous cleaning and degreasing of the surface of the annealed strip; continuous washing of the cleaned and degreased surface of the strip; continuous pickling of the surface of the washed strip;
continuous washing of the surface of the pickled strip;
drying of the surface of the washed strip;
continuous production of a chromium-free conversion coating on the surface of the dried conversion coated strip by

(A) a no-rinse process by treatment with a solution of silanes in a polar organic solvent, or
a no-rinse process by treatment with an aqueous solution of 5 to 10 wt.-% hexafluorotitanic acid (H_2TiF_6) and 2.5 to 5 wt.-% hexafluorozirconic acid (H_2ZrF_6), or

(B) a rinse process by treatment with an aqueous solution of < 1 wt.-% diammonium dimolybdate ($(\text{NH}_4)_2\text{Mo}_2\text{O}_7$) and 5 to 10 wt.-% hexafluorozirconic acid (H_2ZrF_6);

optional washing of the surface of the conversion coated strip;
 continuous drying of the surface of the conversion coated and optionally washed strip;
 continuous coiling of the dried strip onto a second coil.

[0017] Cleaning and degreasing is preferably made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of an initial solution comprising 0.10 to 1.0 wt.% bisoctyl dimethyl ammonium chloride, 5 to 10 wt.% potassium hydroxide, 5 to 10 wt.% phosphate (P) and < 5 wt.% cationic tenside.

[0018] In a first embodiment of the invention, pickling is preferably made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of an initial solution comprising 65 to 80 wt.% ortho phosphoric acid.

[0019] In a second embodiment of the invention, pickling is preferably made by spraying the strip with an aqueous solution of 5 to 30 g/l, preferably 8 to 15 g/l, of a first initial solution comprising 25 to 50 wt.% sulphuric acid and 5 to 15 wt.% non ionic tenside, and 0.1 to 10 g/l, preferably 1 to 3 g/l, of a second initial solution comprising 5 to 7 wt.% hydrofluoric acid.

[0020] In a first embodiment of the invention, the conversion coating is preferably made by spraying the strip with a solution of 50 to 200 g/l, preferably 80 to 120 g/l, of an initial solution comprising silane and 10 to 25 wt.% ethanol.

[0021] In a second embodiment of the invention, the conversion coating is preferably made by spraying the strip with an aqueous solution of 10 to 160 g/l, preferably 30 to 50 g/l, of a first initial solution comprising 5 to 10 wt.% hexafluorotitanic acid and 2.5 to 5 wt.% hexafluorozirconic acid, and 1 to 10 g/l, preferably 7 to 9 g/l, of a second initial solution comprising 20 to 21 wt.% silica.

[0022] In a third embodiment of the invention, the conversion coating is preferably made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of a first initial solution comprising < 1 wt.% diammonium dimolybdate and 5 to 10 wt.% hexafluorozirconic acid, and 0.01 to 0.3 g/l, preferably 0.1 to 0.3 g/l, of a second initial solution comprising 10 to 25 wt.% ammonium fluoride and 10 to 25 wt.% ammonium hydrogen difluoride.

[0023] In a third embodiment of the invention, the conversion coating is preferably made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of a first initial solution comprising < 1 wt.% diammonium dimolybdate and 5 to 10 wt.% hexafluorozirconic acid, and 0.01 to 0.3 g/l, preferably 0.1 to 0.3 g/l, of a second initial solution comprising 10 to 25 wt.% ammonium fluoride and 10 to 25 wt.% ammonium hydrogen difluoride, and 0 to 2 g/l, preferably 0.05 to 0.2 g/l, of a third initial solution comprising 25 wt.% polycarboxylic acid in water.

[0024] In the preferred no rinse process according to the invention, a conventionally cleaned and rinsed metal surface, after rinsing with deionized water and drying and/or removal of the water film by squeegees, is wetted in any manner with the solution of silanes in the polar organic solvent aqueous treatment solution in such a quantity that around 2 to 20 ml and preferably around 5 to 10 ml of the polar organic treatment solution are applied per square meter of surface area.

[0025] The treatment solutions in the preferred no rinse process according to the invention may be applied to the precleaned metal strips by any method which is capable of producing a uniform, defined liquid film on the metal surface in the quantity ranges indicated. The roller application process using two to four rollers ("chemcoater") has proved to be particularly effective, although wetting of the strip by spraying or immersion and subsequent removal of the excess liquid film, for example by plastic-coated equalizing rollers or an adjustable air knife, is also suitable. The temperature of the treatment solution may be in the range from 15°C to 30°C and is preferably in the range from 20°C to 25°C.

[0026] The liquid film applied to the metal surface is allowed to react thereon for about 1 to 40 seconds, after which the film is dried and heat-treated at elevated temperature. However, the process steps of contact with the metal surface and drying may also be combined. After drying, a formable, water-insoluble solid film with a weight per unit area of around 5 to 50 mg Si/m² and preferably around 10 to 30 mg Si/m² is left on the metal surface. The drying and/or heat treatment of the liquid film applied to the metal surface, or rather of the chemicals applied with it, may be carried out at temperatures of around 80°C to 140°C, temperatures in the range from 110°C to 120°C being preferred.

[0027] Both acidic and alkaline cleaners are suitable for the cleaning pretreatment of the metal surfaces to be wetted in accordance with the invention. The layers obtained with the treatment solution according to the invention provide a uniform finish of the substrate. In combination with suitable organic coatings subsequently applied, they satisfy the requirements of the food packaging industry.

[0028] The following example relates to a no-rinse process with a conversion coating by treatment with a solution of silanes in ethanol.

1. cleaning and degreasing with surfactant-containing alkaline or acidic cleaners -- for example GARDOCLEAN S 5664, 20 g/l -- applied by spraying at a treatment temperature of 50°C to 65°C for treatment times of 2 to 5 s,
2. rinsing with process water,
3. pickling with an aqueous solution of 20 g/l phosphoric acid (H₃PO₄) or 10.6 g/l sulfuric acid (H₂SO₄) with 2 g/l hydrofluoric acid (HF) applied by spraying at a treatment temperature of 50°C to 60°C for treatment times of 2 to 5 s,
4. rinsing with deionized water,
5. drying,
6. application of the pretreatment -- for example 100g/l OXSILAN® MM-0705 using a coater at a treatment temperature

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of 18°C to 25°C, 20 mg Si/m²

7. drying (with OXSILAN® at 110°C to 120°C)

[0029] Chemical composition, broad and preferred of treatment solutions for the process steps of degreasing, pickling and conversion related to rinse and no rinse processes are included in the following tables.

Table 1: No rinse process, conversion with silanes

Process step	Initial Solution	Bath concentration [g/l]	
		broad range	preferred range
Degreasing (spraying)	Gardoclean S 5664	5-50	15-25
Pickling 1 (spraying)	Gardobond H 7173	5-50	15-25
Pickling 2 (spraying)	Gardoclean S 5240/2	5-30	8-15
	Gardobond H 7269	0.1-10	1-3
Conversion (no rinse)	Oxsilan MM-0705	50-200	80-120

Table 2: No rinse process, conversion with Zr/Ti

Process step	Initial Solution	Bath concentration [g/l]	
		broad range	preferred range
Degreasing (spraying)	Gardoclean S 5664	5-50	15-25
Pickling 1 (spraying)	Gardobond H 7173	5-50	15-25
Pickling 2 (spraying)	Gardoclean S 5240/2	5-30	8-15
	Gardobond H 7269	0.1-10	1-3
Conversion (no rinse)	Gardobond X 4591	10-160	30-50
	GTB 10437B (Additive)	1-10	7-9

Table 3: Rinse process, conversion with Zr/Mo

Process step	Initial Solution	Bath concentration [g/l]	
		broad range	preferred range
Degreasing (spraying)	Gardoclean S 5664	5-50	15-25
Pickling (spraying)	Gardobond H 7173	5-50	15-25
Conversion 1 (rinse)	Permatreat 1903 A	5-50	30-50
	Gardobond H 7255	0.01-0.3	0.1-0.3
Conversion 2 (rinse)	Permatreat 1903 A	5-50	15-25
	Gardobond H 7255	0.01-0.3	0.1-0.3
	Gardolene D 6815	0-2	0.05-0.2

Table 4: Chemical Composition of the Initial Solutions

Initial Solution	Chemical composition	[weight-%]
Gardoclean S 5664	bisoctyl dimethyl ammonium chloride potassium hydroxide phosphate (P) cationic tenside	0.10-1.0 5-10 5-10 <5
Gardobond H 7173	ortho phosphoric acid	65-80
Gardoclean S 5240/2	sulfuric acid non ionic tenside	25-50 5-15
Gardobond H 7269	hydrofluoric acid	5-7
Oxsilan MM-0705	silane ethanol	10-25
Gardobond X 4591	hexafluorotitanic acid hexafluorozirconic acid	5-10 2.5-5
GTB 10437B additive	Silica	20-21
Permatreat 1903 A	diammonium dimolybdate hexafluorozirconic acid	<1 5-10
Gardobond H 7255	ammonium fluoride ammonium hydrogen difluoride	10-25 10-25
Gardolene D 6815	polycarboxylic acid in water (polymer)	25

Claims

- Method of producing an aluminium or aluminium alloy strip with a heat-seal lacquer on a first surface and an epoxide based stove lacquer on the second surface,
characterised in that
a chromium-free conversion coating is produced on the first and second surface of the aluminium or aluminium alloy strip in a continuous production line before applying the heat-seal lacquer and the stove lacquer, the chromium-free conversion coating is produced by
 - a no-rinse process by treatment with a solution of silanes in a polar organic solvent, or
 - a no-rinse process by treatment with an aqueous solution of 5 to 10 wt.-% hexafluorotitanic acid (H_2TiF_6) and 2.5 to 5 wt.-% hexafluorozirconic acid (H_2ZrF_6), or
 - a rinse process by treatment with an aqueous solution of < 1 wt.-% diammonium dimolybdate ($(\text{NH}_4)_2\text{Mo}_2\text{O}_7$) and 5 to 10 wt.-% hexafluorozirconic acid (H_2ZrF_6).
- Method of producing a chromium-free conversion coating on a surface of an aluminium or aluminium alloy strip in a continuous production line, the method comprising the steps of
 - continuous uncoiling of a rolled aluminium or aluminium alloy strip from a first coil;
 - continuous annealing of the uncoiled strip;
 - continuous cleaning and degreasing of the surface of the annealed strip; continuous washing of the cleaned and degreased surface of the strip; continuous pickling of the surface of the washed strip;
 - continuous washing of the surface of the pickled strip;
 - drying of the surface of the washed strip;
 - continuous production of a chromium-free conversion coating on the surface of the dried conversion coated strip; optional washing of the surface of the conversion coated strip; continuous drying of the surface of the conversion coated and optionally washed strip;
 - continuous coiling of the dried strip onto a second coil;**characterised in that**
the chromium-free conversion coating is produced by

(A) a no-rinse process by treatment with a solution of silanes in a polar organic solvent, or a no-rinse process by treatment with an aqueous solution of 5 to 10 wt.-% hexafluorotitanic acid (H_2TiF_6) and 2.5 to 5 wt.-% hexafluorozirconic acid (H_2ZrF_6), or

(B) a rinse process by treatment with an aqueous solution of <1 wt.-% diammonium dimolybdate ($(\text{NH}_4)_2\text{Mo}_2\text{O}_7$) and 5 to 10 wt.-% hexafluorozirconic acid (H_2ZrF_6).

3. Method according to claim 2, wherein cleaning and degreasing is made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of an initial solution comprising 0.10 to 1.0 wt.-% bisoctyl dimethyl ammonium chloride, 5 to 10 wt.-% potassium hydroxide, 5 to 10 wt.-% phosphate (P) and < 5 wt.-% cationic tenside.
4. Method according to claim 2, wherein pickling is made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of an initial solution comprising 65 to 80 wt.-% ortho phosphoric acid.
5. Method according to claim 2, wherein pickling is made by spraying the strip with an aqueous solution of 5 to 30 g/l, preferably 8 to 15 g/l, of a first initial solution comprising 25 to 50 wt.-% sulphuric acid and 5 to 15 wt.-% non ionic tenside, and 0.1 to 10 g/l, preferably 1 to 3 g/l, of a second initial solution comprising 5 to 7 wt.-% hydrofluoric acid.
6. Method according to claim 2, wherein the conversion coating is made by spraying the strip with a solution of 50 to 200 g/l, preferably 80 to 120 g/l, of an initial solution comprising silane and 10 to 25 wt.-% ethanol.
7. Method according to claim 2, wherein the conversion coating is made by spraying the strip with an aqueous solution of 10 to 160 g/l, preferably 30 to 50 g/l, of a first initial solution comprising 5 to 10 wt.-% hexafluorotitanic acid and 2.5 to 5 wt.-% hexafluorozirconic acid, and 1 to 10 g/l, preferably 7 to 9 g/l, of a second initial solution comprising 20 to 21 wt.-% silica.
8. Method according to claim 2, wherein the conversion coating is made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of a first initial solution comprising < 1 wt.-% diammonium dimolybdate and 5 to 10 wt.-% hexafluorozirconic acid, and 0.01 to 0.3 g/l, preferably 0.1 to 0.3 g/l, of a second initial solution comprising 10 to 25 wt.-% ammonium fluoride and 10 to 25 wt.-% ammonium hydrogen difluoride.
9. Method according to claim 2, wherein the conversion coating is made by spraying the strip with an aqueous solution of 5 to 50 g/l, preferably 15 to 25 g/l, of a first initial solution comprising < 1 wt.-% diammonium dimolybdate and 5 to 10 wt.-% hexafluorozirconic acid, and 0.01 to 0.3 g/l, preferably 0.1 to 0.3 g/l, of a second initial solution comprising 10 to 25 wt.-% ammonium fluoride and 10 to 25 wt.-% ammonium hydrogen difluoride, and 0 to 2 g/l, preferably 0.05 to 0.2 g/l, of a third initial solution comprising 25 wt.-% polycarboxylic acid in water.



EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 11 January 2012	Examiner Handrea-Haller, M
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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