(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 243 863 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
20.06.2012 Bulletin 2012/25

(21) Application number: **10159892.8**

(22) Date of filing: **14.04.2010**

(51) Int Cl.:
C23C 22/34 $^{(2006.01)}$
C23C 22/08 $^{(2006.01)}$
C23C 22/10 $^{(2006.01)}$
C23C 22/33 $^{(2006.01)}$
C23C 22/44 $^{(2006.01)}$
C23C 22/53 $^{(2006.01)}$
C23C 22/73 $^{(2006.01)}$
C23C 22/83 $^{(2006.01)}$
C23G 1/20 $^{(2006.01)}$
C23G 1/10 $^{(2006.01)}$
B05D 7/00 $^{(2006.01)}$

(54) Continuous chemical patination/satinising treatment process for zinc-titanium alloys

Fortlaufendes, chemisches Patinierungs-/Satinierungsverfahren für Zink-Titan-Legierungen

Procédé chimique continu de patinage/satinage des alliages de zinc-titane

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: **21.04.2009 IT MI20090665**

(43) Date of publication of application:
27.10.2010 Bulletin 2010/43

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WO-A-03/018872

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Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a continuous chemical patination/satinising treatment process for zinc-titanium alloys used in the construction industry, in particular for roofs, facades, guttering, interiors or architectural works.

Prior art

[0002] Zinc-titanium alloy laminates are widely used in the construction industry, especially for roofing and cladding. The natural appearance of these claddings can be varied by particular pre-patination surface treatments.

[0003] Said processes must give coil surfaces having a chemical composition complying with Standard EN 988 - 1998 (see Table 1) an attractive appearance with a patinated effect, specific colouring, such as antique-look zinc, excellent antifinger properties, and high corrosion resistance.

Table 1

Element	Standard EN 988 - 1998
Al	< 0.0150%
Cu	0.0800 - 1.0000%
Pb	< 0.0030%
Cd	< 0.0030%
Fe	< 0.0020%
Sn	< 0.0010%
Ti	0.0600 - 0.2000%

[0004] The known process normally comprises the following stages:

- degreasing with an alkaline grease-removal liquid in aqueous solution
- first rinse with continuously fresh water
- acid treatment involving chemical patination/satinising with specific products
- second rinse with continuously fresh water
- final passivation treatment
- drying of wet film.

[0005] EP 827785 describes a process for the treatment of zinc-titanium laminates characterised by the use of a pickling bath based on nitric and sulphuric acid and a passivation stage with a polymer containing chromate.

Disclosure of the invention

[0006] An improved process has now been found which is characterised, after the second rinse with water, by a pre-passivation stage followed by drying with hot air to prevent the formation of surface zinc oxides, and the use of a polyacrylic resin as antifinger agent in the final passivation treatment.

[0007] The process of the invention comprises the following stages in particular:

- degreasing;
- first rinse with continuously fresh water;
- acid treatment involving chemical patination/satinising;
- second rinse with continuously fresh water;
- pre-passivation treatment with a chromium-free bath containing zirconium and/or titanium and aluminium compounds;
- air drying;
- passivation treatment comprising a first stage of treatment with a conventional inorganic component based on chromium 3 and/or 6 or chromium-free, and a second stage of treatment with an antifinger agent consisting of an aqueous solution of an acrylic resin consisting of monomers based on butylacrylate, methylmethacrylate and acrylic acid, having the following characteristics:

pH < 6;
MW ≥ 250000;
TG (glass transition temperature) between 30 and 45°C;
dry residue between 30 and 50%;

possibly mixed with corrosion inhibitors such as zinc oxide and P205;

- drying of wet film.

[0008] Degreasing serves to eliminate all trace of oils, fats, cleaning paste, oxides and any other impurities from the coil surface, in order to have a perfectly clean metal surface ready for subsequent treatments.

[0009] Normally, said degreasing is performed with liquid products in aqueous solution at an alkaline pH (10-14). The use concentration is between 1% and 10%, and the temperature of the working bath between 50°C and 70°C, for a treatment time of between 5 and 40 seconds, with spray pressures of between 1 and 4 bars. The main elements of the degreasing bath are listed in Table 2 below.

Table 2

Element	Concentration
KOH or NaOH	2 - 20 g/l
P_2O5	2 - 20 g/l
Surfactants	200 - 3000 ppm
Sequestering additives	1 - 10 g/l

[0010] P_2O_5 is present either as orthophosphates (monosodium, disodium or trisodium phosphate) or as polyphosphates (tripolyphosphate or neutral pyrophosphate), all in the form of sodium or potassium salts.

[0011] The most commonly used surfactants are ethoxylated fatty alcohols with alcohol C9-C11 chain, C12-C13 or C12-C18, having different degrees of ethoxylation or containing different numbers of ethylene oxide moles.

[0012] The sequestering additives are organic compounds selected from nitriloacetic acid, sodium gluconate, gluconic acid, ethylenediaminetetraacetic acid disodium, ethylenediaminetetraacetic acid trisodium, phosphonates, acrylates and polyacrylates.

[0013] The first rinse with continuously fresh water serves to eliminate all trace of the preceding stage; the temperature is normally between 30°C and 60°C, with times ranging between 5 and 30 seconds, and spray application.

[0014] The chemical patination/satinising treatment is performed by pickling the zinc-titanium alloy with a surface attack between 5 and 20 g/m^2.

[0015] The treatment is usually performed with a specific product at a pH of between 0 and 2, used at concentrations of between 10 and 15%. The temperature of the working bath can be between 50% and 70%, for a reaction time of between 10 and 30 seconds; the spray pressures must be between 1 and 4 bars.

[0016] The main elements of the patination/satinising bath are listed in Table 3 below.

Table 3

Element	Concentration
H_2SO_4	10-150 g/l
Surfactants	1 - 15 g/l
Process accelerant as NO_3	100 - 6000 ppm
Sequestering agents	1-100 g/l
Elements deriving from pickling of the alloy	
Zn	< 100 g/l
Other metals originating from the alloy	< 100 mg/l

[0017] The process accelerator can consist of NO_3 donor compounds such as nitric acid, ammonium nitrate, nickel nitrate, sodium nitrate, zinc nitrate, iron nitrate or cobalt nitrate, or nitrogenous organic compounds such as nitroguanidine, used alone or mixed together. The surfactants and agents are the same as already described.

[0018] The second rinse with continuously fresh water is performed as for the first rinse, to eliminate all trace of the preceding stage; the temperature is normally between 30°C and 60°C, with times ranging between 5 and 30 seconds, and spray application.

[0019] Pre-passivation, which prevents the formation of zinc-oxides on the surface by increasing the anti-corrosion properties of the coil, is performed by treatment with a chromium-free bath containing zirconium and/or titanium and aluminium compounds.

[0020] The typical composition of a pre-passivation bath according to the invention is set out in Table 4 below. The concentration of the product ranges between 1 and 5%, the temperature between 30 and 60°C, and the treatment times between 1 and 10 seconds; the product can be applied by spraying or immersion, and the pH value is < 5.

Table 4

Element	Concentration
Zr	100 - 5000 mg/l
Ti	100 - 5000 mg/l
Al	10 - 500 mg/l
NH_3	100 - 1000 ppm

[0021] The zirconium compounds are preferably selected from fluorozirconic acid, ammonium zirconium carbonate and potassium fluozirconate; the aluminium compounds are selected from aluminium oxide of various extractions (aluminas), aluminium fluoride and aluminium bifluoride; the titanium compounds are selected from fluotitanic acid, titanium oxalate, titanium oxide and potassium fluotitanate.

[0022] Drying is then performed with hot air from 50 to 90°C.

Final passivation treatment

[0023] The antifinger passivating product is applied with a Chem-Coater machine in two separate application stages, with a wet film drying step between each stage.

[0024] The inorganic component is applied at the first stage. Depending on the process required, the inorganic component can be one of three different types:

"Chromium 3 - Chromium 6 Version" (Version 1)

[0025] The product consists of chromic acid, chromium phosphate, corrosion inhibitors such as zinc phosphate and zinc chromate, and reducing agents such as gluconic acid, citric acid, saccharose, hydroxylamine, methanol, hydrogen peroxide and starch. The application takes place continuously at a temperature of between 15°C and 40°C; the concentration used depends on the wet film applied, which ranges between 2 and 10 ml/m^2; it is generally between 10 and 50%, so that the end result is a total chromium deposit of 20 to 100 mg/m^2; its value is calculated from the mg of chromium, on the basis that 1 mg/m^2 of Cr = 16 mg/m^2 of total coating.

[0026] An example of the composition of the bath is shown in Table 5 below.

Table 5

Element	Concentration
Total chromium (= chromium 3 + chromium 6)	5 - 20%
P_2O_5	1 - 5%
Zinc	2 - 8%
"Chromium 3 Version" (Version 2)	

[0027] The product consists of phosphoric acid, chromium phosphate, chromium nitrate, complexing agents selected from salified phosphonates or acids, gluconic acid, citric acid, tartaric acid, EDTA, glycolic acid and/or polyacrylates, corrosion inhibitors such as colloidal silicon dioxides in suspension, possibly having different particle sizes, generally below 30 μm, and with a SiO_2 content of between 10 and 50%, and finally, organic wetting agents based on alkoxypolypropoxypolyethoxy-ethyl-benzylether or belonging to the perfluoroderivative family. The application takes place continuously at a temperature of between 15°C and 40°C; the concentration used depends on the wet film applied, which ranges between 2 and 10 ml/m^2; it is generally between 30 and 70%, so that the end result is a total chromium deposit of 30 to 80 mg/m^2; its value is calculated from the mg of chromium, on the basis that 1 mg/m^2 of Cr = 32 mg/ m^2 of total coating.

[0028] An example of the composition of the bath is shown in Table 6 below.

Table 6

Element	Concentration
Total chromium (= chromium 3)	20 - 200 g/l
P_2O_5	10-150 g/l
NO_3	3 - 50 g/l
SiO_2	20 -200 g/l
"Chromium-free - Chromium Version" (Version 3)	

[0029] The product consists of silanes, selected from the families of 1-propylamine,3-(triethoxysilyl)-silane and trimethoxy[3-(oxiranylmethoxy)-propyl]-silane, titanium salts deriving from fluotitanic acid, titanium oxalate, titanium oxide or potassium fluorotitanate, alkaline phosphates such as monobasic or dibasic ammonium phosphate, mono-, bi- or tribasic sodium phosphate, acid or neutral potassium pyrophosphate, alkaline nitrates such as ammonium nitrate, sodium nitrate or potassium nitrate, sequestering agents selected from nitriloacetic acid, sodium gluconate, gluconic acid, ethylenediaminetetraacetic acid disodium, ethylenediaminetetraacetic acid trisodium, phosphonates, acrylates and polyacrylates, and corrosion inhibitors based on heavy metals such as vanadium, molybdenum, tungsten and cerium. The product should be applied at room temperature, in concentrations ranging between 80 and 100%, in such a way that the titanium deposit is between 4 and 8 mg/m^2 and the SiO_2 deposit between 70 and 140 mg/m^2; its value is calculated from the mg of titanium, on the basis that 1 mg/m^2 of Ti = 160 mg/m^2 of total coating.

[0030] An example of the composition of the bath is shown in Table 7 below.

Table 7

Element	Concentration
SiO_2	10 - 150 g/l
P_2O_5	10- 150 g/l
V	≤ 100 ppm
Ti	≤ 200 ppm

[0031] Drying is then performed with hot air from 50 to 90°C.

[0032] An antifinger agent is applied at the second stage, namely an aqueous solution of corrosion inhibitors such as zinc oxide and P_2O_5 and an acrylic resin consisting of monomers based on butylacrylate, methylmethacrylate and acrylic acid, having the following characteristics:

pH < 6; MW ≥ 250000; TG (glass transition temperature) between 30 and 45°C; dry residue between 30 and 50%.

[0033] In the case of version 1 only, the antifinger passivation product can also be applied in a single stage, with a Chem-Coater machine. Depending on the final chromium deposit desired, the bath is prepared with 1 part inorganic to 2 parts organic component, or 1 part inorganic to 3 parts organic component. The quantity of mixture applied is 2 to 6 ml/m^2. There is a partial reduction of chromium from 6 to 3 during this stage.

[0034] The wet film is then dried at a belt temperature of 80 to 140°C.

Laboratory test procedures

Degreasing:

[0035]

Element	Concentration
KOH	4 g/l
P_2O_5 from neutral potassium pyrophosphate	5 g/l
Surfactants with C9-C11 chain + 5 and 6 moles of OE = ethylene oxide	500 ppm
Sodium gluconate	3 g/l
Use concentration of product	3 - 5%
Temperature	50 - 60°C
Treatment time	10 sec.
Spray pressure	2 bars

First rinse

[0036]

Continuously fresh water	-
Temperature	30°C
Treatment time	10 sec.
Spray pressure	2 bars

Chemical patination/satinising treatment:

[0037]

Element	Concentration
H_2SO_4	60 g/l
HNO_3	6 g/l
Surfactants with C9-C11 chain + 5 and 6 moles of OE = ethylene oxide	1500 ppm
Sodium gluconate	10 g/l
Use concentration of product	10%
Temperature	60 - 70°C
Treatment time	10 sec.
Spray pressure	2 bars

Second rinse

[0038]

Continuously fresh water	-
Temperature	30°C
Treatment time	10 sec.
Spray pressure	2 bars

Pre-passivation

[0039]

Element	Concentration
Zr (from fluorozirconic acid)	500 mg/l
Ti (from fluotitanic acid)	300 mg/l
Al (from alumina)	50 mg/l
NH_3	50 ppm
Use concentration of product	2 - 3%
Temperature	50°C
Treatment time	2 sec.
pH	4

[0040] Drying is typically performed with hot air at a temperature of between 60 and 80°C.

Final passivation

[0041] First stage: "Chromium 3 - Chromium 6 Version"

Element	Concentration
Total chromium (= chromium 6 + chromium 3)	13%
P_2O_5	3%
Zinc	3%
Reducing agent used	starch
Wet film applied	1 - 4 ml/m^2
Temperature	room

[0042] First stage: "Chromium 3 version"

Element	Concentration
Total chromium (= chromium 3)	40 g/l
P_2O_5	20 g/l
NO_3	5 g/l
SiO_2	40 g/l
Complexing agent used	Citric acid
Type of silica used	Particle size 15 μm - dry 30%
Type of wetting agent	perfluoroderivative
Wet film applied	1 - 4 ml/m^2
Temperature	room

[0043] First stage: "Chromium-free version"

Element	Concentration
SiO_2 (from 1-propylamine,3-(triethoxysilyl)- silane and/or trimethoxy[3-(oxiranylmethoxy) propyl]-silane	100 g/l
P_2O_5 (from monobasic ammonium phosphate)	20 g/l
V	100 ppm
Ti (from fluotitanic acid)	200 ppm
Complexing agent used	phosphonate
Nitrate used	ammonium nitrate
Type of inhibitor selected	vanadium
Temperature	room

[0044] Drying is typically performed with hot air at a temperature of between 60 and 80°C.

[0045] Second stage: all versions.

Resin used Resin used	Pure acrylic, new formulation, inhibited, with dry residue = 30%, pH = 4, TG = 32°C
Wet film applied	3-6 ml/m^2

Single-stage application: "Chromium 3 - Chromium 6 Version"

[0046]

Dose ratios	Inorganic ingredient 1 part - Organic ingredient 2 parts Inorganic ingredient 1 part - Organic ingredient 3 parts
Wet film applied	3 - 4 ml/m^2
Temperature	room

[0047] Drying can be performed with hot air at a temperature of between 100 and 120°C.

Examples

[0048] The laboratory tests were performed to compare the results obtained with (i) cycles not including the pre-passivation stage (conventional cycle) and (ii) other cycles which were identical to the preceding ones except that they included the pre-passivation stage and subsequent drying.

[0049] Two-stage application of the final passivating product and single-stage application were tested in the cycles relating to the "Chromium 3 - Chromium 6 version"; 1:2 and 1:3 dose ratios of the two components were tested in the latter case.

[0050] Both the above-mentioned silanes, subsequently marked α and β, were tested in the cycles relating to the "chromium-free version", both separately and in combined.

[0051] Only the acrylic resin according to the invention was used in the organic component of the final passivation stage in all the cycles.

[0052] For convenience, the way in which the various cycles tested were marked is shown in Table 8 below.

Table 8

Code	Pre-passivation	Passivation version	Passivation	Component dose ratio	Type of silane
A 1	No	1	Biphasic		

(continued)

Code	Pre-passivation	Passivation version	Passivation	Component dose ratio	Type of silane
A 1.2	No	1	Monophasic	2 : 1	
A 1.3	No	1	Monophasic	3 : 1	
A 2	No	2	Biphasic		
A 3.1	No	3	Biphasic		α
A 3.2	No	3	Biphasic		β
A 3.3	No	3	Biphasic		$\alpha + \beta$
B 1	Yes	1	Biphasic		
B 1.2	Yes	1	Monophasic	2 : 1	
B 1.3	Yes	1	Monophasic	3 : 1	
B 2	Yes	2	Biphasic		
B 3.1	Yes	3	Biphasic		α
B 3.2	Yes	3	Biphasic		β
B 3.3	Yes	3	Biphasic		$\alpha + \beta$

[0053] After application of the cycles, the zinc-titanium alloy panels treated were subjected to corrosion-resistance tests in a salt spray (fog) chamber, in accordance with Standard ASTM B 117, unprotected panels and panels with protected edges being checked for the appearance of the first white oxides.

[0054] Table 9 shows the results obtained, expressed as hours of exposure before the appearance of the first white oxidation phenomena.

Table 9

Code	Hours of exposure	Code	Hours of exposure
A 1	72	B 1	96
A 1.2	72	B 1.2	96
A 1.3	72	B 1.3	96
A 2	60	B 2	72
A 3.1	60	B 3.1	72
A 3.2	60	B 3.2	72
A 3.3	72	B.3.3	96

Claims

1. A process of continuous chemical patination/satinising treatment of zinc-titanium alloys comprising the following stages:

    - degreasing with alkaline grease-removal liquid in aqueous solution;
    - first rinse with continuously fresh water;
    - chemical acid patination/satinising treatment;
    - second rinse with continuously fresh water;
    - pre-passivation treatment with a chromium-free bath containing zirconium and/or titanium and aluminium compounds;
    - air drying;
    - passivation treatment comprising a first stage of treatment with a conventional inorganic component based on chromium 3 and/or 6 or chromium-free, and a second stage of treatment with an antifinger agent consisting

of an aqueous solution of an acrylic resin consisting of monomers based on butylacrylate, methylmethacrylate and acrylic acid, having the following characteristics:

pH < 6;
MW ≥ 250000;
TG (glass transition temperature) between 30 and 45°C;
dry residue between 30 and 50%;

possibly mixed with corrosion inhibitors such as zinc oxide and P205;
- drying of wet film.

2. A process as claimed in claim 1, wherein the zirconium and/or titanium and aluminium compounds in the pre-passivation bath are selected from fluorozirconic acid, ammonium zirconium carbonate and potassium fluorozirconate; aluminium oxide of various extractions (aluminas), aluminium fluoride and aluminium difluoride; fluorotitanic acid, titanium oxalate, titanium oxide and potassium fluorotitanate.

3. A process as claimed in claim 1 or 2, wherein the passivation comprises treatment with a bath containing chromium 3 and chromium 6 compounds.

4. A process as claimed in claim 3, wherein the bath contains chromic acid, chromium phosphate, zinc phosphate and zinc chromate and reducing agents.

5. A process as claimed in claim 1 or 2, wherein the passivation comprises treatment with a bath containing chromium 3 compounds.

6. A process as claimed in claim 5, wherein the bath contains phosphoric acid, chromium phosphate, chromium nitrate, complexing agents, corrosion inhibitors and organic wetting agents based on alkoxypolypropoxypolyethoxy-ethylbenzylether or belonging to the class of perfluoroderivatives.

7. A process as claimed in claim 1 or 2, wherein the passivation comprises treatment with a chromium-free bath.

8. A process as claimed in claim 7, wherein the bath contains silanes, selected from the classes of 1-propylamine, 3-(triethoxysilyl)-silane and trimethoxy[3-(oxiranylmethoxy)propyl]-silane, titanium salts deriving from fluorotitanic acid, titanium oxalate, titanium oxide or potassium fluorotitanate, alkaline phosphates, alkaline nitrates, sequestering agents selected from nitriloacetic acid, sodium gluconate, gluconic acid, ethylenediaminetetraacetic acid disodium, ethylenediaminetetraacetic acid trisodium, phosphonates, acrylates, polyacrylates, and corrosion inhibitors based on heavy metals selected from vanadium, molybdenum, tungsten and cerium.

Patentansprüche

1. Verfahren einer kontinuierlichen chemischen Patinierungs-/Satinierungsbehandlung von Zink-Titan-Legierungen, das die nachstehenden Schritte umfasst:

- Entfetten mit einer alkalischen Fettentfernungsflüssigkeit in einer wässrigen Lösung:
- erstes Spülen mit kontinuierlich frischem Wasser;
- chemische Säure-Patinierungs-/-Santinierungsbehandlung;
- zweites Spülen mit kontinuierlich frischem Wasser;
- Vorpassivierungsbehandlung mit einem chromfreien Bad, das Zirkonium- und/oder Titan- und Aluminiumverbindungen enthält;
- Lufttrocknen;
- Passivierungsbehandlung, die eine erste Behandlungsstufe mit einer herkömmlichen anorganischen Komponente, die auf Chrom 3 oder 6 basiert oder chromfrei ist, und eine zweite Behandlungsstufe mit einem Antifingermittel umfasst, das aus einer wässrigen Lösung eines Acrylsäureharzes, das aus auf Butylacrylat, Methylmethacrylat und Acrylsäure basierenden Monomeren besteht und die nachstehenden Eigenschaften aufweist:

pH-Wert < 6;
Mm ≥ 250000;

TG (Glasübergangstemperatur) zwischen 30 und 45 °C;
Trockenrückstand zwischen 30 und 50%;

gegebenenfalls im Gemisch mit Korrosionshemmern wie Zinkoxid und P2O5 besteht;
- Trocknen des feuchten Films.

2. Verfahren wie in Anspruch 1 beansprucht, wobei die Zirkonium- und/der Titan- und Aluminiumverbindungen in dem Vorpassivierungsbad aus Fluorozirkonsäure, Ammoniumzirkoniumcarbonat und Kaliumfluorozirkonaht; Aluminiumoxid von verschiedenen Extraktionen (Aluminas), Aluminiumfluorid und Aluminiumdifluorid; Fluorotitansäure, Titanoxalat, Titanoxide und Kaliumfluorotitanat ausgewählt werden.

3. Verfahren wie in Anspruch 1 oder 2 beansprucht, wobei die Passivierung eine Behandlung mit einem Bad umfaßt, das Chrom 3- und Chrom 6-Verbindungen enthält.

4. Verfahren wie in Anspruch 3 beansprucht, wobei das Bad Chromsäure, Chromphosphat, Zinkphosphat und Zinkchromat und Reduktionsmittel enthält.

5. Verfahren wie in Anspruch 1 oder 2 beansprucht, wobei die Passivierung eine Behandlung mit einem Bad umfasst, das Chrom 3-Verbindungen enthält.

6. Verfahren wie in Anspruch 5 beansprucht, wobei das Bad Phosphorsäure, Chromphosphat, Chromnitrat, Komplexierungsmittel, Korrosionshemmer und organische Benetzungsmittel enthält, die auf Alkoxypolypropoxypolyethoxyethylbenzylether basieren oder zu der Klasse von Perfluorderivaten gehören.

7. Verfahren wie in Anspruch 1, oder 2 beansprucht, wobei die Passivierung eine Behandlung mit einem chromfreien Bad umfasst.

8. Verfahren wie in Anspruch 7 beansprucht, wobei das Bad Silane, ausgewählt aus den Klassen von 1-Propylamin-3-(triethoxysilyl)silan und Tri-methoxy[3-(oxiranylmethoxy)propyl]silan, Titansalze, die sich von Fluorotitansäure, Titanoxalat, Titanoxid oder Kaliumfluorotitanat ableiten, alkalische Phosphate, alkalische Nitrate, Sequestriermittel, ausgewählt aus Nitriloessigsäure, Natriumgluconat, Gluconsäure, Ethylendiamintetraessigsäure-Dinatrium, Ethylendiamintetraessigsäure-Trinatrium, Phosphonaten, Acrylaten, Polyacrylaten, und Korrosionshemmer, basierend auf Schwermetallen, ausgewählt aus Vanadium, Molybdän, Wolfram und Cer, enthält.

Revendications

1. Procédé de traitement de patine/satinage chimique continu des alliages de zinc-titane comprenant les étapes suivantes :

- dégraissage avec un liquide dégraissant alcalin dans une solution aqueuse ;
- premier rinçage avec une eau renouvelée en continu ;
- traitement de patine/satinage par acide chimique ;
- deuxième rinçage avec une eau renouvelée en continu ;
- traitement de pré-passivation avec un bain exempt de chrome contenant des composés de zirconium et/ou de titane et d'aluminium ;
- séchage à l'air ;
- traitement de passivation comprenant une première étape de traitement avec un composant inorganique conventionnel à base de chrome 3 et/ou 6 ou sans chrome, et une deuxième étape de traitement avec un agent anti-empreinte digitale constitué d'une solution aqueuse d'une résine acrylique constituée de monomères à base d'acrylate de butyle, de méthacrylate de méthyle et d'acide acrylique, ayant les caractéristiques suivantes :

pH < 6 ;
PM (Poids moléculaire) ≥ 250 000 ;
TV (température de transition vitreuse) comprise entre 30 et 45°C ;
résidu sec compris entre 30 et 50% ;
éventuellement mélangé avec des inhibiteurs de corrosion, tels que l'oxyde de zinc et le P_2O_5 ;

- séchage du film humide.

2. Procédé tel que revendiqué selon la revendication 1, dans lequel les composés de zirconium et/ou de titane et d'aluminium dans le bain de pré-passivation sont choisis parmi l'acide fluorozirconique, le carbonate d'ammonium et de zirconium et le fluorozirconate de potassium ; l'oxyde d'aluminium de différentes extractions (alumines), le fluorure d'aluminium et le difluorure d'aluminium, l'acide fluorotitanique, l'oxalate de titane, l'oxyde de titane et le fluorotitanate de potassium.

3. Procédé tel que revendiqué selon la revendication 1 ou 2, dans lequel la passivation comprend un traitement avec un bain contenant des composés de chrome 3 et de chrome 6.

4. Procédé tel que revendiqué selon la revendication 3, dans lequel le bain contient de l'acide chromique, du phosphate de chrome, du phosphate de zinc et du chromate de zinc et des agents réducteurs.

5. Procédé tel que revendiqué selon la revendication 1 ou 2, dans lequel la passivation comprend un traitement avec un bain contenant des composés de chrome 3.

6. Procédé tel que revendiqué selon la revendication 5, dans lequel le bain contient de l'acide phosphorique, du phosphate de chrome, du nitrate de chrome, des agents complexants, des inhibiteurs de corrosion et des agents mouillants organiques à base d'alcoxypolypropoxypolyéthoxy-éthyl-benzyléther ou appartenant à la classe des dérivés perfluorés.

7. Procédé tel que revendiqué selon la revendication 1 ou 2, dans lequel la passivation comprend un traitement avec un bain exempt de chrome.

8. Procédé tel que revendiqué selon la revendication 7, dans lequel le bain contient des silanes, choisis dans les classes de I-propylamine,3-(triéthoxysilyl)-silane et de triméthoxy[3-(oxyranylméthoxy)propyl]-silane, des sels de titane dérivant de l'acide fluorotitanique, oxalate de titane, l'oxyde de titane ou le fluorotitanate de potassium, des phosphates alcalins, des nitrates alcalins, des agents séquestrants choisis parmi l'acide nitriloacétique, le gluconate de sodium, l'acide gluconique, l'acide éthylènediaminetétraacétique disodique, l'acide éthylènediaminetétraacétique trisodique, les phosphonates, les acrylates, les polyacrylates, et des inhibiteurs de corrosion à base de métaux lourds choisis parmi le vanadium, le molybdène, le tungstène et le cérium.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 827785 A **[0005]**