



(11)

EP 1 612 294 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.01.2006 Bulletin 2006/01

(51) Int Cl.:
C23C 22/56 (2006.01) **C23C 22/34** (2006.01)
C23C 22/36 (2006.01)

(21) Application number: **05105831.1**

(22) Date of filing: **29.06.2005**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR**
Designated Extension States:
AL BA HR LV MK YU

(30) Priority: **02.07.2004 IT 2004169**

(71) Applicant: **ITALTECNO S.R.L.**
41100 Modena MO (IT)

(72) Inventors:
• **Dalla Barba, Walter**
41100 Modena (IT)
• **Vincenzi, Fabio**
41057 Spilamberto MO (IT)
• **Vincenzi, Federico**
41100 Modena (IT)

(74) Representative: **Modiano, Micaela Nadia**
Modiano Gardi Patents SAS
Via Meravigli 16
20123 Milano (IT)

(54) **Bath and associated method for the conversion coating of articles made of aluminium and alloys thereof**

(57) A bath and an associated method for the conversion coating of articles made of aluminum and alloys thereof; the bath comprises at least one manganese (Mn) carrier in a aqueous solution with a non-basic pH; the method comprises cleaning the surface of an article made of aluminum or alloy thereof to be treated and converting a layer of the surface thus cleaned into a protective coating by applying the bath to the clean surface.

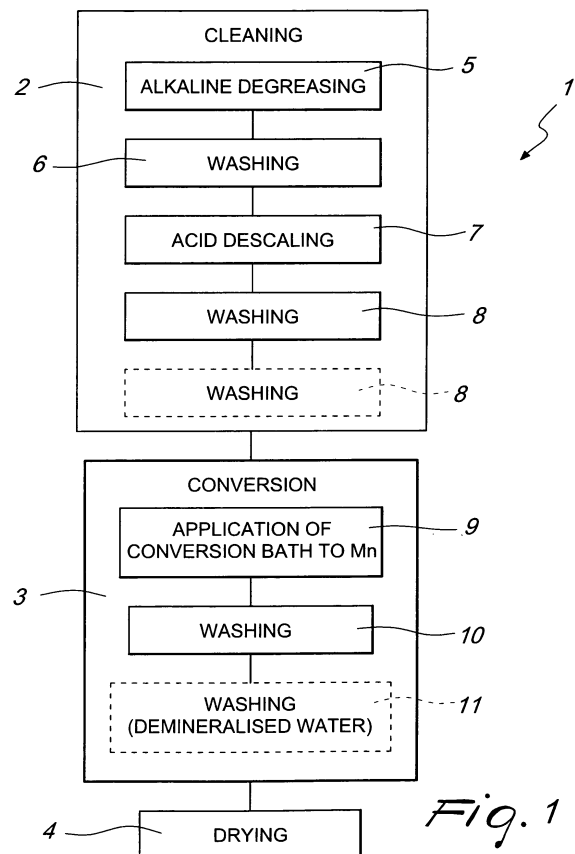


Fig. 1

Description

[0001] The present invention relates to a bath for the conversion coating of articles made of aluminum and alloys thereof and to the associated method.

[0002] It is known that metallic materials, in contact with various environments, are subject to corrosion phenomena which cause their gradual deterioration, modification and destruction.

[0003] Among the many known methods for preventing corrosion and protecting against it, there are those which act on the control of the chemical and physical characteristics of the metallic material by coating it with metallic or nonmetallic protective coatings.

[0004] Among these, inorganic coatings obtained by conversion of the metallic material are known; i.e., said coatings are the result of the conversion (transformation caused by chemical reactions) of a surface layer, having a thickness on the order of 0.5-2 μm , of the unstable metallic material into a stable and corrosion-resistant layer.

[0005] Inorganic conversion coatings can be formed by means of chemical or electrochemical processes affecting the metallic material in suitable baths, the composition of which determines the nature of the resulting coating.

[0006] With particular reference to aluminum and alloys thereof, known inorganic conversion coatings include chromate-based ones, phosphochromate-based ones, and chromium-free ones.

[0007] In all three cases, the coating process substantially follows three stages: cleaning of the surface to be coated;

conversion of the clean surface into a protective inorganic coating, respectively by chromating, phosphochromating, and in the absence of chromium;

drying of the resulting coating.

[0008] Since aluminum is amphoteric, cleaning the surface to be treated comprises generally a step for alkaline degreasing and a step for acid descaling (also termed "neutralization" or "activation" of the surface), each of which is followed by at least one wash.

[0009] In the case of phosphochromating, the conversion baths of which are particularly aggressive, it is possible to limit or even eliminate the step of acid descaling and the subsequent wash.

[0010] Conversion occurs by applying a conversion bath to the clean surface; the application times and temperature and the qualitative and quantitative composition of the bath vary depending on the type of coating to be provided: chromate-based, phosphochromate-based, or chromium-free.

[0011] The bath can be applied by immersion or spraying.

[0012] Application is followed by one or more washes; in general, by a first wash with mains water and by a second wash with demineralized/deionized water.

[0013] The conversion coating obtained by chromating

and phosphochromating has an amorphous structure and contains water of imbibition, which must be eliminated by subjecting the coated surface to slow drying at ambient temperature or at low temperatures (on the order of 70-80 $^{\circ}\text{C}$), so as to avoid the formation of cracks.

[0014] The bath for chromium conversion (chromating) is an aqueous solution of chromates (hexavalent chromium), acids, fluorides and optionally accelerating agents, with a pH that can vary between 1.5 and 2.5.

[0015] Reactions occur between the clean aluminum surface and the conversion bath which form a coating constituted by a layer that contains chromium chromates ($\text{Cr}(\text{OH})_2\text{HCrO}_4$) and optionally basic aluminum oxide (AlOOH) in addition to other compounds, which depend on the composition of the bath, such as for example, in the case of accelerated baths, chromium ferrocyanide ($\text{CrFe}(\text{CN})_6$). The coating obtained by chromating can be identified visually by its typical coloring, which varies from iridescent yellow to brownish yellow and is caused by the hexavalent state of the chromium present in the form of chromates.

[0016] The bath for phosphorus-chromium conversion (phosphochromating) is an aqueous solution of acid phosphates, acid and alkaline chromates, complexed and free fluorides, and optional accelerating agents.

[0017] Reactions occur between the clean aluminum surface and the conversion bath which lead to the formation of a coating constituted by a layer containing chromium phosphate (CrPO_4) and aluminum phosphate (AlPO_4).

[0018] The coating obtained by phosphochromating can be identified visually by the typical green coloring, caused by the trivalent state of the chromium, which is present in the form of phosphate.

[0019] The chromium-free conversion bath is an aqueous solution of fluorides together with titanium or zirconium; reactions occur between the clean aluminum surface and the conversion bath which lead to the formation of a coating constituted by a layer containing aluminum oxide (Al_2O_3) and aluminum fluorotitanium ($\text{AlOF}\cdot\text{TiO}_2$, AlOF TiOF_2).

[0020] These known protection methods are not free from drawbacks, including the fact that inorganic conversion coatings obtained by chromating or phosphochromating use hexavalent chromium, which is toxic and noxious to the health of the operators assigned to performing the corresponding processes and pollutes the environment.

[0021] It is noted in fact that the wastewater of chromating and phosphochromating conversion processes contain hexavalent chromium, in addition to fluorides and ferrocyanides (if used as accelerating agents), which are highly pollutant; this wastewater, before being released, must be subjected to long and complex treatments, the cost of which affects substantially the overall process cost.

[0022] Chromium-free and titanium- or zirconium-based inorganic conversion coatings instead have

the drawback of being substantially colorless, and this, differently from chromating treatments (which are brownish-yellow) and phosphochromating treatments (which are green), on the one hand prevents the operators assigned to the corresponding process from checking visually the actual execution of the process or of the quality of the coating obtained thereby (continuity, uniformity, etc) and on the other hand forces the execution of periodic chemical tests, which are in themselves less effective.

[0023] It is noted that conversion systems can be installed in-line, for example, with systems for the subsequent painting of aluminum parts; in this case, parts that are not coated or are coated incompletely and unevenly may reach the painting step.

[0024] Another disadvantage of chromium-free processes for inorganic conversion coating consists of the fact that they have a reduced yield with respect to chromating and phosphochromating processes and depend to a greater extent on the initial steps for cleaning the surfaces to be treated, which accordingly must be performed with greater care and monitoring.

[0025] In order to obviate these drawbacks, a conversion coating process is also known from Italian Industrial Patent Application No. M02003A185, in the name of this same Applicant, which uses a chromium-free bath substantially constituted by a manganese carrier, preferably potassium permanganate (KMnO_4), in an aqueous solution at an alkaline pH.

[0026] By means of this process, it is possible to obtain colored protective coatings, so as to allow direct visual assessment of the effectiveness of the performed treatment despite not using chromium.

[0027] However, even this coating method has some drawbacks, linked in particular to the fact that it does not allow to obtain uniform coatings of the treated articles, since in an alkaline environment the soda tends to react with the aluminum, interfering with the formation of the protective coating, and to difficulty in execution, in view of the fact that existing plants are mostly made of materials suitable for using acid solutions and therefore would have to be replaced with plants preset to work in an alkaline environment.

[0028] Further, since the treatment steps that are generally provided upstream of the conversion coating step occur in an acid environment, it is necessary to provide intermediate washes, which are needed in order to transition from an acid environment to an alkaline environment, inevitably extending the time requirements of the cycle and increasing its costs.

[0029] Not least, the basicity of the bath that is used does not allow to introduce in the solution salts of zirconium and/or titanium, which as is known assist the conversion process and increase the corrosion resistance of the resulting coating.

[0030] The aim of the present invention is to eliminate the drawbacks noted above, by providing a bath for the conversion coating of articles made of aluminum and al-

loys thereof, which allows to obtain uniform protective coatings having high resistance to corrosion and can be used in currently existing plants without requiring particular structural adaptations thereof and does not entail the execution of additional preliminary treatments.

[0031] Within this aim, an object of the present invention is to provide a bath that is not toxic or noxious to the health of the operators assigned to the corresponding process, does not pollute the environment, and allows operators to perform a straightforward and complete visual check of the effectiveness of the treatment performed on all the processed articles.

[0032] Another object of the present invention is to provide a method for conversion coating of articles made of aluminum and alloys thereof that can be performed simply and effectively by using known plants and technologies, has a high yield and has wastewater that can be treated easily at low costs.

[0033] Another object of the present invention is to provide a structure that is simple, relatively easy to provide in practice, safe in use, effective in operation, and has a relatively low cost.

[0034] In view of this aim and of these and other objects, which will become better apparent hereinafter, a bath for the conversion coating of articles made of aluminum and alloys thereof is provided which comprises at least one manganese (Mn) carrier, characterized in that said manganese (Mn) carrier is in an aqueous solution with a pH that is not basic and therefore is neutral or acid.

[0035] Preferably, the bath according to the invention comprises a manganese carrier in an aqueous solution with acid pH.

[0036] The manganese carrier is preferably constituted by potassium permanganate (KMnO_4) and is present in quantities which can vary between 1 and 10 g/l (liter of bath), preferably 5 g/l.

[0037] The acidity of the bath corresponds to pH values comprised between 2 and 4, preferably substantially equal to 2.6.

[0038] It should be noted that the manganese carrier has a protective effect, since it reacts with the surface of the article to be treated, "converting" it into a protective coating, and a coloring effect on said coating.

[0039] Advantageously, the bath can contain at least one titanium (Ti) carrier and/or at least one zirconium (Zr) carrier, which increase the corrosion resistance of the resulting coating.

[0040] The titanium carrier is preferably constituted by fluorotitanic acid (H_2TiF_6) and is comprised in quantities variable between 0.2 and 2 g/l (liter of bath).

[0041] The zirconium carrier is preferably constituted by fluorozirconic acid (H_2ZrF_6) and is present in quantities that can vary between 0.1 and 1 g/l (liter of bath).

[0042] If the fluorotitanic acid and/or the fluorozirconic acid are absent or are present in small quantities, close to the minimum values of the ranges described above, it is possible to introduce conveniently in the bath at least one fluoride carrier acid.

[0043] The fluoride carrier acid is preferably constituted by hydrofluoric acid (HF) and is present in quantities comprised between 0.1 and 0.6 g/l.

[0044] It is also possible to replace the components of the bath with others that are equivalent thereto and to add to the bath additives which assist the conversion process.

[0045] The water used for the bath is preferably demineralized water or softened mains water.

[0046] The method for the conversion coating of articles made of aluminum and alloys thereof according to the invention is shown schematically in Figure 1 by means of a block diagram which identifies its various steps of execution.

[0047] The method 1 comprises a step 2 for cleaning the surface of the article made of aluminum or alloy thereof to be treated, a step 3 for converting a layer of the surface thus cleaned into a protective coating, and a step 4 for drying the resulting protective coating.

[0048] The present description does not describe in detail the cleaning step 2 and the drying step 4 and the corresponding plants, since they are similar to the ones used in known technologies for conversion coating of aluminum (chromating, phosphochromating, chromium-free).

[0049] The cleaning step 2 consists substantially of an alkaline degreasing 5, followed by a wash 6, and by an acid descaling 7 (neutralization or activation), followed by one or more washes 8; it is designed to remove from the surface to be treated all the pollutant particles, including the oxides that naturally coat aluminum.

[0050] The conversion step 3 comprises the application 9, to the surface cleaned in the preceding step, of a bath which contains a manganese (Mn) carrier in an aqueous solution having a non-basic and preferably acid pH, as described above.

[0051] The application 9, which can be performed with the known immersion or spray techniques, not shown, occurs at a temperature that can vary between 15 and 40 °C, preferably 20 °C, for a time that can vary between 30 seconds and 5 minutes, preferably 2 minutes.

[0052] Reactions occur between the clean surface made of aluminum or alloy thereof and the bath which lead to the formation of a conversion coating (i.e., produced by the transformation of a surface layer of aluminum), which is constituted by a layer that contains manganese dioxide (MnO₂), aluminum oxide (Al₂O₃), and optionally titanium and zirconium oxides; if further additives are used, said layer might also include additional reaction compounds.

[0053] The coating has a thickness which can vary between 0.5 and 2 μm, has an amorphous structure and a gold yellow/brown coloring.

[0054] At the end of the application 9, the surfaces coated with the conversion coating are subjected to at least one wash 10 with mains water or preferably demineralized water, optionally containing traces of hydrogen peroxide, and preferably to at least one wash 11 with

demineralized water, similar to the washes used in known chromating, phosphochromating and chromium-free coating technologies.

[0055] It is necessary to eliminate from the resulting coating the water of imbibition that is trapped therein by subjecting it to the drying step 4, which can be performed at ambient temperature or in heated environments.

[0056] The following examples are given merely by way of illustration of the present invention and must not be understood as limiting the scope of the present invention as defined by the accompanying claims.

Example 1

[0057] A bath for the inorganic conversion coating of aluminum and alloys thereof is prepared which is constituted by an acid aqueous solution (pH 2.6) which contains:

- potassium permanganate (KMnO₄) 5 g/l;
- fluorotitanic acid (H₂TiF₆) 0.65 g/l;
- fluorozirconic acid (H₂ZrF₆) 0.16 g/l;
- hydrofluoric acid (HF) 0 g/l.

[0058] The bath is applied to a clean surface of an article made of aluminum or alloy thereof at a temperature of 20 °C and for 2 minutes.

Example 2

[0059] A bath for the inorganic conversion coating of aluminum and alloys thereof is prepared which is constituted by an acid aqueous solution (pH 2.6) which contains:

- potassium permanganate (KMnO₄) 5 g/l;
- fluorotitanic acid (H₂TiF₆) 0 g/l;
- fluorozirconic acid (H₂ZrF₆) 0 g/l;
- hydrofluoric acid (HF) 0.3 g/l.

[0060] The bath is applied to a clean surface of an article made of aluminum or alloy thereof at a temperature of 20 °C and for 2 minutes.

Example 3

[0061] A bath for the inorganic conversion coating of aluminum and alloys thereof is prepared which is constituted by an acid aqueous solution (pH 2.6) which contains:

- potassium permanganate (KMnO₄) 5 g/l;
- fluorotitanic acid (H₂TiF₆) 0.40 g/l;
- fluorozirconic acid (H₂ZrF₆) 0.16 g/l;
- hydrofluoric acid (HF) 0.1 g/l.

[0062] The bath is applied to a clean surface of an article made of aluminum or alloy thereof at a temperature

of 20 °C and for 2 minutes.

Example 4

[0063] A bath for the inorganic conversion coating of aluminum and alloys thereof is prepared which is constituted by an acid aqueous solution (pH 2.6) which contains:

- potassium permanganate (KMnO_4) 5 g/l;
- fluorotitanic acid (H_2TiF_6) 0 g/l;
- fluoro-zirconic acid (H_2ZrF_6) 0.3 g/l;
- hydrofluoric acid (HF) 0.1 g/l.

[0064] The bath is applied to a clean surface of an article made of aluminum or alloy thereof at a temperature of 20 °C and for 2 minutes.

[0065] In practice it has been found that the described invention achieves the proposed aim and objects.

[0066] The bath according to the invention in fact allows to obtain a compact and uniform conversion coating on the surface of the treated articles, which by being colored (gold yellow/brown) allows operators to perform an immediate visual check of the actual execution of the coating process and/or of the quality of the resulting coating (continuity, uniformity, defects, etc).

[0067] Moreover, the bath is not toxic, does not harm the health of the operators and does not pollute the environment.

[0068] The conversion coating obtained with the bath according to the invention protects aluminum or alloys thereof against corrosion and can act as a foundation for the subsequent application of paints or varnishes.

[0069] The method according to the invention can be performed with technologies and plants that are already known in the field, has a good yield and produces wastewater that has a reduced environmental impact with respect to wastewater produced with traditional chromium-based baths and can be treated simply and at lower cost.

[0070] The invention thus conceived is susceptible of numerous modifications and variations, all of which are within the scope of the appended claims.

[0071] All the details may further be replaced with other technically equivalent ones.

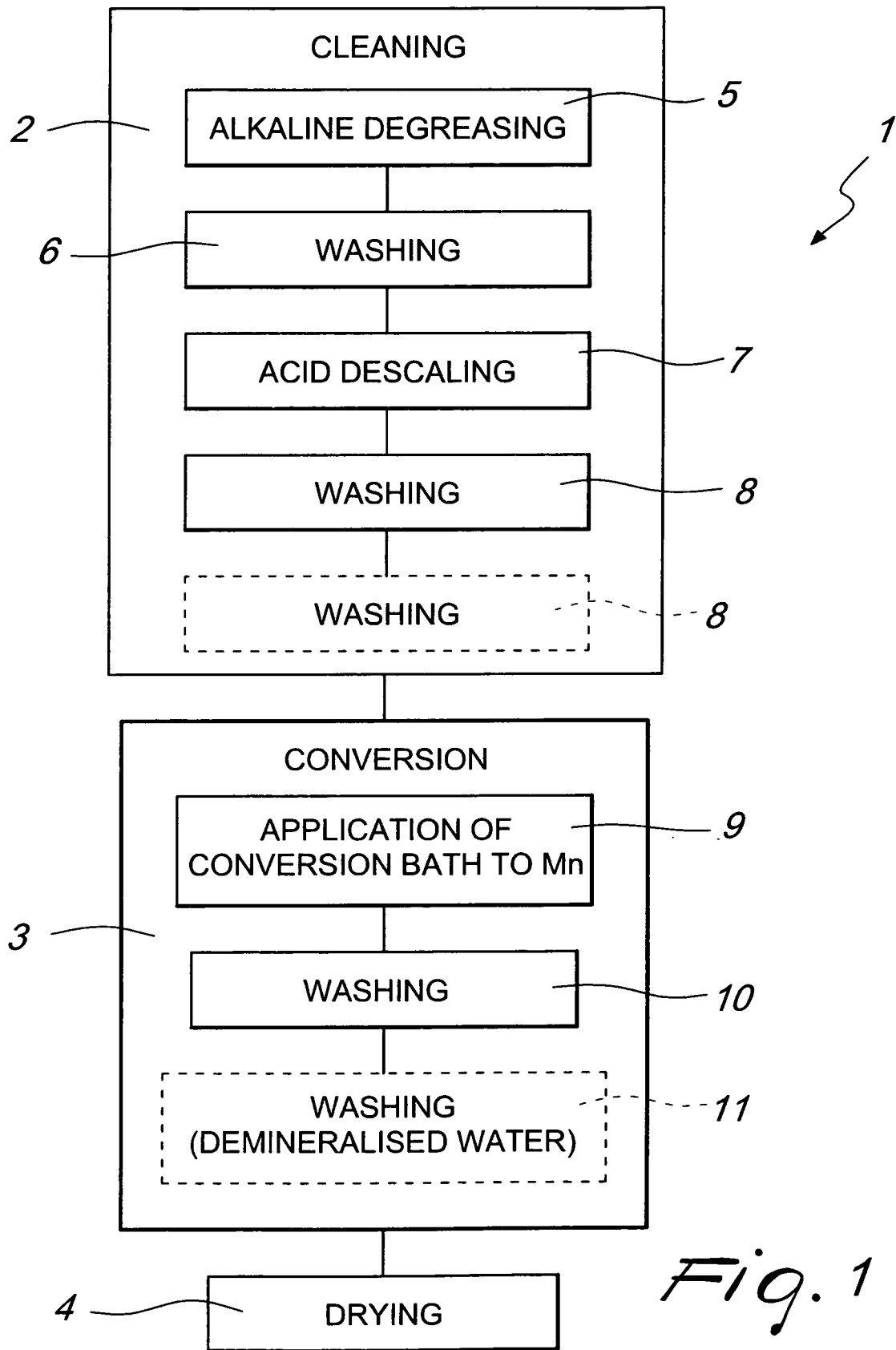
[0072] The disclosures in Italian Patent Application No. M02004A000169, from which this application claims priority, are incorporated herein by reference.

[0073] Where technical features mentioned in any claim are followed by reference signs, those reference signs have been included for the sole purpose of increasing the intelligibility of the claims and accordingly such reference signs do not have any limiting effect on the interpretation of each element identified by way of example by such reference signs.

Claims

1. A bath for the conversion coating of articles made of aluminum and alloys thereof, comprising at least one manganese (Mn) carrier, **characterized in that** said manganese (Mn) carrier is in an aqueous solution with a non-basic pH.
2. The bath according to claim 1, **characterized in that** said pH is acid.
3. The bath according to one or more of the preceding claims, **characterized in that** said pH can vary between 2 and 4.
4. The bath according to one or more of the preceding claims, **characterized in that** said pH is substantially equal to 2.6.
5. The bath according to one or more of the preceding claims, **characterized in that** said manganese carrier comprises potassium permanganate (KMnO_4).
6. The bath according to one or more of the preceding claims, **characterized in that** said manganese carrier is present in quantities that can vary between 1 and 10 g/l (liter of bath).
7. The bath according to one or more of the preceding claims, **characterized in that** said manganese carrier is present in a quantity equal to 5 g/l (liter of bath).
8. The bath according to one or more of the preceding claims, **characterized in that** it comprises at least one titanium (Ti) carrier.
9. The bath according to claim 8, **characterized in that** said titanium carrier comprises fluorotitanic acid (H_2TiF_6).
10. The bath according to one or more of the preceding claims, **characterized in that** said titanium carrier is present in quantities that can vary between 0.2 and 2 g/l (liter of bath).
11. The bath according to one or more of the preceding claims, **characterized in that** it comprises at least one zirconium (Zr) carrier.
12. The bath according to claim 11, **characterized in that** said zirconium carrier comprises fluoro-zirconic acid (H_2ZrF_6).
13. The bath according to one or more of the preceding claims, **characterized in that** said zirconium carrier is present in quantities that can vary between 0.1 g/l and 1 g/l (liter of bath).

14. The bath according to one or more of the preceding claims, **characterized in that** it comprises at least one fluoride carrier acid.
15. The bath according to claim 14, **characterized in that** said fluoride carrier acid is hydrofluoric acid (HF).
16. The bath according to one or more of the preceding claims, **characterized in that** said fluoride carrier acid is present in quantities that can vary between 0.1 and 0.6 g/l (liter of bath).
17. The bath according to one or more of the preceding claims, **characterized in that** it comprises:
- potassium permanganate (KMnO_4) 5 g/l;
 - fluorotitanic acid (H_2TiF_6) 0.65 g/l;
 - fluorozirconic acid (H_2ZrF_6) 0.16 g/l;
 - hydrofluoric acid (HF) 0 g/l.
18. The bath according to one or more of the preceding claims, **characterized in that** it comprises:
- potassium permanganate (KMnO_4) 5 g/l;
 - fluorotitanic acid (H_2TiF_6) 0 g/l;
 - fluorozirconic acid (H_2ZrF_6) 0 g/l;
 - hydrofluoric acid (HF) 0.3 g/l.
19. The bath according to one or more of the preceding claims, **characterized in that** it comprises:
- potassium permanganate (KMnO_4) 5 g/l;
 - fluorotitanic acid (H_2TiF_6) 0.40 g/l;
 - fluorozirconic acid (H_2ZrF_6) 0.16 g/l;
 - hydrofluoric acid (HF) 0.1 g/l.
20. The bath according to one or more of the preceding claims, **characterized in that** it comprises:
- potassium permanganate (KMnO_4) 5 g/l;
 - fluorotitanic acid (H_2TiF_6) 0 g/l;
 - fluorozirconic acid (H_2ZrF_6) 0.3 g/l;
 - hydrofluoric acid (HF) 0.1 g/l.
21. A method for the conversion coating of articles made of aluminum and alloy thereof, comprising the steps that consist in cleaning the surface of an article made of aluminum or alloy thereof to be treated and in converting a layer of the surface thus cleaned into a protective coating, **characterized in that** the conversion step comprises the application to said clean surface of a bath according to one or more of claims 1 to 20.
22. The method according to claim 21, **characterized in that** said conversion step occurs at a temperature that can vary between 15 and 40 °C.
23. The method according to one or more of the preceding claims, **characterized in that** said conversion step occurs at a temperature on the order of 20 °C.
24. The method according to one or more of the preceding claims, **characterized in that** said bath is applied to said clean surface for a time that can vary between 30 seconds and 5 minutes.
25. The method according to one or more of the preceding claims, **characterized in that** said bath is applied to said clean surface for 2 minutes.
26. The method according to one or more of the preceding claims, **characterized in that** said application step consists in immersing said clean surface in said bath.
27. The method according to one or more of the preceding claims, **characterized in that** said application step consists in spraying said bath onto said clean surface.
28. The method according to one or more of the preceding claims, **characterized in that** said conversion step comprises at least one wash, which follows said application.
29. The method according to one or more of the preceding claims, **characterized in that** it comprises drying said inorganic protective coating.
30. The method according to one or more of the preceding claims, **characterized in that** said protective coating comprises manganese dioxide (MnO_2) and aluminum oxide (Al_2O_3), titanium (Ti) oxides, and/or zirconium (Zr) oxides.
31. The method according to one or more of the preceding claims, **characterized in that** said protective coating has a thickness that can vary between 0.5 and 2 μm .





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 99/60186 A (HENKEL CORPORATION; NAKADA, KAZUYA; KAWAGUCHI, MOTOKI; MAEDA, KAZUHIRO) 25 November 1999 (1999-11-25) * page 7, lines 16-21 * * page 10; table 1 * * page 11 - page 13; examples 2-5; table 2 * * page 6, line 35 - page 7, line 2 * * claims 1-3 * * page 8, lines 8-16,34,35 * * page 9, lines 23-30 * * page 10, lines 3-7; table 2 * * page 8, line 36 - page 9, line 1 * * claims 4-7 *	1-14, 21-31	C23C22/56 C23C22/34 C23C22/36
X	DE 40 31 710 A1 (HENKEL KGAA, 4000 DUESSELDORF, DE) 9 April 1992 (1992-04-09) * column 2, lines 30-55 * * column 3, lines 1-8,30-33,40-52,55-63 * * examples 3,4 * * claims 1-6 * * column 4, lines 21-50,65,66 * * claims 8-11 *	1-3,5,6, 8,9,11, 12,14, 21-29	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C23C
X	EP 1 447 460 A (NIPPON PAINT CO., LTD) 18 August 2004 (2004-08-18) * page 6, line 45, paragraphs 18,20 * * page 10; example 11; table 1 * * claims 4,5 * * page 8, paragraph 35; table 1 * ----- -/--	1-3,5, 11-16, 21,24,26	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 29 September 2005	Examiner Handrea-Haller, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 10 5831

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	CH 136 060 A (DR. OTTO SPRENGER PATENTVERWERTUNG JIROTKA M. B. H) 31 October 1929 (1929-10-31) * page 2, lines 10,11,36-43 * * claims 1-3,5 *	1,2,5, 14,15	
E	EP 1 571 237 A (NIHON PARKERIZING CO., LTD; TOYOTA JIDOSHA KABUSHIKI KAISHA; DAIHATSU) 7 September 2005 (2005-09-07) * page 10, lines 18-28, paragraph 60; example 7 *	1-3,5,8, 14,15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 29 September 2005	Examiner Handrea-Haller, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

3
EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 10 5831

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-09-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9960186 A	25-11-1999	AU 4308099 A CA 2332620 A1 EP 1177329 A1	06-12-1999 25-11-1999 06-02-2002
DE 4031710 A1	09-04-1992	NONE	
EP 1447460 A	18-08-2004	CN 1530461 A JP 2004270031 A US 2004217328 A1	22-09-2004 30-09-2004 04-11-2004
CH 136060 A	31-10-1929	NONE	
EP 1571237 A	07-09-2005	AU 2003289323 A1 CA 2509772 A1 WO 2004055237 A1 JP 2004190121 A	09-07-2004 01-07-2004 01-07-2004 08-07-2004