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

(11) EP 1 447 461 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
12.12.2007 Bulletin 2007/50

(21) Application number: **01976326.7**

(22) Date of filing: **24.10.2001**

(51) Int Cl.:
C23G 1/02 *(2006.01)* ***C23F 1/16*** *(2006.01)*
C23F 3/06 *(2006.01)*

(86) International application number:
PCT/ES2001/000401

(87) International publication number:
WO 2003/035933 (01.05.2003 Gazette 2003/18)

(54) **PRODUCT AND METHOD FOR CLEANING TITANIUM SURFACES**

PRODUKT UND VERFAHREN ZUR REINIGUNG VON TITANOBERFLÄCHEN

PRODUIT NETTOYANT ET PROCEDE DE NETTOYAGE DE SURFACES EN TITANE

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

(43) Date of publication of application:
18.08.2004 Bulletin 2004/34

(73) Proprietors:
- **Fundacion Inasmet**
  20009 San Sebastián (Guip zcoa) (ES)
- **Fundacion Museo Guggenheim Bilbao**
  48009 Bilbao (Vizcaya) (ES)

(72) Inventors:
- **CANO IRANZO, Francisco**
  E-20012 San Sebastián (Gipuzkoa) (ES)
- **VAQUERO TXAPARTEGI, Maria Isabel**
  E-20120 Hernani (Gipuzkoa) (ES)
- **PELAYO RIVERA, Alberto**
  E-20012 San Sebastian (Gipuzkoa) (ES)

(74) Representative: **Carpintero Lopez, Francisco et al**
HERRERO & ASOCIADOS, S.L.
Alcalá, 35
28014 Madrid (ES)

(56) References cited:
EP-A- 1 029 953
WO-A-01/00906
US-A- 3 844 859
US-A- 5 217 569

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 447 461 B1

Description

AREA OF THE INVENTION

[0001] The invention concerns a cleaning product to clean titanium surfaces and its application in a procedure to clean titanium surfaces such as titanium facades and panels.

BACKGROUND OF THE INVENTION

[0002] The excellent resistance of titanium and its alloys to corrosion is due to the formation of a protective film of oxides, which is continuous, stable and adheres strongly to the surface. Owing to the high affinity of titanium for oxygen, this film of oxides forms spontaneously as soon as a recent cut of the material is exposed to the atmosphere.

[0003] The nature, composition and thickness of the layer of protective oxides formed on the surface of the titanium depend on environmental conditions. In most aqueous environments, the oxide formed is TiO_2, although also a mixture of TiO_2, Ti_2O_3 and TiO can also be formed. The naturally formed oxide films reach thicknesses of around 10 nm, which are not visible with the naked eye.

[0004] Some factors can alter the characteristics and composition of the TiO_2 layer, including the temperature or affinity of titanium for certain gases. Also, the presence of contamination or dirt on the metal surface can produce discontinuities in the surface that can give rise to severe localized corrosion processes. In the case of titanium panels used in construction and exposed to aggressive environmental, industrial and urban atmospheres, this type of phenomenon, which alters the surface characteristics of the panels and their composition, has been observed.

[0005] Cleaning and surface passivation methods used in normal conditions to eliminate this type of oxide and surface contamination require immersion processes that use different types of solutions. These include acid pickling, electropolishing or mechanical processes. These methods are not viable in panels used for construction purposes owing to their high cost and because they can alter the surface characteristics of the original panels.

[0006] Document EP1029953 discloses a method for preparying titanium surfaces for use a polyaniline coated light-absorbing surfaces. The titanium is subjected to alkaline degreasing followed by an acid descaling which produces a roughened surface and a chemical conversion treatment and finally a hydrolisis. Consequently, the surface appearance of the titanium is deliberately altered.

[0007] There is, therefore, the need for a new method to clean surfaces containing titanium, such as the titanium panels used in construction, that can help to overcome all or most of the problems described here.

SUMMARY OF THE INVENTION

[0008] The invention, in general, deals with the problem of providing a method to clean titanium surfaces such as the titanium panels used to build facades.

[0009] The solution provided by the invention is based on the development of a cleaning product that includes, separately, (i) a descaling substance, which contains an active agent that acts on the metal surface, composed of a mixture of inorganic acids, and (ii) a fixative, which inhibits and neutralizes the action of the descaling substance, and also in the application of this cleaning product to clean titanium surfaces.

[0010] The application of the cleaning product and the cleaning method provided by this invention permit easy and precise cleaning of the titanium surface without damaging it.

[0011] This cleaning product and its application to clean titanium surfaces are both the objectives of this invention.

DETAILLED DESCRIPTION OF THE INVENTION

[0012] The invention provides a cleaning product, useful for cleaning titanium surfaces, that includes, separately, (A) a descaling or cleaning substance, from hereon called the descaling substance, which contains an active agent that acts on the metal surface, which is composed of a mixture of inorganic acids, and, (B) a fixative or neutralizer, from hereon referred to as the fixative, which inhibits and neutralizes the action of the descaling substance.

[0013] More specifically, the cleaning product of the invention corresponds, separately, to:

A) a descaling substance comprised of:

A.1) a mixture of nitric acid and hydrofluoric acid;
A.2) a thickening agent;
A.3) a surfactant;
A.4) an indicator;

A.5) water; and, optionally,
A.6) a propellant; and

B) a fixative substance that contains:

B.1) an alkaline aqueous solution;
B.2) a thickener;
B.3) a surfactant;
B.4) water; and
B.5) a propellant.

A. Composition of descaling substance

[0014] The composition of the descaling substance consists of water, an active agent and auxiliary agents (thickener, surfactant and indicator), as well as a propellant.

[0015] The active agent is comprised of a mixture of nitric and hydrofluoric acid, and acts on the metal surface (Ti), providing the chemical reaction responsible for eliminating the contamination, impurities and oxides. Beneficially, the active agent also has a protective effect to prevent progression of the cleaning chemical reaction on the metal substrate. The active agent, usually added in the form of an aqueous solution, is present in the descaling substance in a concentration ranging from 1 to 20% in weight relative to the total descaling composition. In a specific application, this active agent consists of a mixture of nitric acid and hydrofluoric acid that contains between 1% and 10% in weight of nitric acid compared to the total descaling composition and between 0.1% and 1% in weight of hydrofluoric acid relative to the total descaling composition, and the weight ratio of nitric acid: hydrofluoric acid is 10:1.

[0016] The thickener is introduced in the descaling substance as a stabilizer, also giving it viscosity and selected rheological characteristics. As a thickening agent, a water-soluble organic pseudoplastic thickener can be used, for example, of cellulotic type or a natural gum, for example xanthane gum. The thickening agent can be present in the descaling substance in a concentration ranging from 0.1% to 1% in weight relative to the total descaling composition.

[0017] The surfactant alters the surface tension of the descaling substance, favoring the formation of foam, stabilization of this substance and dispersion of its components. Potential surfactants include ionic ones (anionic or cationic), in concentrations ranging from 0.1 to 1% in weight compared to the total descaling composition. In one specific application this surfactant is sodium dodecyl sulphate.

[0018] The indicator is introduced in the descaling substance to indicate, by a color change, the time of neutralization of the descaling substance applied on the metallic surface by the fixative substance. The indicator is present in the descaling substance at a concentration less than 0.1% in weight relative to the total weight of descaling substance. In one application the indicator used is phenolphthalein.

[0019] The water present in the descaling substance can come from the active agent (if the acids present are supplied in aqueous solution) and/or from the auxiliary agents (if these are provided dissolved or suspended in water) and/or from water added to make up the descaling solution.

[0020] The descaling substance can take one of several different forms, for example, it can be a foam, gel or a spray gel. Depending on its form of preparation and packaging, the descaling substance may or may not contain a propellant.

[0021] The propellant is a substance that provides the packaged descaling substance with a high internal pressure that results in its forced ejection onto the metallic surface to be cleaned. The propellant can be a liquated or compressed gas.

[0022] Liquated gases are substances that are liquid at ambient temperature, due to the effect of pressure, and that become gaseous at atmospheric pressure. At a specific temperature, the high working pressure is constant and equals the vapor pressure of the liquated propellant. Vaporization of the propellant into the atmosphere favors spray formation or conversion into fine droplets of the non-volatile compounds in solution favoring the formation of microfoams. Examples of liquated gases include hydrocarbons and hydrofluorocarbons (HFC), which can be used at a concentration ranging from 5% to 20% in weight relative to the total descaling composition. In one specific application, the propellant is hydrofluorocarbon identified as HFC 134a (1,1,1,2-tetrafluoroethane).

[0023] Compressed gases are substances injected at appropriate pressures that maintain the excess pressure on the surface of the descaling substance in the container, forcing this to the exterior in the same way as an embolus that acts on the surface of a liquid, especially in the case of insoluble gases. As the contents are discharged, the gas occupies an increasingly larger volume, its initial pressure is reduced and, therefore, the initial working conditions change. Nitrogen, carbon dioxide, nitrous oxide and air can be used in appropriate amounts at the required working pressure.

[0024] As mentioned previously, the preparation and packaging of the descaling compound depends on the form or type of viscous vehicle concerned. As an example, this descaling compound can take the form of:

a) foam (FD), when the propellant used is a liquated gas;
b) spray gel (SPD), when the propellant used is a compressed gas; or
c) gel (GD), when it does not contain propellant.

[0025] The foam and spray gel products are prepared in pressurized containers resistant to acid media, from the following components [active agent, auxiliary agents (in gel form or as an aqueous mixture of thickener, surfactant and indicator), water and gas propellant, in the proportions appropriate to satisfy the percentages defined for the final desired product]. In this case, application of the descaling substance is done, for example, by spraying with a gun, with a maximum interval of 3 hours between filling the container and application of the product, preferably less than 1 hour.

[0026] The gel type product is prepared in acid-resistant containers from the following components [active agent, gel or aqueous mixture of auxiliary agents (thickener, surfactant and indicator) and water, in appropriate proportions to satisfy the percentages defined for the final desired product]. In this case, application of the product is done, for example by sponge trowel, with a maximum time interval between filling the container and using the product of 3 hours, and preferably under 1 hour.

B. Fixative substance

[0027] The fixative is comprised of a neutralizing active agent that stops the action of the descaling agent, neutralizing it, some auxiliary agents (thickener and surfactant), water and a propellant.

[0028] The neutralizing active agent inhibits the action of the acid present in the descaling substance when the fixative is applied to the metallic surface thus reducing the likelihood of a too aggressive attack of the acid on the metallic surface, neutralizing the cleaning product and favoring its collection and elimination. As a neutralizing active agent, a base can be used, generally in the form of an aqueous solution, capable of neutralizing the acid present in the descaling substance. As an example, this base can be an alkaline metal hydroxide, for example, sodium hydroxide, in a concentration of between 1% and 20% in weight relative to the total fixative composition, or trisodium phosphate, in a concentration of between 1% and the maximum permitted concentration relative to the fixative.

[0029] The thickener has the same function as mentioned previously relative to the descaling substance. In this case, as a thickening agent, preferentially, inorganic products with a silicate base are used, for example, sepiolite, at a concentration ranging from 1 to 8% in weight relative to the total fixative composition, since this type of thickener can also neutralize the hydrofluoric acid of the descaling substance.

[0030] The surfactant fulfils the same function as that mentioned for the descaling substance. The surfactant present in the fixative can correspond to ionic surfactants (anionic or cationic), that can be the same or different to those used in the descaling substance. The surfactant can be present in the fixative in a concentration ranging from 0.1 to 1% in weight relative to the total fixative composition.

[0031] The water present in the fixative can either come from the neutralizing active agent (if the base is supplied in aqueous solution) and/or from auxiliary agents (in the case that these are supplied dissolved or suspended in water) and/or of water that is incorporated to make up the volume of the fixative.

[0032] The propellant, which can be a liquated gas or a compressed gas, fulfils the same function as that mentioned previously relative to the descaling substance. The propellant present in the fixative compound can be the same as or different to that used in the descaling substance(if this contains propellant). The propellant can be present in the fixative substance in a concentration ranging from 5 to 20% in weight relative to the total fixative composition when the propellant is a liquated gas, for example, a hydrocarbon or a HFC, such as HFC 134a. Alternatively, when the propellant is a compressed gas, for example, nitrogen, carbon dioxide, nitrous oxide or air, this propellant is used, as mentioned previously, in the appropriate quantity at the working temperature required.

[0033] The fixative can take any suitable form of presentation such as foam(FF) when the propellant is a liquated gas or in the form of spray gel (SGF) when the propellant is a compressed gas.

[0034] Both products (foam and spray gel) are kept in pressurized containers resistant to alkaline media, and are composed of the following components [neutralizing active agents, auxiliary agents (in the form of gel or an aqueous mixture of thickener and surfactant) in proportions that satisfy the percentages defined for the final desired product and propellant gas]. Application of the fixative substance is done, for example, by spraying with a gun, with a maximum interval between filling the container and application of the product of 3 hours, but preferably less than 1 hour.

[0035] In one specific application, the invention provides a cleaning product, useful for cleaning titanium surfaces, that also has, separately, the characteristics listed in Table 1.

Table 1

Cleaning Product

A) A descaling compound that contains:

(continued)

Cleaning Product

	A mixture of:	
	Nitric acid (HNO_3)	1-10%
	Hydrofluoric acid (HF) In a weight ratio HNO_3 : HF of 10:1	0.1-1%
	A thickening agent	0.1-1%
	A surfactant	0.1-1%
	An indicator	<0.1%
	A propellant (liquated gas)	5-20%
	Water (as required for)	100%
	Where the percentages are percentages in weight relative to the total descaling composition; and	
B)	a fixative substance containing:	
	A base	5-15%
	A thickening agent	2-8%
	A surfactant	0.1-1%
	A propellant (liquated gas)	5-20%
	Water (as required for)	100%
	Where the percentages are percentages in weight relative to the total fixative composition.	

[0036] In one specific application of the cleaning product the composition of which is recorded in Table 1, in the descaling composition the active agent is a mixture of 60%HNO_3 and 48% HF, the thickening agent is xanthane gum, the surfactant is sodium dodecyl sulphate, the indicator is phenolphthalein and the propellant (liquated gas) is HFC 134a.

[0037] Similarly, in one specific application of the cleaning product the composition of which is shown in Table 1, in the fixative composition, the base is sodium hydroxide, the thickening agent is sepiolite, the surfactant is sodium dodecyl sulfate and the propellant (liquated gas) is HFC 134a.

[0038] The cleaning product of the invention is useful for cleaning titanium surfaces, especially, titanium building facades. Therefore, the invention provides a method to clean titanium surfaces that consists of using the cleaning product of this invention. More specifically, this method corresponds to the following stages of:

a) applying the descaling substance of the cleaning product of the invention to the titanium surface to be cleaned and letting it act for a period of time;
b) applying the fixative composition of the cleaning product of the invention to the titanium surface previously treated with this descaling substance in stage a), and leaving it to act for a period of time;
c) aspiration of the surfaces previously treated with these descaling and fixative compounds in stages a) and b); and
d) rinsing the treated titanium surface after completing stage c).

[0039] Stage a) or the descaling stage consists in applying the descaling substance of the cleaning product of the invention, homogeneously over the whole titanium surface to be cleaned, which is preferentially dry. Where necessary, the titanium surface is dried using instruments that do not cause mechanical damage of the metallic surface. Depending on the form of presentation of the descaling substance, this is administered in one way or another. For example, foam descaling substances (FD) and spray gel descaling substances (SGD) are applied using the appropriate spray gun, while the gel descaling substance (GD) is applied with a sponge trowel taking care not to cause mechanical damage of the metallic surface. After applying the descaling substance to the metallic surface this should be left to act for a period ranging from 15 seconds to 10 minutes before applying the fixative.

[0040] Stage b) or the fixative stage consists in applying the fixative of the cleaning product of the invention to the metallic surface previously treated with the descaling substance in stage a) ensuring that the surface is completely and homogeneously covered. The fixative as foam (FF) and spray gel (SGF) are applied using an appropriate spray gun. After applying the fixative, this is left to act for 30 seconds to 5 minutes before proceeding to the following stage, confirming beforehand that the active neutralizing agent of the fixative substance has neutralized the acid present in the fixative, indicated by the color change of the indicator, or, alternatively, by the use of pH paper indicator strips.

[0041] After the fixation stage, stage c) or the aspiration stage is carried out, in which the previously treated titanium surfaces are aspirated to remove the cleaning products from this previously treated surface. This aspiration is applied carefully using the appropriate equipment to avoid producing chemical or mechanical damage to the metallic surface.

[0042] Finally, after aspiration, step d) or the rinsing is carried out, in which a water jet at a temperature between 5 and 30°C is applied to eliminate the remains of products used in previous stages.

[0043] In one specific application, the titanium surface to be cleaned is a titanium building facade or titanium panels to be used for the construction of facades.

[0044] The following example illustrates application of the invention and should not in any way be considered to limit its scope of application.

EXAMPLE 1

Cleaning of a titanium panel

1.1 Cleaning product

[0045] Several cleaning products were prepared with formulations included among the compositions recorded in Table 2.

Table 2

Composition of cleaning products of the invention

A)	Descaling substance composed of a mixture of:	
	HNO_3 60%	1-10%
	HF 48%	0.1-1%
	Weight ratio HNO_3 :H of 10:1	
	xanthane gum	0.1-1%
	sodium docedyl sulphate	0.1-1%
	phenolphthalein	<0.1%
	HFC 134a (liquated gas)	5-20%
	Water (as required for)	100%
	Where the percentages are percentages in weight relative to the total in the descaling compound; and	
B)	Fixative containing:	
	NaOH	5-15%
	sepiolite	2-8%
	Sodium dodecyl sulphate	0.1-1%
	HFC 134a (liquated gas)	5-20%
	Water (as required for)	100%
	Where the percentages are percentages in weight relative to the total amount of fixative.	

[0046] Both the descaling substance and the fixative are prepared and packaged in foam form by incorporating different compounds in the desired amounts.

1.2 Cleaning method

[0047] Titanium panels will be cleaned using cleaning products prepared according to Example 1.1. This will be done by following the protocol described below:

a) Descaling : the descaling substance of the cleaning product used in each case is applied by spraying the surface of the titanium panels using a spray gun and leaving the product to act for a period ranging from 30 seconds to 3 minutes;

b) Fixing: the fixative of the cleaning product used in each case is applied to the titanium panels previously treated with the descaling substance using a spray gun and left to act for a period ranging from 30 seconds to 2 minutes;

c) Aspiration: the products formed and the remains left on the previously treated titanium panels are aspirated with the help of an aspiration system that is neither chemically or mechanically aggressive; and

d) Rinsing: with water jets at a temperature between 5 and 30°C, to eliminate the remains of products from previous stages.

[0048] The cleaning products tested showed their efficacy at cleaning the treated titanium panels.

Claims

1. A cleaning product that is composed, separately, of:

A) a descaling substance that consists of:

A.1) a mixture of nitric acid and hydrofluoric acid;
A.2) a thickener;
A.3) a surfactant;
A.4) an indicator;
A.5) water; and, optionally,
A.6) a propellant; and

B) a fixative that consists of:

B.1) a base;
B.2) a thickener;
B.3) a surfactant;
B.4) water; and
B.5) a propellant.

2. Cleaning product according to Claim 1, in which this mixture of nitric acid and hydrofluoric acid is present in this descaling substance at a concentration ranging from 1% to 20% in weight relative to the total descaling compound.

3. Cleaning product according to Claim 1, in which the weight ratio of nitric acid: hydrofluoric acid is 10:1.

4. Cleaning product according to Claim 1, in which the thickener present in the descaling compound is of water-soluble organic pseudoplastic type.

5. Cleaning product according to Claim 4, in which this water-soluble organic pseudoplastic thickener is selected from cellulotic type thickeners and natural gums.

6. Cleaning product according to Claim 5, in which this thickener is xanthane gum.

7. Cleaning product according to Claim 1, in which this descaling substance contains this thickener in a concentration ranging from 0.1% to 1% in weight relative to the total descaling composition.

8. Cleaning product according to Claim 1, in which the surfactant present in the descaling substance is selected from anionic and cationic surfactants.

9. Cleaning product according to Claim 8, in which this surfactant is sodium dodecyl sulphate.

10. Cleaning product according to Claim 1, in which this descaling substance contains this surfactant in a concentration ranging from 0.1 to 1% in weight relative to the total descaling composition.

11. Cleaning product according to Claim 1, in which this indicator is phenophthalein.

12. Cleaning product according to Claim 1, in which this indicator is present in the descaling substance at a concentration lower than 0.1% in weight relative to the total descaling composition.

13. Cleaning product according to Claim 1, in which the propellant present in this descaling composition is a liquated gas selected from among hydrocarbons and hydrofluorocarbons (HFC).

14. Cleaning product according to Claim 13, in which the propellant is HFC 134a.

15. Cleaning product according to Claim 1 in which this descaling composition contains a liquated gas as a propellant at a concentration ranging from 5% to 20% in weight relative to the total descaling composition.

16. Cleaning product according to Claim 1, in which this propellant present in the descaling substance is a compressed gas.

17. Cleaning product, according to Claim 16, in which this compressed gas is nitrogen, carbon dioxide, nitrous oxide or air.

18. Cleaning product according to Claim 1, in which the base, present in this fixative composition is either an alkaline metal hydroxide or trisodium phosphate.

19. Cleaning product according to Claim 18, in which this base present in the fixative composition is sodium hydroxide.

20. Cleaning product according to Claim 1 in which this base is present in this fixative at a concentration ranging from 1 to 20% relative to the total fixative composition.

21. Cleaning product according to Claim 1, in which the thickening agent present in the fixative is an inorganic silicate-based thickener.

22. Cleaning product according to Claim 21, in which this thickening agent is sepiolite.

23. Cleaning product according to Claim 1 in which this fixative contains the thickening agent in a concentration ranging from 1% to 8% in weight relative to the total fixative composition.

24. Cleaning product according to Claim 1 in which the surfactant present in the fixative composition is selected from anionic or cationic surfactants.

25. Cleaning product according to Claim 24, in which this surfactant is sodium dodecylsulphate.

26. Cleaning product according to Claim 1, in which this fixative contains this surfactant at a concentration ranging from 0.1% to 1% in weight relative to the total of fixative composition.

27. Cleaning product according to Claim 1 in which this propellant present in the fixative is a liquated gas chosen from hydrocarbons or hydrofluorocarbons (HFC).

28. Cleaning product according to Claim 27, in which this propellant is HFC 134a.

29. Cleaning product according to Claim 1 in which this fixative contains a liquated gas as a propellant in a concentration ranging from 5% to 20% in weight of the total said fixative.

30. Cleaning product according to Claim 1, in which the propellant present in this fixative is a compressed gas.

31. Cleaning product according to Claim 30 in which this compressed gas is nitrogen, carbon dioxide, nitrous oxide or air.

32. Cleaning product according to Claim 1, that includes, separately:

A) a descaling substance containing:

A mixture of:

Nitric acid (HNO_3)	1-10%
Hydrofluoric acid (HF)	0.1-1%
In which the weight ratio HNO_3:HF is 10:1	
A thickener	0.1-1%
A surfactant	0.1-1%
An indicator	<0.1%
A propellant (liquated gas)	5-20%

(continued)

Water (as required for)	100%

Where the percentages are percentages in weight relative to the total descaling substance; and

B) a fixative containing:

A base	5-15%
A thickener	2-8%
A surfactant	0.1-1%
A propellant (liquated gas)	5-20%
Water (as required for)	100%

Where the percentages are percentages in weight relative to the total fixative composition.

33. Cleaning product according to Claim 32, which includes, separately:

A) A descaling substance containing

A mixture of:

HNO_3 60%	1-10%
HF 48%	0.1-1%
With a weight ratio HNO_3:HF of 10:1	
Xanthane gum	0.1-1%
Sodium dodecylsulphate	0.1-1%
Phenolphthalein	<0.1%
HFC 134a (liquated gas)	5-20%
Water (as required for)	100%

Where the percentages are percentages in weight relative to the total descaling composition; and

B) a fixative containing:

NaOH	5-15%
sepiolite	2-8%
sodium dodecylsulphate	0.1-1%
HFC 134a (liquated gas)	5-20%
Water (as required for)	100%

Where the percentages are percentages in weight relative to the total fixative composition.

34. Cleaning product according to Claim 1, in which the descaling composition is presented as foam, spray gel or gel.

35. Cleaning product according to Claim 1, in which the fixative is present as foam or spray gel.

36. A method for cleaning titanium surfaces that refers to the application of a cleaning product according to any of Claims 1 to 35 that includes the following stages:

a) application of the descaling substance of the said cleaning product on the surface to be cleaned and leaving this to act for a given period of time;
b) application of the fixative of this cleaning product to the titanium surface previously treated with this descaling substance in stage a), and leaving this to act for a given period of time;
c) aspiration of the titanium surface previously treated with these descaling and fixative substances in stages

a) and b); and
d) rinsing the treated titanium surface after carrying out stage c).

37. Method according to Claim 36, in which the application of this descaling substance to the titanium surface to be cleaned is done by a spray gun or by a sponge trowel, and left to act for a period of time ranging from 15 seconds to 10 minutes before applying the fixative.

38. Method according to Claim 36 in which the application of this fixative on the titanium surface to be cleaned, previously treated with the descaling substance is done using a spray gun, and is left to act for a period ranging from 15 seconds to 5 minutes before starting stage c) after confirming that the neutralization has taken place.

39. Method according to Claim 36, in which rinsing of the treated titanium surface is done with water jets at a temperature ranging from 5°C to 30°C.

Patentansprüche

1. Reinigungsprodukt, das separat zusammengesetzt ist aus:

A) einer Entzunderungssubstanz, bestehend aus:

A.1) einer Mischung aus Salpetersäure und Flusssäure;
A.2) einem Verdickungsmittel;
A.3) einem oberflächenaktiven Stoff;
A.4) einem Indikator;
A.5) Wasser; und optional
A.6) einem Treibmittel; und

B) einem Fixationsmittel, bestehend aus:

B.1) einer Base;
B.2) einem Verdickungsmittel;
B.3) einem oberflächenaktiven Stoff;
B.4) Wasser; und
B.5) einem Treibmittel.

2. Reinigungsprodukt nach Anspruch 1, bei dem diese Mischung aus Salpetersäure und Flusssäure in dieser Entzunderungssubstanz in einer Konzentration zwischen 1 und 20 Gewichtsprozent bezogen auf die gesamte Entzunderungszusammensetzung vorliegt.

3. Reinigungsprodukt nach Anspruch 1, bei dem das Gewichtsverhältnis von Salpetersäure zu Flusssäure 10:1 beträgt.

4. Reinigungsprodukt nach Anspruch 1, bei dem das in der Entzunderungszusammensetzung vorhandene Verdikkungsmittel vom wasserlöslichen organischen pseudoplastischen Typ ist.

5. Reinigungsprodukt nach Anspruch 4, bei dem dieses wasserlösliche organische pseudoplastische Verdickungsmittel aus Verdickungsmittels vom Zellstofftyp und natürlichen Gummis ausgewählt ist.

6. Reinigungsprodukt nach Anspruch 5, bei dem das Verdickungsmittel Xanthan-Gummi ist.

7. Reinigungsprodukt nach Anspruch 1, bei dem die Entzunderungssubstanz das Verdickungsmittel in einer Konzentration zwischen 0,1 und 1 Gewichtsprozent bezogen auf die gesamte Entzunderungszusammensetzung enthält.

8. Reinigungsprodukt nach Anspruch 1, bei dem der in der Entzunderungssubstanz vorhandene oberflächenaktive Stoff unter anionischen und kationischen oberflächenaktiven Stoffen ausgewählt ist.

9. Reinigungsprodukt nach Anspruch 8, bei dem der oberflächenaktive Stoff Natriumdodecylsulfat ist.

10. Reinigungsprodukt nach Anspruch 1, bei dem die Entzunderungssubstanz den oberflächenaktiven Stoff in einer Konzentration zwischen 0,1 und 1 Gewichtsprozent bezogen auf die gesamte Entzunderungszusammensetzung enthält.

11. Reinigungsprodukt nach Anspruch 1, bei dem der Indikator Phenophthalein ist.

12. Reinigungsprodukt nach Anspruch 1, bei dem der Indikator in der Entzunderungssubstanz in einer Konzentration von weniger als 0,1 Gewichtsprozent bezogen auf die gesamte Entzunderungszusammensetzung vorliegt.

13. Reinigungsprodukt nach Anspruch 1, bei dem das in der Entzunderungszusammensetzung vorhandene Treibmittel ein verflüssigtes Gas ist, das unter Kohlenwasserstoffen und Fluorkohlenwasserstoffen (HFC) gewählt ist.

14. Reinigungsprodukt nach Anspruch 13, bei dem das Treibmittel HFC 134a ist.

15. Reinigungsprodukt nach Anspruch 1, bei dem die Entzunderungszusammensetzung als Treibmittel ein verflüssigtes Gas in einer Konzentration zwischen 5 und 20 Gewichtsprozent bezogen auf die gesamte Entzunderungszusammensetzung enthält.

16. Reinigungsprodukt nach Anspruch 1, bei dem das in der Entzunderungssubstanz vorhandene Treibmittel ein Druckgas ist.

17. Reinigungsprodukt nach Anspruch 16, bei dem das Druckgas Stickstoff, Kohlendioxid, Stickoxid oder Luft ist.

18. Reinigungsprodukt nach Anspruch 1, bei dem die in der Fixationsmittelzusammensetzung vorhandene Base entweder ein Alkalimetallhydroxid oder Trinatriumphosphat ist.

19. Reinigungsprodukt nach Anspruch 18, bei dem die in der Fixationsmittelzusammensetzung vorhandene Base Natriumhydroxid ist.

20. Reinigungsprodukt nach Anspruch 1, bei dem die Base in dem Fixationsmittel in einer Konzentration zwischen 1 und 20 Gewichtsprozent bezogen auf die gesamte Fixationsmittelzusammensetzung vorliegt.

21. Reinigungsprodukt nach Anspruch 1, bei dem das in dem Fixationsmittel vorliegende Verdickungsmittel ein anorganische auf Silicat basierendes Verdickungsmittel ist.

22. Reinigungsprodukt nach Anspruch 21, bei dem das Verdickungsmittel Sepiolith ist.

23. Reinigungsprodukt nach Anspruch 1, bei dem das Fixationsmittel das Verdickungsmittel in einer Konzentration zwischen 1 und 8 Gewichtsprozent bezogen auf die gesamte Fixationsmittelzusammensetzung enthält.

24. Reinigungsprodukt nach Anspruch 1, bei dem der in der Fixationsmittelzusammensetzung vorhandene oberflächenaktive Stoff aus anionischen oder kationischen oberflächenaktiven Stoffen gewählt ist.

25. Reinigungsprodukt nach Anspruch 24, bei dem der oberflächenaktive Stoff Natriumdodecylsulfat ist.

26. Reinigungsprodukt nach Anspruch 1, bei dem das Fixationsmittel den oberflächenaktiven Stoff in einer Konzentration zwischen 0,1 und 1 Gewichtsprozent bezogen auf die gesamte Fixationsmittelzusammensetzung enthält.

27. Reinigungsprodukt nach Anspruch 1, bei dem das in dem Fixationsmittel vorhandene Treibmittel ein verflüssigtes Gas ist, das unter Kohlenwasserstoffen und Fluorkohlenwasserstoffen (HFC) gewählt ist.

28. Reinigungsprodukt nach Anspruch 27, bei dem das Treibmittel HFC 134a ist.

29. Reinigungsprodukt nach Anspruch 1, bei dem das Fixationsmittel als Treibmittel ein verflüssigtes Gas in einer Konzentration zwischen 5 und 20 Gewichtsprozent bezogen auf das gesamte Fixationsmittel enthält.

30. Reinigungsprodukt nach Anspruch 1, bei dem das in dem Fixationsmittel vorhandene Treibmittel ein Druckgas ist.

31. Reinigungsprodukt nach Anspruch 30, bei dem das Druckgas Stickstoff, Kohlendioxid, Stickoxid oder Luft ist.

32. Reinigungsprodukt nach Anspruch 1, das separat aufweist:

A) eine Entzunderungssubstanz, enthaltend:

eine Mischung aus:

Salpetersäure (HNO_3	1-10%
Flusssäure (HF)	0,1-1%
wobei das Gewichtsverhältnis von HNO_3:HF beträgt:	10:1
ein Verdickungsmittel	0,1-1%
einen oberflächenaktiven Stoff	0,1-1%
einen Indikator	<0,1%
ein Treibmittel (verflüssigtes Gas)	5-20%
Wasser (je nach Bedarf)	100%

wobei die Prozentanteile Gewichtsprozentanteile bezogen auf die gesamte Entzunderungssubstanz sind; und
B) ein Fixationsmittel, enthaltend:

eine Base	5-15%
ein Verdickungsmittel	2-8%
einen oberflächenaktiven Stoff	0,1 - 1%
ein Treibmittel (verflüssigtes Gas)	5-20%
Wasser (je nach Bedarf)	100%

wobei die Prozentanteile Gewichtsprozentanteile bezogen auf die gesamte Fixationsmittelzusammensetzung sind.

33. Reinigungsprodukt nach Anspruch 32, welches separat enthält:

A) eine Entzunderungssubstanz, aufweisend:

eine Mischung aus:

HNO_3 60%	1-10%
HF 48%	0,1-1%
mit einem Gewichtsverhältnis von HNO_3:HF von 10: 1	
Xanthan-Gummi	0,1-1%
Natriumdodecylsulfat	0,1-1%
Phenolphthalein	<0,1%
HFC 143a (verflüssigtes Gas)	5-20%
Wasser (je nach Bedarf)	100%

wobei die Prozentanteile Gewichtsprozentanteile bezogen auf die gesamte Entzunderungszusammensetzung sind; und
B) ein Fixationsmittel, aufweisend:

NaOH	5-15%
Sepiolith	2-8%
Natriumdodecylsulfat	0,1-1%

(fortgesetzt)

HFC 143a (verflüssigtes Gas)	5-20%
Wasser (je nach Bedarf)	100%

wobei die Prozentanteile Gewichtsprozentanteile bezogen auf die gesamte Fixationsmittelzusammensetzung sind.

34. Reinigungsprodukt nach Anspruch 1, bei dem die Entzunderungszusammensetzung als Schaum, Sprühgel oder Gel vorliegt.

35. Reinigungsprodukt nach Anspruch 1, bei dem das Fixationsmittel als Schaum oder Sprühgel vorliegt.

36. Verfahren zum Reinigen von Titanoberflächen, bezogen auf die Anwendung eines Reinigungsprodukts nach einem der Ansprüche 1 bis 35, wobei das Verfahren die folgenden Schritte umfasst:

a) Aufbringen der Entzunderungssubstanz des Reinigungsprodukts auf der zu reinigenden Oberfläche und Belassen derselben zum Einwirken über eine bestimmte Zeitdauer;
b) Aufbringen des Fixationsmittels des Reinigungsprodukts auf die zuvor im Schritt a) mit der Entzunderungssubstanz behandelten Titanoberfläche und Belassen desselben zum Einwirken über eine bestimmte Zeitdauer;
c) Absaugen der in den Schritten a) und b) zuvor mit der Entzunderungs- und Fixationsmittelsubstanz behandelten Titanoberfläche; und
d) Abspülen der behandelten Titanoberfläche nach der Durchführung des Schritts c).

37. Verfahren nach Anspruch 36, bei dem das Aufbringen der Entzunderungssubstanz auf die zu reinigende Titanoberfläche mittels einer Spritzpistole oder einem Schwammputzbrett erfolgt und diese zum Einwirken über einen Zeitraum von 15 Sekunden bis 10 Minuten belassen wird, bevor das Fixationsmittel aufgebracht wird.

38. Verfahren nach Anspruch 36, bei dem das Aufbringen des Fixationsmittels auf die zu reinigende, zuvor mit der Entzunderungssubstanz behandelte Titanoberfläche mittels einer Spritzpistole erfolgt, und dieses zum Einwirken über einen Zeitraum zwischen 15 Sekunden und 5 Minuten belassen wird, bevor der Schritt c) nach der Feststellung, dass die Neutralisierung stattgefunden hat, begonnen wird.

39. Verfahren nach Anspruch 36, bei dem das Abspülen der behandelten Titanoberfläche mit Wasserstrahlen bei einer Temperatur zwischen 5°C und 30°C erfolgt.

Revendications

1. Produit nettoyant composé, séparément, de:

A) une substance décapante qui consiste en :

A.1) un mélange d'acide nitrique et d'acide fluorhydrique;
A.2) un agent épaississant ;
A.3) un agent tensio-actif ;
A.4) un indicateur ;
A.5) de l'eau ; et, éventuellement,
A.6) un agent de propulsion ; et

B) un fixatif consistant en :

B.1) une base ;
B.2) un agent épaississant ;
B.3) un agent tensio-actif;
B.4) de l'eau ; et
B.5) un agent de propulsion.

2. Produit nettoyant selon la revendication 1, dans lequel ce mélange d'acide nitrique et d'acide fluorhydrique est

présent dans cette substance décapante, en une concentration allant de 1 % à 20 % en poids par rapport au composé décapant total.

3. Produit nettoyant selon la revendication 1, dans lequel le rapport pondéral d'acide nitrique : acide fluorhydrique est de 10 : 1.

4. Produit nettoyant selon la revendication 1, dans lequel l'agent épaississant présent dans le composé décapant est du type pseudoplastique organique soluble dans l'eau.

5. Produit nettoyant selon la revendication 4, dans lequel cet agent épaississant pseudoplastique organique soluble dans l'eau est choisi parmi les agents épaississants de type cellulolytique et les gommes naturelles.

6. Produit nettoyant selon la revendication 5, dans lequel cet agent épaississant est la gomme de xanthane.

7. Produit nettoyant selon la revendication 1, dans lequel cette substance décapante contient cet agent épaississant en une concentration allant de 0,1 % à 1 % en poids par rapport à la composition décapante totale.

8. Produit nettoyant selon la revendication 1, dans lequel l'agent tensio-actif présent dans la substance décapante est choisi parmi des agents tensio-actifs anioniques et cationiques.

9. Produit nettoyant selon la revendication 8, dans lequel cet agent tensio-actif est le dodécylsulfate de sodium.

10. Produit nettoyant selon la revendication 1, dans lequel cette substance décapante contient cet agent tensio-actif en une concentration allant de 0,1 à 1 % en poids par rapport à la composition décapante totale.

11. Produit nettoyant selon la revendication 1, dans lequel cet indicateur est la phénophtaléine.

12. Produit nettoyant selon la revendication 1, dans lequel cet indicateur est présent dans la substance décapante, en une concentration inférieure à 0,1 % en poids par rapport à la composition décapante totale.

13. Produit nettoyant selon la revendication 1, dans lequel l'agent de propulsion présent dans cette composition décapante est un gaz de liquation choisi parmi les hydrocarbures et les hydrofluorocarbones (HFC).

14. Produit nettoyant selon la revendication 13, dans lequel l'agent de propulsion est le HFC 134a.

15. Produit nettoyant selon la revendication 1, dans lequel cette composition décapante contient un gaz de liquation comme agent de propulsion, en une concentration allant de 5 % à 20 % en poids par rapport à la composition décapante totale.

16. Produit nettoyant selon la revendication 1, dans lequel cet agent de propulsion présent dans la substance décapante est un gaz comprimé.

17. Produit nettoyant selon la revendication 16, dans lequel ce gaz comprimé est l'azote, le dioxyde de carbone, l'oxyde nitreux ou l'air.

18. Produit nettoyant selon la revendication 1, dans lequel la base, présente dans cette composition fixative est un hydroxyde métallique alcalin ou un phosphate trisodique.

19. Produit nettoyant selon la revendication 18, dans lequel cette base présente dans la composition fixative est l'hydroxyde de sodium.

20. Produit nettoyant selon la revendication 1, dans lequel cette base est présente dans ce fixatif, en une concentration allant de 1 à 20 % par rapport à la composition fixative totale.

21. Produit nettoyant selon la revendication 1, dans lequel l'agent épaississant présent dans le fixatif est un agent épaississant à base de silicate inorganique.

22. Produit nettoyant selon la revendication 21, dans lequel cet agent épaississant est la sépiolite.

23. Produit nettoyant selon la revendication 1, dans lequel ce fixatif contient l'agent épaississant, en une concentration allant de 1 % à 8 % en poids par rapport à la composition fixative totale.

24. Produit nettoyant selon la revendication 1, dans lequel l'agent tensio-actif présent dans la composition fixative est choisi parmi les agents tensio-actifs anioniques ou cationiques.

25. Produit nettoyant selon la revendication 24, dans lequel cet agent tensio-actif est le dodécylsulfate de sodium.

26. Produit nettoyant selon la revendication 1, dans lequel ce fixatif contient cet agent tensio-actif, en une concentration allant de 0,1 % à 1 % en poids par rapport au total de la composition fixative.

27. Produit nettoyant selon la revendication 1, dans lequel cet agent de propulsion présent dans le fixatif est un gaz de liquation choisi parmi les hydrocarbures ou hydrofluorocarbones (HFC).

28. Produit nettoyant selon la revendication 27, dans lequel cet agent de propulsion est le HFC 134a.

29. Produit nettoyant selon la revendication 1, dans lequel ce fixatif contient un gaz de liquation comme agent de propulsion, en une concentration allant de 5 % à 20 % en poids du total dudit fixatif.

30. Produit nettoyant selon la revendication 1, dans lequel l'agent de propulsion présent dans ce fixatif est un gaz comprimé.

31. Produit nettoyant selon la revendication 30, dans lequel ce gaz comprimé est l'azote, le dioxyde de carbone, l'oxyde nitreux ou l'air.

32. Produit nettoyant selon la revendication 1, qui inclut, séparément :

A) une substance décapante contenant :

un mélange de :

acide nitrique (HNO_3)	1-10%
acide fluorhydrique (HF)	0,1-1 %
dans lequel le rapport pondéral HNO_3 : HF est 10 : 1	
un agent épaississant	0,1-1 %
un agent tensio-actif	0,1-1 %
un indicateur	<0,1 %
un agent de propulsion (gaz de liquation)	5-20 %
eau (telle que requise pour)	100 %

où les pourcentages sont des pourcentages en poids par rapport à la substance décapante totale ; et
B) un fixatif contenant :

une base	5-15 %
un agent épaississant	2-8 %
un agent tensio-actif	0,1-1 %
un agent de propulsion (gaz de liquation)	5-20 %
eau (telle que requise pour)	100 %

où les pourcentages sont des pourcentages en poids par rapport à la composition fixative totale.

33. Produit nettoyant selon la revendication 32, qui inclut, séparément :

A) une substance décapante contenant :

un mélange de :

HNO_3 60 %	1-10 %
HF 48 %	0,1-1 %
avec un poids pondéral suivant :	
HNO_3 : HF de 10 : 1	
gomme de xanthane	0,1-1%
dodécylsulfate de sodium	0,1-1 %
phénolphtaléine	<0,1 %
HFC 134a (gaz de liquation)	5-20 %
eau (telle que requise pour)	100 %

où les pourcentages sont des pourcentages en poids par rapport à la composition décapante totale ; et
B) un fixatif contenant :

NaOH	5-15 %
sépiolite	2-8 %
dodécylsulfate de sodium	0,1-1 %
HFC 134a (gaz de liquation)	5-20 %
eau (telle que requise pour)	100 %

où les pourcentages sont des pourcentages en poids par rapport à la composition fixative totale.

34. Produit nettoyant selon la revendication 1, dans lequel la composition décapante est présentée sous la forme de mousse, de gel en spray ou de gel.

35. Produit nettoyant selon la revendication 1, dans lequel le fixatif est présent sous la forme de mousse ou de gel en spray.

36. Procédé de nettoyage de surfaces en titane faisant référence à l'application d'un produit nettoyant selon l'une quelconque des revendications 1 à 35, qui inclut les étapes suivantes :

a) application de la substance décapante dudit produit nettoyant sur la surface à nettoyer et temps de repos pour laisser agir pendant une période donnée ;
b) application du fixatif de ce produit nettoyant sur la surface en titane traitée précédemment avec cette substance décapante à l'étape a), et temps de repos pour laisser agir pendant une période donnée ;
c) aspiration de la surface en titane traitée précédemment avec ces substances décapantes et fixatives aux étapes a) et b) ; et
d) rinçage de la surface en titane traitée après réalisation de l'étape c).

37. Procédé selon la revendication 36, dans lequel l'application de cette substance décapante sur la surface en titane à nettoyer est réalisée grâce à un pistolet de pulvérisation ou grâce à une taloche-éponge, et on la laisse agir pendant une période allant de 15 secondes à 10 minutes avant d'appliquer le fixatif.

38. Procédé selon la revendication 36, dans lequel l'application de ce fixatif sur la surface en titane à nettoyer, traitée préalablement avec la substance décapante, est réalisée en utilisant un pistolet de pulvérisation, et on le laisse agir pendant une période allant de 15 secondes à 5 minutes, avant de démarrer l'étape c), suite à la confirmation que la neutralisation a eu lieu.

39. Procédé selon la revendication 36, dans lequel l'étape de rinçage de la surface en titane traitée est effectuée à l'aide de jets d'eau à une température allant de 5 °C à 30 °C.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1029953 A **[0006]**