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(54) RENDERING SURFACES HYDROPHOBIC AND OLEOPHOBIC

(71) We, WACKER-CHEMIE G.M.B.H., a body corporate organised according to the laws of the Federal Republic of Germany, of 8 München 22, Prinzregentenstrasse 22, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process and composition for rendering surfaces hydrophobic and oleophobic, that is to say for rendering surfaces repellent to both water and oil.

Glass and asbestos surfaces may be rendered hydrophobic and oleophobic by treating them with, for example, a mixture of a solution or dispersion of a fluorine-containing polymer imparting water-repellency and a solution or emulsion of an organosilicon compound imparting oil-repellency, as described in U.S. Patent Specification No. 3 385 812. The fluorine-containing polymer used is one consisting of fluorine, carbon, hydrogen, oxygen and phosphorus or sulphur and nitrogen atoms, and the organosilicon compound used is one containing silicon-bonded hydrogen atoms.

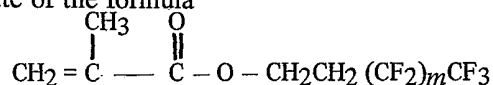
The present invention provides a process for rendering hydrophobic and oleophobic, the surface of an inorganic material having open pores, which comprises applying to the surface (a) (i) a solution or dispersion of a fluorine-containing organic polymer consisting of fluorine and carbon atoms and, optionally, atoms of one or more elements selected from chlorine, hydrogen, oxygen, sulphur, phosphorus and nitrogen or (ii) an aqueous solution of a water-soluble polymer of an olefinically unsaturated carboxylic acid, and (b) a solution of an organosilicon compound having an average of from 0.9 to 1.8 hydrocarbon radicals per silicon atom and in which any silicon valency not satisfied by a hydrocarbon radical is satisfied by an oxygen atom.

The process of the present invention has a number of advantages over the process of U.S. Patent Specification No. 3 385 812 described above. In particular, it has the advantage that it does not require the use of organosilicon compounds containing silicon-bonded hydrogen atoms: such organosilicon compounds are less readily obtainable than other organosilicon compounds, and hydrogen can split off from them during storage, which can entail a danger of explosion.

Surfaces that may be rendered hydrophobic and oleophobic by the process of the invention are the surfaces of inorganic materials having open pores, that is pores that are in contact with the surrounding medium. (As regards the term "open pores" cf. E. Uhlein, *Römpps Chemisches Wörterbuch*, Stuttgart 1969, pp. 698-699.) Examples of open-pored inorganic materials are unglazed porous brickyard products, for example, building bricks (porous), cooperating and non-cooperating ceiling bricks, light-weight bricks, light-weight construction plates, tubes, cable protection covers, roof tiles, building terracotta and earthenware; unglazed sintered brick-yard products, for example, surface clinker bricks, clinker conduits (for water systems), paving clinker, floor and wall tiles and plates, acid-resistant tiles, split clinker flags, dividing-wall bricks, cell-wall bricks, and clinkered building terracotta; expanded clay products ("Lecca" - Trade Mark) which are used as structural elements for

light-weight construction, and light-weight construction elements; concrete, asbestos cement, mortar, lime sandstone, and natural stone, for example, natural sandstone, travertine and other limestones.

5 The fluorine-containing organic polymer that may be used according to the invention is one that will impart oil-repellency to the surface and that consists of fluorine and carbon atoms and, optionally, chlorine and/or hydrogen and/or oxygen and/or sulphur and/or phosphorus and/or nitrogen atoms. Fluorine-containing polymers of the type defined that have previously been known or used for rendering organic substances (*e.g.* organic fibres) or inorganic substances oleophobic or oil-repellent may be used according to the present invention. Examples of suitable fluorine-containing organic polymers are polytetrafluoroethylene, polytrifluorochloroethylene, copolymers of tetrafluoroethylene and hexafluoropropylene, copolymers of trifluorochloroethylene and one or more other olefinically unsaturated monomers (*e.g.* vinylidene fluoride, vinyl chloride, vinyl acetate, methyl methacrylate, and styrene), fluorinated acrylic resins *e.g.* polymers of 1,1-dihydroperfluorobutyl acrylate and copolymers of *n*-butyl acrylate, *N*-methylol acrylamide and at least 35 % by weight of a methacrylate of the formula



20 in which *m* denotes an integer from 1 to 13.

The water-soluble polymer of an olefinically unsaturated carboxylic acid used according to the invention may be one that has previously been known or used for rendering organic textile materials dirt-repellent. Examples of suitable olefinically unsaturated carboxylic acids are acrylic acid, methacrylic acid, itaconic acid, vinylacetic acid, and fumaric acid. The polymer may be a homopolymer, a copolymer of two or more olefinically unsaturated carboxylic acids, or a copolymer of one or more olefinically unsaturated carboxylic acid(s) and one or more other olefinically unsaturated monomers (*e.g.* an acrylate, styrene, or vinyl chloride).

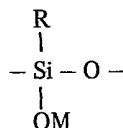
30 The fluorine-containing organic polymer may be applied to the surface to be treated in the form of an aqueous dispersion or in the form of a solution or dispersion in an organic liquid diluent. The water-soluble polymer of an olefinically unsaturated carboxylic acid is used in the form of an aqueous solution. If desired, both a fluorine-containing organic polymer and a water-soluble polymer of an olefinically unsaturated carboxylic acid may be applied to the surface to be treated.

35 The amount of the fluorine-containing organic polymer and/or the water-soluble polymer of an olefinically unsaturated carboxylic acid in the solution or dispersion is advantageously within the range of from, 0.05 to 25 % by weight, preferably from 0.5 to 20 % by weight, based on the weight of the said polymer(s) and the solvent or dispersing medium.

40 The organosilicon compound used to impart water-repellency to the material is advantageously an alkali metal hydrocarbon siliconate in which the or each hydrocarbon radical is an alkyl radical having up to 5 carbon atoms or a phenyl radical. Such compounds have the advantage of being readily obtainable and readily soluble in water, the most common solvent. The alkali metal hydrocarbon siliconate may suitably be a monomeric compound of the general formula

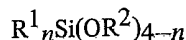


45 or a polymeric compound comprising units of the general formula



50 in which formulae, each R denotes an alkyl radical having up to 5 carbon atoms or a phenyl radical, and each M denotes an alkali metal atom, preferably a sodium or potassium atom.

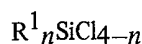
55 The organosilicon compound may alternatively be, for example, an organosilane of the general formula



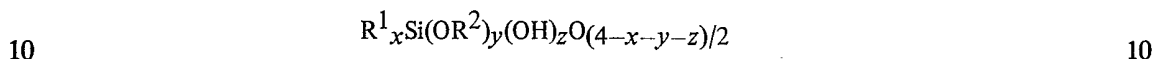
60 in which each R¹ denotes a hydrocarbon radical free of aliphatic unsaturation and having up to 14 carbon atoms, each R² denotes an alkyl radical or an alkoxyalkyl radical, each having up to 5 carbon atoms, and *n* denotes 0, 1, 2 or 3 and has an average value within the range of from 0.9 to 1.8. A partial hydrolysate, having not more than 10 silicon atoms per molecule, of such an organosilane may be used.

65 Another suitable organosilicon compound is a reaction product of a silane of the general

formula



5 in which R^1 and n are defined as above, and ethylene glycol or diethylene glycol. 5
Yet another suitable organosilicon compound is an organopolysiloxane having more than 10 silicon atoms per molecule and consisting of units of the general formula



in which R^1 and R^2 are defined as above, each of x , y and z denotes 0, 1, 2 or 3, the sum $x + y + z$ does not exceed 3, the average value of x is within the range of from 0.9 to 1.8, preferably from 0.9 to 1.3, the average value of each of y and z is within the range of from 0.00 to 0.20 with the proviso that at least one of y and z has an average value of at least 0.01.

15 Examples of alkyl radicals denoted by R or R^2 in any of the above formulae are methyl, ethyl, n-propyl, isopropyl and n-pentyl radicals. An example of an alkoxy alkyl radical denoted by R^2 , is a methoxyethyl radical. Examples of hydrocarbon radicals denoted by R^1 are alkyl radicals, for example, methyl, ethyl, n-propyl, isopropyl, sec-butyl, decyl and tetradecyl radicals; aryl radicals, for example, phenyl radicals; alkaryl radicals, for example, tolyl radicals; and aralkyl radicals for example, benzyl radicals. 20

The solvent used for dissolving the organosilicon compound is suitably water or a mixture of water and a water-miscible organic solvent, when the organosilicon compound is an alkali metal hydrocarbonsiliconate or a water-soluble organosilane. Otherwise, the solvent is suitably an organic solvent, which may be either water miscible or water-immiscible. Examples of suitable water-miscible solvents are alcohols for example, ethanol, isopropanol and diacetone alcohol; ketones, for example, acetone and methyl ethyl ketone; and dimethylformamide. Examples of water-immiscible solvents are hydrocarbons, for example, toluene, xylene and trimethylbenzene; chlorohydrocarbons, for example, trichloroethylene; esters, for example, ethyl acetate; and ethers, for example, di-n-butyl ether. 25

30 The solution of the organosilicon compound advantageously contains from 0.01 to 25 %, preferably from 0.1 to 10 %, by weight of the organosilicon compound, based on the weight of the organosilicon compound and the solvent.

The application of (a) the solution or dispersion of the fluorine-containing polymer or the aqueous solution of the water-soluble polymer of an olefinically unsaturated carboxylic acid and of (b) the solution of the organosilicon compound to the surface to be rendered hydrophobic may be effected in either order or simultaneously. When the application of component (a) is effected simultaneously with the application of component (b), the two components may be used in the form of a mixture. Such a mixture will be in the form of a mixed solution of the organosilicon compound and the fluorine containing polymer or the water-soluble polymer of an olefinically unsaturated carboxylic acid or in the form of a dispersion of the fluorine-containing polymer with the organosilicon compound dissolved in the dispersing medium (also known as the outer phase of the dispersion). Such a mixture may be prepared simply by mixing the various components in any sequence. 35

The solutions and/or dispersions used in the present process may contain various auxiliaries. Examples of auxiliaries that may be present (some of which will not be appropriate for particular solutions or dispersions) are dispersants, for example, protective colloids and emulsifiers; catalysts to promote crosslinking of the organosilicon compounds, for example, metal salts, e.g. zinc octoate, or titanium and aluminium alcoholates; organic and inorganic fillers; organic and inorganic pigments; soluble dyestuffs; perfumes; and binders. 40

The solution or dispersion of the fluorine-containing polymer or the solution of the water-soluble polymer of a carboxylic acid is advantageously applied to the surface to be rendered oleophobic in an amount within the range of from 1 to 2000 g/m², preferably from 150 to 800 g/m². The solution of the organosilicon compound is also advantageously applied to the surface to be rendered hydrophobic in an amount of from 1 to 2000 g/m², preferably from 150 to 800 g/m². When the two components (a) and (b) are applied in the form of a mixture, the amount of the mixture applied to the surface to be rendered hydrophobic and oleophobic is advantageously within the range of from 1 to 1000 g/m², preferably from 80 to 500 g/m². 45

It is advantageous to apply the organosilicon compound and the fluorine-containing polymer or the water-soluble polymer of an olefinically unsaturated carboxylic acid in a respective weight ratio within the range of from 2 : 1 to 20 : 1, preferably about 5 : 1. 50

The application of the solution(s) and/or dispersion(s) to the surface to be treated may be effected in any manner known for the application of a solution or dispersion to the surface of a solid material, for example, by spraying, casting, coating, rolling or immersing. 55

60 It is possible to treat all surfaces or the entire surface of a material according to the present 65

process, or to treat only one surface or only part of the surface of a material, for example, to treat only the upper side of a floor tile.

It is preferable to apply the two components (a) and (b) simultaneously to the surface to be treated. This may be effected either by applying them as a mixture or in some other manner, for example by simultaneously spraying them from two or more nozzles. If the two components are not applied simultaneously, it is advantageous to apply the solution of the organosilicon compound before applying the other solution or dispersion, which may be applied before and/or after the solution of the organosilicon compound has dried. If the solution or dispersion of the fluorine-containing polymer or the aqueous solution of the water-soluble polymer of an olefinically unsaturated carboxylic acid is applied before the solution of the organosilicon compound is applied, it is advantageous to use an aqueous dispersion of the fluorine-containing polymer or an aqueous solution of the water-soluble polymer of an olefinically unsaturated carboxylic acid and to apply the solution of the organosilicon compound before the said aqueous dispersion or the said aqueous solution has dried.

If desired, two or more solutions of an organosilicon compound used according to the invention may be applied to the surface to be treated. Two or more dispersions and/or solutions of a fluorine-containing polymer used according to the invention, or two or more aqueous solutions of a water-soluble polymer of an olefinically unsaturated carboxylic acid used according to the invention, or one or more solutions and/or dispersions of the first-mentioned polymer and one or more solutions of the second-mentioned polymer, may also be applied to the surface to be treated. The second coating may be identical to or different from the first coating, and any subsequent coatings may also be identical to or different from previous coatings.

After application of the various solutions and/or dispersions to the surface to be treated, the said solutions and/or dispersions are dried. This drying may be effected at room temperature or may be accelerated by heating to a temperature of up to 250°C. During drying, crosslinking or hardening of the organosilicon compound occurs.

The present process has the advantage over a process for rendering a surface solely oleophobic, that the water-repellency also imparted to the surface prevents or hinders the migration to the surface of salts and other substances, which could impair the appearance or oil-repellency of the material. It also has the advantage that the oil-repellency achieved by the present process is often better than that achieved by a process for rendering a surface solely oleophobic.

The following examples illustrate the process of the invention and compare the results obtained with those obtained from processes for rendering a surface solely oleophobic or solely hydrophobic.

Parts and percentages given in the examples are by weight unless otherwise stated.

The water-repellency and oil-repellency of the treated surfaces in the examples were assessed as follows, unless stated otherwise:

(a) Water-repellency

A 0.5 ml droplet of water was applied to the treated surface and the time taken for it to disappear, by absorption or evaporation, was measured. The longer is this time, the greater is the degree of water-repellency.

(b) Oil-repellency

A 0.2 ml droplet of mineral oil and a 0.2 ml droplet of edible oil (commercially available under the Trade Mark "Mazola") were each applied to the treated surface. The time taken for each drop to be absorbed was measured. The longer is this time, the greater is the degree of oil-repellency. The diameter of the stain produced on the surface by the mineral oil droplet was also measured. The smaller is this diameter, the greater is the degree of oil-repellency.

The unglazed ceramic plates used in the examples all had open pores and (except where otherwise stated) in the untreated state had a high oil-absorption and a high water-absorption.

Throughout the examples, an asterisk indicates a comparative test not according to the invention.

Example 1

350 g/m² of the following solutions and dispersions were coated onto respective unglazed ceramic plates. The coated plates were allowed to dry by being stored in air at room temperature for 4 days and then their oil-repellency and water-repellency were assessed. The results are given in Table 1.

- (i) 3.6 % aqueous solution of potassium methylsiliconate.
- (ii) 0.25 % aqueous dispersion of a copolymer of trifluorochloroethylene and vinyl fluoride.
- (iii) 0.25 % dispersion of a copolymer of trifluorochloroethylene and vinyl fluoride in a 3.6 % aqueous solution of potassium methylsiliconate.

Table 1

	Treatment	Water absorption	Mineral oil absorption	Edible oil absorption	Stain diameter (mm)	
5	none *	5 sec	70 min	60 min	27	5
10	(i) *	270 min	12 h	12 h	17	10
	(ii) *	2 min	35 h	31.5 h	11	
	(iii)	240 min	> 14 d	12 d	11	
15	<i>Example 2</i>					15
	The following solutions and dispersions were coated onto unglazed ceramic plates:					
	(i) 450 g/m ² of the solution under Example 1 (i) and immediately thereafter (within 1 min) 180 g/m ² of a 4 % aqueous dispersion of a low-molecular-weight polymer of 1,1-dihydroperfluorobutyl acrylate.					20
20	(ii) * 450 g/m ² of the solution under Example 1 (i).					20
	(iii) * 320 g/m ² of the 4 % aqueous dispersion under Example 2 (i)					
	(iv) * 320 g/m ² of a 10 % aqueous dispersion of polytrifluorochloroethylene.					
	The coated plates were dried for 20 min at 150°C.					
	The plates treated according to (i), (iii) and (iv) were all oil-repellent.					
25	The water-repellency of the plates was assessed by placing the untreated rear side of each plate about 5 mm deep in a 2 % aqueous solution of magnesium sulphate, with the following results:					25
	(i) and (ii) The sides of the plates were unchanged after 3 days in the solution and remained unchanged on drying.					30
30	(iii) The side of the plate showed small moist spots after 17 h, and exhibited efflorescence of the salt on drying.					30
	(iv) The side of the plate became dark and wet and exhibited efflorescence on drying.					
35	<i>Example 3</i>					35
	400 g/m ² of the following solutions and dispersions were coated onto unglazed ceramic plates. The coated plates were dried at room temperature in air for 4 days and their mineral-oil repellency properties were then assessed. The results are given in Table 2.					
	(i) 1.5 % aqueous dispersion of polytrifluorochloroethylene with 7.5 % of potassium methylsiliconate dissolved in the outer phase.					40
40	(ii) 7.5 % aqueous solution of potassium methylsiliconate.					40
	(iii) 1.5 % aqueous dispersion of polytrifluorochloroethylene.					
	Table 2					
45	Treatment	Mineral oil absorption	Stain diameter (mm)			45
	(i)	> 14 d	10			
50	(ii) *	22 h	12			50
	(iii) *	94 h	11			
55	Water was quickly absorbed by the plates treated according to (iii), but repelled by the other plates.					55
	<i>Example 4</i>					
	125 g/m ² of the following solutions and dispersions were coated onto respective ceramic plates having a water-absorption of less than 2.5 %.					
60	(i) a 10 % solution of a mixture of methyltri(methoxyethoxy)silane and n-propyltris(methoxyethoxy)silane (molar ratio 6:3) in a 3:1 mixture of isopropanol and water, with 0.75 % of a low-molecular-weight polymer of 1,1-dihydroperfluorobutyl acrylate dispersed therein.					60
65	(ii) a 10 % solution as under (i), with 1 % of a copolymer of trifluorochloroethylene and vinyl fluoride dispersed therein.					65

- (iii) a 10 % solution as under (i), with no polymeric component.
 (iv) a 1 % aqueous dispersion of a copolymer as under (ii).

The plates were stored in air at room temperature for 4 days and then heated to 150°C for 10 min. The water-repellency and oil-repellency were assessed. The results are given in Table 3.

Table 3

	Treatment	Water absorption	Mineral oil absorption	Edible oil absorption	
10	(i)	345 min	> 6 d	> 6 d	10
	(ii)	230 min	> 6 d	> 6 d	
15	(iii) *	378 min	6 d	4.5 d	15
	(iv) *	15 min	> 6 d	> 6 d	
20	none *	10 min	13h	12 h	20

Example 5

200 g/m² of the following solutions and dispersions were coated onto respective ceramic plates having a water-absorption of less than 2.5 %:

- 25 (i) a solution in toluene of 0.3 % of a low-molecular-weight polymer of 1,1-dihydroperfluorobutylacrylate and 2.5 % of an organopolysiloxane consisting of 20 mole % of dimethyl siloxane units and 80 mole % of monomethylsiloxane units and containing 8 % of ethoxy groups and 6 % of silicon-bonded hydroxy groups.
 (ii) a solution as under (i) but containing only 0.2 % of the said polymer.
 30 (iii) a 5 % solution in toluene of the organopolysiloxane as under (i).
 The plates were dried by heating at 150°C for 25 min. Their repellency properties were determined after cooling, and are given in Table 4.

Table 4

	Treatment	Water absorption	Mineral oil absorption	Edible oil absorption	Stain diameter (mm)	
35						35
40	(i)	420 min	> 26 d	> 26 d	11	40
	(ii)	410 min	23 d	11 d	11	
45	(iii) *	436 min	7 d	2 d	19	45
	none *	5 min	5 d	1.5 d	28	

Example 6

- 50 Concrete slabs, measuring 20 cm x 20 cm x 4 cm, were produced from a mixture of 450 parts of white cement, 450 parts of standard sand (grain I-fine), 900 parts of standard sand (grain II - coarse) and 270 parts of water, according to DIN 1164 (December 1958), using a wooden frame and a smooth support. The wooden frames were removed when the concrete had solidified, and after a further 24 h the concrete slabs were removed from their respective supports. They were allowed to dry at room temperature for 36 days.

Each slab was then immersed to half-height with the smooth side downward for one minute in one of the solutions (i), (ii) and (iii) in Example 5. 620 g/m² of solution was absorbed. The slabs were then dried in air at room temperature for 5 days.

- 60 The treated and untreated surfaces of the slabs were then treated with an aqueous red-pigment dispersion from a spray nozzle (commercially available under the name "Plaka"). After 2 days, the sprayed surfaces were treated with toluene in an attempt to remove the coloration of the pigment. The coloration could easily be removed almost completely from the surfaces treated with solutions (i) and (ii), but could not be removed, even with great effort, from the surface treated with solution (iii) or from the untreated surfaces.

- 65 The water-repellency of the surfaces treated according to the invention (i) and (ii))

prevented substantial penetration of the aqueous dyestuff and their oil-repellency prevented substantial penetration of the dispersant and thus also of the pigment.

Example 7

Concrete slabs of the size given in Example 6 were prepared as in Example 6, except that they were dried for 7 weeks at room temperature instead of for 36 days.

Two slabs each were then immersed to half-height for one minute in the following respective solutions:

- (i) a solution similar to that under Example 5 (i) but containing 0.5 % of the polymer and 1.25 % of the organopolysiloxane.
- (ii) a solution similar to that under Example 5 (i) but containing 0.33 % of the polymer and 2.6 % of the organopolysiloxane.
- (iii) a solution similar to that under Example 5 (i) but containing 0.25 % of the polymer and 3.0 % of the organopolysiloxane.
- (iv)* a solution as under Example 5 (iii).

About 600 g/m² of solution was absorbed by each slab.

Each of the above solutions was also coated respectively onto one side of each of two roof tiles (unglazed brickyard products with a porous body) and onto one side of each of two asbestos cement slabs. About 500 g/m² of solution was used on the roof tiles and about 150 g/m² of solution on the asbestos cement slabs.

One of each pair of the building materials was then stored for 4 weeks at room temperature and protected from weathering. The other of each pair was, directly after application of the respective solution, exposed at an inclination of 45° to the weather in Burghausen, Oberbayern, Germany for 4 weeks.

The treated and untreated surfaces of all of the tiles and slabs were subsequently written on using a felt-tip pen (commercially available under the name "Edding"). After 24 hours, the writing on each surface was rubbed with a piece of paper soaked in toluene. The writing on all surfaces treated according to (i), (ii) or (iii) could easily be removed in this manner, irrespective of the material and of whether the surface had been weathered. The writing could not be removed in this manner from the untreated surfaces nor from the surface treated according to (iv), again irrespective of the material and of whether it had been weathered.

Example 8

Unglazed ceramic plates were coated as follows:

- (i) 450 g/m² of a solution as under Example 1 (i) were applied, and the coating was dried at 150°C for 25 minutes. After cooling to room temperature, 330 g/m² of a solution as under Example 7 (iii) were applied, and the coating was dried at 150°C for 10 minutes.
- (ii) 450 g/m² of a solution as under Example 1 (i) were applied. Within one minute of the first application while the coating was still wet, 70 g/m² of a dispersion as under Example 1 (ii) were applied. Drying was then effected for 10 min at 150°C.
- (iii)* 450 g/m² of a solution as under Example 1 (i) were applied, and the coating was dried at 150°C for 25 minutes.

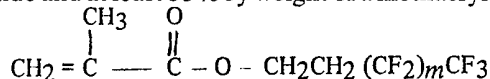
All the treated surfaces were found to be water-repellent.

A few drops of mineral oil and of edible oil were applied to each treated surface, and removed after 6 hours by means of absorbent paper. The surface treated according to (iii) had a dark stain showing that it was not oil-repellent, whereas no marks showed on the surfaces treated according to (i) and (ii).

WHAT WE CLAIM IS:

1. A process for rendering hydrophobic and oleophobic, the surface of an inorganic material having open pores, which comprises applying to the surface (a) (i) a solution or dispersion of a fluorine-containing organic polymer consisting of fluorine and carbon atoms and, optionally, atoms of one or more elements selected from chlorine, hydrogen, oxygen, sulphur, phosphorus and nitrogen or (ii) an aqueous solution of a water-soluble polymer of an olefinically unsaturated carboxylic acid, and (b) a solution of an organosilicon compound having an average of from 0.9 to 1.8 hydrocarbon radicals per silicon atom and in which any silicon valency not satisfied by a hydrocarbon radical is satisfied by an oxygen atom.

2. A process as claimed in claim 1, wherein the fluorine-containing organic polymer is polytetrafluoroethylene, polytrifluorochloroethylene, a copolymer of tetrafluoroethylene and hexafluoropropylene, a copolymer of trifluorochloroethylene and one or more other olefinically unsaturated monomers, a fluorinated acrylic resin, or a copolymer of N-butyl acrylate, N-methylol acrylamide and at least 35 % by weight of a methacrylate of the formula



in which m denotes an integer from 1 to 13.

3. A process as claimed in claim 1 or claim 2, wherein component (a) is an aqueous

dispersion of the fluorine-containing organic polymer.

4. A process as claimed in claim 1 or claim 2, wherein component (a) is a solution or dispersion in an organic liquid of the fluorine-containing organic polymer.

5. A process as claimed in claim 1, wherein the water-soluble polymer of an olefinically unsaturated carboxylic acid is a polymer of one or more monomers selected from acrylic acid, methacrylic acid, itaconic acid, vinylacetic acid, and fumaric acid.

6. A process as claimed in any one of claims 1 to 5, wherein the fluorine-containing polymer or the water-soluble polymer of an olefinically unsaturated carboxylic acid is present in the solution or dispersion (a) in an amount within the range of from 0.05 to 25% by weight, based on the weight of the respective polymer and the solvent or dispersing medium.

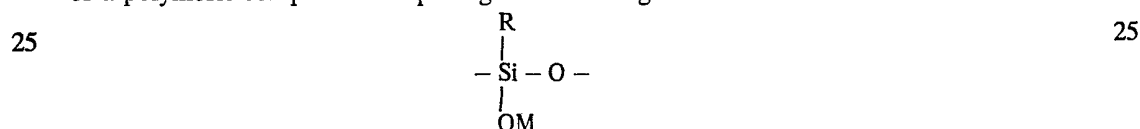
7. A process as claimed in any one of claims 1 to 5, wherein the fluorine-containing polymer or the water-soluble polymer of an olefinically unsaturated carboxylic acid is present in the solution or dispersion (a) in an amount within the range of from 0.5 to 20% by weight, based on the weight of the respective polymer and the solvent or dispersing medium.

8. A process as claimed in any one of claims 1 to 7, wherein the organosilicon compound is an alkali metal hydrocarbonsiliconate in which the or each hydrocarbon radical is an alkyl radical having up to 5 carbon atoms or a phenyl radical.

9. A process as claimed in any one of claims 1 to 7, wherein the organosilicon compound is a monomeric compound of the general formula



or a polymeric compound comprising units of the general formula



in which formulae, each R denotes an alkyl radical having up to 5 carbon atoms or a phenyl radical, and each M denotes an alkali metal atom.

10. A process as claimed in claim 9, wherein, in the general formulae, M denotes a sodium or potassium atom.

11. A process as claimed in any one of claims 1 to 7, wherein the organosilicon compound is an organosilane of the general formula



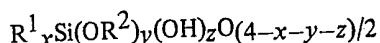
in which each R^1 denotes a hydrocarbon radical free of aliphatic unsaturation and having up to 14 carbon atoms, each R^2 denotes an alkyl radical or an alkoxyalkyl radical, each having up to 5 carbon atoms, and n denotes 0, 1, 2 or 3 and has an average value within the range of from 0.9 to 1.8, or is a partial hydrolysate, having not more than 10 silicon atoms per molecule, of such an organosilane.

12. A process as claimed in any one of claims 1 to 7, wherein the organosilicon compound is a reaction product of a silane of the general formula



in which R^1 and n are defined as in claim 11, and ethylene glycol or diethylene glycol.

13. A process as claimed in any one of claims 1 to 7, wherein the organosilicon compound is an organopolysiloxane having more than 10 silicon atoms per molecule and consisting of units of the general formula



in which R^1 and R^2 are defined as in claim 11, each of x , y and z denotes 0, 1, 2 or 3, the sum $x + y + z$ does not exceed 3, the average value of x is within the range of from 0.9 to 1.8, the average value of each of y and z is within the range of from 0.00 to 0.20 with the proviso that at least one of y and z has an average value of at least 0.01.

14. A process as claimed in any one of claims 8 to 10, wherein the organosilicon compound is dissolved in water or a mixture of water and a water-miscible organic solvent.

15. A process as claimed in any one of claims 11 to 13, wherein the organosilicon compound is dissolved in an organic solvent.

16. A process as claimed in any one of claims 1 to 15, wherein the organosilicon compound is present in the solution (b) in an amount within the range of from 0.01 to 25% by weight, based on the weight of the organosilicon compound and the solvent.

17. A process as claimed in any one of claims 1 to 15, wherein the organosilicon compound is present in the solution (b) in an amount within the range of from 0.1 to 10% by weight, based on the weight of the organosilicon compound and the solvent.

5 18. A process as claimed in any one of claims 1 to 17, wherein the organosilicon compound and the fluorine-containing polymer or the water-soluble polymer of an olefinically unsaturated carboxylic acid are applied in a respective weight ratio within the range of from 2:1 to 20:1. 5

19. A process as claimed in any one of claims 1 to 18, wherein the solution or dispersion (a) is applied to the surface in an amount within the range of from 1 to 2000 g/m².

10 20. A process as claimed in any one of claims 1 to 18, wherein the solution or dispersion (a) is applied to the surface in an amount within the range of from 150 to 800 g/m². 10

21. A process as claimed in any one of claims 1 to 20, wherein the solution (b) is applied to the surface in an amount within the range of from 1 to 2000 g/m².

15 22. A process as claimed in any one of claims 1 to 20, wherein the solution (b) is applied to the surface in an amount within the range of from 150 to 800 g/m². 15

23. A process as claimed in any one of claims 1 to 18, wherein component (a) and component (b) are applied simultaneously.

24. A process as claimed in claim 23, wherein component (a) and component (b) are applied in admixture with one another.

20 25. A process as claimed in claim 24, wherein the mixture of component (a) and component (b) is applied to the surface in an amount within the range of from 1 to 1000 g/m². 20

26. A process as claimed in claim 24, wherein the mixture of component (a) and component (b) is applied to the surface in an amount within the range of from 80 to 500 g/m².

25 27. A process as claimed in any one of claims 1 to 22, wherein component (b) is applied before component (a). 25

28. A process as claimed in any one of claims 1 to 22, wherein component (b) is applied after component (a) but before component (a) has dried.

29. A process as claimed in any one of claims 1 to 28, wherein, subsequent to their application, the two components are dried at a temperature of up to 250°C.

30 30. A process as claimed in claim 1, carried out substantially as described in any one of the examples herein. 30

31. A surface treated by a process as claimed in any one of claims 1 to 30.

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