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(71) Applicants (for all designated States except US): **DOW CORNING CORPORATION** [US/US]; 2200 West Salzburg Road, Midland, MI 48686-0994 (US). **DAIKIN INDUSTRIES, LTD.** [JP/JP]; Umeda Center Building, 2-4-12, Nakazaki-nishi, Kita-ku, Osaka, Osaka, 530-8323 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BUTLER, Derek** [GB/GB]; 246 Sunnyside Gladstone Road, Barry CF62 8NG (GB). **HUPFIELD, Peter, Chesire** [GB/GB]; Parc-y-gelli Henfwlch Road, Trevaughan SA33 6AA (GB). **REED, Samantha** [GB/GB]; 2 Burreed Close Watersedge, Cardiff CF 3 ORL (GB).

(74) Agents: **LUNA, Susan, M.** et al.; Dinsmore & Shohl LLP, One Dayton Center, Suite 1300, One South Main Street, Dayton, OH 45402-2023 (US).

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(54) Title: COMPOSITION FOR TREATING MASONRY

(57) Abstract: A composition for treating masonry to improve its stain resistance as well as providing water and oil repellency is provided which utilizes a fluorine-containing polymer and at least one silicon compound selected from silanes and siloxanes. The composition may be dispersed in an organic solvent for application to a masonry substrate followed by elimination of the solvent.



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COMPOSITION FOR TREATING MASONRY

This invention relates to a composition for treating masonry to improve its stain resistance and water- and oil-repellency.

5 WO-A-2004/108779 describes a fluoropolymer for masonry treatment produced from a fluoromonomer which is a fluoroalkyl ester of an alpha-substituted acrylate and a comonomer having a functional group reactive with active hydrogen, for example a silane, phosphate, carboxylate, sulphate or glycidyl group. The fluoropolymer is applied to masonry from an organic solvent.

10 JP-A-07-109317 discloses a treatment agent comprising a fluoropolymer which is a copolymer of a monomer having a fluoroalkyl group and a silicone-based vinyl monomer. US-A-6037429 discloses treating porous substrates to render them repellent to water- and oil-based stains with a water-soluble fluoropolymer containing only carbon atoms in the backbone, with pendent fluoroaliphatic groups, carboxyl-containing groups, oxyalkylene or polyoxyalkylene groups, and silyl groups. EP-A-1225187 discloses the treatment of ceramics with a copolymer of a fluoroalkyl-containing monomer, a fluorine-free monomer and a monomer containing a silyl group. These treatments or these treatment agents, however, do not have both sufficient water repellency and sufficient oil repellency, and cannot impart sufficient soil resistance for a masonry-treatment agent.

20 US-A-5872180 describes a composition for treating textile substrates to render them oil-, water- and soil-repellent, comprising a fluorine-containing acrylic polymer and a fluorine-free poly(meth)acrylate. The composition can optionally contain an organosilsesquioxane. However, this has not been practically used as a masonry-treatment agent.

25 The compositions described in WO-A-2004/108779 impart excellent oil repellency and stain resistance to masonry substrates. There is however a need for a composition which additionally imparts improved water repellency to the masonry.

Described below are the environmental problems raised by perfluorooctanoic acid (PFOA). The results of the latest researches [a report of the Environmental Protection
30 Agency (EPA), "PRELIMINARY RISK ASSESSMENT OF THE DEVELOPMENTAL

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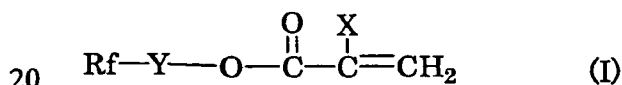
TOXICITY ASSOCIATED WITH EXPOSURE TO PERFLUOROOCTANOIC ACID AND ITS SALTS" (<http://www.epa.gov/opptintr/pfoa/pfoara.pdf>)] have taught that PFOA (perfluorooctanoic acid), one of long chain fluoroalkyl compounds, is proved to have a danger to burden the environment. Under such a situation, EPA announced on

5 April 14, 2003 that the scientific investigation on PFOA should be more intensively executed. On the other hand, the Federal Register (FR Vol.68, No.73/April 16, 2003 [FRL-7303-8], <http://www.epa.gov/opptintr/pfoa/pfoafr.pdf>), EPA Environmental News FOR RELEASE: MONDAY APRIL 14, 2003 EPA INTENSIFIES SCIENTIFIC INVESTIGATION OF A CHEMICAL PROCESSING AID

10 (<http://www.epa.gov/opptintr/pfoa/pfoaprs.pdf>) and EPA OPPT FACT SHEET April 14, 2003 (<http://www.epa.gov/opptintr/pfoa/pfoafacts.pdf>) have published that telomers have a possibility to produce PFOA when decomposed or metabolized (herein, the telomer means a long chain fluoroalkyl group), and also that telomers have been widely used in foam fire extinguishers, care products, washing materials, carpets, textiles, paper, leather,

15 etc., in order to impart water and oil repellency and soil resistance to them.

A composition according to the invention for masonry treatment comprises a fluorine-containing polymer (A) and at least one silicon compound. The fluorine-containing polymer (A) comprises repeating units derived from a fluorine-containing monomer of the formula:



wherein X is a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, a CFX¹ X² group in which X¹ and X² are each a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom or an iodine atom, a cyano group, a linear or branched fluoroalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted benzyl group, or a substituted

25 or unsubstituted phenyl group;

Y is an aliphatic group having 1 to 10 carbon atoms, an aromatic or cycloaliphatic group having 6 to 10 carbon atoms, a -CH₂ CH₂ N(R¹) SO₂ - group in which R¹ is an alkyl group having 1 to 4 carbon atoms, or a -CH₂ CH(OY¹) CH₂ - group in which Y¹ is a hydrogen atom or an acetyl group; and

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Rf is a linear or branched fluoroalkyl or fluoroalkenyl group having 1 to 21 carbon atoms, or a fluoroether group having a total of 1 to 200 repeating units selected from the repeating units $-\text{C}_3\text{F}_6\text{O}-$, $-\text{C}_2\text{F}_4\text{O}-$ and $-\text{CF}_2\text{O}-$. The silicon compound is selected from silanes and siloxanes of the general formula $\text{R}_a\text{SiO}_{(4-a/2)}$ wherein each R is a monovalent organic group, which can be the same or different, and denotes for example a hydrocarbon, substituted hydrocarbon, hydroxyl, hydrocarbonoxy or substituted hydrocarbonoxy group and has an average value of from 0.25 to 4.

The invention includes a method of treating masonry to enhance its stain resistance and water resistance, which comprises applying a composition as described above to the masonry. The fluorine-containing polymer (A) and the silicon compound may for example be dispersed in an organic solvent, which is eliminated after application to the masonry.

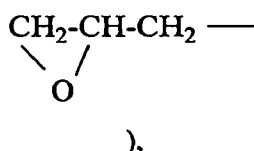
When the Rf group in the formula (I) is a fluoroalkyl group or a fluoroalkenyl group, the Rf group is preferably a perfluoroalkyl group or a perfluoroalkenyl group. The fluoroalkyl group or the fluoroalkenyl group has 1 to 21 carbon atoms, particularly 1 to 6 carbon atoms, for example, 1 to 4 carbon atoms. Examples of the fluoroalkyl group include $-\text{CF}_3$, $-\text{CF}_2\text{CF}_3$, $-\text{CF}_2\text{CF}_2\text{CF}_3$, $-\text{CF}(\text{CF}_3)_2$, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$, $-\text{CF}_2\text{CF}(\text{CF}_3)_2$, $-\text{C}(\text{CF}_3)_3$, $-(\text{CF}_2)_4\text{CF}_3$, $-(\text{CF}_2)_2\text{CF}(\text{CF}_3)_2$, $-\text{CF}_2\text{C}(\text{CF}_3)_3$, $-\text{CF}(\text{CF}_3)\text{CF}_2\text{CF}_2\text{CF}_3$, $-(\text{CF}_2)_5\text{CF}_3$, $-(\text{CF}_2)_3\text{CF}(\text{CF}_3)_2$, $-(\text{CF}_2)_4\text{CF}(\text{CF}_3)_2$, $-(\text{CF}_2)_7\text{CF}_3$, $-(\text{CF}_2)_5\text{CF}(\text{CF}_3)_2$, $-(\text{CF}_2)_6\text{CF}(\text{CF}_3)_2$, and $-(\text{CF}_2)_9\text{CF}_3$.

Y is an aliphatic group having 1 to 10 carbon atoms, an aromatic group or a cycloaliphatic group, each having 6 to 10 carbon atoms, a group $-\text{CH}_2\text{CH}_2\text{N}(\text{R}^1)\text{SO}_2-$ group (in which R^1 is an alkyl group having 1 to 4 carbon atoms) or a $-\text{CH}_2\text{CH}(\text{OY}^1)\text{CH}_2-$ group (in which Y^1 is a hydrogen atom or an acetyl group). The aliphatic group is preferably an alkylene group, particularly having 1 to 4 carbon atoms, for example, 1 or 2 carbon atoms. The aromatic group and the cycloaliphatic group may be substituted or unsubstituted.

The fluoroether group has at least one repeating unit (an oxyperfluoroalkylene group) selected from the group consisting of the repeating units: $-\text{C}_3\text{F}_6\text{O}-$, $-\text{C}_2\text{F}_4\text{O}-$ and $-\text{CF}_2\text{O}-$. The $-\text{C}_3\text{F}_6\text{O}-$ group is $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ or $-\text{CF}_2\text{C}(\text{CF}_3)\text{FO}-$. The $-\text{C}_2\text{F}_4\text{O}-$ group is

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generally $-\text{CF}_2\text{CF}_2\text{O}-$. The total number of the oxyperfluoroalkylene repeating units is 1 to 200, for example, 1 to 100, and particularly 5 to 50. The fluoroether group has a terminal group which is directly bonded to the oxyperfluoroalkylene repeating unit. Examples of the terminal group include a hydrogen atom, a halogen atom (e.g., a fluorine atom), an alcohol group (e.g., HOCH_2-), an epoxy group (for example,



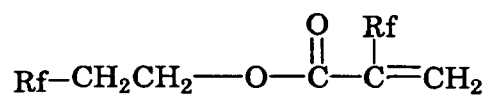
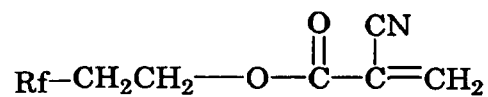
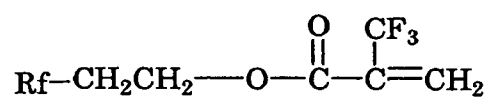
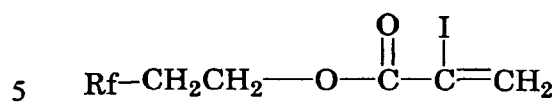
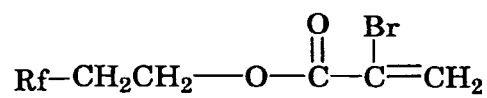
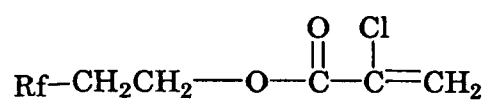
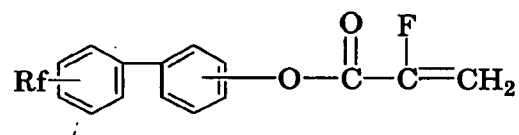
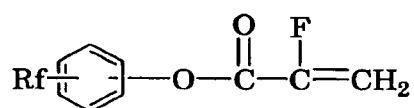
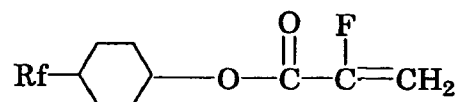
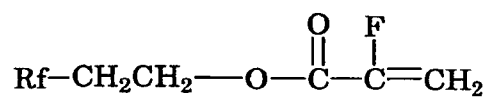
an amine group (e.g., $\text{H}_2\text{N}-$), a carboxylic acid group (e.g., $\text{HOOC}-$), an acid halide group (e.g., $\text{F}(\text{O}=\text{C})-$) and a chloromethyl group ($\text{ClH}_2\text{C}-$). The fluoroether group may have a fluoroalkylene group having 1 to 10 carbon atoms, particularly a perfluoroalkylene group, in addition to the oxyperfluoroalkylene repeating unit and the terminal group. Examples of the fluoroalkylene group having 1 to 10 carbon atoms are $-\text{CF}_2-$ and $-\text{CF}_2\text{CF}_2-$.

Examples of the fluoroether group (particularly, a perfluoroether group) which is an example of the Rf group include the following:

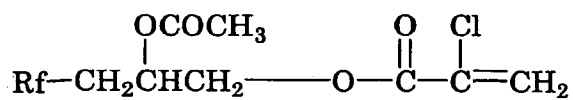
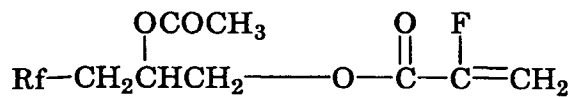
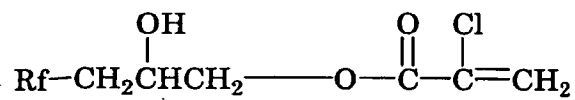
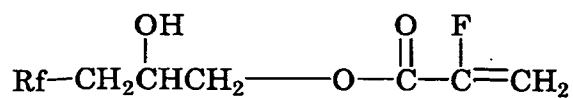
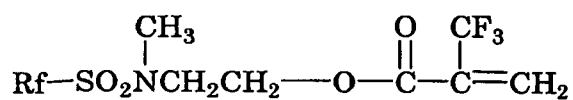
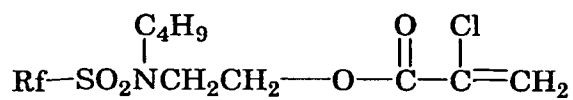
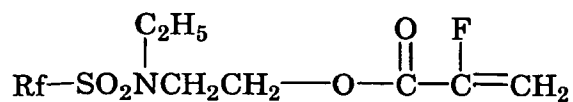
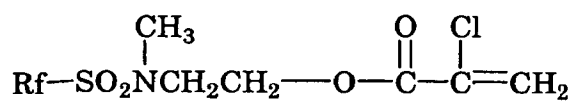
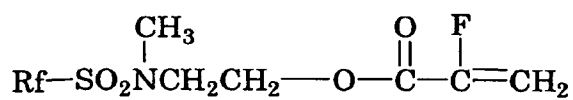
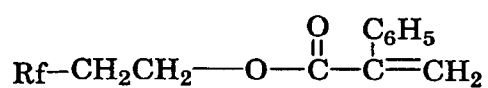
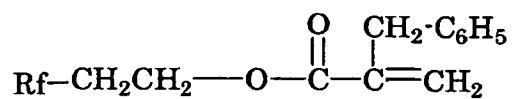
- 15 F- $(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_n$ - CF_2CF_2- (n is a number of 1 to 200),
 F- $(\text{CF}_2\text{C}(\text{CF}_3)\text{FO})_n$ - CF_2CF_2- (n is a number of 1 to 200),
 F- $(\text{CF}_2\text{C}(\text{CF}_3)\text{FO})_n$ - $(\text{CF}_2\text{O})_m$ - CF_2CF_2-
 (the total of n and m is 1 to 200), and
 F- $(\text{CF}_2\text{CF}_2\text{O})_n$ - $(\text{CF}_2\text{O})_m$ - CF_2CF_2-
 20 (the total of n and m is 1 to 200).

Examples of the fluorine-containing monomer include the following:

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wherein Rf is a linear or branched fluoroalkyl or fluoroalkenyl group having 1 to 21 carbon atoms, or a fluoroether group having totally 1 to 200 repeating units selected from the group consisting of the repeating units: -C₃F₆O-, -C₂F₄O- and -CF₂O-.

According to one aspect of the invention, the fluorine-containing polymer contains
 5 units derived from a monomer having a functional group reactive with active hydrogen, for example a monomer having a carbon-carbon double bond and a functional group reactive with active hydrogen. Examples of the functional group reactive with active hydrogen include a silane group, a phosphate or phosphoric acid group, a carboxylate or carboxylic acid group, a sulfonate or sulfonic acid group, and a glycidyl group.

10 A monomer having the silane group is preferably a compound having a silane group (particularly a terminal silane group) and a carbon-carbon double bond. The monomer having the silane group may be a terminal silane coupling agent.

Specific examples of the silane group-containing monomer are as follows:

- CH₂=CHCO₂(CH₂)₃Si(OCH₃)₃,
 15 CH₂=CHCO₂(CH₂)₃Si(OC₂H₅)₃,
 CH₂=C(CH₃)CO₂(CH₂)₃Si(OCH₃)₃
 (γ-methacryloxypropyltrimethoxysilane),
 CH₂=C(CH₃)CO₂(CH₂)₃Si(OC₂H₅)₃,
 CH₂=CHCO₂(CH₂)₃SiCH₃(OC₂H₅)₂,
 20 CH₂=C(CH₃)CO₂(CH₂)₃SiC₂H₅(OCH₃)₂,
 CH₂=C(CH₃)CO₂(CH₂)₃Si(CH₃)₂(OC₂H₅),
 CH₂=C(CH₃)CO₂(CH₂)₃Si(CH₃)₂OH,
 CH₂=CHCO₂(CH₂)₃SiCH₃[ON(CH₃)C₂H₅]₂,
 CH₂=C(CH₃)CO₂(CH₂)₃SiC₆H₅[ON(CH₃)C₂H₅]₂,
 25 CH₂=CHSi(OCH₃)₃,
 CH₂=CHSi(OC₂H₅)₃,
 CH₂=CHSiCH₃(OCH₃)₂,
 CH₂=CHSi(CH₃)₂(OC₂H₅),
 CH₂=CHSi(CH₃)₂SiCH₃(OCH₃)₂,
 30 CH₂=CHSiCH₃[ON(CH₃)C₂H₅]₂

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vinyltrichlorosilane, and vinyl tris(2-methoxyethoxy)silane.

Specific examples of a monomer having the phosphate group include 2-methacryloyloxyethyl acid phosphate, 2-acryloyloxyethyl acid phosphate, acid phosphoxypropyl methacrylate, 3-chloro-2-acid phosphoxypropyl methacrylate, and 2-methacryloyloxyethyl acid phosphate monoethanolamine half salt.

Specific examples of a monomer having the carboxylate group include methacrylic acid, acrylic acid, 2-methacryloyloxyethyl succinic acid, 2-acryloyloxyethyl succinic acid, 2-methacryloyloxyethyl phthalate, 2-acryloyloxyethyl phthalate, 2-methacryloyloxyethyl hexahydrophthalate, 2-acryloyloxyethyl hexahydrophthalate, 2-acryloyloxypropyl phthalate, 2-acryloyloxypropyl hexahydrophthalate, 2-acryloyloxypropyl tetrahydrophthalate, maleic anhydride and citraconic anhydride.

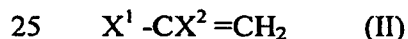
Specific examples of a monomer having the sulfonate group include acrylamide-tert.-butyl sulfonic acid, and 2-acrylamide-2-methylpropane sulfonic acid.

Specific examples of a monomer having the glycidyl group include glycidyl methacrylate and glycidyl acrylate.

The amount of the monomer having a functional group reactive with hydrogen atom may be from 0.01 parts to 50 parts by weight, from 0.1 parts to 20 parts by weight, based on 100 parts by weight of the fluorine-containing polymer.

The fluorine-containing polymer may contain an other monomer, in addition to the fluorine-containing monomer (I) and the monomer having a functional group. The other monomer may be a fluorine-free monomer. The fluorine-free monomer may be an alkyl group-containing monomer.

The fluorine-free monomer may be a fluorine-free alkyl (meth)acrylate. The fluorine-free alkyl (meth)acrylate is generally a monomer of the formula:



wherein X^1 is an alkyl carboxylate group (the number of carbon atoms in the alkyl group: 1 to 18), and X^2 is a hydrogen atom or a methyl group. The fluorine-containing polymer may not contain the fluorine-free alkyl (meth)acrylate.

The fluorine-containing polymer may contain the other monomer other than the fluorine-free alkyl (meth)acrylate. Examples of the other monomer are R_f group-free monomers such as ethylene, vinyl halide (for example, vinyl chloride), vinylidene halide (for example, vinylidene chloride), styrene, vinyl alkyl ketone, isoprene, chloroprene, butadiene, benzyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, glycerol mono(meth)acrylate, methoxypolyethyleneglycol (meth)acrylate, polypropyleneglycol (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, dimethylamino (meth)acrylate, trimethyl-(2-hydroxy-3-methacryloyloxypropyl) ammonium chloride and 3-chloro-2-hydroxypropyl methacrylate.

10 The amount of the other monomer may be from 0 to 100 parts by weight, for example, from 0 to 90 parts by weight, particularly from 1 to 70 parts by weight, based on 100 parts by weight of the fluorine-containing monomer (I).

 The fluorine-containing polymer can be prepared by any of conventional polymerization methods. The conditions of polymerization reaction can be arbitrarily
15 selected. The polymerization procedure includes a bulk polymerization, a solution polymerization and an emulsion polymerization. The solution polymerization is generally preferable.

 The molecular weight of the fluorine-containing polymer may be generally from 5,000 to 1,000,000 (for example, measured in GPC and in terms of polystyrene).

20 The silicon compound can be a silane or a siloxane, or a mixture of two or more silanes, or a mixture of two or more siloxanes, or a mixture of one or more silanes and one or more siloxanes. The silanes and siloxanes are generally of the formula $R_aSiO_{(4-a/2)}$ wherein each R is a monovalent organic group, which can be the same or different, denotes a hydrocarbon, substituted hydrocarbon, hydroxyl, hydrocarbonoxy or substituted
25 hydrocarbonoxy group and a has an average value of from 0.25 to 4. Examples of preferred substituted hydrocarbon groups are aminoalkyl or fluoroalkyl.

 The silicon compound can for example be a silane of the general formula R_4Si , wherein each R is a monovalent organic group, which can be the same or different, denotes for example a hydrocarbon, substituted hydrocarbon, hydroxyl, hydrocarbonoxy
30 or substituted hydrocarbonoxy group. Preferably at least one of the groups R in such a

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silane is a hydrocarbonoxy or substituted hydrocarbonoxy group. The silane can for example be a trialkoxysilane of the formula $R^2(R^3O)_3Si$ in which R^2 and R^3 each represent a monovalent organic group an optionally substituted hydrocarbyl group. R^2 can for example be an alkyl group having 1 to 18 carbon atoms optionally substituted by a hydroxyl, halogen, amino, alkoxy or epoxy group. Each R^3 can for example be an alkyl group having 1 to 6 carbon atoms such as a methyl or ethyl group. The silane can alternatively be a dialkoxysilane of the formula $(R^2)_2(R^3O)_2Si$ or a monoalkoxysilane of the formula $(R^2)_3R^3OSi$ in which R^2 and R^3 each have the meanings given above. The silane can alternatively be a tetraalkoxysilane $(R^3O)_4Si$.

- 10 Examples of specific silanes that can be used in the composition of the invention are trialkoxysilanes such as isobutyltrimethoxysilane, n-octyltrimethoxysilane, isobutyltriethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, isopropyltrimethoxysilane, n-hexyltrimethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, 3-glycidylpropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-amino-2-methylpropyltrimethoxysilane, 3-mercapto-2-methylpropyltrimethoxysilane, 3-glycidyl-2-methylpropyltrimethoxysilane, 3-(2-aminoethylamino)-2-methylpropyltrimethoxysilane or stearyltrimethoxysilane, dialkoxysilanes such as diisobutyldimethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, n-octylmethyldimethoxysilane, 3-glycidylpropylmethyldimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-aminopropylmethyldiethoxysilane or 3-(2-aminoethylamino)-2-methylpropylmethyldimethoxysilane, monoalkoxysilanes such as triisobutylmethoxysilane, trimethylethoxysilane, trimethylmethoxysilane, diisobutylmethylethoxysilane or triethylmethoxysilane, or tetraalkoxysilanes such as tetraethoxysilane (ethyl orthosilicate) or a partially condensed ethylsilicate.

- The silicon compound can alternatively or additionally be a siloxane of the general formula $R_aSiO_{(4-a/2)}$ wherein each R is a monovalent organic group, which can be the same or different, denotes a hydrocarbon, substituted hydrocarbon, hydroxyl, hydrocarbonoxy or substituted hydrocarbonoxy group and a has an average value of from

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0.25 to 3, preferably 0.5 to 2.4. Such a siloxane can for example be a predominantly linear polydiorganosiloxane in which most of the groups R are hydrocarbon groups and a has a value close to 2, for example in the range 1.8 to 2.4. Alternatively the siloxane can be a cyclic polydiorganosiloxane or a branched siloxane fluid polymer, or can be a branched
5 siloxane resin in which a has a value of less than 2, for example 0.5 to 1.2.

Examples of predominantly linear polydiorganosiloxanes are polydialkylsiloxanes such as polydimethylsiloxane (PDMS) or a poly(methylalkylsiloxane) in which the alkyl group has 2 or more, for example 2 to 18, carbon atoms, or a poly(methylphenyl)silicone. Such a polydialkylsiloxane can contain a minor proportion of other groups such as alkoxy
10 groups, hydroxyl groups or hydrogen atoms attached to Si. The linear polydiorganosiloxane can have various terminal groups. It may have terminal trialkylsilyl groups such as trimethylsilyl, or can have dialkylalkoxysilyl, alkylalkoxysilyl or trialkoxysilyl terminal groups, or can be silanol-terminated by having terminal groups including Si-bonded hydroxyl such as dialkylhydroxysilyl terminal groups. Silanol-
15 terminated siloxanes may be preferred as giving the best adhesion to a masonry substrate of any of the polydiorganosiloxanes. A predominantly linear polydiorganosiloxane used in the composition of the invention can for example contain from 2 to 500 siloxane units, particularly 4 to 50 siloxane units. The predominantly linear polydiorganosiloxane can be mixed with a cyclic polydiorganosiloxane such as decamethylcyclopentasiloxane or
20 octamethylcyclotetrasiloxane. Alternatively such a cyclic polydiorganosiloxane can be used instead of the linear polydiorganosiloxane.

If the silane or siloxane contains silanol groups or S-bonded alkoxy groups, the composition may contain a catalyst for condensation of such groups, for example a titanate ester such as titanium butoxide.

25 Examples of branched silicone resins are resins comprising mainly $\text{RSiO}_{3/2}$ siloxane units, known as T units. In such T resins the value of a in the formula $\text{R}_a\text{SiO}_{(4-a/2)}$ is about 1. The group R is a monovalent organic group and can for example be alkyl such as methyl, ethyl or isobutyl, or substituted alkyl, or can be aryl such as phenyl. The T resins can optionally additionally contain $\text{R}_3\text{SiO}_{1/2}$ units (M units) and/or $\text{SiO}_{4/2}$ units (Q
30 units) and/or R_2SiO units. Alternative branched silicone resins which can be used in the

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composition of the invention are resins comprising mainly M units and Q units. Branched siloxane fluid polymers can be formed from reactive polydiorganosiloxanes such as silanol-terminated polydimethylsiloxane by reaction with a alkyltrialkoxysilane to introduce T and Q units.

5 The proportion of fluorine-containing polymer and silicon compound in the composition of the invention is usually in the range 0.1 to 30 parts by weight of silicon compound per part of fluorine-containing polymer. For many masonry applications a proportion in the range 0.2 to 20 parts, and especially 0.25 to 4 parts, by weight of silicon compound per part of fluorine-containing polymer is used. The preferred proportion of
10 fluorine-containing polymer and silicon compound can vary for different masonry applications. For example a relatively high proportion of silicon compound may be preferred for application to reinforced concrete, where water resistance is particularly important to inhibit corrosion of the metal reinforcing bars. For application to dressed stone buildings, a relatively high proportion of fluorine-containing polymer may be
15 preferred to give maximum resistance to external stains.

 The fluorine-containing polymer and silicon compound can be dissolved together in an organic solvent to form the composition of the invention. Examples of suitable organic solvents include esters such as butyl acetate or t-butyl acetate, alcohols such as 2-butanol, pentanol, isopropanol or 1-butanol, ether-alcohols, ketones, halogenated
20 hydrocarbons such as tetrachlorohexafluorobutane and/or hydrocarbons such as white spirit or methylcyclopentane. The total concentration of the fluorine-containing polymer and the silicon compound in the solvent can for example be 0.1 to 50% by weight and is usually in the range 1 to 15%.

 The masonry treating composition of the invention can optionally contain an
25 organic wax, an antifreezing agent, a viscosity-adjusting agent, a surfactant, an antioxidant, a pH adjuster, a defoaming agent, an antiseptic agent and/or a flame retardant, as required, in addition to the fluorine-containing polymer and the silicon compound.

 The masonry substrate to which the composition of the invention is applied can for example be natural stone, for example marble, granite or limestone, concrete, artificial
30 stone, brick or tile.

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The composition of the invention can for example be applied to the masonry substrate by coating, spraying, brushing or dipping. The organic solvent is eliminated by drying the treated masonry, for example at 0°C to 200°C, or by simply allowing the solvent to evaporate. The total amount of fluorine-containing polymer and silicon
5 compound applied on the masonry can be 0.05 to 200g, for example 0.1 to 50g, especially 1 to 20g per square metre of surface area of the masonry.

Masonry treated with the composition of the invention has the excellent oil repellency and resistance to staining and to soil adhesion given by the fluorine-containing polymer described in WO-A-2004/108779 and additionally is rendered more hydrophobic,
10 as shown by a reduced water uptake. This improved hydrophobicity prevents efflorescence from the masonry, inhibits corrosion of reinforcing bars in concrete and improves resistance to water based stains. Although WO-A-2004/108779 describes the use of a silane-containing comonomer in the fluorine-containing polymer, we have found that the addition of a silicon compound to the composition improves the hydrophobicity of
15 the treated masonry. Moreover, the use of a separate silicon compound allows the proportion of silicon compound to fluorine-containing polymer to be varied according to the masonry substrate to be treated.

The invention is illustrated by the following Examples, in which parts and percentages are by weight.

20 Example 1

A fluorine-containing polymer (nonafluorohexyl chloracrylate/ stearyl acrylate/ methacryloxypropyltrimethoxysilane copolymer) was prepared as described in Example 2 of WO-A-2004/108779 and was dissolved at 15% in t-butyl acetate. 20g of this solution was added to a solution of 20g n-octyltrimethoxysilane in 10g t-butyl acetate to form a
25 masonry treating composition according to the invention.

The above composition was applied to concrete (as specified in British Standard BS3712) at 300 g/m² by brushing and was allowed to dry for 2 days.

Contact angles on the treated substrate of water and hydrocarbon oil (hexadecane) were measured using 1µl droplets. 3 measurements were taken across the block. The
30 results are shown in Table 1 below.

Table 1 - Contact angle test

	Water	Hexadecane
Measurement 1 °	131.00	77.30
Measurement 2 °	129.40	79.30
Measurement 3 °	128.70	89.30
Average contact angle °	129.70	81.96

The treated substrate was stained with one drop of each of the staining materials: olive oil, black coffee, black tea, red wine, coca-cola, tomato ketchup, horizontally across the block. This was repeated so that there were three rows of stains across the block.

- 5 After 5 minutes, the stains in the first row were removed using a paper tissue. The appearance was scored from 1-5 (5 being the best – the stain has completely been removed) and recorded. After 2 hours, the stains in the second row were removed using a paper tissue and score and the appearance was scored and recorded. The stains were then scrubbed with a wet tissue paper, allowed to dry and the appearance was again recorded.
- 10 After 24 hours, the stains in the third row were removed using a paper tissue and the appearance was scored. The stains were then scrubbed with a wet tissue paper, allowed to dry and the appearance was again recorded. The stains were then scrubbed with a hard paint brush, and the appearance of the stains on the substrate was again scored and recorded. The results are shown in Table 2 below.

15 Table 2 - Stain resistance test

	5 mins	2 hrs		24hrs		
	Dry	Dry	Wet	Dry	Wet	Brush
Olive oil	5	4	4	4	3	3
Black coffee	3	2	2	1	3	3
Black tea	5	4	4	2	4	4
Red wine	5	4	4	4	4	4
Coca-cola	5	5	5	4	5	5
Tomato ketchup	5	3	5	4	4	4
Total	28	22	24	19	23	23
Overall score	139					

The treated substrate was weighed and was placed on glass rods in a tray of water, so only the treated surface of the substrate was touching the surface of the water, to measure water-pick up. The weight of the block was measured after 15 minutes, 2 hours and 24 hours in contact with water. The results are shown in Table 3 below.

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Table 3 - Water pick-up test (initial weight of block 438.69g)

<u>Time of immersion</u>	<u>Weight including water absorbed</u>	<u>% Weight of water absorbed</u>
15 mins	439.11	0.10
2 hrs	439.31	0.14
24 hrs	440.68	0.45

In a comparative example, the fluorine-containing polymer of Example 2 of WO-A-2004/108779 and was dissolved at 6% in t-butyl acetate and this solution was applied to BS3712 concrete at 300 g/m² by brushing and was allowed to dry for 2 days. The treated concrete was the tested as described in Example 1. The results are shown in Tables 4 to 6 below.

Table 4 - Contact angle test

	<u>Water</u>	<u>Hexadecane</u>
Measurement 1 °	141.00	109.60
Measurement 2 °	129.00	101.90
Measurement 3 °	143.90	105.50
<u>Average contact angle °</u>	137.96	105.66

Table 5 - Stain resistance test

	<u>5 mins</u>	<u>2 hrs</u>		<u>24hrs</u>		
	<u>Dry</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Brush</u>
Olive oil	5	5	5	5	5	5
Black coffee	3	3	3	1	3	4
Black tea	4	4	4	4	4	5
Red wine	3	3	3	2	2	2
Coca-cola	5	5	5	3	4	4
Tomato ketchup	4	4	5	3	5	5
Total	24	24	25	18	23	25
<u>Overall score</u>	139					

10

Table 6 - Water pick-up test (Initial weight of block = 460.19g)

<u>Time of immersion</u>	<u>Weight including water absorbed</u>	<u>% Weight of water absorbed</u>
15 mins	460.73	0.12
2 hrs	461.80	0.35
24 hrs	466.99	1.45

It can be seen from Tables 2 and 5 that the composition of Example 1 gave equal anti-staining performance to the composition of the comparative example. It can be seen

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from Tables 3 and 6 that concrete treated with the composition of Example 1 had substantially lower water uptake than the concrete treated with the composition of the comparative example.

Example 2

- 5 Example 1 was repeated using isobutyltriethoxysilane in place of the octyltriethoxysilane. The test results for the treated concrete are set out in Tables 7 to 9 below.

Table 7 - Contact angle test

	<u>Water</u>	<u>Hexadecane</u>
Measurement 1 °	140.00	94.60
Measurement 2 °	136.80	102.00
Measurement 3 °	138.80	89.30
Average contact angle °	138.53	95.30

10 Table 8 - Stain resistance test

	<u>5 mins</u>	<u>2 hrs</u>		<u>24hrs</u>		
	<u>Dry</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Brush</u>
Olive oil	5	5	5	5	5	5
Black coffee	4	3	3	1	2	3
Black tea	4	3	2	1	4	4
Red wine	3	2	2	2	2	2
Coca-cola	5	3	4	3	4	4
Tomato ketchup	3	3	5	3	5	5
Total	24	19	21	15	22	23
<u>Overall score</u>	124					

Table 9 - Water pick-up test (Initial weight of block = 453.93g)

<u>Time of immersion</u>	<u>Weight including water absorbed</u>	<u>% Weight of water absorbed</u>
<u>15 mins</u>	454.52	0.13
<u>2 hrs</u>	454.86	0.20
<u>24 hrs</u>	456.29	0.51

- It can be seen from Tables 6 and 9 that concrete treated with the composition of Example 2 had substantially lower water uptake than the concrete treated with the composition of the comparative example.
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Example 3

- 10g of a solution at 15% in t-butyl acetate of the fluorine-containing polymer prepared as described in Example 2 of WO-A-2004/108779 was added to a solution of 20g isobutyltrimethoxysilane in 20g methylcyclopentane to form a masonry treating composition according to the invention. This composition was applied to concrete and tested as described in Example 1. The results are set out in Tables 10 to 12 below.

Table 10 - Contact angle test

	<u>Water</u>	<u>Hexadecane</u>
Measurement 1 °	115.20	75.60
Measurement 2 °	121.10	86.60
Measurement 3 °	132.00	87.40
Average contact angle °	122.76	83.20

Table 11 - Stain resistance test

	<u>5 mins</u>	<u>2 hrs</u>		<u>24hrs</u>		
	<u>Dry</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Brush</u>
Olive oil	5	5	5	5	5	5
Black coffee	5	4	4	1	4	4
Black tea	4	4	4	3	4	5
Red wine	4	2	3	1	3	3
Coca-cola	5	5	5	2	4	5
Tomato ketchup	5	4	4	3	3	4
Total	28	24	25	15	23	26
<u>Overall score</u>	141					

Table 12 - Water pick-up test (Initial weight of block = 435.94g)

<u>Time of immersion</u>	<u>Weight including water absorbed</u>	<u>% Weight of water absorbed</u>
<u>15 mins</u>	436.36	0.09
<u>2 hrs</u>	436.75	0.18
<u>24 hrs</u>	437.81	0.43

- It can be seen from Tables 5 and 11 that the composition of Example 3 gave equal anti-staining performance to the composition of the comparative example. It can be seen from Tables 6 and 12 that concrete treated with the composition of Example 3 had substantially lower water uptake than the concrete treated with the composition of the comparative example.

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Example 4

The process of Example 3 was repeated with the difference that t-butyl acetate was used in place of methylcyclopentane as the solvent for the isobutyltrimethoxysilane. The results of the tests on concrete treated with the composition of Example 4 are shown in

5 Tables 13 to 15 below.

Table 13 - Contact angle test

	<u>Water</u>	<u>Hexadecane</u>
Measurement 1 °	136.80	115.50
Measurement 2 °	142.50	109.10
Measurement 3 °	136.70	114.40
Average contact angle °	138.66	113.00

Table 14 - Stain resistance test

	<u>5 mins</u>	<u>2 hrs</u>		<u>24hrs</u>		
	<u>Dry</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Brush</u>
Olive oil	4	4	4	4	4	4
Black coffee	1	1	1	1	2	2
Black tea	1	1	1	3	3	3
Red wine	1	1	1	2	2	2
Coca-cola	4	3	3	2	2	2
Tomato ketchup	1	1	1	3	3	3
Total	12	11	11	15	16	16
<u>Overall score</u>	81					

10 **Table 15 - Water pick-up test (Initial weight of block = 455.71g)**

<u>Time of immersion</u>	<u>Weight including water absorbed</u>	<u>% Weight of water absorbed</u>
15 mins	456.37	0.14
2 hrs	456.48	0.17
24 hrs	456.90	1.19

Example 5

Example 4 was repeated using n-octyltrimethoxysilane in place of the isobutyltrimethoxysilane. The results of the tests on concrete treated with the composition of Example 5 are shown in Tables 16 to 18 below.

15

Table 16 - Contact angle test

	<u>Water</u>	<u>Hexadecane</u>
Measurement 1 °	140.20	105.20
Measurement 2 °	139.30	111.00
Measurement 3 °	145.50	108.60
Average contact angle °	141.66	108.26

Table 17 - Stain resistance test

	<u>5 mins</u>	<u>2 hrs</u>		<u>24hrs</u>		
	<u>Dry</u>	<u>Dry</u>	<u>Wet</u>	<u>Dry</u>	<u>Wet</u>	<u>Brush</u>
Olive oil	3	2	2	3	3	3
Black coffee	3	3	3	1	3	3
Black tea	3	3	3	3	4	4
Red wine	3	2	2	1	2	2
Coca-cola	5	5	5	3	4	4
Tomato ketchup	4	4	4	2	4	4
Total	21	19	19	13	20	20
<u>Overall score</u>	112					

5 Table 18 - Water pick-up test (Initial weight of block = 453.78g)

<u>Time of immersion</u>	<u>Weight including water absorbed</u>	<u>% Weight of water absorbed</u>
15 mins	454.27	0.11
2 hrs	454.59	0.18
24 hrs	455.60	0.40

It can be seen from Tables 6 and 18 that concrete treated with the composition of Example 5 had substantially lower water uptake than the concrete treated with the composition of the comparative example.

Example 6

- 10 A solution in n-butyl acetate of the fluorine-containing polymer prepared as described in Example 2 of WO-A-2004/108779 was added to a solution of a branched siloxane fluid polymer in n-butyl acetate to form a masonry treating composition containing 2.8% of the fluorine-containing polymer and 1.2% branched siloxane fluid polymer in n-butyl acetate. The branched siloxane fluid polymer is a mixed hydrolysate of
- 15 80% silanol-terminated PDMS, 9% methyltrimethoxysilane, 5% n-octyltriethoxysilane, 2% titanium tetrabutoxide and 4% cyclic PDMS.

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The above composition was applied to limestone at 283 g/m^2 by brushing and was allowed to dry for 2 days.

The treated limestone was tested for stain resistance as described in Example 1, except that stain resistance after 5 minutes was not measured and the final scrubbing with a brush was not carried out. The results are shown in Table 19 below.

Table 19

Stain	2 hr		24 hr	
	Dry	Wet	Dry	Wet
Olive Oil	5	5	5	5
Black Coffee	4	5	0	4
Black Tea	4	5	0	5
Red Wine	3	5	0	4
Coca Cola	5	5	1	4
Tomato ketchup	5	5	5	5
Totals	26	30	12	28

The contact angles of water and hexadecane on the treated limestone were 125.5° and 54.8° respectively.

The water uptake of the treated limestone was measured as described in Example 1. After 15 mins it was 0.08wt%, after 2 hrs it was 0.17wt% and after 24 hrs it was 0.24wt%.

Example 7

A masonry treating composition was prepared as described in Example 6 using t-butyl acetate as solvent in place of n-butyl acetate. The composition was applied to limestone at 278 g/m^2 and the treated limestone was tested as described in Example 6. The results are shown in Table 20 below.

Table 20

Stain	2 hr		24 hr	
	Dry	Wet	Dry	Wet
Olive Oil	5	5	5	5
Black Coffee	3	4	0	4
Black Tea	4	4	0	5
Red Wine	3	4	0	4
Coca Cola	5	5	3	5
Tomato ketchup	4	5	5	5
Totals	24	27	13	28

The contact angles of water and hexadecane on the treated limestone were 120.7° and 62.8° respectively.

- The water uptake of the treated limestone after 15 mins was 0.08wt%, after 2 hrs was 0.09wt% and after 24 hrs was 0.18wt%.

Example 8

- The solution of fluorine-containing polymer described in Example 6 was added to a solution of isobutyltrimethoxysilane in n-butyl acetate to form a masonry treating composition containing 3% of the fluorine-containing polymer and 2% isobutyltrimethoxysilane in n-butyl acetate. The composition was applied to limestone at 286 g/m² and the treated limestone was tested as described in Example 6. The results are shown in Table 21 below.

Table 21

Stain	2 hr		24 hr	
	Dry	Wet	Dry	Wet
Olive Oil	5	5	4	4
Black Coffee	4	5	0	4
Black Tea	4	5	0	5
Red Wine	2	2	0	3
Coca Cola	4	5	4	5
Tomato ketchup	3	3	3	3
Totals	22	25	11	24

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The contact angles of water and hexadecane on the treated limestone were 142.1° and 71.0° respectively.

The water uptake of the treated limestone after 15 mins was 0.58wt%, after 2 hrs was 4.22wt% and after 24 hrs was 4.36wt%.

5 Example 9

Example 8 was repeated using n-octyltriethoxysilane in place of the isobutyltrimethoxysilane. The stain test results are shown in Table 22 below.

Table 22

Stain	2 hr		24 hr	
	Dry	Wet	Dry	Wet
Olive Oil	5	5	5	5
Black Coffee	5	5	1	4
Black Tea	5	5	1	4
Red Wine	4	4	3	4
Coca Cola	5	5	3	4
Tomato ketchup	5	5	3	4
Totals	26	30	12	28

The contact angles of water and hexadecane on the treated limestone were

10 131.6° and 75.5° respectively.

The compositions of Examples 6, 8 and 9 were each applied to BS3712 concrete test pieces at about 300g/m² and after drying were tested for water uptake. The water uptake was:

Example 6 – 2.0% after 2 hours and 3.0% after 24 hours

15 Example 8 – 1.2% after 2 hours and 3.2% after 24 hours

Example 9 – 0.8% after 2 hours and 1.6% after 24 hours.

By comparison, the water uptake of concrete to which the solution in n-butyl acetate of the fluorine-containing polymer of Example 6 had been applied was 6.8% after 2 hours and 9.3% after 24 hours.

Example 10

Example 8 was repeated using a silanol-terminated polydimethylsiloxane of degree of polymerisation around 14 siloxane units in place of the isobutyltrimethoxysilane. The stain test results are shown in Table 23 below.

5 **Table 23**

Stain	2 hr		24 hr	
	Dry	Wet	Dry	Wet
Olive Oil	4	4	5	5
Black Coffee	4	4	0	4
Black Tea	4	5	2	4
Red Wine	3	4	4	4
Coca Cola	5	5	4	5
Tomato ketchup	4	5	4	5
Totals	24	27	19	27

The contact angles of water and hexadecane on the treated limestone were 137.2° and 65.5° respectively.

The water uptake of the treated limestone after 15 mins was 0.09wt%, after 2 hrs was 0.5wt% and after 24 hrs was 0.75wt%.

10 **Examples 11 to 27**

Using the fluorine-containing polymer of Example 1 and the general procedure of Example 1 with various solvents for the silicon compound and various additives, masonry treating compositions were prepared having the following formulations shown in Table 24, the amounts being given in parts by weight.

15 **Table 24**

	Ex.11	Ex.12	Ex.13	Ex.14	Ex.15	Ex.16	Ex.17	Ex.18	Ex.19
Fluoropolymer	1.55	1.55	1.58	1.56	1.53	1.58	1.55	1.55	1.58
n-octyl triethoxysilane	20.50	20.30	20.60	20.30	20.50	20.30			
Isobutyl triethoxysilane							20.50	20.35	20.65
Linear siloxane				1.02					

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Branched siloxane					1.02				
Butyl acetate	8.75	8.75	8.92	8.84	8.67	8.92	8.80	8.81	8.92
2-butanol	20.50	155.00	22.50	21.60	20.20	17.60	20.51	15.51	22.52
Chlorobenzo-trifluoride		5.10				2.40		5.11	
Surfactant			1.06						1.11

Table 24 (continued)

	Ex.20	Ex.21	Ex.22	Ex.23	Ex.24	Ex.25	Ex.26	Ex.27
Fluoropolymer	1.56	1.54	1.58	1.59	1.55	1.55	1.55	1.55
Isobutyltriethoxysilane	20.33	20.51	20.32					
n-octyltriethoxysilane				20.50	20.52	20.51	20.51	20.51
Linear siloxane	1.05							
Branched siloxane		1.03						
Butyl acetate	8.86	8.74	8.98	9.04	8.75	8.77	8.76	8.80
2-butanol	21.69	20.22	17.64					20.76
Isopropanol				20.50				
Pentanol					20.53			
1-butanol						20.55		
Hexanol							20.50	
Chlorobenzotrifluoride			2.44					
Titanium butoxide								0.51

The linear siloxane used in Examples 14 and 20 is a silanol-terminated polydimethylsiloxane of degree of polymerisation around 14 siloxane units.

- 5 The branched siloxane used in Examples 15 and 21 is a mixed hydrolysate of 80% silanol-terminated PDMS, 9% methyltrimethoxysilane, 5% n-octyltriethoxysilane, 2% titanium tetrabutoxide and 4% cyclic PDMS.

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The masonry treating compositions of Examples 11 to 27 were each applied to concrete and tested as described in Example 1. The results are summarised in Table 25 below.

- A comparison of the water pick-up values in Tables 6 and 25 shows the improvement in water resistance given by all the compositions of Examples 11 to 27.

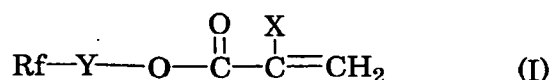
Table 25

<u>Ex. no</u>	<u>Stain resistance</u>						<u>Overall Score</u>	<u>Static contact angle</u>		<u>Water pick-up 24hrs Wt %</u>
	<u>5m Dry</u>	<u>2hr Dry</u>	<u>2hr Wet</u>	<u>24hrs Dry</u>	<u>24hrs Wet</u>	<u>24hrs Brush</u>		<u>Water °</u>	<u>Hexadecane °</u>	
11	22	20	20	16	19	21	118	127.3	58.5	0.19
12	21	20	20	18	21	22	122	119.1	61.1	1.19
13	20	19	19	17	20	19	114	75.43	34.86	0.41
14	17	18	18	11	11	11	86	126.95	70.9	0.29
15	22	18	18	15	17	19	109	126.05	83.63	0.19
16	21	19	20	15	18	19	112	125.7	90.4	0.22
17	22	20	21	17	21	21	122	122.68	86.68	0.24
18	25	22	22	17	22	23	131	127.59	61.13	0.33
19	20	18	21	16	16	20	111	120.8	64.62	0.27
20	25	21	21	18	20	20	125	134.67	79.4	0.26
21	19	18	17	14	20	20	108	132.92	89.74	0.21
22	23	23	23	18	23	23	133	137.05	83.97	0.24
23	22	20	20	13	20	20	115	112.5	77.96	0.25
24	22	20	20	16	19	20	117	133.54	91.15	0.27
25	20	19	20	16	20	20	115	124.87	87.14	0.2
26	20	19	20	14	19	20	112	138.97	98.72	0.17
27	22	22	22	15	18	18	117	136.44	91.95	0.21

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CLAIMS

1. A composition for masonry treatment, comprising a fluorine-containing polymer (A) comprising repeating units derived from a fluorine-containing monomer of the formula:



- wherein X is a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, a CFX¹ X² group in which X¹ and X² are each a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom or an iodine atom, a cyano group, a linear or branched fluoroalkyl group having 1 to 20 carbon atoms, a substituted or unsubstituted benzyl group, or a substituted or unsubstituted phenyl group;

- Y is an aliphatic group having 1 to 10 carbon atoms, an aromatic or cycloaliphatic group having 6 to 10 carbon atoms, a -CH₂ CH₂ N(R¹)SO₂ - group in which R¹ is an alkyl group having 1 to 4 carbon atoms, or a -CH₂ CH(OY¹)CH₂ - group in which Y¹ is a hydrogen atom or an acetyl group; and

- Rf is a linear or branched fluoroalkyl or fluoroalkenyl group having 1 to 21 carbon atoms, or a fluoroether group having a total of 1 to 200 repeating units selected from the repeating units -C₃F₆O-, -C₂F₄O- and -CF₂O- ;
characterised in that the composition also contains at least one silicon compound selected from silanes and siloxanes of the general formula R_nSiO_(4-n/2) wherein each R is a monovalent organic group, which can be the same or different.

2. A composition according to claim 1, wherein the Rf group in the fluorine-containing monomer (a) has 1 to 4 carbon atoms.

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3. A composition according to Claim 1 or Claim 2, wherein the fluorine-containing polymer (A) also contains repeating units derived from a monomer having a functional group reactive with active hydrogen.

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4. A composition according to Claim 3, wherein the said functional group is selected from a silane group, a phosphate or phosphoric acid group, a carboxylate or carboxylic acid group, a sulfonate or sulfonic acid group and a glucidyl group.
5. A composition according to any of Claims 1 to 4, wherein the fluorine-containing polymer (A) also contains repeating units derived from a monomer having a non reactive functional group.
6. A composition according to Claim 4, wherein the monomer having a non reactive functional group is an alkyl (meth)acrylate or contains a polyether group.
7. A composition according to any of Claims 1 to 6, characterized in that in the silicon compound each R denotes a hydrocarbon, substituted hydrocarbon, hydroxyl, hydrocarbonoxy or substituted hydrocarbonoxy group and a has an average value of from 0.25 to 4.
8. A composition according to any of Claims 1 to 7, characterized in that the silicon compound comprises a silane of the formula $R^2(R^3O)_3Si$ in which R^2 is a monovalent organic group and each R^3 represents an alkyl group having 1 to 6 carbon atoms.
9. A composition according to Claim 8, wherein R^2 represents an alkyl group having 1 to 18 carbon atoms optionally substituted by a hydroxyl, halogen, alkoxy or epoxy group.
10. A composition according to any of Claims 1 to 7, characterized in that the silicon compound comprises a siloxane of the general formula $R_aSiO_{(4-a/2)}$ wherein each R is a monovalent organic group, which can be the same or different, and a has an average value of from 0.5 to 2.4.

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11. A composition according to Claim 10, wherein each R represents a hydrocarbon, substituted hydrocarbon, hydroxyl, hydrocarbonoxy or substituted hydrocarbonoxy group.
12. A composition according to Claim 11, wherein at least one R represents an aminoalkyl or fluoroalkyl group.
13. A composition according to any of Claims 10 to 12, characterized in that the siloxane is a predominantly linear polydiorganosiloxane.
14. A composition according to Claim 13, characterised in that the predominantly linear polydiorganosiloxane contains T and Q branching.
15. A composition according to Claim 10, characterized in that the siloxane is a branched siloxane resin.
16. A composition according to any of Claims 1 to 15, characterized in that the composition additionally contains an organic wax, an antifreezing agent, a viscosity-adjusting agent, a surfactant, an antioxidant, a pH adjuster, a defoaming agent, an antiseptic agent and/or a flame retardant.
17. A composition according to any of Claims 1 to 16, characterized in that the fluorine-containing polymer (A) and the silicon compound are dispersed in an organic solvent.
18. A method of treating masonry to enhance its stain resistance and water resistance, which comprises applying a composition according to Claim 17 to the masonry and then eliminating the organic solvent.