



US 20030106161A1

(19) **United States**

(12) **Patent Application Publication**  
**Enomoto et al.**

(10) **Pub. No.: US 2003/0106161 A1**

(43) **Pub. Date: Jun. 12, 2003**

(54) **TREATMENT OF TEXTILE PRODUCT FOR IMPARTING WATER AND OIL REPELLENCY**

**Publication Classification**

(51) **Int. Cl.<sup>7</sup> ..... D06M 10/00**  
(52) **U.S. Cl. .... 8/115.51**

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(57) **ABSTRACT**

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A textile having sufficient water repellency, oil repellency and soil releasability before and after cleaning can be prepared by a method of preparing a treated textile has the steps of (1) preparing a treatment liquid containing a water- and oil-repellent agent and a stain blocking agent, (2) bringing the pH of the treatment liquid to at most 7, (3) applying the treatment liquid to the textile, (4) thermally treating the textile with steam, and (5) washing the textile with water and dehydrating the textile, wherein the water- and oil-repellent agent has a combination of (A) a fluorine-containing polymer comprising a repeat unit derived from vinyl chloride and/or vinylidene chloride, and (B) a fluorine-containing polymer free from a repeat unit derived from vinyl chloride and/or vinylidene chloride.

(21) Appl. No.: **10/181,897**

(22) PCT Filed: **Jan. 17, 2001**

(86) PCT No.: **PCT/JP01/00243**

(30) **Foreign Application Priority Data**

Jan. 25, 2000 (JP) ..... 2000-015769

## TREATMENT OF TEXTILE PRODUCT FOR IMPARTING WATER AND OIL REPELLENCY

### FIELD OF THE INVENTION

[0001] The present invention relates to a treatment for imparting water repellency, oil repellency, soil releasability and durability thereof to a textile. A method of the present invention is particularly useful for carpet.

### RELATED ART

[0002] Hitherto, various treatment methods have been proposed in order to impart water repellency, oil repellency and soil releasability to a textile such as a carpet. For example, a process of treating a textile comprising decreasing the pH of a treatment liquid, applying the treatment liquid to the textile, thermally treating the textile with steam, washing the textile with water, and dehydrating the textile (hereinafter, sometimes referred to as "Exhaust process") is proposed.

[0003] A method comprising the Exhaust process is proposed in U.S. Pat. Nos. 5,073,442, 5,520,962 and 5,516,337, and International Publication WO 98/50619.

[0004] U.S. Pat. No. 5,073,442 discloses a method of treating a textile, comprising conducting an Exhaust process by using a water- and oil-repellent agent comprising a fluorine-containing compound, a formaldehyde condensation product and an acrylic polymer. U.S. Pat. No. 5,520,962 discloses a method of treating a carpet, comprising conducting an Exhaust process by using a fluorine-containing compound and a polymeric binder. U.S. Pat. No. 5,516,337 discloses a method of treating a textile, comprising conducting an Exhaust process by using a fluorine-containing water- and oil-repellent agent and a metal compound such as aluminum sulfate. International Publication WO 98/50619 discloses a method of treating a carpet, comprising conducting an Exhaust process by using a fluorine-containing water- and oil-repellent agent and a salt such as a magnesium salt.

[0005] Sufficient water repellency, oil repellency and soil releasability cannot be obtained by conducting the Exhaust process in accordance with these methods.

### SUMMARY OF THE INVENTION

[0006] An object of the present invention is to give a textile excellent in water repellency, oil repellency, soil releasability and durability thereof, when an Exhaust process is conducted with using a water- and oil-repellent agent having a specified composition.

[0007] The present invention provides a method of treating a textile, comprising steps of:

- [0008] (1) preparing a treatment liquid comprising a water- and oil-repellent agent,
- [0009] (2) adjusting pH of the treatment liquid to at most 7, preferably at most 2,
- [0010] (3) applying the treatment liquid to the textile,
- [0011] (4) thermally treating the textile with steam, and
- [0012] (5) washing the textile with water and dehydrating the textile,

[0013] wherein the water- and oil-repellent agent comprises a combination of (A) a fluorine-containing polymer comprising a repeat unit derived from vinyl chloride and/or vinylidene chloride, and (B) a fluorine-containing polymer free from a repeat unit derived from vinyl chloride and/or vinylidene chloride.

[0014] The present invention also provides a textile prepared by the above-mentioned method.

### DETAILED DESCRIPTION OF THE INVENTION

[0015] The procedure used in the present invention is an Exhaust process which comprises decreasing the pH of the treatment liquid comprising the fluorine-containing polymer, applying the treatment liquid to the textile, washing the textile with water, and dehydrating the textile.

[0016] In the step (1) of the method of the present invention, the treatment liquid comprising the water- and oil-repellent agent, which is applied to the textile, is prepared. The treatment liquid comprising the water- and oil-repellent agent may be in the form of a solution or an emulsion, particularly an aqueous emulsion.

[0017] In the step (2) in the method of the present invention, the pH of the treatment liquid is brought to at most 7. The pH of the treatment liquid is preferably at most 3, more preferably at most 2. The pH can be decreased by addition of an acid, such as an aqueous solution of citric acid and an aqueous solution of sulfamic acid, to the treatment liquid.

[0018] In the step (3) of the method of the present invention, the treatment liquid is applied to the textile. The water- and oil-repellent agent can be applied to a substrate to be treated (that is, the textile) by a known procedure. The application of the treatment liquid can be conducted by immersion, spraying and coating. Usually, the treatment liquid is diluted with an organic solvent or water, and is adhered to surfaces of the substrate by a well-known procedure such as an immersion coating, a spray coating and a foam coating to a fabric (for example, a carpet cloth), a yarn (for example, a carpet yarn) or an original fiber. If necessary, the treatment liquid is applied together with a suitable crosslinking agent, followed by curing. It is also possible to add mothproofing agents, softeners, antimicrobial agents, flame retardants, antistatic agents, paint fixing agents, crease-proofing agents, etc. to the treatment liquid. The concentration of the water- and oil-repellent agent active component (that is, the fluorine-containing polymer) in the treatment liquid contacted with the substrate may be from 0.05 to 10% by weight. The stain blocking agent may be used in the concentration of, for example, 0 to 1,000 parts by weight, particularly 1 to 500 parts by weight, in terms of the solid content, based on 100 parts by weight of the fluorine-containing polymer.

[0019] In the step (4) of the method of the present invention, the textile is thermally treated. The thermal treatment can be conducted by applying a steam (for example, 90° C. to 110° C.) to the textile under a normal pressure for e.g., 10 seconds to 10 minutes.

[0020] In the step (5) of the method of the present invention, the textile is washed with water and dehydrated. The thermally treated textile is washed with water at least once. Then, in order to remove excess water, the textile is dehy-

drated by a usual dehydration procedure such as a centrifuging and vacuuming procedure.

[0021] After the step (5), the textile can be dried.

[0022] The water- and oil-repellent agent used in the present invention comprises two fluorine-containing polymers, that is, the fluorine-containing polymer (A) and the fluorine-containing polymer (B).

[0023] The fluorine-containing polymer (A) is the fluorine-containing polymer comprising a repeat unit derived from vinyl chloride and/or vinylidene chloride. The fluorine-containing polymer (B) is the fluorine-containing polymer free from a repeat unit derived from vinyl chloride and/or vinylidene chloride.

[0024] The fluorine-containing polymers (A) and (B) may be a polymer derived from a fluoroalkyl group-containing monomer such as a fluoroalkyl group-containing (meth)acrylate, a fluoroalkyl group-containing maleate or fumarate, and a fluoroalkyl group-containing urethane.

[0025] The fluorine-containing polymer (A) may be, for example, a polymer comprising:

[0026] (A-I) a repeat unit derived from a monomer having a fluoroalkyl group, and

[0027] (A-II) a repeat unit derived from vinyl chloride and/or vinylidene chloride. An example of the fluorine-containing polymer (A) is a copolymer comprising:

[0028] (A-I) a repeat unit derived from a monomer having a fluoroalkyl group,

[0029] (A-II) a repeat unit derived from vinyl chloride and/or vinylidene chloride,

[0030] (A-III) a repeat unit derived from a fluorine-free monomer, and

[0031] (A-IV) a repeat unit derived from a crosslinkable monomer.

[0032] The fluorine-containing polymer (B) may be, for example, a copolymer which comprises

[0033] (B-I) a repeat unit derived from a monomer having a fluoroalkyl group, and which does not comprise a repeat unit derived from vinyl chloride and/or vinylidene chloride. An example of the fluorine-containing polymer (B) is a copolymer which comprises:

[0034] (B-I) a repeat unit derived from a monomer having a fluoroalkyl group,

[0035] (B-II) a repeat unit derived from a fluorine-free monomer, and

[0036] (B-III) a repeat unit derived from a crosslinkable monomer, and which does not comprise a repeat unit derived from vinyl chloride and/or vinylidene chloride.

[0037] The repeat units (A-I) and (B-I) are preferably a repeat unit derived from a (meth)acrylate ester having a fluoroalkyl group.

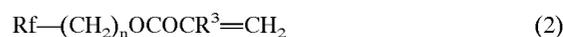
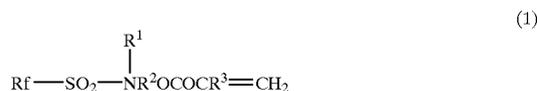
[0038] The fluoroalkyl group-containing (meth)acrylate ester may be of the formula:



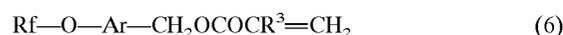
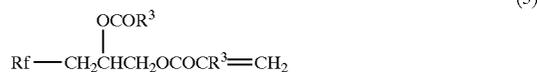
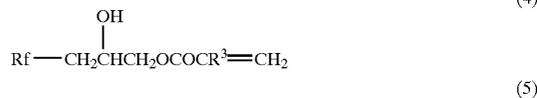
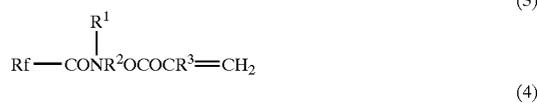
[0039] wherein Rf is a fluoroalkyl group having 3 to 21 carbon atoms, R<sup>1</sup> is a hydrogen atom or a methyl group, and A is a divalent organic group.

[0040] In the above formula, A may be a linear or branched alkylene group having 1 to 20 carbon atoms, a —SO<sub>2</sub>N(R<sup>21</sup>)R<sup>22</sup>— group or a —CH<sub>2</sub>CH(OR<sup>23</sup>)CH<sub>2</sub>— group (R<sup>21</sup> is an alkyl group having 1 to 10 carbon atoms, R<sup>22</sup> is a linear or branched alkylene group having 1 to 10 carbon atoms, and R<sup>23</sup> is a hydrogen atom or an acyl group having 1 to 10 carbon atoms).

[0041] Examples of the fluoroalkyl group-containing (meth)acrylate are as follows:

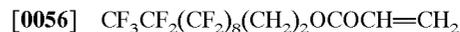
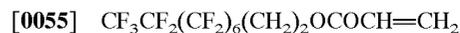
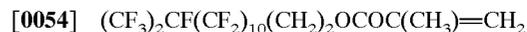
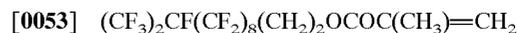
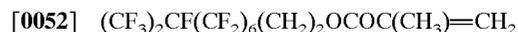
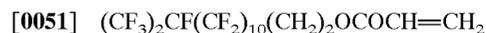
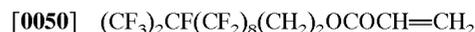
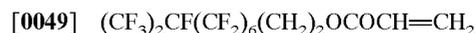
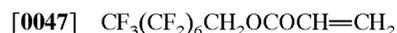


[0042]

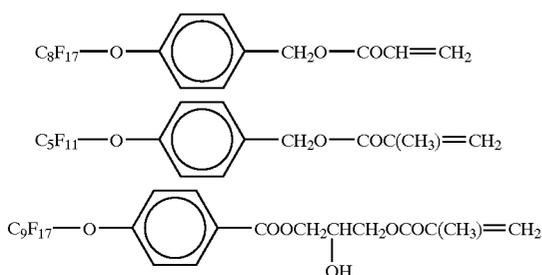


[0043] wherein Rf is a fluoroalkyl group having 3 to 21 carbon atoms, R<sup>1</sup> is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R<sup>2</sup> is an alkylene group having 1 to 10 carbon atoms, R<sup>3</sup> is a hydrogen atom or a methyl group, and Ar is arylene group optionally having a substituent, and n is an integer of 1 to 10.

[0044] Specific examples of the fluoroalkyl group-containing (meth)acrylate are as follows:



- [0057]  $\text{CF}_3\text{CF}_2(\text{CF}_2)_{10}(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$   
 [0058]  $\text{CF}_3\text{CF}_2(\text{CF}_2)_6(\text{CH}_2)_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$   
 [0059]  $\text{CF}_3\text{CF}_2(\text{CF}_2)_8(\text{CH}_2)_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$   
 [0060]  $\text{CF}_3\text{CF}_2(\text{CF}_2)_{10}(\text{CH}_2)_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$   
 [0061]  $\text{CF}_3(\text{CF}_2)_7\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$   
 [0062]  $\text{CF}_3(\text{CF}_2)_7\text{SO}_2\text{N}(\text{C}_2\text{H}_5)(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$   
 [0063]  $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_8\text{CH}_2\text{CH}(\text{OCOCH}_3)$   
 $\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$   
 [0064]  $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOCH}=\text{CH}_2$



[0065] The repeat units (A-III) and (B-II) are preferably derived from a fluorine-free vinyl monomer. Non-limiting examples of preferable monomer constituting the repeat units (A-III) and (B-II) include, for example, ethylene, vinyl acetate, acrylonitrile, styrene, alkyl (meth)acrylate, polyethyleneglycol (meth)acrylate, polypropyleneglycol (meth)acrylate, methoxypolyethyleneglycol (meth)acrylate, methoxypolypropyleneglycol (meth)acrylate, vinyl alkyl ether and isoprene.

[0066] The monomer constituting the repeat units (A-III) and (B-II) may be a (meth)acrylate ester having an alkyl group. The number of carbon atoms of the alkyl group may be from 1 to 30, for example, from 6 to 30, e.g., from 10 to 30. For example, the monomer constituting the repeat units (A-III) and (B-II) may be acrylates of the general formula:



[0067] wherein  $\text{A}^1$  is a hydrogen atom or a methyl group, and  $\text{A}^2$  is an alkyl group of  $\text{C}_n\text{H}_{2n+1}$  ( $n=1$  to 30). The copolymerization with this monomer can improve various properties such as water- and oil-repellency and soil releasability; cleaning durability, washing durability and abrasion resistance of said repellency and releasability; solubility in solvent; hardness; and feeling, according to necessity.

[0068] The crosslinkable monomer constituting the repeat units (A-IV) and (B-III) may be a fluorine-free vinyl monomer having at least two reactive groups. The crosslinkable monomer may be a compound having at least two carbon-carbon double bonds, or a compound having at least one carbon-carbon double bond and at least one reactive group.

[0069] Examples of the crosslinkable monomer include diacetoneacrylamide, (meth)acrylamide, N-methylolacrylamide, hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl

(meth)acrylate, butadiene, chloroprene and glycidyl (meth)acrylate, to which the crosslinkable monomer is not limited. The copolymerization with this monomer can improve various properties such as water- and oil-repellency and soil releasability; cleaning durability and washing durability of said repellency and releasability; solubility in solvent; hardness; and feeling, according to necessity.

[0070] The fluorine-containing polymer (A) and the fluorine-containing polymer (B) preferably has a weight average molecular weight of 2,000 to 1,000,000, for example, 10,000 to 200,000.

[0071] Preferably, the amount of the repeat unit (A-I) is from 40 to 89.9% by weight, more preferably from 50 to 79.5% by weight,

[0072] the amount of the repeat unit (A-II) is from 5 to 50% by weight, more preferably from 10 to 40% by weight,

[0073] the amount of the repeat unit (A-III) is from 5 to 54.9% by weight, more preferably from 10 to 40% by weight, and

[0074] the amount of the repeat unit (A-IV) is from 0.1 to 10% by weight, more preferably 0.5 to 5% by weight,

[0075] based on the fluorine-containing polymer (A).

[0076] Preferably, the amount of the repeat unit (B-I) is from 39 to 94.9% by weight, more preferably from 50 to 89.5% by weight,

[0077] the amount of the repeat unit (B-II) is from 5 to 60% by weight, more preferably from 10 to 40% by weight, and

[0078] the amount of the repeat unit (B-III) is from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight,

[0079] based on the fluorine-containing polymer (B).

[0080] A weight ratio of the fluorine-containing polymer (A) to fluorine-containing polymer (B) in this mixture may be from 1:99 to 99:1, for example, from 10:90 to 90:10, particularly from 70:30 to 90:10.

[0081] The fluorine-containing polymer (A) and (B) in the present invention can be produced by any polymerization method, and the conditions of the polymerization reaction can be arbitrary selected. The polymerization method includes, for example, solution polymerization and emulsion polymerization. Among them, emulsion polymerization is particularly preferred.

[0082] The method of producing the fluorine-containing polymer (A) is explained hereinafter.

[0083] In the solution polymerization, there can be used a method of dissolving a monomer (A-I), a monomer (A-III) and a crosslinking monomer (A-IV) in an organic solvent in the presence of a polymerization initiator, replacing the atmosphere by nitrogen, charging vinyl chloride and/or vinylidene chloride (A-II) and stirring the mixture with heating at the temperature within the range from 50° C. to 120° C. for 1 hour to 10 hours. Examples of the polymerization initiator include azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene

hydroperoxide, t-butyl peroxyphthalate and diisopropyl peroxydicarbonate. The polymerization initiator is used in the amount within the range from 0.01 to 5 parts by weight based on 100 parts by weight of the monomers.

[0084] The organic solvent is inert to the monomer and dissolves them, and examples thereof include pentane, hexane, heptane, octane, cyclohexane, benzene, toluene, xylene, petroleum ether, tetrahydrofuran, 1,4-dioxane, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, tetrachlorodifluoroethane and trichlorotrifluoroethane. The organic solvent may be used in the amount within the range from 50 to 1,000 parts by weight based on 100 parts by weight of the monomers (A-I) to (A-IV).

[0085] In the emulsion polymerization, there can be used a method of emulsifying a monomer (A-I), a monomer (A-III) and a crosslinking monomer (A-IV) in water in the presence of a polymerization initiator and an emulsifying agent, replacing the atmosphere by nitrogen, charging vinyl chloride and/or vinylidene chloride (A-II) and copolymerizing with stirring at the temperature within the range, for example, from 50° C. to 80° C. for 1 hour to 10 hours. As the polymerization initiator, for example, water-soluble initiators (e.g., benzoyl peroxide, lauroyl peroxide, L-butyl perbenzoate, 1-hydroxycyclohexyl hydroperoxide, 3-carboxypropionyl peroxide, acetyl peroxide, azobisisobutyramidine dihydrochloride, azobisisobutyronitrile, sodium peroxide, potassium persulfate and ammonium persulfate) and oil-soluble initiators (e.g., azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxyphthalate and diisopropyl peroxydicarbonate) are used. The polymerization initiator is used in the amount within the range from 0.01 to 5 parts by weight based on 100 parts by weight of the monomers.

[0086] In order to obtain a copolymer dispersion in water, which is superior in storage stability, it is desirable that the monomers are atomized in water by using an emulsifying device capable of applying a strong shattering energy (e.g., a high-pressure homogenizer and an ultrasonic homogenizer) and then polymerized with using the oil-soluble polymerization initiator. As the emulsifying agent, various emulsifying agents such as an anionic emulsifying agent, a cationic emulsifying agent and a nonionic emulsifying agent can be used in the amount within the range from 0.5 to 10 parts by weight based on 100 parts by weight of the monomers. When the monomers (A-I) to (A-IV) are not completely compatibilized, a compatibilizing agent capable of sufficiently compatibilizing them (e.g., a water-soluble organic solvent and a low-molecular weight monomer) is preferably added to these monomers. By the addition of the compatibilizing agent, the emulsifiability and copolymerizability can be improved.

[0087] Examples of the water-soluble organic solvent include acetone, methyl ethyl ketone, ethyl acetate, propylene glycol, dipropylene glycol monomethyl ether, dipropylene glycol, tripropylene glycol and ethanol. The water-soluble organic solvent may be used in the amount within the range from 1 to 50 parts by weight, e.g., from 10 to 40 parts by weight, based on 100 parts by weight of water.

[0088] The fluorine-containing polymer (B) can be prepared in the same manner as in the fluorine-containing polymer (A), except that vinyl chloride or vinylidene chloride is not used.

[0089] A liquid containing the fluorine-containing polymer (A) and a liquid containing the fluorine-containing polymer (B), which are separately prepared, are mixed and optionally a medium (for example, water or an organic solvent) is added to give the water- and oil-repellent agent.

[0090] The substrate to be treated in the present invention is preferably a textile, particularly a carpet. The textile includes various examples. Examples of the textile include animal- or vegetable-origin natural fibers such as cotton, hemp, wool and silk; synthetic fibers such as polyamide, polyester, polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride and polypropylene; semisynthetic fibers such as rayon and acetate; inorganic fibers such as glass fiber, carbon fiber and asbestos fiber; and a mixture of these fibers. The present invention can be suitably used in carpets made of nylon fibers, polypropylene fibers and/or polyester fibers, because the present invention provides excellent resistance to a detergent solution and brushing (mechanical).

[0091] The textile may be in any form such as a fiber and a fabric. When the carpet is treated with the water- and oil-repellent agent, the carpet may be formed after the fibers or yarns are treated with the water- and oil-repellent agent, or the formed carpet may be treated with the water- and oil-repellent agent. Examples of the substrate to be treated include glass, paper, wood, leather, fur, asbestos, brick, cement, metal and oxide, ceramics, plastic, coated surface and plaster, in addition to the textile.

## EXAMPLES

[0092] The following Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof. The water repellency, oil repellency, soil releasability and fluorine adhesion amount of the carpets obtained in the Examples and Comparative Example were evaluated.

[0093] Test procedures of the water repellency, the oil repellency, the soil releasability, fluorine adhesion amount and cleaning are as follows.

### [0094] (1) Water repellency

[0095] A droplet of a isopropyl alcohol (IPA)/water mixture liquid shown in Table 1 is softly positioned on a carpet surface, and a maximum content of IPA (% by volume) in the liquid which maintains the droplet shape is taken as the result of the water repellency.

[0096] Specific procedure is as follows.

[0097] A carpet treated for giving repellency is stored in a thermo-hygrostat having a temperature of 21° C. and a humidity of 65% for at least 4 hours. A test liquid (having the composition shown in Table 1) which has been also stored at 21° C. is used. The temperature of a measurement room is controlled to be 21° C. Droplets of the test liquid in an amount of 50  $\mu$ L are softly dropped by a micropipette on the carpet and the diameter of the droplets is 5 mm. The micropipette is vertically stood and droplets are softly dropped. Five droplets are positioned. If 4 or 5 droplets remain on the carpet after standing for 10 seconds, it is

evaluated that the test liquid passes the test. The maximum content of IPA (% by volume) in the test liquid which passes the test is taken as the result of the water repellency.

TABLE 1

Mixing composition (% by volume)	
Isopropyl alcohol	Water
100	0
90	10
80	20
70	30
60	40
50	50
40	60
30	70
25	75
20	80
15	85
10	90
5	95
2	98
0	100

[0098] (2) Oil repellency

[0099] According to AATCC-TM-118-1992, five droplets of the test solution shown in Table 2 are positioned on a carpet and the penetration state after 30 seconds is observed. A maximum point corresponding to the test solution, four droplets of which exhibit no penetration, is taken as the oil repellency.

TABLE 2

Point	Test solution	Surface tension (mN/m, 25° C.)
0	Inferior to 1	—
1	Nujol	31.2
2	Mixture liquid of n-Hexadecane (35 wt. parts)/ nujol (65 wt. parts)	29.6
3	n-Hexadecane	27.3
4	n-Tetradecane	26.7
5	n-Dodecane	25.0
6	n-Decane	23.5

[0100] (3) Soil releasability (Stain proof property)

[0101] A carpet sample piece (size: 18.2 cm in a direction of tufting, and 8.9 cm in a direction perpendicular to a tufting direction) treated with a water- and oil-repellent agent and a blank carpet piece (size: 18.2 cm in direction of tufting, and 8.9 cm in a direction perpendicular to tufting direction) are kept to stand for at least 4 hours in an atmosphere of 21° C. and 65% RH. Before the soil releasability test, L\*, a\* and b\* of the carpet pieces are measured at five spots. Two carpet pieces are adhered with a double-sided tape to an internal surface of a pot of a ball mill. 10 g of dry soil (artificial soil having the composition shown in Table 3, dried in a desiccator for at least 48 hours) is charged in the pot and then a lid is put on the pot. The pot is slightly shaken so that the dry soil is positioned almost uniformly on the carpet test piece. The lid of the pot is taken off, the carpet samples are removed, and then 50 ceramic balls (according

to AATCC Test Method 123-1989) are charged into the pot, and the lid is firmly put on the pot. In the ball mill apparatus, the pot is rotated at 80 rpm for 7 minutes and 30 seconds. The lid of the pot is taken off, the carpet samples are removed, and then the double-sided tapes are peeled off. Excess dry soil on a front surface of the carpet test piece is removed by a vacuum cleaner. The vacuum cleaner is applied to the front surface in each direction (longitudinal and transverse directions) for back and forth five times. Finally, the vacuum cleaner is applied also to the back surface for back and forth once. L\*, a\* and b\* of each carpet piece without excess dry soil are measured at five spots by a color difference meter (CR-310 manufactured by MINOLTA Co., Ltd., having a circular detection part having the diameter of 50 mm).

[0102] A color difference ( $\Delta E^*ab$ ) of the carpet surface is calculated according to the following equation from L\*, a\* and b\* before soil releasability test and L\*, a\* and b\* after soil releasability test. Since the measurement for each carpet sample is conducted at five spots, the calculation is conducted by using a value at the same spot.

$$\Delta E^*ab = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

[0103]  $\Delta L^*$ : difference of L\* before and after soil releasability test

[0104]  $\Delta a^*$ : difference of a\* before and after soil releasability test

[0105]  $\Delta b^*$ : difference of b\* before and after soil releasability test

[0106] An average of  $\Delta E^*ab$  is determined for each carpet test sample, and this average is taken as  $\Delta E$ , which is a result of soil releasability.

TABLE 3

Components of artificial soil	Amount (wt %)
Peat moss (dark)	38.4
Portland cement	18
Kaolin clay	18
Silica (200 mesh)	18
Carbon black	1.05
Red iron oxide	0.30
Mineral oil	6.25

[0107] (4) Adhesion amount of fluorine

[0108] The content of fluorine (ppm) present on a carpet fiber after the Exhaust treatment is measured by an oxygen combustion method.

[0109] (5) Cleaning

[0110] A carpet fabric treated with a water- and oil-repellent agent is cleaned according to AATCC-TM-171-1995. The detail of the cleaning procedure is as follows. A carpet piece having a size of 8.9 cm×18.2 cm is fixed on a test pedestal. A steam cleaner (having functions of suction and warm water injection) is applied to the carpet surface from back and forth once, with suction and spraying of 60° C. water, and then applied to the carpet surface from back and forth once, with suction alone. The above procedure is defined as once of the cleaning. After a given number of times of the cleaning is conducted, the carpet is dried at 105° C. for 15 minutes in hot-air dryer to complete the cleaning.

[0111] The water repellency, the oil repellency, the soil releasability and the fluorine adhesion amount are measured before and after the cleaning.

[0112] The carpet of the present invention preferably has the water repellency of at least 90 and the oil repellency of at least 5 before the cleaning, and the water repellency of at least 40 and the oil repellency of at least 2 after 10 times of the cleaning.

#### Preparative Example 1

##### Preparation of (a) a Fluorine-containing Water- and Oil-repellent Agent Containing Vinyl Chloride

[0113]  $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_2(\text{CF}_2\text{CF}_2)_n\text{CF}_2\text{CF}_3$  (a mixture of compounds wherein n is 3, 4 and 5 in a weight ratio of 5:3:1) (FA), stearyl acrylate (StA), N-methylolacrylamide (N-MAM), 3-chloro-2-hydroxypropyl methacrylate (TOPOLEN M), deionized water, n-laurylmercaptan (LSH, a chain transfer agent), octadecyltrimethyl ammonium chloride (CATION 2ABT, a cationic emulsifier), polyoxyethylenealkylphenyl ether (EMULGEN 985, a nonionic emulsifier), polyoxyethylene-alkylphenyl ether (NONION HS-208, a nonionic emulsifier), sorbitan monopalmitate (NONION PP-40R, a nonionic emulsifier) and dipropylene glycol monomethyl ether (DPM) were mixed in the amounts shown in Table 4 to give a mixture liquid.

[0114] This mixture liquid was heated at 60° C. and emulsified by a high pressure homogenizer. The resultant emulsion was charged into a 1 L autoclave and subjected to a nitrogen gas replacement to remove a dissolved oxygen. Vinyl chloride having a purity of 99% (VCl) was charged in the amount shown in Table 4 and then an initiator, azobisisamide dipropane (V-50) was charged in the amount shown in Table 4. With stirring, the copolymerization reaction was conducted for 60° C. at 8 hours to give a vinyl chloride-containing copolymer emulsion, which was diluted with water to give an emulsion having a solid content of 30% by weight.

#### Preparative Example 2

##### Preparation of (b) a Fluorine-containing Water- and Oil-repellent Agent Free of Vinyl Chloride

[0115]  $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_2(\text{CF}_2\text{CF}_2)_n\text{CF}_2\text{CF}_3$  (a mixture of compounds wherein n is 3, 4 and 5 in a weight ratio of 5:3:1) (FA), stearyl acrylate (StA), 2-hydroxyethyl methacrylate (2ERA), glycidyl methacrylate (BLENMER G), N-methylolacrylamide (N-MAM), 3-chloro-2-hydroxypropyl methacrylate (TOPOLEN M), deionized water, n-laurylmercaptan (LSH), polyoxyethylene-alkylphenyl ether sulfate ammonium (HITENOL N-17, an anionic emulsifier), polyoxyethylenealkylphenyl ether (NONION HS-220, a nonionic emulsifier), sorbitan monolaurate (LP-20R, a nonionic emulsifier) and dipropylene glycol monomethylether (DPM) were mixed in the amounts shown in Table 4 to give a mixture liquid.

[0116] This mixture liquid was heated at 60° C. and emulsified by a high pressure homogenizer. The resultant emulsion was charged into a 1 L autoclave and subjected to a nitrogen gas replacement to remove a dissolved oxygen. Then, an initiator, ammonium persulfate (APS) was charged in the amount shown in Table 4. With stirring, the copoly-

merization reaction was conducted for 60° C. at 8 hours to give a fluorine-containing copolymer emulsion, which was diluted with water to give an emulsion having a solid content of 30% by weight.

TABLE 3

	Composition ratio of charged monomers (weight (g))	
	Pre. Ex. 1	Pre. Ex. 2
SFA	90.4	79.2
STA	6.0	19.1
VCl (vinyl chloride)	14.7	—
2EHA	—	19.1
BLENMER G	—	2.6
N-MAM	2.4	3.0
TOPOLEN M	0.6	1.3
LSH	0.8	0.24
Ammonium persulfate	—	0.56
azobisisamide dipropane	0.76	—
NONION PP-40R	1.92	—
NONION HS-208	4.20	—
NONION HS-220	—	1.72
LP-20R	—	2.16
EMULGEN 985	1.92	—
CTION 2ABT	2.0	—
HITENOL N-17	—	5.20
Pure water	236	244

#### Example 1

[0117] 0.9 Grams of a mixture liquid of the fluorine-containing water- and oil-repellent agent (a) (which is a fluorine-containing water- and oil-repellent agent containing vinyl chloride) produced in Preparative Example 1 and the fluorine-containing water- and oil-repellent agent (b) (which is a water- and oil-repellent agent free of vinyl chloride) produced in Preparative Example 2 (the mixing weight ratio of 8 to 2 in terms of solid) and 5 g of a stain blocking agent FX-657 (manufactured by 3M) were diluted with water to 1,000 g to give a mixture liquid. The solid weight ratio of the water- and oil-repellent agent and the stain blocking agent was 1:5.6. The pH of the mixture liquid was adjusted to 1.5 by adding a 10% aqueous solution of sulfamic acid to give a treatment liquid.

[0118] A carpet (8.9 cm×18.2 cm, nylon 6,6, cut piled, density: 36 oz/yd<sup>2</sup>) was immersed in the treatment liquid for 30 seconds. Then, the carpet was squeezed to give the WPU (wet pick up) of 300%. Then, a normal pressure steamer treatment (the temperature of 100° C. to 107° C.) was conducted for 90 seconds under the state that a pile surface of the carpet is upward. Then, the carpet was lightly rinsed with 2 L of water, and centrifugally dehydrated to give the WPU of about 25%. Finally, the carpet was thermally cured at 110° C. for ten minutes. Then, this carpet was cleaned (five times or ten times). The water repellency, the oil repellency, the soil releasability and the fluorine adhesion amount were evaluated before and after the cleaning. The results are shown in Tables A to D.

#### Comparative Example 1

[0119] 0.8 Grams of the fluorine-containing water- and oil repellent agent (a) and 5 g of the stain blocking agent FX-657 (manufactured by 3M) were diluted with water to 1,000 g to give a mixture liquid. The solid weight ratio of the

water- and oil-repellent agent and the stain blocking agent was 1:6.3. The pH of the mixture liquid was adjusted to 1.5 by adding a 10% aqueous solution of sulfamic acid. Then, the treatment and evaluation were conducted in the same manner as in Example 1. The results are shown in Tables A to D.

#### Comparative Example 2

[0120] 1.0 Grams of the fluorine-containing water- and oil repellent agent (b) and 5 g of the stain blocking agent FX-657 (manufactured by 3M) were diluted with water to 1,000 g to give a mixture liquid. The solid weight ratio of the water- and oil-repellent agent and the stain blocking agent was 1:5. The pH of the mixture liquid was adjusted to 1.5 by adding a 10% aqueous solution of sulfamic acid. Then, the treatment and evaluation were conducted in the same manner as in Example 1. The results are shown in Tables A to D.

#### Comparative Example 3

[0121] 5.7 Grams of a commercially available emulsion repellent agent (solid concentration: 21% by weight) [a mixture of a fluorine-containing oil repellent agent containing chlorine (6% by weight) and a stain blocking agent (a phenol-formaldehyde condensation product) (15% by weight)] was diluted with water to 1,000 g to give a mixture liquid. The pH of the mixture liquid was adjusted to 1.5 by adding a 10% aqueous solution of sulfamic acid. Then, the treatment and evaluation were conducted in the same manner as in Comparative Example 1. The results are shown in Tables A to D.

#### Comparative Example 4

[0122] 5.7 Grams of a commercially available emulsion repellent agent (solid concentration: 21% by weight) [a mixture of a fluorine-containing oil repellent agent containing chlorine (6% by weight) and a stain blocking agent (a phenol-formaldehyde condensation product) (15% by weight)] and 12.5 g of MgSO<sub>4</sub> were diluted with water to 1,000 g to give a mixture liquid. The pH of the mixture liquid was adjusted to 1.5 by adding a 10% aqueous solution of sulfamic acid. Then, the treatment and evaluation were conducted in the same manner as in Comparative Example 1. The results are shown in Tables A to D.

TABLE A

Results of water repellency evaluation					
Number of times of cleaning	Com. Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4
0	90	80	100	X	40
5	90	70	90	X	30
10	40	40	40	X	30

Note)

X: cannot pass a test liquid (IPA:water = 0:100 (vol %))

[0123]

TABLE B

Results of oil repellency evaluation					
Number of times of cleaning	Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4
0	5	3	6	0	5
5	4	2	6	0	4
10	2	0	4	0	4

[0124]

TABLE C

Results of soil releasability (delta E value)					
Number of times of cleaning	Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4
0	16.5	16.5	19.8	24.9	18.9
5	18.0	16.7	21.7	25.7	19.6
10	19.5	19.6	22.8	25.1	21.1

Delta E value of untreated carpet is 25.6 at the number of cleaning times of 0.

[0125]

TABLE D

Results of fluorine adhesion amount measurement (ppm)					
Number of times of cleaning	Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4
0	292	273	300	10	259
5	285	262	300	9	225
10	235	173	279	8	216

1. A method of preparing a treated textile, comprising steps of:

- (1) preparing a treatment liquid comprising a water- and oil-repellent agent,
- (2) adjusting pH of the treatment liquid to at most 7, preferably at most 2,
- (3) applying the treatment liquid to the textile,
- (4) thermally treating the textile with steam, and
- (5) washing the textile with water and dehydrating the textile,

wherein the water- and oil-repellent agent comprises a combination of (A) a fluorine-containing polymer comprising a repeat unit derived from vinyl chloride and/or vinylidene chloride, and (B) a fluorine-containing polymer free from a repeat unit derived from vinyl chloride and/or vinylidene chloride.

2. The method according to claim 1, wherein the fluorine-containing polymer (A) comprises:

- (A-I) a repeat unit derived from a monomer having a fluoroalkyl group, and
- (A-II) a repeat unit derived from vinyl chloride and/or vinylidene chloride.

3. The method according to claim 1, wherein the fluorine-containing polymer (A) comprises:

- (A-I) a repeat unit derived from a monomer having a fluoroalkyl group,
- (A-II) a repeat unit derived from vinyl chloride and/or vinylidene chloride,
- (A-III) a repeat unit derived from a fluorine-free monomer, and
- (A-IV) a repeat unit derived from a crosslinkable monomer.

4. The method according to claim 1, wherein the fluorine-containing polymer (B) comprises

- (B-I) a repeat unit derived from a monomer having a fluoroalkyl group, and does not comprise a repeat unit derived from vinyl chloride and/or vinylidene chloride.

5. The method according to claim 1, wherein the fluorine-containing polymer (B) comprises:

- (B-I) a repeat unit derived from a monomer having a fluoroalkyl group,
- (B-II) a repeat unit derived from a fluorine-free monomer, and
- (B-III) a repeat unit derived from a crosslinkable monomer, and does not comprise a repeat unit derived from vinyl chloride and/or vinylidene chloride.

6. A textile obtainable by the method according to claim 1.

7. A carpet obtainable by the method according to claim 1.

8. The carpet according to claim 7, wherein the carpet comprises a nylon fiber, a propylene fiber and/or a polyester fiber.

9. The carpet according to claim 7, which has the water repellency of at least 90 and the oil repellency of at least 5

before the cleaning, and the water repellency of at least 40 and the oil repellency of at least 2 after 10 times of the cleaning,

wherein the numerical value of the water repellency is a maximum content of IPA (% by volume) in a test solution resulting from the test that five droplets of an isopropyl alcohol (IPA)/water mixture test solution are softly positioned on a carpet surface, the penetration state of the droplets after 10 seconds are observed and at least four droplets do not exhibit the penetration, and

the numerical value of the oil repellency is a maximum value of oil repellency according to AATCC-TM-118-1992 resulting from the test that five droplets of a test solution are softly positioned on a carpet surface, the penetration state of the droplets after 30 seconds are observed and at least four droplets do not exhibit the penetration.

10. A water- and oil-repellent agent used in a method of preparing a treated textile, comprising steps of:

- (1) preparing a treatment liquid comprising a water- and oil-repellent agent,
- (2) adjusting pH of the treatment liquid to at most 7, preferably at most 2,
- (3) applying the treatment liquid to the textile,
- (4) thermally treating the textile, and
- (5) washing the textile with water and dehydrating the textile,

wherein the water- and oil-repellent agent comprises a combination of (A) a fluorine-containing polymer comprising a repeat unit derived from vinyl chloride and/or vinylidene chloride, and (B) a fluorine-containing polymer free from a repeat unit derived from vinyl chloride and/or vinylidene chloride.

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