



(11) **EP 1 753 906 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Claims EN 2

(48) Corrigendum issued on:
04.01.2012 Bulletin 2012/01

(45) Date of publication and mention
of the grant of the patent:
25.05.2011 Bulletin 2011/21

(21) Application number: **05724326.3**

(22) Date of filing: **02.03.2005**

(51) Int Cl.:
D06M 15/277 (2006.01) D06M 15/576 (2006.01)

(86) International application number:
PCT/US2005/006756

(87) International publication number:
WO 2005/103362 (03.11.2005 Gazette 2005/44)

(54) **TEXTILE TREATMENTS USING FLUOROPOLYMER-BRANCHED SILICONE POLYETHERS**

TEXTILBEHANDLUNGEN UNTER VERWENDUNG VON FLUORPOLYMERVERZWEIGTEN
SILICONPOLYETHERN

TRAITEMENTS DE TEXTILES AU MOYEN DE POLYETHERS DE SILICONE RAMIFIE-
FLUOROPOLYMERE

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

(30) Priority: **12.04.2004 US 561622 P**

(43) Date of publication of application:
21.02.2007 Bulletin 2007/08

(73) Proprietor: **Dow Corning Corporation**
Midland, MI 48686-0994 (US)

(72) Inventor: **VAZQUEZ, Fernando**
Greensboro, NC 27410 (US)

(74) Representative: **Polypatent**
Postfach 40 02 43
51410 Bergisch Gladbach (DE)

(56) References cited:
EP-A- 0 312 949 WO-A-03/078504
US-A- 4 283 519 US-A- 4 631 208
US-A- 4 781 844

EP 1 753 906 B9

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

DescriptionCross reference to related applications

5 **[0001]** Not applicable.

Field of the invention

10 **[0002]** This invention relates to the treatment of textiles by a fluoropolymer - branched silicone polyether composition. The fluoropolymer - branched silicone polyether compositions are prepared by combining a fluoropolymer and a branched silicone polyether. The resulting compositions improve the hand or feel of the fabric without significantly diminishing oil repellency nor stain release properties associated with fluoropolymers. The branched silicone polyethers can be used alone to improve the feel of fabrics, without diminishing the hydrophilicity of the fabric.

15 Background of the invention

[0003] Silicones are used as textile treatments to impart a variety of properties, but in particular are used for improving the feel or hand of treated fabrics. For example, reference may be had to US Patent 4,781,844 (November 1, 1988), US Patent 4,978,462 (December 18, 1960), and US 6,171,515 (January 9, 2001), for a description of the general state of the art. The '515 patent in particular provides a detailed overview on the use of various silicones in the textile industry.

[0004] Fluorocarbons are extensively used in the textile industry to impart water and oil repellency to fabrics. They are also used to provide stain release properties. However, one of the major drawbacks of fluorocarbon treatments is the harsh feel imparted to the fabric surface. The increasing use of fluoropolymers in apparel fabrics and garments demands a higher level of softness.

25 **[0005]** There have been several attempts to combine various fluorocarbons and silicones into a single textile treatment to offer the combined benefits of each. However, such attempts have usually resulted in comprising one or more fabric attributes. For example, the addition of a silicone to a fluorocarbon treatment composition may improve the hand of the fabric, but the oil repellency of the combined treatment is often much worse when compared to the fluorocarbon treated fabrics. Thus, there is a need to identify fluorocarbon based textile treating compositions that maintain the attributes associated with fluorocarbon treatments, but improve the deficiencies, such as poor hand.

30 **[0006]** The present inventor has discovered certain silicones, namely branched silicone polyethers, when combined with fluoropolymers, provide textile treatments that provide the positive attributes of fluoropolymers, while providing improved hand of the treated fabrics.

35 Summary of the invention

[0007] The present invention provides a composition comprising;

- 40 A) a fluoropolymer, and
B) a branched silicone polyether.

[0008] The invention further relates to a method of treating fibers or textiles comprising;

- 45 I) combining
A) a fluoropolymer,
B) a branched silicone polyether, and
II) applying the product of step I on fibers or textiles.

50 Detailed description of the invention

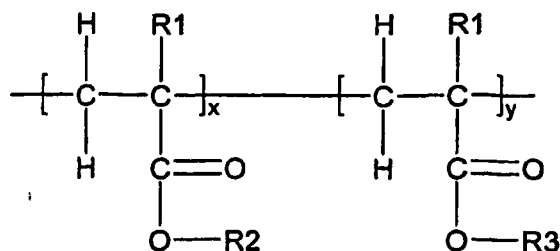
[0009] The present invention provides a composition comprising;

- 55 A) a fluoropolymer, and
B) a branched silicone polyether.

[0010] Component A) is a fluoropolymer. The fluoropolymer can be any fluorocarbon polymer, either used neat, or

alternatively in an emulsion form, that is known in the art for treating fibers, fabrics, or textiles. Typically, the fluoropolymer is selected from a fluoroalkyl acrylate copolymer, a fluorinated polyurethane, an emulsion of a fluoroalkyl acrylate copolymer, or an emulsion of a fluorinated polyurethane.

[0011] A fluoroalkyl acrylate copolymer is illustrated by the formula shown below.



In the above structure, R1 is hydrogen or an alkyl group such as methyl; R2 represents a fluorocarbon group such as $-(\text{CH}_2)_m(\text{CF}_2)_n\text{CF}_3$; R3 represents an alkyl group such as $-(\text{CH}_2)_n\text{CH}_3$; m is 0-5; n is 2-19; and x and y have values dependent upon the desired chain length.

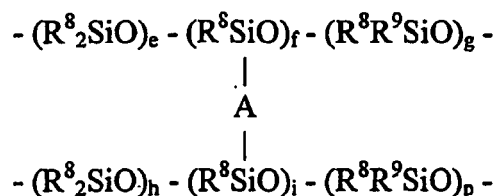
[0012] Emulsions containing fluoroalkyl acrylate copolymers are commercially available from companies such as Daikin Industries Ltd., Osaka, Japan, under their trademark Noveon Inc., Charlotte, North Carolina, under the trade mark UNIDYNE™ such as UNIDYNE™ TG-532 and UNIDYNE™ TG-992; and Ciba Specialty Chemicals Corp, High Point, North Carolina under their trademark ZONYL® such as ZONYL® CO. Emulsions containing fluorinated polyurethanes are commercially available from companies such as E.I. DuPont de Nemours, Wilmington, Delaware, under their trademark ZONYL® such as Zonyl® 7910.

[0013] Component B) is a branched silicone polyether. As used herein, a "branched silicone polyether", (abbreviated herein as BSPE) is a cross-linked organopolysiloxane polymer having at least one polyoxyalkylene group. This class of compounds has been generally described by Bahr et.al. in U.S. Patent Nos. 4,853,474 and 5,136,068, to teach cross-linked organopolysiloxane polymers suitable as Component B). Compounds suitable as component B) include organopolysiloxane-polyoxyalkylene polymer molecules which are intentionally cross-linked through a cross-linking agent joined thereto by nonhydrolyzable bonds and being free of internal hydrolyzable bonds.

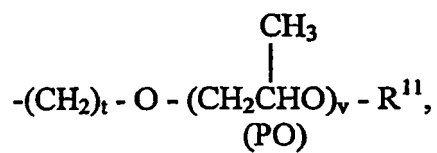
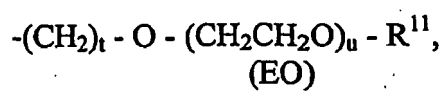
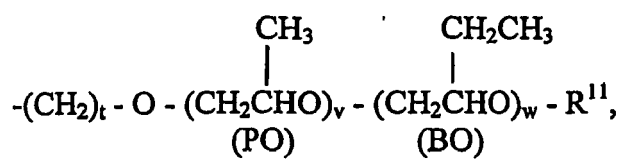
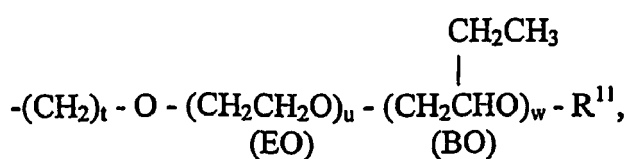
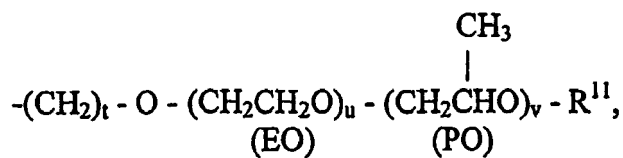
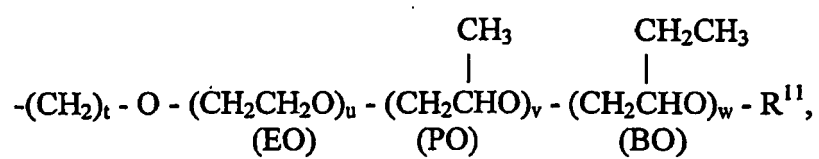
[0014] Component B) may be obtained by a method comprising preparing a cross-linked organopolysiloxane polymer and combining a polyoxyalkylene group therewith or by a method comprising preparing a linear polyorganosiloxane having a polyoxyalkylene group combined therewith and cross-linking the same.

[0015] The cross-linking in this system can be attained through a variety of mechanisms. Those skilled in the art will readily recognize the systems wherein the required components are mutually compatible to carry out the method of preparing component B). By way of illustration, an extensive bibliography of siloxane polymer chemistry is provided in Siloxane Polymers, S.J. Clarson and J.A. Semlyen eds., PTR Prentice Hall, Englewood Cliffs, N.J., (1993).

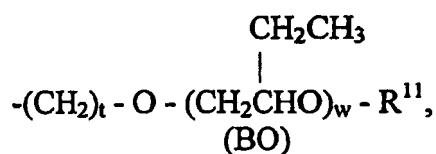
[0016] In the present invention, typically component B) is a compound having a viscosity of 100 to 100,000 mm²/s at 25°C and having the unit formula:



wherein R⁸ is a monovalent hydrocarbon group, A is a group having its formula selected from $(\text{CH}_2)_q-(\text{R}^{10}_2\text{SiO})_r\text{Si}(\text{CH}_2)_s$ or $\text{O}(\text{R}^{10}_2\text{SiO})_r\text{SiO}$ wherein R¹⁰ denotes a monovalent hydrocarbon group, q has a value of 2 to 10, r has a value of 1 to 5000, s has a value of 2 to 10, R⁹ denotes a group having its formula selected from the group consisting of:



and



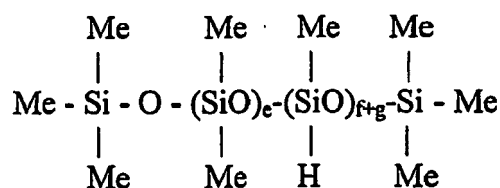
wherein R¹¹ is selected from a hydrogen atom, an alkyl group, an aryl group, or an acyl group, t has a value of 0 to 6, u has a value of from greater than zero to 150, v has a value of from greater than zero to 150, and w has a value of from greater than zero to 150, e has a value of 1 to 1000, f has a value of from greater than zero to 30, g has a value of 1 to 1000, h has a value of 1 to 1000, i has a value of from greater than zero to 30, p has a value of 1 to 1000. In the formula hereinabove EO, PO, and BO denote ethylene oxide, propylene oxide, and butylene oxide groups, respectively. The groups R⁸ and R¹⁰ can be the same or different as desired and are preferably alkyl groups or aryl groups and it is highly preferred that they are both methyl.

[0017] In the formulae hereinabove, e has a value of 1 to 500 or alternatively a value of 1 to 250, f has a value of from greater than zero to 20, or alternatively from 1 to 15, g has a value of 1 to 100 or alternatively 1 to 50, h has a value of 1 to 500 or alternatively 1 to 250, i has a value of from greater than zero to 20 or alternatively 1 to 15, p has a value of 1 to 100, or alternatively 1 to 50, q has a value of 2 to 6, r has a value of 1 to 2500, or alternatively 20 to 1000, s has a value of 2 to 6, t has a value of 0 to 3, u has a value of from 1 to 100 or alternatively 5 to 50, v has a value of from 1 to 100 or alternatively 5 to 50, w has a value of from 1 to 100 or alternatively 1 to 50.

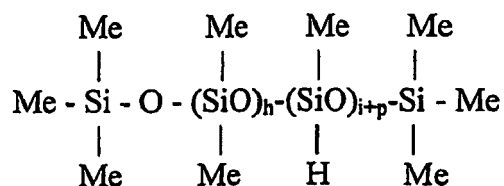
[0018] Typically the cross-linked organopolysiloxane polymer of component B) is triorganosiloxy endblocked at each terminal of the polymer, and it is highly preferred that the polymer is trimethylsiloxy endblocked at each terminal of the cross-linked polymer.

[0019] A specific example of the method for producing the crosslinked organopolysiloxane polymers will now be described. Preparation of a crosslinked organopolysiloxane polymer can be done through the following steps: (I) a charging step in which a linear polysiloxane having hydrogen atoms in its side chains, a polysiloxane having vinyl groups and a catalyst for promoting the reaction, particularly platinum catalysts such as an isopropanol solution of H₂PtCl₆·6H₂O with a 2% methanol solution of sodium acetate are put in a reactor, (II) an agitation/heating step in which agitation is conducted, for example, at 40°C for 30 minutes, (III) an input step in which a polyoxyalkylene and a solvent (isopropanol) are put in the reactor, (IV) a reflux step in which the isopropanol is refluxed, for example, at 80°C for 1.5 to 2 hours while monitoring the reaction rate of Si-H, (V) a stripping step in which the isopropanol is stripped, for example, at 130°C under a reduced pressure of 25 mmHg, and (VI) a final step in which the reduced pressure condition of step (V) is released and the reaction mixture is cooled to 60°C to obtain a final product.

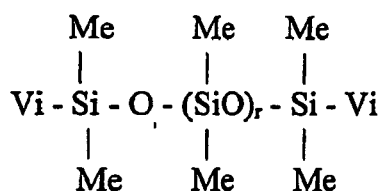
[0020] An example of a linear polysiloxane having hydrogen atoms in its side chains suitable for step (I) is a polysiloxane having its formula selected from:



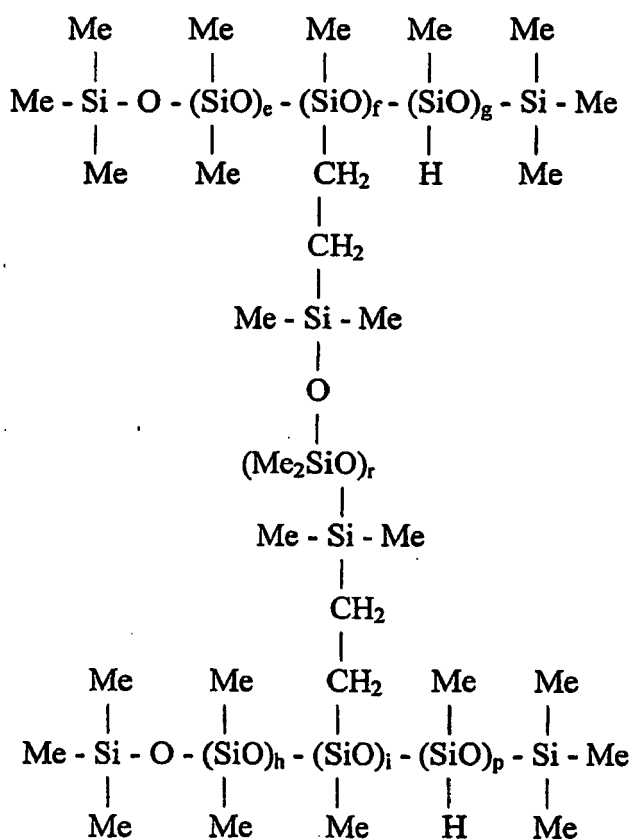
or



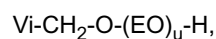
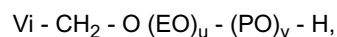
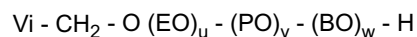
wherein Me hereinafter denotes methyl and e, f, g, h, i, and p are as defined above. An example of a polysiloxane having vinyl groups suitable for step (I) is a polysiloxane having the formula:

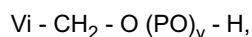
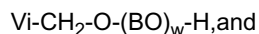


wherein Me denotes methyl, Vi hereinafter denotes vinyl, and r is as defined above. The reaction of these two compounds in step (II) results in a cross-linked siloxane polymer having the formula

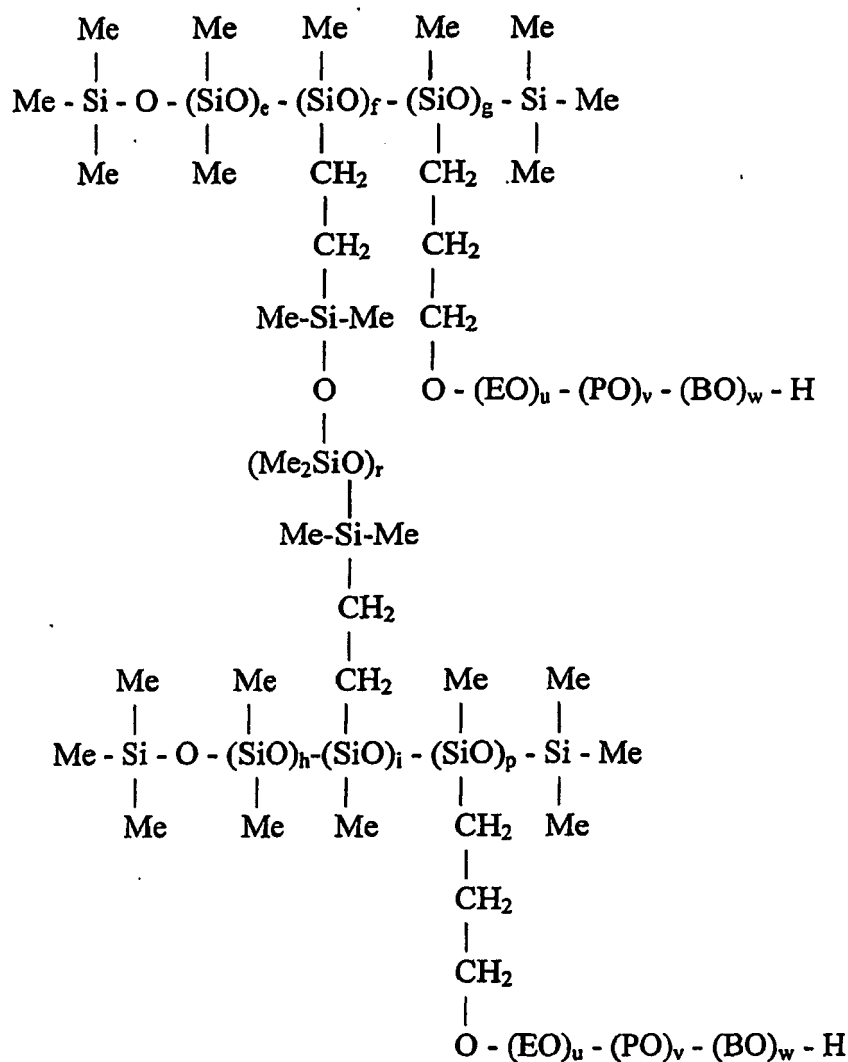


[0021] Introduction of a polyoxyalkylene group into the obtained crosslinked organopolysiloxane polymer (steps III-VI) can be accomplished by reacting the crosslinked polymer with a polyoxyalkylene compound having its formula selected from the group consisting of





wherein Vi, EO, PO, and BO are as denoted hereinabove, and u, v, and w are as defined above.
The resulting compounds are cross-linked organopolysiloxane polymers having the formula



wherein Me, EO, PO, BO, e, f, g, h, i, p, and r are as defined hereinabove, u has a value of 0 to 150, v has a value of 0 to 150, and w has a value of 0 to 150, with the proviso that the value of u+v+w is at least one.

[0022] The compositions of the present invention are prepared by combining components A) and B), either before adding them to the finishing bath, by adding them separately into the finishing bath using any conventional mixing techniques, or by adding them in separate sequential steps onto the fibrous substrate. Typically, components A) and B) are combined such that the weight ratio of component A)/component B) is from 1/99 to 99/1.

[0023] The invention further provides a method of treating fibers or textiles comprising;

l) combining,

A) a fluoropolymer,

B) a branched silicone polyether, and

II) applying the product of step I on fibers or textiles.

[0024] The first step of the method is mixing a fluoropolymer and a branched silicone polyether either before adding them to the finishing bath or by adding them separately into the finishing bath or by adding them through separate sequential steps onto the fibrous substrate. The fluoropolymer A) and the branched silicone polyether B) are the same as described supra. Finishing bath may also include additional components such as, but not limited to, durable press reactants, such as dimethyloldihydroxyethylene urea (DMDHEU), reactant catalysts such as Magnesium Chloride/Citric Acid, softeners such as polyethylene emulsions, process aids such as wetting agents and other. Mixing can be performed by any conventional known techniques such as milling, blending, homogenizing, sonolating or stirring. These mixing procedures can be conducted either in a batch or continuous process.

[0025] The second step of the method comprises applying to fibers or textiles the product resulting from combining components A) and B), also referred herein as the treatment composition or the separate components A) and B) in sequential steps. The amount applied is a "hand improving" effective amount of the treatment composition and is applied to the fiber and/or textile by any convenient method. For example, the treatment composition can be applied by padding, dipping, spraying or exhausting. When the treatment composition comprises more than one solution, dispersion, or emulsion; the solutions, dispersions, and emulsions can be applied simultaneously or sequentially to the textiles. After the treatment composition is applied to the fiber and/or fabric, it can be dried by heat

[0026] The fiber/textile treatment composition can be applied to the fiber and/or textile during making the fibers or textiles, or later such as during laundering textiles. After application, carriers (if any) can be removed from the treatment composition for example by drying the composition at ambient or elevated temperature. The amount of treatment composition applied to the fibers and textiles is typically sufficient to provide 0.1 to 15 weight percent of the composition on the fibers and textiles, based on their dry weight, preferably in an amount of 0.2 to 5 weight percent based on the dry weight of the fiber or textile.

[0027] Fibers and textiles that can be treated with the treatment composition include natural fibers such as cotton, silk, linen, and wool; regenerated fibers such as rayon and acetate; synthetic fibers such as polyesters, polyamides, polyacrylonitriles, polyethylenes, and polypropylenes; combinations, and blends thereof. The form of the fibers can include threads, filaments, tows, yarns, woven fabrics, knitted materials, non-woven materials, paper, carpet, and leather.

[0028] The treatment composition of this invention has advantages such that it can impart combined benefits of attributes associated with silicones and fluorocarbons. Silicones generally provide superior hand to fabrics, whereas fluorocarbons contribute water repellency, oil repellency, and stain release to textiles. *Hand* for purposes of the invention means the softness and smoothness of the fabric. The present compositions and methods provide oil repellency properties to fibers or textiles, but without a significant detriment to the hand of treated fibers.

EXAMPLES

[0029] The following examples are presented to further illustrate the compositions and methods of this invention, but are not to be construed as limiting the invention, which is delineated in the appended claims. All parts and percentages in the examples are on a weight basis and all measurements were obtained at about 23°C, unless indicated to the contrary.

Treatment of Textiles and Test Methods

[0030] Fabrics were obtained from Testfabrics Incorporated, Pittston, Pennsylvania, and included a 100 percent cotton twill Tribecka series khaki, and a No. 7409 Dacron 54 /Cotton (65/35) Bleached Broadcloth and Interlock cotton knit style 460, as the standardized fabrics for use. Neither fabric had any prefinished treatment.

Oil Repellency: Hydrocarbon Resistance Test Protocol- American Association of Textile Chemists & Colorists (AATCC) Test Method 118-1997

[0031] In this test method, a series of oils are designated with numbers 1 thru 8. The surface tension of the oil decreases as the number of the oil increases, i.e., the number 1 oil has the highest surface tension whereas the number 8 oil has a lowest surface tension. Each fabric is tested with the number oil (Kaydol) up to the number 8 oil (n-heptane), and the wetting or wicking into the fabric is noted. Values based on a rating scale of A, B, C, and D, are assigned to each oil as an indication of the contact angle of the oil applied to the surface, and at a C value, wicking and wetting of the fabric is noted, with full wicking being a rating of D. Value A is the best, value B is passing, value C indicates failure, and value D is the worst. The test protocol consists of placing 5 drops of each oil on the test fabric, waiting 30 +/-2 seconds, and then assigning a score for the oil. If the score is B or better, the next higher numbered oil is tested. A score of 8A is considered the best score since it would indicate that there was no or little if any wicking and/or wetting of the fabric even with the oil having the lowest surface tension.

Water Repellency: Spray Test - AATCC Test Method 22-1996

[0032] An AATCC spray tester was used for this test. The tester included a stand with a 45 °incline, above which a separatory funnel was mounted having an attached spray nozzle hanging above it. Fabric samples are fastened into a metal hoop, and placed on the incline, and the nozzle head is positioned 6 inches above it. Then, 250 milliliter of distilled water is allowed to play down onto the fabric. The wetting pattern is compared to a standard rating scale. A rating of 100 indicates no sticking or wetting of the upper surface; a rating of 90 indicates a slight random sticking or wetting of the upper surface; a rating of 80 indicates a wetting of the upper surface at the spray points; a rating of 70 indicates a partial wetting of the whole of upper surface; a rating of 50 indicates a complete wetting of the whole of the upper surface; a rating of 0 indicates a complete wetting of the whole of the upper and lower surfaces.

Water/IPA Drop Test

[0033] This method was used to evaluate the water repellency of the interlock cotton knit. In this method, solutions with ratios of water and isopropyl alcohol (IPA) from 100:0 to 0:100 are prepared, and 5 drops of each solution are placed on the surface to observe whether penetration occurs within 10 seconds. The higher the ratio of IPA in the solution, the lower the surface tension, the more difficult to repel and therefore the higher rating given, e.g. a fabric repelling 100% IPA was given a rating of 100.

Hand Testing

[0034] A panel of expert evaluators rated the fabric softness using a scale of 1 to 5. A value of 5 was used for the softest fabric and a value of 1 was given to the least soft fabric.

Finishing Procedure

[0035] Four different fluoropolymer emulsions were used in the design of the finishing formulations. Three emulsions were compositions containing a fluoroalkyl acrylate copolymers, and the other emulsion was a composition containing a fluorinated polyurethane. The emulsions containing the fluoroalkyl acrylate copolymers were obtained from Noveon Corporation, sold as Unydine® TG-532 and Unidyne® TG-992, Daikin Industries, sold as Unydine® 571 and Ciba Specialty Chemicals, sold as Zonal® CO. The emulsion containing the fluorinated polyurethane was obtained from E.I. Dupont de Nemours, Wilmington, Delaware, sold as ZONYL® 7910. All these compositions are known to provide good stain repellency and/or stain release to textile substrates made of all types of fibers and fiber blends. The required amount of the emulsion components was added to the water finishing bath in order to deposit the specified amount of solids on fabric. Swatches of test fabric were cut from single bolts of fabric into square measuring 15" X 15".

[0036] Finishing bath was applied to the fabric by padding where it is impregnated with the bath liquor followed by squeezing through a nip to leave a specific quantity of liquor on the substrate. After padded, the fabric was dried and cured in a laboratory stenter at 170°C, for 90 sec.

Materials

[0037] The following materials were used in the examples, as detailed below.

BSPE 1 = **Dow Corning® 2-5563** a branched silicone polyether (Dow Corning Corporation, Midland, MI)

BSPE 2 = **Dow Corning® 2-5785** a branched silicone polyether (Dow Corning Corporation, Midland, MI)

[0038] Solutions of each were prepared and applied in a stain repellent and release fabric finish formulations to different fabric substrates. The representative finishing systems were based on either fluoroalkyl acrylate copolymers or a fluorinated urethanes.

Typical Stain Repellent Finish Formulation

Product	wt %
Branched Silicone Polyether Solution (20% Actives)	2-8
Fluoropolymer Emulsion (20-30% Solids)	4-8
Durable Press Reactant	12.0

EP 1 753 906 B9

(continued)

Product	wt %
Durable Press Resin Catalyst	3.0
Non Re-wettable Surfactant	0.1
Water	Balance

Example 1

[0039] Evaluation of BSPE's/fluoropolymer fabric treatment based on Unidyne® TG-532 System (Noveon Inc.) on 100% Khaki Cotton Twill, 1% Silicone, 1% Fluoropolymer

[0040] Unidyne®-532 is a fluoroalkyl acrylate copolymer emulsion (aprox 19% actives, 25% solids) from Noveon Inc. Table 1 below shows that both BSPE 1 and BSPE 2 had and minimum impact or even improved the oil repellency in the Unidyne TG-532 system. In this fabric, which was treated with 1% Si, hand for BSPE 1 was perceived better than BSPE 2. As shown, branched spe's were compared with a commercially available amino-functional silicone, commonly used for fiber treatment.

Table 1

Oil Repellency(1) (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Unidyne® TG-532 Only	B	B+	A-	A	A	A	A
Unidyne® TG-532 & BSPE I	C	B	A-	A	A	A	A
Unidyne® TG-532 & BSPE II	B	A-	A	A-	A	A	A
Unidyne® TG-532 & Aminofunctional Silicone	C	C	C+	B-	B+	A-	A
(1) Ratings: A - Pass, B -Borderline pass, C & D fail							

Hand Rating(1)

Treatment	Unidyne® TG-532 Only	Unidyne® TG-532 & SBG I	Unidyne® TG-532 & SBG II	Unidyne® TG-532 & Aminofunctional Silicone
Rating	1	4.6	4.5	4.25
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest.				

Example 2

[0041] Evaluation of BSPE's/fluoropolymer fabric treatment based on Unidyne® TG-532 System (Noveon Inc.) on 65/35 polycotton woven, 1% Silicone, 1 % Fluoropolymer Solids

[0042] On polycotton both Branched spe's had a minimum impact on the oil repellency provided by the fluoropolymer while providing very good softness to the treated fabric. Softness for branched spe's was similar and perceived as mid-range among all the silicones evaluated (evaluation included conventional amino-functional silicones as well). Both branched spe's showed no impact on water repellency for polycotton. Results are shown in the tables below:

Oil Repellency(1) (Hydrocarbon Resistance Test-AATCC 118-1992)

Treatment /Oil	7	6	5	4	3	2	1
Unidyne® TG-532 Only	B-	B-	A	A	A	A	A
Unidyne® TG-532 & BSPE I	B-	B-	B+	A-	A	A	A

EP 1 753 906 B9

(continued)

Oil Repellency(1) (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Unidyne® TG-532 & BSPE II	B-	B	B	A-	A	A	A
Unidyne® TG-532 & Aminofunctional Silicone	C	C+	C+	B-	B-	A-	A
(1) Ratings: A - Pass, B - Borderline pass, C & D fail							

Water Repellency, Spray Rating (AATCC-22)				
Treatment	Unidyne® TG-532 Only	Unidyne® TG-532 & SBG I	Unidyne® TG-532 & SBG II	Unidyne® TG-532 & Aminofunctional Silicone
Rating	100	100	100	80

Hand Rating(1)				
Treatment	Unidyne® TG-532 Only	Unidyne® TG-532 & SBG I	Unidyne® TG-532 & SBG II	Unidyne® TG-532 & Aminofunctional Silicone
Rating	1	3	3	5
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest.				

Example 3

[0043] Evaluation of BSPE's/fluoropolymer fabric treatment based on Unidyne® TG-532 System (Noveon Inc.) on 100% Cotton knit, 0. 7% Silicone , 1.4% FC

[0044] The branched silicone polyethers were evaluated on a 100% cotton knit, using 0.7% silicone and 1.4% fluorocarbon, following the procedures of example 1. The results are summarized in Table 3 below.

Table 3

Oil Repellency(1) (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Unidyne® TG-532 Only	B+	B+	A-	A	A	A	A
Unidyne® TG-532 & BSPE I	B+	B+	A-	A	A	A	A
(1) Ratings: A - Pass, B - Borderline pass, C & D fail							

Hand Rating(1)			
Treatment	Unidyne® TG-532 Only	Unidyne® TG-532 & BSPE	
Rating	1	4	
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest			

Example 4

[0045] Evaluation of BSPE's/fluoropolymer fabric treatment based on Zonyl® CO System (Ciba Specialty Chemicals

EP 1 753 906 B9

Corp.) on Polycotton fabric, at 0.5% Silicone, 1% Fluoropolymer Zonyl® CO is described as a perfluoroalkyl acrylic copolymer with average of 16% actives (13-19% actives according to MSDS).

[0046] In polycotton, all the materials tested, except the competitive, performed well showing no impact on oil repellency. As far as water repellency BSPE 1 does not show any impact. Regarding softness, the BSPE provided good to this type of fabric when compared to the aminofunctional silicone included in the testing.

Table 4

Oil Repellency ₍₁₎ (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Zonyl® CO Only	B-	B-	B	A	A	A	A
Zonyl®CO & BSPE I	B-	B-	B	A-	A-	A	A
Zonyl® CO & Aminofunctional	B-	B-	B	B	A-	A	A
(1) Ratings: A - Pass, B - Borderline pass, C & D fail							

Water Repellency, Spray Rating (AATCC-22)			
Treatment	Zonyl® CO Only	Zonyl® CO & BSPE I	Zonyl® CO & Aminofunctional
Rating	100	100	100

Hand Rating ₍₁₎			
Treatment	Zonyl® CO Only	Zonyl® CO & BSPE I	Zonyl® CO & Aminofunctional
Rating	1	3.75	4.5
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest,			

Example 5

[0047] Evaluation of BSPE's/fluoropolymer fabric treatment based on Zonyl® CO System (Ciba Specilaty Chemicals Corp.) on Cotton Khaki, at 0.5% Silicone, 1% Fluoropolymer

Oil Repellency (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Zonyl® CO Only BSPE II	B-	B	A-	A-	A	A	A
Zonyl® CO & Aminofunctional	D	C	C	B-	A-	A	A
(1) Ratings: A - Pass, B - Borderline pass, C & D fail							

Hand Rating ₍₁₎			
Treatment	Zonyl® CO Only	Zonyl® CO & BSPE II	Zonyl® CO & Aminofunctional
Rating	1	4	4.3
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest			

Example 6

[0048] Evaluation of BSPE's/fluoropolymer fabric treatment based on Zonyl® CO System (Ciba Specilaty Chemicals Corp.) on Cotton Khaki, 1% Silicone, 1% FC

Oil Repellency ₍₁₎ (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Zonyl® CO Only	B-	B-	B	B+	A-	A	A
Zonyl® CO & BSPE I	B-	B-	B-	B	A-	A	A
Zonyl® CO & Other Silicone	-	-	-	C	B-	B	A-
(1) Ratings: A - Pass, B - Borderline pass, C & D fail							

Water Repellency, Spray Rating (AATCC-22)			
Treatment	Zonyl® CO Only	Zonyl® CO & BSPE	Zonyl® CO & Other Silicone
Rating	100	85	75

Hand Rating ₍₁₎			
Treatment	Zonyl® CO Only	Zonyl® CO & BSPE I	Zonyl® CO & Other Silicone
Rating	1	4	5
Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest.			

Example 7

Evaluation of BSPE's/fluoropolymer fabric treatment based on Zonyl® 7910 Stain Release fabric treatment on Khaki Cotton Twill, 1% Silicone 1.0 % FC

[0049] Zonyl® 7910 is described as a fluorinated urethane with 30-35% solids content. Performance of BSG I was compared with an epoxy/polyether functional silicone which is a material normally recommended in this application

Oil Repellency ₍₁₎ (Hydrocarbon Resistance Test-AATCC 118-1992)							
Treatment /Oil	7	6	5	4	3	2	1
Zonyl® 7910 Only	-				C	B+	B+
Zonyl® 7910 & BSPE I	-	-	B-	B	B	B+	B+
Zonyl® 7910 & BSPE II	-	-	B-	B	B	B+	B+
Zonal® 7910 and Epoxy/polyether functional silicone			C	B-	B-	B	B+
(1) Ratings: A - Pass, B - Borderline pass, C & D fail							

Stain Release Rating ₍₁₎ (AATCC 130-2000)			
Treatment /Oil	Vegetable Oil	Mineral Oil	Dirty Motor Oil
Zonyl® 7910 Only	4.2	3.5	1
Zonyl® 7910 & BSPE I	4.4	3.9	2.3
Zonyl® 7910 & BSPE II	4.5	3.8	2.5

EP 1 753 906 B9

(continued)

Stain Release Rating ₍₁₎ (AATCC 130-2000)			
Treatment /Oil	Vegetable Oil	Mineral Oil	Dirty Motor Oil
Zonyl® 7910 & Epoxy/polyether functional silicone	4.3	4.0	2.1
(1) Rating: Best - 5, Worst -1			

Hand Rating (1)				
Treatment	Zonyl® 7910 Only	Zonyl® 7910& BSPE I	Zonyl® 7910 & BSPE II	Zonyl® 7910 & Epoxy/ polyether Silicone
Rating	1	4.5	5	4.0
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest				

Example 8

Evaluation of BSPE's/fluoropolymer fabric treatment in Stain Release Systems

[0050] Unidyne™ TG-992 is described as a fluoroacrylate copolymer emulsion with 20-25% solids. Performance of BSG I was compared with an epoxy/polyether functional silicone which is the standard material used in this application

Stain Release Rating ₍₁₎ (AATCC 130-2000)		
Treatment /Oil	Mineral Oil	Dirty Motor Oil
Unidyne TG-992 Only	4	1.2
Unidyne TG-992 & BSPE I	3.75	1.6
Unidyne TG-992 & Epoxy/polyether functional Silicone	3.5	1.7
(1) Rating: Best-5, Worst-1		

Hand Rating ₍₁₎				
Treatment	Unidyne Only	Unidyne & Epoxy/polye ther silicone	Unidyne & BSPE I	
Rating	1	2.5	3.6	
(1) Relative Hand Rating obtained from a panel of expert evaluators:1 is the least soft, 5 is the softest				

Example 9

Branched spe's as Hydrophilic Textile Finishes

[0051] Branched spe's have shown that can provided very good softness to textile substrates with minimum impact on their natural absorbency.

Absorbency, sec(1) (AATCC)		
Treatment /Oil	Cotton Knit	Cotton Terry
Untreated	< 1	< 1

(continued)

Absorbency, sec(1) (AATCC)		
Treatment /Oil	Cotton Knit	Cotton Terry
BSPE I	<1	<1
BSPE II	<1	<1
Premium Silicone Hydrophilic Softener	2.7	10 sec

Hand Ratings ₍₁₎				
Treatment	Untreated	BSPE I	BSPE II	Premium Silicone Hydrophilic Softener
Cotton Knit	1	3.5	4.5	5
Cotton Towel	1	3	4	5
(1) Relative Hand Rating obtained from a panel of expert evaluators: 1 is the least soft, 5 is the softest.				

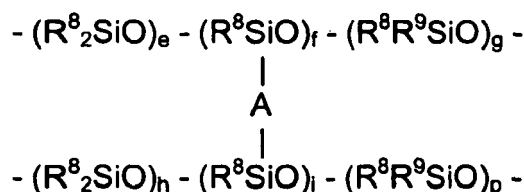
Whiteness Index ₍₁₎				
Treatment	Untreated	BSPE I	BSPE II	Premium Silicone Hydrophilic Softener
Cotton Knit	79.9	79.7	79.6	77.9
Cotton Towel	123.6	123.2	123.1	118.2
(1) Hunter Lab Colorimeter. Fabric dried at 170C for 2 min.				

Claims

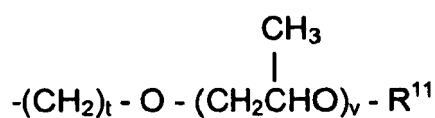
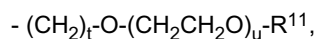
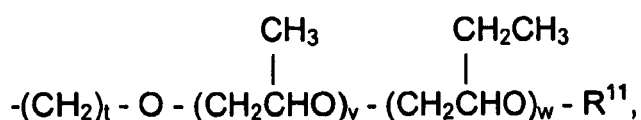
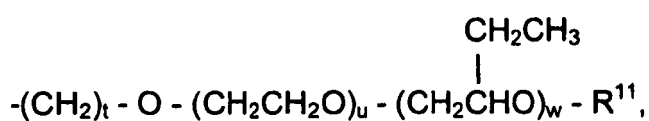
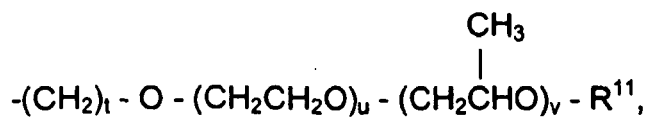
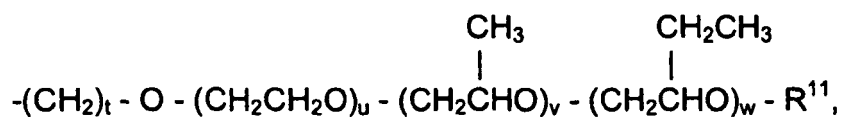
1. A fabric treatment composition comprising;

- A) a fluoropolymer,
B) a branched silicone polyether.

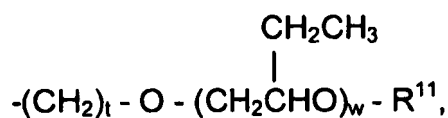
2. The fabric treatment composition according to Claim 1, wherein the branched silicone polyether is a organopolysiloxane comprising the unit formula:



wherein R^8 is a monovalent hydrocarbon group,
 A is a group having its formula selected from $(CH_2)_q-(R^{10}_2SiO)_rSi(CH_2)_s$ or $O(R^{10}_2SiO)_r-SiO$ wherein R^{10} denotes a monovalent hydrocarbon group,
 q has a value of 2 to 10,
 r has a value of 1 to 5000,
 s has a value of 2 to 10,
 R^9 denotes a group having its formula selected from the group consisting of:



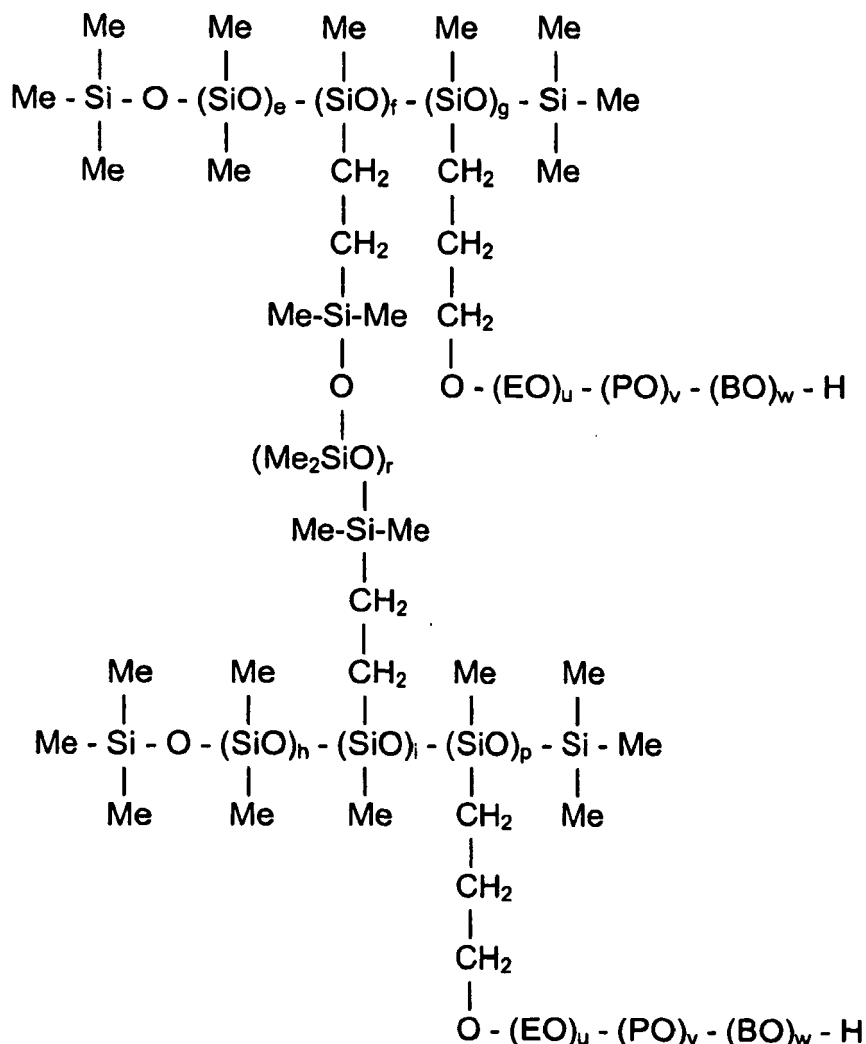
and



wherein R^{11} is selected from a hydrogen atom, an alkyl group, an aryl group, or an acyl group,
 t has a value of 0 to 6,
 u has a value of from greater than zero to 150,
 v has a value of from greater than zero to 150,
 w has a value of from greater than zero to 150,
 e has a value of 1 to 1000,
 f has a value of from greater than zero to 30,
 g has a value of 1 to 1000, h has a value of 1 to 1000,

i has a value of from greater than zero to 30, and p has a value of 1 to 1000.

3. The fabric treatment composition according to Claim 1, wherein the branched silicone polyether is a organopolysiloxane having the formula:



wherein Me denotes methyl, EO denotes ethylene oxide, PO denotes propylene oxide, BO denotes butylene oxide, e has a value of 1 to 1000, f has a value of from greater than zero to 30, g has a value of 1 to 1000, h has a value of 1 to 1000, i has a value of from greater than zero to 30, p has a value of 1 to 1000, r has a value of 1 to 5000, u has a value of 0 to 150, v has a value of 0 to 150, and w has a value of 0 to 150, with the proviso that the value of u+v+w is at least one.

4. The fabric treatment composition according to Claim 1, 2 or 3, wherein the fluoropolymer is selected from a fluoroalkyl acrylate copolymer, a fluorinated polyurethane, an emulsion of a fluoroalkyl acrylate copolymer, or an emulsion of a fluorinated polyurethane.
5. A method of treating fibers or textiles comprising;

l) combining,

- A) a fluoropolymer,
B) a branched silicone polyether, and

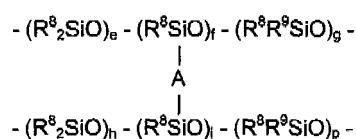
II) applying the product of step I on fibers or textiles.

Patentansprüche

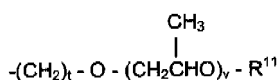
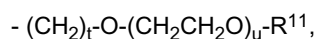
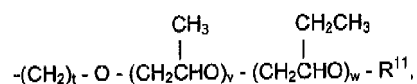
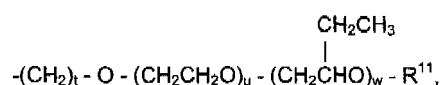
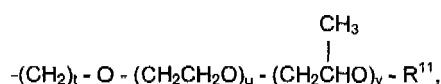
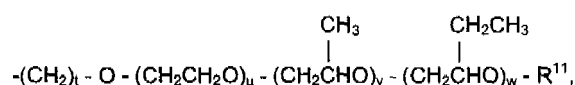
1. Faserbehandlungszusammensetzung enthaltend:

- A) ein Fluorpolymer,
- B) einen verzweigten Siliconpolyether.

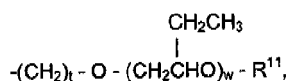
2. Faserbehandlungszusammensetzung nach Anspruch 1, wobei der verzweigte Siliconpolyether ein Organopolysiloxan ist, das die Einheitenformel:



aufweist, worin R^8 eine einbindige Kohlenwasserstoffgruppe ist,
A eine Gruppe ist, deren Formel ausgewählt ist aus $(CH_2)_q-(R^{10}_2SiO)_rSi(CH_2)_s$ oder $O(R^{10}_2SiO)_r-SiO$, worin R^{10} für eine einbindige Kohlenwasserstoffgruppe steht,
q einen Wert von 2 bis 10 aufweist,
r einen Wert von 1 bis 5000 aufweist,
s einen Wert von 2 bis 10 aufweist,
 R^9 für eine Gruppe steht, deren Formel ausgewählt ist aus der Gruppe bestehend aus:

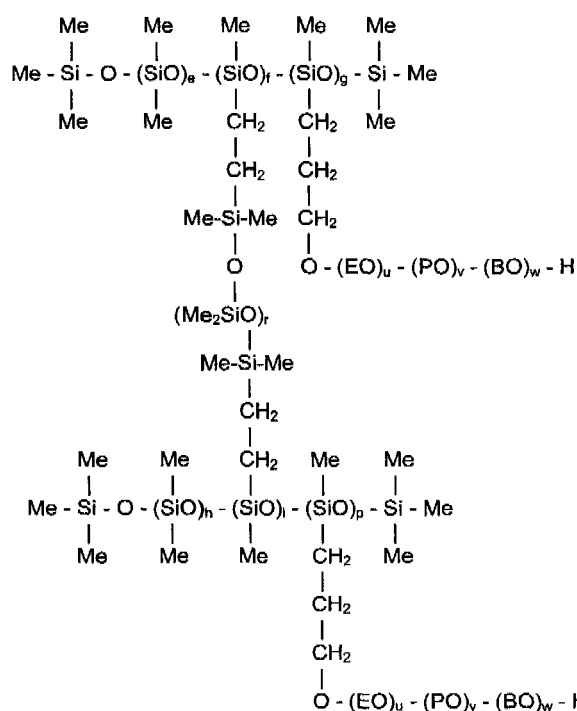


und



worin R^{11} ausgewählt ist aus einem Wasserstoffatom, einer Alkylgruppe, einer Arylgruppe oder einer Acylgruppe, t einen Wert von 0 bis 6 aufweist, u einen Wert von größer als null bis 150 aufweist, v einen Wert von größer als null bis 150 aufweist, w einen Wert von größer als null bis 150 aufweist, e einen Wert von 1 bis 1000 aufweist, f einen Wert von größer als null bis 30 aufweist, g einen Wert von 1 bis 1000 aufweist, h einen Wert von 1 bis 1000 aufweist, i einen Wert von größer als null bis 30 aufweist und p einen Wert von 1 bis 1000 aufweist.

3. Faserbehandlungszusammensetzung nach Anspruch 1, wobei der verzweigte Siliconpolyether ein Organopolysiloxan mit der Formel:



ist, worin Me für Methyl steht, EO für Ethylenoxid steht, PO für Propylenoxid steht, BO für Butylenoxid steht, e einen Wert von 1 bis 1040 aufweist, f einen Wert von größer als null bis 30 aufweist, g einen Wert von 1 bis 1000 aufweist, h einen Wert von 1 bis 1000 aufweist, i einen Wert von größer als null bis 30 aufweist, p einen Wert von 1 bis 1000 aufweist, r einen Wert von 1 bis 5000 aufweist, u einen Wert von 0 bis 150 aufweist, v einen Wert von 0 bis 150 aufweist und w einen Wert von 0 bis 150 aufweist, unter der Voraussetzung, dass der Wert von $u+v+w$ wenigstens eins ist.

4. Faserbehandlungszusammensetzung nach Ansprüchen 1, 2 oder 3, wobei das Fluorpolymer ausgewählt ist aus Fluoralkyl-Acrylat-Copolymer, einem fluorierten Polyurethan, einer Emulsion eines Fluoralkyl-Acrylat-Copolymers oder einer Emulsion eines fluorierten Polyurethans.

5. Verfahren zur Behandlung von Fasern oder Textilien umfassend:

I) Vereinigen von

- A) einem Fluorpolymer,
B) einem verzweigten Siliconpolyether und

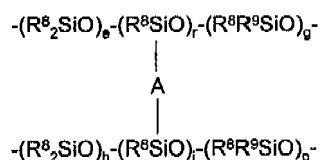
II) Aufbringen des Produkts aus Schritt I auf Fasern oder Textilien.

Revendications

1. Composition pour le traitement de textiles comprenant :

- A) un fluoropolymère,
B) un silicone polyéther ramifié.

2. Composition pour le traitement de textiles selon la revendication 1, dans laquelle le silicone polyéther ramifié est un organopolysiloxane comprenant la formule d'unité :



dans laquelle R⁸ est un groupe hydrocarboné monovalent,

A est un groupe présentant sa formule choisie parmi (CH₂)_q-(R¹⁰₂SiO)_rSi(CH₂)_s ou O(R¹⁰₂SiO)_r-SiO où R¹⁰

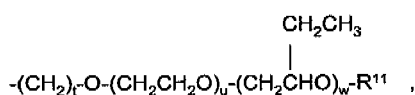
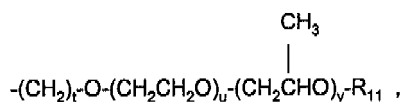
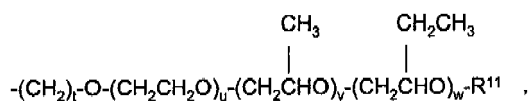
indique un groupe hydrocarboné monovalent,

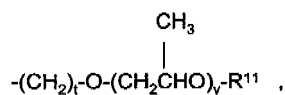
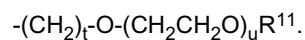
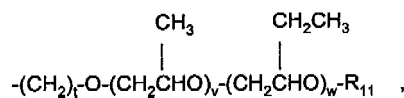
q présente une valeur de 2 à 10,

r présente une valeur de 1 à 5 000,

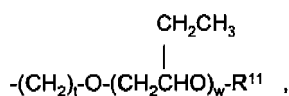
s présente une valeur de 2 à 10,

R⁹ indique un groupe présentant sa formule choisie dans le groupe constitué de :





et



où R^{11} est choisi parmi un atome d'hydrogène, un groupe alkyle, un groupe aryle ou un groupe acyle, t présente une valeur de 0 à 6,

u présente une valeur supérieure à zéro jusqu'à 150,

v présente une valeur supérieure à zéro jusqu'à 150,

w présente une valeur supérieure à zéro jusqu'à 150,

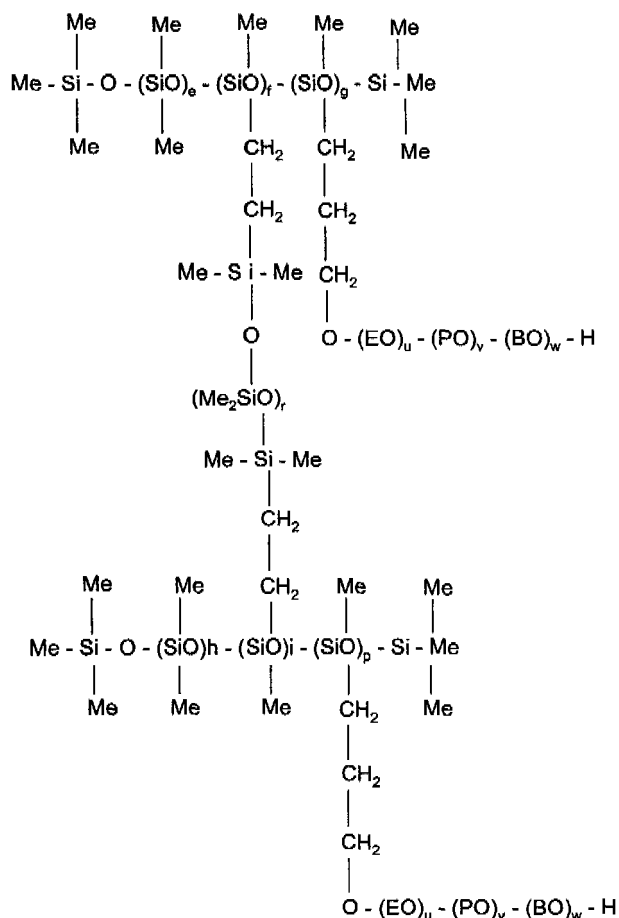
e présente une valeur de 1 à 1 000,

f présente une valeur supérieure à zéro jusqu'à 30,

g présente une valeur de 1 à 1 000, h présente une valeur de 1 à 1 000,

i présente une valeur supérieure à zéro jusqu'à 30, et p présente une valeur de 1 à 1 000.

3. Composition pour le traitement de textiles selon la revendication 1, dans laquelle le silicone polyéther ramifié est un organopolysiloxane présentant la formule :



dans laquelle Me indique le groupe méthyle, EO indique l'oxyde d'éthylène, PO indique l'oxyde de propylène, BO indique l'oxyde de butylène, e présente une valeur de 1 à 1 000, f présente une valeur supérieure à zéro jusqu'à 30, g présente une valeur de 1 à 1 000, h présente une valeur de 1 à 1 000, i présente une valeur supérieure à zéro jusqu'à 30, p présente une valeur de 1 à 1 000, r présente une valeur de 1 à 5 000, u présente une valeur de 0 à 150, v présente une valeur de 0 à 150 et w présente une valeur de 0 à 150, à condition que la valeur de u+v+w est au moins égale à 1.

4. Composition pour le traitement de textiles selon la revendication 1, 2 ou 3, dans laquelle le fluoropolymère est choisi parmi un copolymère d'acrylate de fluoroalkyle, un polyuréthane fluoré, une émulsion d'un copolymère d'acrylate de fluoroalkyle ou une émulsion d'un polyuréthane fluoré.

5. Procédé pour le traitement de fibres ou de textiles comprenant les étapes consistant:

1) à combiner,

A) un fluoropolymère,

B) un silicone polyéther ramifié, et

II) à appliquer le produit de l'étape I sur des fibres ou des textiles.

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- US 4781844 A [0003]
- US 4978462 A [0003]
- US 6171515 B [0003]
- US 4853474 A [0013]
- US 5136068 A [0013]

Non-patent literature cited in the description

- Siloxane Polymers. PTR Prentice Hall, 1993 [0015]