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(54) Title: TREATMENT OF FIBROUS SUBSTRATES WITH SILSESQUIOXANES AND STAINBLOCKERS

(57) **Abstract:** This invention relates to a method for imparting soil-resistant, stain-resistant and optional water-repellent properties to fibrous substrates (such as carpet fibers) by applying an acidic, aqueous treating composition containing at least one silsesquioxane, at least one stainblocker to the substrate. The composition may further contain a metal salt and/or a fluorochemical or hydrocarbon repellent material.

TREATMENT OF FIBROUS SUBSTRATES WITH SILSESQUIOXANES AND STAINBLOCKERS

FIELD OF THE INVENTION

This invention relates to a method for imparting soil-resistant, stain-resistant and optional water-repellent properties to fibrous substrates (such as carpet fibers) by applying an acidic aqueous treating composition containing at least one silsesquioxane, at least one stainblocker to the substrate. The composition may further contain a metal salt and/or a fluorochemical or hydrocarbon repellent material and/or an additional antisoiling materials such as a silicate.. The composition may be a solution, dispersion or emulsion.

This invention also relates to the treating composition used to impart soil resistance, stain resistance and optional water repellency to the carpet.

This invention also relates to treated carpet made according to the method of this invention.

BACKGROUND OF THE INVENTION

Various patents describe methods for exhausting stainblockers onto a fibrous substrate such as nylon carpet to impart to the substrate good stain resistance to acid colorants.

U.S. Pat. No. 4,822,373 (Olson et. al) describes treated fibrous polyamide substrate having applied thereto (a) a partially sulfonated novolac resin and (b) methacrylic acid-containing polymers, and combinations thereof.

U.S. Pat. No. 4,875,901 (Payet et al.) discloses a method for providing fibrous polyamide substrates with stain resistance by contacting the substrate with an aqueous solution comprising a normally solid, water-soluble, partially sulfonated novolac resin and a water-soluble polyvalent metal salt.
U.S. Pat. No. 5,001,004 (Fitzgerald et al.) describes stain-resistant, polyamide textile substrates treated with compositions comprising hydrolyzed ethylenically unsaturated aromatic/maleic anhydride polymers and processes for their preparation. World Published Patent Application WO 92/10605 (Pechhold) describes a polyamide fibrous substrate having deposited upon it a water-soluble

or water-dispersible hydrolyzed or monoesterified alpha-olefin/maleic anhydride copolymer.

World Published Patent Application WO 98/50619 (Clark et al.) describes a method for imparting repellency, stain-resistance and soil-resistance to carpets by applying to the carpet via an immersion process an aqueous treating solution comprising a hydrocarbon material, a stainblocking material, and a salt.

U.S. Pat. No. 5,073,442 (Knowlton et al.) describes a method for enhancing the soil- and/or stain-resistant characteristics of polyamide and wool fabric by applying to the fabric an aqueous solution containing sulfonated phenol formaldehyde compound, modified wax emulsion and acrylic resin.

U.S. Pat. No. 3,493,424 (Mohrlok et al.) describes fibrous materials which are given antislip, dulling, and/or dry-soiling resistance properties by applying a colloidal suspension of a silsesquioxane, followed by drying the material.

U.S. Pat. No. 4,351,736 (Steinberger et al.) describes a textile pile-stabilizing impregnating agent comprising a colloidal suspension of silicic acid and organosilsesquioxanes.

U.S. Pat. No. 4,781,844 (Kortmann et al.) describes a textile finishing agent comprising an aqueous colloidal suspension of an organosilsesquioxane-containing sol and an organic polymer resin containing perfluoroalkyl groups which imparts soil resistance.

SUMMARY OF THE INVENTION

This invention relates to a method for imparting soil-resistant, stain-resistant and optional repellent properties to fibrous polyamide substrates (such as carpet fibers) by applying an acidic aqueous treating composition containing at least one silsesquioxane and at least one stainblocker to the substrate. The composition may further contain metal salt and/or a fluorochemical or hydrocarbon repellent material. None of the treating compositions and methods described in the art discloses a method for treating a fibrous substrate using a composition comprising a silsesquioxane and a stainblocker to simultaneously achieve good antisoiling and good stain resistance properties. The compositions are surprisingly stable. Normally the stainblockers tend to be anionic while the silsesquioxane materials tend to be cationic; the combination of the two generally results in precipitation of one or more components and compromises the stainblocking properties of the composition.

Specifically, this invention relates to a method for imparting in-depth repellency, stain resistance and soil resistance to a fibrous substrate comprising the steps of:

(a) contacting the fibrous substrate with an aqueous acidic solution comprising a silsesquioxane and a stainblocker,

(b) treating the wet treated fibrous substrate (preferably by steaming) using a combination of a sufficiently high temperature and a sufficient long time to effectively exhaust the treating materials onto the fibrous substrate; and

(c) drying the wet treated substrate.

Preferably the composition further comprises a polyvalent metal salt exhausting aid and a fluorochemical repellent material having a receding contact angle to n-hexadecane of 45° or higher or a hydrocarbon repellent material having a receding contact angle to n-hexadecane of 35° or higher. The use of divalent metal salts are described in U.S. 4,875,901 (Payet et al.).

In one embodiment, a fibrous substrate is first treated exhaustively by contacting substrate fibers with the aqueous treatment composition of this invention. Following this exhaustion process, the wet fibrous substrate is then heated in a water-saturated atmosphere such as a steam box for a time sufficient to affix the treating materials onto each fiber surface. The heated wet fibrous substrate may be subsequently rinsed with water and is dried in an oven at sufficient temperature to effectively activate the materials.

This invention also describes the resulting treated fibrous substrate which exhibit excellent anti-soiling, anti-staining and repellency performance. The fibrous substrate, having had penetration of the fibers, offers significant protection again dry soiling when compared to untreated carpet as demonstrated by several cycles of "walk-on" tests, resists staining by aqueous acid staining agents such as red Kool-Aid™ drink, and, with the inclusion of the hydrocarbon repellent, exhibits excellent dynamic water resistance (i.e., the treated carpet resists penetration by water-based drinks spilled from a height).

As used herein, a "stainblocking material" or “stainblocker” refers to a material which, when applied to a substrate, enhances the ability of the substrate to resist staining, for example, by natural or artificial colorants found in food or other household items. Preferably, the stain resistance is accomplished without permanently and visibly changing (to the unaided eye) the color of the substrate, except for a slight yellowing of the substrate that is associated with the use of some known stainblocking materials, although it is most preferred that no permanent and visible yellowing of the substrate occur.

The function of the exhaustive treating process is to contact the entirety of each fiber of the fibrous substrate with silsesquioxane, stainblocker and the optional materials. Specifically, the exhaustive treating process can be any of several commonly encountered wet processing operations, including flex-nip, otting, fluidcon, KFA, puddle foamer and padding. Other application methods are envisioned, including applying the composition as part of a cleaning or detergent composition.

To impart antisoiling resistance to the fibrous substrates, the treating compositions of this invention contain silsesquioxanes. Useful silsesquioxanes include compounds of the formula $RSiO_{3/2}$ where R is an optionally substituted alkyl or aryl of up to 7 carbon atoms, and/or cocondensates of hydrosylates of tetraalkoxysilanes with organotrialkoxysilanes having $RSiO_{3/2}$ or SiO_2 units. Useful silsesquioxanes are described in U.S. Pat. Nos. 3,493,424, 4,351,736 and 4,781,844. Preferred silsesquioxanes are neutral or anionic silsesquioxanes, prior to addition to the composition.

To provide in-depth resistance of fibrous substrates to acid staining agents, the treating compositions of this invention contain stainblockers. Useful stainblockers are typically sulfonated or carboxylated polymers, including sulfonated aromatic resins, polymers that are derived from at least one or more (α- and/or β-substituted) acrylic acid monomers, and hydrolyzed copolymers of maleic anhydride and at least one or more ethylenically unsaturated monomers such as styrene and α-olefins. Also suitable as stainblockers are blends of at least two or more of these polymers, reaction products of at least two or more monomers from which these stainblockers may be derived, reaction products of at least one or more monomers from which the polymers may be derived and at least one of the polymers, and materials obtained by polymerizing at least one or more of the monomers in the presence of one or more of the polymers. Non-sulfonated phenolics such as tannic acid or phenolic resin obtained from dihydroxydiphenyl sulfone and formaldehyde may also be used. Suitable stainblockers for polyamide carpet are described in detail in U.S. Pat. No. 5,952,409 (Boardman et al.). In the case of polyamide fibrous substrates, the concentration of stainblocker should be at least 0.75% SOF (solids on fiber) and preferably is at least 2% SOF. However, in the case of hard-to-stain fibrous substrates, such as polypropylene, the amount of stainblocker applied can be as low as 0.01% and is normally used in that case as an emulsion stabilizer.

A suitable repellent is defined as one which exhibits a receding contact angle to *n*-hexadecane of at least 35° for hydrocarbon repellents, or 45^{o}C for fluorochemical repellents, or higher as measured by the Receding Contact Angle Test. Additionally, a suitable repellent material is a hard, glassy, non-tacky material having a glass transition temperature ranging from about 20°C to about 130°C, as measured by the Glass Transition Temperature Test..

The repellant material can be from any chemical class, but hydrocarbon urethanes and amides are preferred. The concentration of hydrocarbon material should be at least 0.01% SOF and is preferably at least 0.05% SOF.

Metal salts may be incorporated into treating solutions having pHs greater than 1.5 to improve the exhaustion efficiency. Nearly any metal salt will suffice, such as sodium chloride, sodium bromide, sodium iodide, sodium sulfate, potassium chloride, ammonium sulfate, lithium sulfate, cesium chloride, tetramethylammonium chloride, zinc sulfate, copper sulfate, aluminum nitrate and zirconium oxyacetate. However, it is preferable that the metal salt be an alkaline earth divalent metal salt, e.g., a salt of magnesium, calcium, strontium or barium, such as magnesium sulfate, magnesium chloride, calcium chloride, calcium acetate, strontium chloride or barium chloride. The optimum divalent metal salts are described in detail in U.S. Pat. No. 4,875,901 (Payet et al.).

The treatment composition is acidic to maximize exhaustion of materials to the fibrous substrate, preferably having a pH of from 1 to 5, more preferably a pH of from 1.5 to 3.5. Any protic acid is suitable but preferably should be an inexpensive, strong acid such as sulfuric acid, and sulfamic acid.

Suitable fibrous substrates includes carpet, fabric, textiles and any substrate woven from fibers such as yarn or thread; carpet is the preferred form of the fibrous substrate. The fiber can be made from any number of thermoset or thermoplastic polymers, such as polyamide, polyester, acrylic and polyolefin; polyamide (e.g. nylon) is the preferred fiber. Where the composition imparts undesirable stiffness or a harsh hand to the fibrous substrate, softening agents such as are known in the art may be added.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A wide variety of stainblocking materials may be used in the stainblocking compositions of the invention. Included among the useful materials are sulfonated aromatic polymers, polymers that are derived from at least one or more α- and/or β-substituted acrylic acid monomers, and hydrolyzed copolymers of at least one or more ethylenically unsaturated monomers and maleic anhydride. Also useful as stainblocking materials are blends of at least two or more of these polymers, reaction products of at least two or more of the monomers from which these polymers may be derived, reaction products of at least one or more of the monomers from which the polymers may be derived and at least one or more of the polymers, and materials obtained by polymerizing at least one or more of the monomers in the presence of one or more of the polymers.

Sulfonated aromatic polymers are a preferred stainblocking material. Desirable examples may comprise a condensation polymer of an aldehyde (e.g., formaldehyde or acetaldehyde) and a sulfonated aromatic compound, or a subsequently sulfonated condensation polymer of an aldehyde and an aromatic compound. Various sulfonated aromatic compounds are available for use in the stainblocking compositions of the invention. However, among the most preferred materials are those which include hydroxyl functionality such as bis(hydroxy phenyl sulfone), hydroxy benzenesulfonic acid, hydroxynaphthalenesulfonic acid, sulfonated 4,4'-dihydroxydiphenylsulfone, and blends thereof. Other useful sulfonated aromatic polymers comprise a copolymer of an ethylenically unsaturated aromatic monomer (e.g., styrene) and a sulfonated ethylenically unsaturated aromatic monomer (e.g., styrene sulfonate).

Another preferred class of stainblocking materials is polymers derived from at least one or more α- and/or β-substituted acrylic acid monomers. These monomers have the general structure $HR^1C=C(R)COOX$, wherein R and R^1 are independently selected from hydrogen, organic radicals and halogens, and X is independently selected from hydrogen, organic radicals and cations. Particularly preferred examples of the resulting polymers are acrylic polymers; i.e., polyacrylic acid, copolymers of acrylic acid and one or more other monomers that are copolymerizable with acrylic acid, and blends of polyacrylic acid and one or more acrylic acid copolymers. Even more preferred, however, are methacrylic polymers which includes polymethacrylic acid, copolymers of methacrylic acid and one or more other monomers that are copolymerizable with methacrylic acid, and blends of polymethacrylic acid and one or more methacrylic acid copolymers.

A third preferred class of stainblocking materials are hydrolyzed copolymers of at least one or more ethylenically unsaturated monomers and maleic anhydride. The ethylenically unsaturated monomers can be alpha-olefin type monomers (e.g. 1-alkenes), alkyl vinyl ethers or, more preferably, aromatic monomers such as styrene.

Quite useful stainblocking materials may be obtained by blending together two or more polymers selected from among the different general classes of polymers described above, reacting together at least two or more monomers from which the different general classes of polymers are derived, reaction products of at least one or more of the monomers from which the polymers may be derived and at least one or more of the polymers, or by polymerizing at least one or more of the monomers in the presence of one or more of the polymers.

For example, one or more α- and/or β-substituted acrylic acid monomers may be polymerized together and, subsequent to the polymerization, blended with a sulfonated aromatic polymer. Alternatively, the α- and/or β-substituted acrylic acid monomers can be polymerized in the presence of a sulfonated aromatic polymer.

In another example, a hydrolyzed copolymer of ethylenically unsaturated monomer and maleic anhydride may be combined with a sulfonated aromatic polymer, and, optionally, a polymer derived from at least one or more α- and/or β-substituted acrylic acid monomers.

By "monomer" is meant a polymerizable single unit (typically of low molecular weight) that provides repeating units in the ultimate polymer, as well as partially reacted materials that can still participate in a polymerization reaction so as to provide repeating units in the ultimate polymer. The expression "at least" recognizes, as explained below, that monomers in addition to those mentioned may participate in the polymerization.

Sulfonated aromatic polymers useful in the invention may be obtained by condensation polymerizing an aldehyde with a sulfonated aromatic compound, the resulting polymer sometimes being referred to herein as either a sulfonated aromatic condensation polymer or as a condensation polymer. The resulting condensation polymer should contain a significant number of sulfonate groups. Preferably, at least one sulfonate group is attached to at least 30% of the monomeric units of the condensation polymer, more preferably between 30% and 70% of the monomeric units. It is also preferred that the resulting condensation polymer be substantially soluble in water to simplify handling and application of the stainblocking composition to a substrate at normal temperatures (about room temperature to 100° C., where "room temperature" refers to a temperature of about 20 to 25° C.).

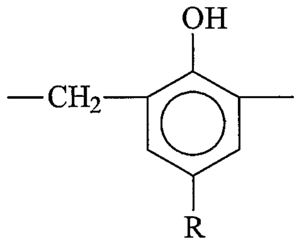
The sulfonated aromatic polymer should have an effective sulfonic acid equivalent weight. By an "effective sulfonic acid equivalent weight" is meant an equivalent weight that is sufficient to impart stain resistance to a substrate treated with the stainblocking composition, while rendering the stainblocking composition sufficiently water soluble or water dispersible to permit application to a substrate at normal temperatures (typically about room temperature to 100° C.). Within these guidelines, the sulfonic acid equivalent weight is preferably about 300 to 1,200, more preferably, about 400 to 900.

Any aldehyde that can be condensation polymerized with a sulfonated aromatic compound may be used in the invention. Suitable examples of such aldehydes include acetaldehyde, benzaldehyde, furfuraldehyde, and, most preferably, formaldehyde. Suitable sulfonated aromatic compounds for forming the condensation polymer include monomers such as benzene sulfonic acid (which, in general, may contain various combinations of alkyl, hydroxy and alkoxy substituents), toluene sulfonic acid, xylene sulfonic acid (e.g., 2,4-dimethyl benzene sulfonic acid), phenyl 4-sulfonic acid, cumene sulfonic acid, dodecylbenzene sulfonic acid, sulfonated diphenyl ether, benzaldehyde sulfonic acid, aminobenzene sulfonic acid, alkoxybenzenesulfonic acid, benzophenone sulfonic acid, sulfonated derivatives of styrene, dodecyl diphenyloxide disulfonic acid, sulfonated derivatives of naphthalene (e.g., naphthalene sulfonic acid), which derivatives may generally contain various combinations of alkyl, hydroxy and alkoxy substituents such as, alkylnaphthalene sulfonic acid (e.g., methylnaphthalene sulfonic acid) and alkoxynaphthalene sulfonic acid.

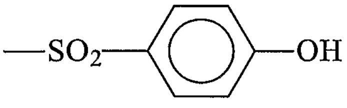
Including hydroxyl functionality in the sulfonated aromatic compound may enhance its solubility in water. Hydroxyl functionality may be introduced into the sulfonated aromatic compound (so as to form a sulfonated hydroxyaromatic compound) by either sulfonating a phenolic compound, or by polymerizing the aldehyde and the sulfonated aromatic compound with a hydroxyaromatic material (preferably a phenolic compound). Phenolic compounds useful in either approach include phenol, halogenated phenol (e.g., chlorophenol or trifluoromethylphenol), naphthol, dihydroxydiphenylsulfide, resorcinol, catechol, hydroxyarylcarboxylic acid (e.g., salicylic acid), hydroxyphenylphenyl ether, phenylphenol, alkylphenol (e.g., nonylphenol or cresol), dihydroxydiphenylsulfone, and bis(hydroxyphenyl)alkane (e.g., 2,2-bis(hydroxyphenyl)propane or 2,2,-bis(hydroxyphenyl)hexafluoropropane). Resulting materials include sulfoalkylated phenol, (e.g., sulfomethylated dihydroxydiphenyl sulfone). Particularly preferred sulfonated hydroxyaromatic compounds include bis(hydroxyphenyl)sulfone, hydroxybenzenesulfonic acid, hydroxynapthalenesulfonic acid, and sulfonated 4,4'-dihydroxydiphenylsulfone.

Enhanced solubility in water may also be obtained by providing the sulfonated aromatic compound as a salt based on, for example, sodium, potassium, or ammonium, such as sodium xylene sulfonate, ammonium xylene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, ammonium cumene sulfonate, potassium toluene sulfonate, potassium cumene sulfonate, and potassium xylene sulfonate.

Particularly preferred condensation polymers consist essentially of repeating units of the formula



where R is the same or different in each unit, and is either hydrogen or a radical selected from the group consisting of --SO_3 X,



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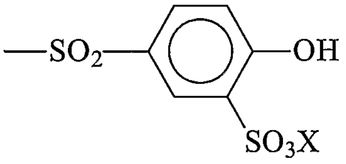


where X is hydrogen or a cation such as sodium or potassium, provided that the resulting polymer contains a sufficient number of sulfonate groups (typically at least 30%). Even more preferred are condensation polymers having these structures and which are water soluble, have at least 40% of the repeating units containing an --SO_3 X radial, and have at least 40% of the repeating units containing the group –SO2-.

Sulfonated aromatic condensation polymers useful in the invention are described in U.S. Pat. No. 4,680,212 (Blyth et al.), U.S. Pat. No. 4,875,901 (Payet et al.), U.S. Pat. No. 4,940,757 (Moss, III et al.), U.S. Pat. No. 5,061,763 (Moss, III et al.), U.S. Pat. No. 5,074,883 (Wang), and U.S. Pat. No. 5,098,774 (Chang).

Sulfonated aromatic condensation polymers useful in the invention can be prepared by methods known to those skilled in the art. Sulfonation of phenolic compounds is described in, for example, Sulfonated and Related Reactions, E. E. Gilbert, Interscience Publishers, 1965. Methods of preparing condensation polymers of sulfonated aromatic compounds with formaldehyde are described in U.S. Pat. No. 1,901,536 (Schafer), U.S. Pat. No. 1,972,754 (Biedernann), U.S. Pat. No. 1,988,985 (Schafer), U.S. Pat. No. 2,112,361 (Fischer), U.S. Pat. No. 2,171,806 (Russell, et al.), U.S. Pat. No. 4,680,212 (Blyth et al.), U.S. Pat. No. 4,940,757 (Moss, III et al.), U.S. Pat. No. 5,061,763 (Moss, III et al.), and Phenolic Resins, A. Knopf et al., Springer-Verlag, 1985.

In general, an aromatic compound such as phenol, naphthalene or naphthol is sulfonated, for example by reacting it with a sulfonating compound such as sulfuric acid, chlorosulfonic acid or alkaline sulfite so as to form a sulfonated aromatic compound. The sulfonated aromatic compound is then condensation polymerized with formaldehyde or other aldehyde, typically under acidic conditions. Mixtures of different sulfonated aromatic compounds can also be polymerized. Typically, one mole of sulfonated aromatic compound is reacted with 0.5 to 1.2 mole of aldehyde. The sulfonated aromatic condensation polymer can be subsequently reacted with a base (e.g., sodium hydroxide, potassium hydroxide, or ammonium hydroxide) so as to form a sulfonic acid salt. Currently marketed condensation polymers are typically sold as a sodium sulfonate salt.

Alternatively, a sulfonated aromatic condensation polymer may be prepared by reacting an unsulfonated hydroxy aromatic compound (e.g., a phenolic compound such as phenol, naphthol, etc.) with an aldehyde such as formaldehyde and then sulfonating the resulting condensation polymer by treatment with fuming sulfuric acid.

Examples of useful, commercially available sulfonated aromatic condensation polymers include Erional™ NW (Ciba-Geigy Limited; containing a naphthalene sulfonic acid polymer with formaldehyde and 4,4'-dihydroxydiphenylsulfone), Erional™ PA (polymer of phenol sulfonic acid, formaldehyde, and 4,4' dihydroxydiphenyl sulfone from Ciba-Geigy), 3M™ brand stain release concentrate FX-369™ (3M Co.), Tamol™ SN (Rohm & Haas Co.), Mesitol™ NBS, Bayprotect CL or CSD™ (Bayer AG), Nylofixan™ P (containing a formaldehyde condensation copolymer of 4,4'-dihydroxydiphenylsulfone and 2,4-dimethylbenzenesulfonic acid, manufactured by Sandoz Corp.), and Intratex™ N (Crompton & Knowles Corp.). The sulfonated aromatic polymers are typically purchased commercially as a 30 to 40% solids aqueous solution that can contain other compounds, including aromatic sulfonic acids and glycols.

The effectiveness of a sulfonated aromatic condensation polymer in imparting stain resistance to a substrate may be improved by providing the condensation polymer in the form of a divalent metal salt. These salts are water soluble and are substantially free of sulfonic acid moieties (i.e., $-SO_3H$ groups); that is, they typically contain less than 1 mole percent sulfonic acid moieties. The salt form of the polymer may be obtained by reacting the condensation polymer with a divalent metal oxide or hydroxide, or the divalent metal salt of a weak acid (e.g., carbonic acid, boric acid, or a carboxylic acid) so as to form an aqueous solution having a pH of at least 3. In another approach, a sulfonated aromatic compound that is used to prepare the condensation polymer may first be converted to a salt (by using a divalent metal oxide or hydroxide, or a divalent metal salt of a weak acid) before reaction with an aldehyde to yield the salt form of the polymer. Suitable divalent metal oxides or hydroxides include oxides and hydroxides of calcium, magnesium and zinc. Divalent metal salts of weak acids include carbonates, bicarbonates, acetates, formates and borates of calcium, magnesium and zinc. Even further improvements in stain resistance may be achieved by adding small amounts (less than 0.1% SOF, more preferably less than 0.05% SOF) of a divalent metal salt (such as those discussed in the additives section below) to the salt form of the polymer. (% SOF refers to the %

solids based on the weight of the fibrous substrate.) Such techniques are described in U.S. 5,098,774 (Chang).

Sulfonated aromatic condensation polymers may discolor with time and assume a yellow tint that can be undesirable, especially depending on the color of the substrate to which the stainblocking composition is applied. Thus, a blue substrate may acquire a greenish cast. One technique for reducing the tendency to change color is to remove color formers inherent in the stainblocking material. This can be accomplished by dissolving the condensation polymer in aqueous base so as to form a solution having a pH of about 8-12, acidifying the aqueous solution to a pH of about 2 to 7.5, heating the acidified material to a temperature of about 50 to 65° C. so as to cause phase separation, removing materials which remain water-soluble after acidification and heating (e.g., by filtering, centrifuging or decanting), and dissolving the resultant water-insoluble material in aqueous base to a final pH of at least about 8, using heat as necessary to effect dissolution. Strong bases (e.g., sodium hydroxide, potassium hydroxide, lithium hydroxide) may be used. Virtually any acid is suitable, e.g. glacial acetic acid, dilute acetic acid, hydrochloric acid, sulfuric acid, oxalic acid, citric acid, or sulfamic acid. Such techniques are described in U.S. Pat. No. 4,833,009 (Marshall).

Another technique for reducing the tendency to change color is to acylate or etherify a portion of the free hydroxyl groups in the condensation polymer. However, acylating or etherifying the free hydroxyl groups can reduce the stainblocking characteristics of the condensation polymer. Thus, the portion of the free hydroxyl groups that are so treated should strike a balance between a reduced tendency to yellow and effective stainblocking. Useful acylating agents include acetic anhydride and ethylchloroformate (conversion of about 50% to 80% of the phenolic hydroxyl groups). Chloroacetic acid is a useful etherifying agent (conversion of about 40% to 60% of the phenolic hydroxyl groups). The acylated and etherified products can be prepared by dissolving the condensation polymer in an aqueous medium having a pH of 7 or above, preferably about 10 or 11 to 13 or 14 (the actual pH depending on the acylating or etherifying agent), and at a temperature that favors acylation or etherification. The water-insoluble phase can be separated from the unwanted water solution by filtering, centrifuging, decanting, etc., and then redissolved in a hydroxyl-functional material, such as ethylene glycol, 1,3-propylene glycol, or 1,3-butylene glycol. Such techniques are described in U.S. Pat. No. 4,963,409 (Liss et al.).

In another embodiment, sulfonated aromatic polymers useful in the invention as stainblocking materials may comprise a copolymer of: (a) one or more ethylenically unsaturated aromatic monomers; and (b) one or more sulfonated ethylenically unsaturated aromatic monomers. Specific examples of ethylenically unsaturated aromatic monomers (a) include styrene, a-methylstyrene, 4-methyl styrene, stilbene, 4-acetoxystilbene, eugenol, isoeugenol, 4-allylphenol, safrole, and mixtures of these materials. Preferably, the sulfonated monomers are water soluble, which can be facilitated by providing the monomer in the form of a salt, for example, salts of alkali metals (e.g., sodium) and ammonium salts. A variety of sulfonated monomers (b) may be used including those which result from sulfonating the ortho and/or para positions of the monomers used to provide ethylenically unsaturated aromatic monomer (a). Particular examples include sodium p-styrene sulfonate, sodium vinyl p-toluene sulfonate, ammonium p-styrene sulfonate.

In the sulfonated aromatic copolymers of this embodiment, the ratio of units derived from monomer (a) to the units derived from monomer (b) is preferably about 0.1 to 10:1, more preferably about 0.9:1. Materials of this type are described in International Patent Publication No. WO 92/07131 (E. I. du Pont de Nemours and Company). The sulfonated aromatic copolymers can be conveniently prepared by a variety of free radical-initiated polymerization reactions using, for example benzoyl peroxide or 2,2'-azobis (2-methylbutyronitrile).

A second class of stainblocking materials useful in the invention are polymers of at least one or more (α-and/or β-substituted) acrylic acid monomers, these materials sometimes being referred to herein as (α-and/or β-substituted) acrylic acid polymers. The use of the parenthetical expression "a-and/or b-substituted" indicates that substitution of the α- and β- positions of the acrylic acid monomer is independently optional. That is, both positions may be substituted, neither position may be substituted, or either one of the two positions may be substituted without the other-position being substituted. Thus, (α-and/or β-substituted) acrylic acid monomers that are useful in preparing the polymers have the general structure HR^1 C=C(R)COOX, wherein R and R^1 are independently selected (i.e., they may be the same or they may be different) from hydrogen, organic radicals or halogen, and X is hydrogen, an organic radical, or a cation. Organic radicals that may be used to provide R and R^1 include aliphatic hydrocarbons (more preferably, alkyl moieties having about 1 to 20, most preferably about 1 to 4 carbon atoms such as methyl, ethyl, propyl and butyl), which, optionally, may be sulfonated or halogenated (for example, by chlorine or fluorine); and aromatic hydrocarbons (more preferably, a phenyl group), which, optionally, may be sulfonated, halogenated (for example, by chlorine or fluorine), hydroxylated (e.g., phenol or naphthol), or combinations thereof (e.g., sulfonated phenol or sulfonated naphthol). Halogens that may be used for R and R^1 include chlorine and fluorine.

Organic radicals that may be used to provide the X group include both aliphatic moieties (which may be linear, branched or cyclic, and preferably containing about 1 to 10 carbon atoms), or aromatic moieties, any of which may, optionally, be halogenated, sulfonated, carboxylated, hydroxylated or ethoxylated, including cationic (e.g., sodium, potassium, ammonium, and quaternary amine) salts of these materials. Cations that may be used to provide X include sodium, potassium, ammonium, and quaternary amine.

Preferred monomers are defined by structures in which R^1 is hydrogen, R is an alkyl group having 1 to 4 carbon atoms, phenyl, phenol, sulfonated phenol, naphthol, chlorine, or fluorine, and X is hydrogen, an alkyl group of 1 to 10 carbon atoms, sodium, potassium or ammonium. The most preferred monomer is methacrylic acid (R^1 and X are hydrogen, R is methyl).

The (α-and/or β-substituted) acrylic acid polymers are preferably sufficiently water-soluble or water dispersible that uniform application and penetration of the polymer into the substrate surface can be achieved at normal application temperatures (about room temperature to 100° C.). However, excessive water solubility may reduce the treated substrate's resistance to staining by acid colorants, as well as the effectiveness of the stainblocking compositions after cleaning the substrate.

The glass transition temperature of the (α-and/or β-substituted) acrylic acid polymers can be as low as about 35° C. although higher glass transition temperatures are preferred. When polymers having high glass transition temperatures (e.g., about 90° C. or higher) are used, an additional benefit of improved soil resistance may be obtained.

The weight average molecular weight and the number average molecular weight of the (α-and/or β-substituted) acrylic acid polymers should be selected so as to provide satisfactory stain resistance, water solubility, viscosity, and ability to be handled in conventional stainblocking material manufacturing and application processes. Preferably, the lower 90 weight percent of the polymer has a weight average molecular weight of about 3,000 to 250,000, and a number average molecular weight of about 500 to 50,000, more preferably about 800 to 10,000. Generally, a larger proportion of water-soluble comonomer is preferred for high molecular weight polymers and a larger proportion of water-insoluble comonomer is preferred for low molecular weight polymers.

In some instances, however, higher molecular weight materials may be useful. For example, a water soluble copolymer of acrylic acid and methacrylic acid may have a weight average molecular weight of about 80,000 to 500,000, more preferably about 100,000 to 350,000, and most preferably about 130,000 to 200,000. In the higher weight average molecular weight copolymers, the acrylic acid preferably comprises about 1 to 20 weight percent, more preferably about 5 to 15 weight percent, while the methacrylic acid correspondingly provides about 99 to 80 weight percent, more preferably, about 95 to 85 weight percent, the sum of the acrylic acid and methacrylic acid equaling 100 weight percent.

Included within the class of (α-and/or β-substituted) acrylic acid polymers are acrylic polymers; i.e., polyacrylic acid, copolymers of acrylic acid and one or more other monomers that are copolymerizable with acrylic acid, and blends of polyacrylic acid and one or more acrylic acid copolymers. These can be produced using well-known techniques for polymerizing ethylenically unsaturated monomers. Also included within the class of (α-and/or β-substituted) acrylic acid polymers, and most preferred, are methacrylic polymers; i.e., polymethacrylic acid, copolymers of methacrylic acid and one or more other monomers that are copolymerizable with methacrylic acid, and blends of polymethacrylic acid and one or more methacrylic acid copolymers. The methacrylic polymers useful in the invention can also be prepared using methods well-known in the art for polymerization of ethylenically unsaturated monomers.

Monomers useful for copolymerization with either the acrylic acid or the methacrylic acid have ethylenic unsaturation. Such monomers include monocarboxylic acids, polycarboxylic acids, and anhydrides of the mono- and polycarboxylic acids; substituted and unsubstituted esters and amides of carboxylic acids and anhydrides; nitriles; vinyl monomers; vinylidene monomers; monoolefinic and polyolefinic monomers; and heterocyclic monomers. Specific representative monomers include acrylic acid, itaconic acid, citraconic acid, aconitic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, cinnamic acid, oleic acid, palmitic acid, vinyl sulfonic acid, vinyl phosphonic acid, and substituted or unsubstituted alkyl and cycloalkyl esters of these acids, the alkyl or cycloalkyl groups having 1 to 18 carbon atoms such as methyl, ethyl, butyl, 2-ethylhexyl, octadecyl, 2-sulfoethyl, acetoxyethyl, cyanoethyl, hydroxyethyl, b-carboxyethyl and hydroxypropyl groups. Also included are amides of the foregoing acids, such as acrylamide, methacrylamide, methylolacrylamide, 1,1-dimethylsulfoethylacrylamide, acrylonitrile, and methacrylonitrile. Various substituted and unsubstituted aromatic and aliphatic vinyl monomers may also be used; for example, styrene, a-methylstyrene, p-hydroxystyrene, chlorostyrene, sulfostyrene, vinyl alcohol, N-vinyl pyrrolidone, vinyl acetate, vinyl chloride, vinyl ethers, vinyl sulfides, vinyl toluene, butadiene, isoprene, chloroprene, ethylene, isobutylene, and vinylidene chloride. Also useful are various sulfated natural oils such as sulfated castor oil, sulfated sperm oil, sulfated soybean oil, and sulfonated dehydrated castor oil. Particularly useful monomers include ethyl acrylate, butyl acrylate, itaconic acid, styrene, sodium sulfostyrene, and sulfated castor oil, either alone or in combination. The methacrylic polymers may be polymerized in the presence of chain transfer agents or other polymers which may incorporate into the methacrylic polymer during polymerization.

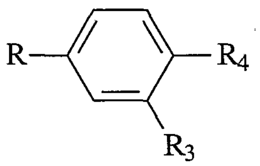
In the methacrylic polymers, the methacrylic acid preferably provides about 20 to 100 weight percent, more preferably about 60 to 90 weight percent, of the polymer. The optimum proportion of methacrylic acid in the polymer depends on the comonomer(s) used, the molecular weight of the copolymer, and the pH at which the material is applied. When water-insoluble comonomers such as ethyl acrylate are copolymerized with methacrylic acid, they may comprise up to about 40 weight percent of the methacrylic polymer. When water-soluble comonomers such as acrylic acid or sulfoethyl acrylate are copolymerized with methacrylic acid, the water soluble comonomers preferably comprise no more than 30 weight percent of the methacrylic polymer and preferably the methacrylic polymer also comprises up to about 50 weight percent water-insoluble monomer.

Commercially available acrylic polymers useful as stainblocking materials include Acrysol™ (available from Rohm and Haas Company) and Carbopol™ from B. F. Goodrich. Commercially available methacrylic polymers generally useful in the present invention include the Leukotan™ family of materials such as Leukotan™ 970, Leukotan™ 1027, Leukotan™ 1028, and Leukotan™ QR 1083, available from Rohm and Haas Company.

Polymers of (α-and/or β-substituted) acrylic acid monomers useful in the stainblocking compositions of the invention are described in U.S. Pat. No. 4,937,123 (Chang et al.), U.S. Pat. No. 5,074,883 (Wang), and U.S. Pat. No. 5,212,272 (Sargent et al.).

A third class of stainblocking materials useful in the invention are hydrolyzed polymers of maleic anhydride and at least one or more ethylenically unsaturated monomers. The unsaturated monomer may be an alpha-olefin monomer or an aromatic monomer, although the latter is preferred. A variety of linear and branched chain alpha-olefins may be used including alkyl vinyl ethers. Particularly useful alpha-olefins are 1-alkenes containing 4 to 12 carbon atoms, such as isobutylene, 1-butene, 1-hexene, 1-octene, 1-decene, and 1-dodecene, with isobutylene and 1-octene being preferred, and with 1-octene being most preferred. A portion of the alpha-olefins can be replaced by one or more other monomers, e.g., up to 50 wt. % of alkyl (C1-4) acrylates, alkyl (C_1-4) methacrylates, vinyl sulfides, N-vinyl pyrrolidone, acrylonitrile, acrylamide, as well as mixture of the same.

A variety of ethylenically unsaturated aromatic monomers may be used to prepare the hydrolyzed polymers. The ethylenically unsaturated aromatic monomers may be represented by the general formula:



wherein R is R^1-CH=C(R^2)- or CH_2 =CH-CH_2 -; R^1 is H-, CH_3- or phenyl R^2 is H- or CH_3 -; R^3 is H- or CH_3 O-; R^4 is H-, CH_3 -, or acetyl and R^3 plus R^4 is -CH_2 -O-CH_2 -O-CH_2 -.

Specific examples of ethylenically unsaturated aromatic monomers include free radically polymerizable materials such as styrene, α-methylstyrene, 4-methyl styrene, stilbene, 4-acetoxystilbene (used to prepare a hydrolyzed polymer from maleic anhydride and 4-hydroxy-stilbene), eugenol, isoeugenol, 4-allylphenol, safrole, mixtures of these materials, and the like. Styrene is most preferred. The utility of some of these materials may be improved by increasing the amount of polymerization initiator or acylating or etherifying the phenolic hydroxy groups.

In the hydrolyzed polymers, the ratio of units derived from ethylenically unsaturated monomer to units derived from maleic anhydride is about 0.4:1 to 1.3:1 when the unsaturated monomer is an alpha-olefin, and is about 1:1 to 2:1 when using an unsaturated aromatic monomer. In any event, a ratio of about 1:1 is most preferred.

Hydrolyzed polymers suitable for use in the invention may be prepared by hydrolyzing ethylenically unsaturated maleic anhydride polymers. Alkali metal hydroxides (such as potassium hydroxide, lithium hydroxide and, most often, sodium hydroxide, as well as blends of these) are suitable hydrolyzing agents. Hydrolysis can be effected in the presence of more than or less than a molar amount of the alkali metal hydroxide. The presence of an alcohol in the hydrolysis mixture should be avoided.

Hydrolyzed polymers of at least one or more alpha-olefin monomers and maleic anhydride useful in the stainblocking compositions of the invention are described in U.S. Pat. No. 5,460,887 (Pechhold). Hydrolyzed polymers of at least one or more ethylenically unsaturated aromatic monomers and maleic anhydride useful in the stainblocking compositions of the invention are described in U.S. Pat. No. 5,001,004 (Fitzgerald et al.).

Quite useful stainblocking materials may be obtained: (1) by blending together at least two or more polymers selected from among the different general classes of polymers described above; (2) by reacting together at least two or more monomers from which the different general classes of polymers are derived; (3) as the reaction product of at least one or more of the monomers from which the polymers may be derived and at least one or more of the polymers; or (4) by polymerizing at least one or more of the monomers in the presence of one or more of the polymers.

For example, one or more (α-and/or β-substituted) acrylic acid monomers may be polymerized together and, subsequent to the polymerization, blended with a sulfonated aromatic polymer. This permits both the carboxyl functionality from the (α-and/or β-substituted) acrylic acid polymer and the sulfonate functionality from the sulfonated aromatic polymer to contribute to the stainblocking properties of the composition. Particularly useful examples of such blends comprise a sulfonated aromatic condensation polymer (e.g., the condensation polymerization product of an aldehyde such as formaldehyde or acetaldehyde, a hydroxyaromatic compound such as bis(hydroxyphenyl)sulfone, phenol or napthol, and phenylsulfonic acid), and methacrylic polymer (e.g., polymethacrylic acid or a copolymer of methacrylic acid and or more of the following monomers: ethyl acrylate, butyl acrylate, itaconic acid, styrene, sodium sulfostyrene, sulfated castor oil, and acrylic acid).

The amounts of the sulfonated aromatic polymer and the (α-and/or β-substituted) acrylic acid polymer used should be sufficient to provide the desired degree of stain resistance to the substrate. Generally, when the substrate is nylon 6,6, lower application levels can be used than when the substrate is nylon 6 or wool. When the substrate is yarn heat-set under moist conditions (e.g., in an autoclave), generally higher application levels are required than when the yarn is heat-set under substantially dry conditions. Preferably, the amount of sulfonated aromatic polymer is at least about 0.1% SOF, more preferably at least about 0.2% SOF, most preferably at least about 0.4% SOF when treating nylon 6,6 carpet fiber. Generally, amounts of sulfonated aromatic polymer in excess of about 2% SOF provide little added benefit. Preferably the amount of (α-and/or β-substituted) acrylic acid polymer is at least about 0.1% SOF, more preferably at least about 0.2% SOF, most preferably at least about 0.4% SOF when treating nylon 6,6 carpet fiber. Generally amounts of (α-and/or β-substituted) acrylic acid polymer in excess of 2% SOF provide little added benefit. Preferably, the amount of sulfonated aromatic polymer used is at least about 0.2% SOF, more preferably at least about 0.4% SOF, based on the weight of the fiber when treating nylon 6 carpet fiber. Preferably, the amount of (α-and/or β-substituted) acrylic acid polymer is at least about 0.2 more, % SOF, preferably at least about 0.4% SOF when treating nylon 6 carpet fiber.

Alternatively, the (α-and/or β-substituted) acrylic acid monomer may be polymerized in the presence of the sulfonated aromatic polymer. Examples of such compositions comprise an α--substituted acrylic acid monomer (e.g., having the structure $H_2C{=}C(R)CO_2H$ wherein R is an alkyl group having 1 to 4 carbon atoms, phenyl, phenol, sulfonated phenol, naphthol, chlorine or fluorine) polymerized in the presence of a sulfonated aromatic condensation polymer (e.g., the condensation polymerization product of an aldehyde such as formaldehyde or acetaldehyde, a hydroxy aromatic compound such as bis(hydroxyphenyl)sulfone, phenol or napthol, and phenylsulfonic acid). Such techniques are described in U.S. Pat. No. 4,940,757 (Moss, III et al.).

A free radical polymerization initiator is added to initiate polymerization of the (α-and/or β-substituted) acrylic acid monomer in the presence of the sulfonated aromatic polymer. Useful initiators include persulfates (e.g., potassium persulfate, ammonium persulfate, or sodium persulfate), peroxides (e.g., sodium peroxide, hydrogen peroxide, benzoyl peroxide, acetyl peroxide, lauryl peroxide, cumyl peroxide, t-butyl peroxide, or t-butyl hydroperoxide), azo compounds (e.g., azo-bis-isobutryonitrile), and hydrochloride salts of azo compounds.

In another embodiment, a stainblocking material may be prepared by reacting a sulfonated hydroxy aromatic compound with isocyanate, carboxylic acid, carboxylic acid anhydride, carboxylic acid chloride, or other carboxylic acid precursor, any of which may be saturated or unsaturated. The ester formed by this reaction may then be reacted by itself or with an (α-and/or β-substituted) acrylic acid, and a free radical polymerization initiator, either in the presence of or in the absence of another sulfonated aromatic polymer. Alternatively, the ester formed from the first reaction may be homopolymerized or copolymerized with an aromatic compound in an aldehyde condensation reaction. The resulting product can be further reacted, either by itself or with an (α-and/or β-substituted) acrylic acid in the presence of a free radical polymerization initiator. Useful free-radical polymerization initiators include persulfates (e.g., ammonium persulfate, sodium persulfate, or potassium persulfate), peroxides (e.g., sodium peroxide, hydrogen peroxide, benzoyl peroxide, acetyl peroxide, lauryl peroxide, cumyl peroxide, t-butyl peroxide, or t-butyl hydroperoxide), an azo compound (e.g., azo-bis-isobutyronitrile), and peracetate (e.g., t-butyl peracetate). Such techniques are described in U.S. Pat. No. 5,310,828 (Williams et al.).

Other useful combinations include hydrolyzed polymers of ethylenically unsaturated monomer and maleic anhydride blended with sulfonated aromatic polymers and/or polymers of (α-and/or β-substituted) acrylic acid. For example, a part of the maleic anhydride (up to 30 weight %) can be replaced by acrylic or methacrylic acid. In another embodiment, a part (preferably 1-75% by weight) of the maleic anhydride can be replaced by maleimide, N-alkyl (C_1-4) maleimides, N-phenyl-maleimide, fumaric acid, itaconic acid, citraconic acid, aconitic acid, crotonic acid, cinnamic acid, alkyl (C_1-18) esters of the foregoing acids, cycloalkyl (C_2-8) esters of the foregoing acids, sulfated castor oil, or the like.

Particularly preferred blends comprise about 95 to 30 weight % of hydrolyzed polymer of ethylenically unsaturated aromatic monomer and maleic anhydride (more preferably, about 85 to 40 weight %), and about 5 to 70 weight % of a sulfonated aromatic condensation polymer, e.g., a sulfonated phenol-formaldehyde condensation polymer (more preferably, about 15 to 60 weight %), wherein the sum of these two components is 100 weight %. Such combinations are described in U.S. Pat. No. 4,833,839 (Fitzgerald et al.).

The emulsifying agent is used in an amount sufficient to provide a stable emulsion, typically about 0.1 to 8%. Typical fluorochemicals are produced by condensation of a fluorinated alcohol or fluorinated primary amine with a suitable anhydride or isocyanate, for example, N-ethyl perfluorooctyl-sulfonamidoethanol and toluene diisocyanate reacted in a 2:1 molar ratio.

The silsesquioxane materials can be any of the types described in U.S. Patent Nos. 4,781,844 (Kortmann, et al), 4,351,736 (Steinberger et al.), 5,073, 442 (Knowlton et al.) or 3,493,424 (Mohrlok et al.). These silsesquioxanes are of the formula R-Si(OR')$_3$ alone or together with silanes of the formula Si(OR')$_4$ and/or R$_2$-Si(OR')$_2$ wherein R represents a substituted or unsubstituted hydrocarbon radical having 1 to 7 carbon atoms, substituents of which may be halogen atoms and mercapto and epoxy groups. R' represents an alkyl radical with 1 to 4 carbon atoms. Preferred silsesquioxanes are those that are neutral or anionic.

The silsesquioxanes may be prepared by adding silanes to a mixture of water, a buffer, a surface active agent and optionally an organic solvent, while agitating the mixture under acidic or basic conditions. It is preferable to add the quantity of silane uniformly and slowly in order to achieve a narrow particle size of 200 to 500 Angstroms. The exact amount of silane that can be added depends on the substituent R and whether an anionic or cationic surface active agent is used.

Copolymers of the silsesquioxanes in which the units can be present in block or random distribution are formed by the simultaneous hydrolysis of the silanes. The preferred amount of silane of the formula $Si(OR')_4$ added is about 2 to 50 percent, relative to the total weight of the silanes employed, prefereably 3 to 20 percent.

The following silanes are useful in preparing the silsesquioxanes of the present invention: methyltrimethoxysilane, methyltriethoxysilane, methyltriisopropoxyoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, propyltrimethoxysilane, isobutyltrimethoxysilane, isobutyltriethoxysilane, 2-ethylbutyltriethoxysilane, tetraethoxysilane, and 2-ethylbutoxytriethoxysilane.

The composition may further comprise a repellent material selected from the group consisting of glassy fluorochemicals having a receding contact angle to n-hexadecane of 45° or higher and glassy hydrocarbons having a receding contact angle to n-hexadecane of 35° or higher.

To impart oil and water repellency as well as soil resistance to a fibrous substrate, the treatments of this invention may contain certain repellent fluorochemical material and/or hydrocarbon material. Suitable fluorochemicals for use in the present invention should exhibit a receding contact angle to n-hexadecane of at least 45° or higher, preferably at least 65° or higher, and more preferably at least 70° or higher, as measured by the Receding Contact Angle Test described herein. Additionally, suitable fluorochemical materials are hard, glassy, non-tacky, non-cationic materials having a glass transition temperature ranging from about 20°C to about 130°C. The fluorochemical material can be from any chemical class, but fluorochemical urethanes are preferred. The fluorochemical material preferably contains a fluoroaliphatic group, and most preferably, a perfluoroaliphatic group. The concentration of fluorochemical material should be at least 0.03% SOF (solids on fiber) and preferably is at least 0. 1 % SOF. The following is a nonexhaustive list of useful fluorochemicals:

F-l - Scotchgard^{Tm} Fabric Protector FC-214-30 - a fluorochemical acrylate/urethane commercially available as a 30% (wt) solids aqueous emulsion from Minnesota Mining, and Manufacturing Company, St. Paul, Minnesota.

F-2 - Scotchgard^{Tm} Rain and Stain Repeller FC-232 - a fluorochemical acrylate/urethane, commercially available as a 30% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-3 - Scotchgard^{Tm} Carpet Protector FC-358 - a fluorochemical carbodiimide, commercially available as a 20% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-4 - 3M Brand Carpet Protector FX-364 - a fluorochemical urethane, commercially available as a 23% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-5 - 3M Brand Protector FX-365 - a fluorochemical urethane commercially available as a 24% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-6 - Scotchgard^{Tm} Carpet Protector FC-1355 - a fluorochemical ester, commercially available as a 45% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-7 - Scotchgard^{Tm} Carpet Protector FC-1367F - a fluorochemical ester, commercially available as a 41 % (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-8 - Scotchgard^{Tm} Carpet Protector FC-1373M - a fluorochemical urethane, commercially available as a 29% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-9 - Scotchgard^{Tm} Carpet Protector FC-1374 - a fluorochemical urethane, commercially available as a 25% (wt) solids aqueous emulsion from Minnesota Mining and Manufacturing Company.

F-10 - Scotchgard^{Tm} Carpet Protector FC-1395 - a fluorochemical urethane, commercially available as a 25% (wt) solids aqueous emulsion from Minnesota Mining, and Manufacturing Company.

F-11 - Duratech^{Tm}carpet treatment - believed to be a fluorochemical urethane/urea, commercially available as a 30% (wt) solids aqueous emulsion from E.I. duPont de Nemours & Co., Wilmington, Delaware F-11A - NRD-372 carpet treatment - believed to be a fluorochemical urethane/urea, commercially available as a 27% (wt) solids aqueous emulsion from E.I. duPont de Nemours & Co.

F-12 - Zonyl^{Tm} 8779 carpet treatment - commercially available as an I I % (wt) solids aqueous emulsion from E.I. duPont de Nemours & Co.

F-13 - Softech^{Tm}97H carpet treatment - believed to be a fluoroalkyl acrylate polymer, commercially available as a 15% (wt) solids aqueous emulsion from Dyetech, Inc., Dalton, Georgia F-14 - ShawguardTm 353 fluoroalkyl acrylate copolymer - commercially available as a 13% (wt) solids aqueous emulsion from Shaw Industries, Inc.

F-15 - Nuva^{Tm} FT fluorochemical acrylate polymer - commercially available as a 22% (wt) solids emulsion from Hoechst Celanese, Charlotte, North Carolina F-16 - BartexTm MAC fluorochemical - commercially available as a 14% (wt) solids emulsion from Trichromatic Carpet, Inc., Quebec, Canada F-17 - BartexTm T11 fluoroalkyl acrylate polymer - commercially available as a 16% (wt) solids emulsion from Trichromatic Carpet, Inc.

F-18 - MeFOSE urethane of Desmodure N-75 Synthesis: 368 g (0.66 eq) of MeFOSE alcohol (C8FI7SOI)N(CH3)C,H40H) and 176 g (0.68 eq) of Desmodur ^{Tm}N75 triisocyanate (a biuret isocyanate trimer derived from hexamethylene triisocyanate, commercially available from Mobay Corp., Pittsburgh, Pennsylvania) was added along with 456 g of methyl ethyl ketone (MEK) by funnel to a 2000 mL three-necked round bottom flask fitted with stirrer and condenser. Heat was applied to the mixture using a heat lamp and agitation was started. I g of dibutyltin dilaurate was added, resulting in a slight exotherm, and the mixture was refluxed for 2.5 hrs. Infrared spectrum analysis of the product showed a small peak at 23 10 cm- 1, indicating, the presence of residual -NCO in the reaction. The reaction product was poured into aluminum trays and the MEK was removed in an oven at 250^{oo}F (121°C). When the solvent had been removed the trays were cooled and the resultant solid urethane was placed into glass bottles.

Emulsification: 100 g of the above solid urethane was added to 250 g of methyl isobutyl ketone (MIBK), and the mixture was heated to approximately 90^{oC} to dissolve the urethane in the solvent. Another mixture consisting of 500 g of water and 5 g of Rhodacal^{Tm} DS-10 surfactant (commercially available from Rhone-Poulenc Corp., Cranberry, New Jersey) was heated to 70°C to dissolve the surfactant. The two liquids were mixed with stirring and were subjected to 12 minutes of emulsification using a Branson Sonifier TM Ultrasonic Horn 450 (commercially available from VWR Scientific). The solution was stripped of organic solvent on a rotary evaporator. The MIBK was co-distilled with a certain amount of water. When inspection revealed the there was no longer any odor of solvent, the amount of solids was measured and sufficient water was added to bring the final emulsion weight percent solids to 14.6%.

F-19 - TG-232D fluoralkyl acrylate copolymer emulsion - available commercially from Advanced Polymers, Inc., Carlstadt, New Jersey

HYDROCARBON MATERIALS Suitable hydrocarbon materials for use in the present invention exhibit a receding contact angle to n-hexadecane of at least 35° or higher as measured by the Receding Contact Angle Test described herein. Additionally, suitable hydrocarbon materials are hard, glassy, non-tacky, non-cationic, fluorine-free materials having at least one aliphatic group and having a glass transition temperature ranging from about 20^{oC} to about 130°C. The aliphatic group is preferably a long-chain aliphatic group containing at least 10 carbon atoms. and more preferably containing between about 12 and about 24 carbon atoms. The hydrocarbon material can be from any chemical class, but hydrocarbon urethanes and amides are preferred. The concentration of hydrocarbon material should be at least 0. 1 % SOF and is preferably at least 0.2% SOF.

H-1 - Octadecyl urethane of Desmodur^{Tm} N100 285 g (1.06 eq) of octadecanol and 228 g (1. 12 eq) of Desmodur^{Tm} N100 trilsocyanate (a biuret isocyanate trimer derived from hexamethylene triisocyanate, commercially available from Mobay Corp., Pittsburgh, Pennsylvania) was added along with 500 g of methyl ethyl ketone (MEK) by funnel to a 2000 mL three-necked round bottom flask fitted with stirrer and condenser. Heat was applied to the mixture using a heat lamp and agitation was started. 500 mg of dibutyltin dilaurate was added, resulting in a slight exotherm, and the mixture was refluxed for 2.5 hrs. Infrared spectrum analysis of the product showed a small peak at 23 10 cm- 1, indicating the presence of residual NCO in the reaction. The reaction product was poured into aluminum trays and the MEK was removed in an oven at 250°F (121^{oC}). When the solvent had been removed the trays were cooled and the resultant solid urethane was placed into glass bottles.

Essentially the same emulsification procedure was followed as was described in the preparation of the emulsion for fluorochemical material F- 18.

The final emulsion weight percent solids was 20.0%.

H-2 - Hexadecyl urethane of Desmodur^{Tm} N100 - Essentially the same procedure for synthesis and emulsification was used to prepare H-2 as was used to prepare H- 1 except that 272 g (1. 12 eq) of hexadecanol replaced 285 - (1.06 eq) of octadecanol. The final emulsion weight percent solids was 20.0%.

H-3 - Tetradecyl urethane of Desmodur^{Tm}N100 - Essentially the same procedure for synthesis and emulsification was used to prepare H-3 as was used to prepare H- I except that 256 g (1.20 eq) of tetradecanol replaced 285 g (1.06 eq) of octadecanol and 244 - (1.28 eq) rather than 228 (1.12 eq) of Desmodur ^{Tm} N 100 triisocvanate was used. The final emulsion weight percent solids was 20.0%.

H-4 - Dodecyl urethane of Desmodur^{Tm}N100 - Essentially the same procedure for synthesis and emulsification was used to prepare H-4 as was used to prepare H- I except that 239 g (1.28 eq) of dodecanol replaced 285 g (1.06 eq) of octadecanol and 261 g (1.37 eq) rather than 228 cy (1. 12 eq) of DesmoduFm NIOO triisocyanate was used. The final emulsion weight percent solids was 20.0%.

H-4A - Octadecyl urethane of Desmodur^{Tm} N75 - Essentially the same procedure for synthesis and emulsification was used to prepare H-4A as was used to prepare H- I except that 284 g (1. 10 eq) of Desmodur Tm N75 replaced 228 g (1. 12 eq) of Desmodur Tm N 100 triisocyanate. The final emulsion weight percent solids was 18.0%.

H-5 - Octadecyl urethane of isophorone diisocyanate - Essentially the same procedure for synthesis and emulsification was used to prepare H-5 as was used to prepare H- I except that 348 g (1.29 eq) rather than 285 g (1.06 eq) of octadecanol was used and 152 g (1.37 eq) of isophorone diisocyanate replaced 228 g (1. 12 eq) of Desmodur Tm NIOO triisocyanate. The final emulsion weight percent solids was 20.0%.

H-6 - Hexadecyl urethane of isophorone diisocyanate - Essentially the same procedure for synthesis and emulsification was used to prepare H-5 as was used to prepare H- I except that 336 g (1.39 eq) of hexadecanol replaced 285 g (1.06 eq) of octadecanol and 164 g (1.47 eq) of isophorone diisocyanate replaced 228 g (1. 12 eq) of Desmodur Tm N 100 triisocyanate. The final emulsion weight percent solids was 20.0%.

H-7 - Octadecyl (2 mol)/1,4-butanediol (1 mol) urethane of hexamethylene diisocyanate (2 mole) Synthesis: 274 g (1.39 eq) of octadecanol and 164 g (1.47 eq) of hexamethylene diisocyanate were added along with 500 g of MEBK by funnel to a 2000 mL three-necked round bottom flask fitted with stirrer and condenser. Heat was applied to the mixture using a heat lamp and agitation was started. 500 g of dibutyltin dilaurate (500 mg) was added, resulting in a slight exotherm, and the mixture was refluxed for 30 minutes. At this point 48 g of butanediol was added and the mixture was refluxed for another 2 hours. Infrared spectrum analysis of the product showed a small peak at 23 10 cm- 1, indicating the presence of residual NCO in the reaction. The reaction product was poured into aluminum trays and the MEK was removed in an oven at 250°F (12 1 °Q. When the solvent had been removed the trays were cooled and the resultant solid urethane was placed into glass bottles.

Emulsification: The same procedure was used for emulsification as was described in the preparation of Hydrocarbon Material H-1. The final emulsion weight percent solids was 20.0%.

H-8 - Octadecyl (2 moles)/1,4-butanediol (1 mole) urethane of isophorone diisocyanate Into a three-necked, 2-L round bottom flask equipped with stirrer and condenser was added 2 10 g (4.12 eq) of isophorone diisocyanate to this was added a solution of 248 g (0.92 eq) of stearyl alcohol in 500 g of dry MEK.

Heating of the mixture was commenced and 250 mg of dibutyltin dilaurate was added. The mixture exothermed, was refluxed for 1 hour, 41g (0.92 eq) of 1,4- butanediol was added, and the mixture was refluxed for an additional 2 hours.

Infrared spectroscopy run on the final mixture revealed a slight excess of isocyanate.

The mixture was poured into shallow pans in an oven for 6 hours at 125^{oC}. The material was collected as a hard white glassy material and was emulsified as described in the preparation of Hydrocarbon Material H-1.

H-9 - Hexadecyl urethane of Vestanat^{Tm} T1890 triisocyanate 75.0 g (0.071 eq) of VestanatTm T1890 trusocyante (commercially available from Hijls America, Inc., Piscataway, New Jersey), 31.9 a of MEK, and 0. 12 g of dibutyltin dilaurate were added to a stirred solution in a three-necked flask containing 51.9 g of hexadecanol in 50 g of MEK heated to 70°C under nitrogen. The temperature of the mixture was increased to 780 C over a 3 minute period, then the mixture was stirred for an additional 3.3 hours. The resulting reaction product was poured into an aluminum pan. The yield was 104.7 g (96% of theoretical).

Essentially the same emulsification procedure was used as described in the preparation of Hydrocarbon Material H-1.

H-10 - Octadecyl aminoalcohol adduct of Epon^{Tm} 828 diepoxide A one pint aluminum can was equipped with an overhead stirrer and a nitrogen purge line. The flask was charged with 152.6 g of EPONTM 828 epoxy resin (epoxy equivalent weight of 187, commercially available from Shell Chemical Co., Houston, Texas) and 42.4 g of bisphenol A (equivalent weight of 114). The reaction was heated to 1250C while being purged with nitrogen. Next, g of bisphenol A and 0.25 g of phosphonium iodide were charged to the flask, and the reaction was heated to 145^{oC}. The reaction exothermed to 175'C and was held at this temperature for I hour. The reaction was cooled to 130°C and 107.6 g of melted octadecylamine (equivalent weight of 269) was added to the reaction. The reaction exothermed to 163°C and then cooled to 125°C. Finally, the reaction was heated at 125°-135°C for 1.5 hours. The reaction was cooled to room temperature and 307g of a glassy solid was collected.

Essentially the same emulsification procedure was used as described in the preparation of Hydrocarbon Material H-1.

H-10A - Octadecyl aminoalcohol adduct of Epon^{Tm} 828 diepoxide A one pint aluminum can was equipped with an overhead stirrer and a nitrogen purge line. The flask was charged with 146 9 of EPON ^{T}" 828 and 50 g of bisphenol A. The reaction was heated to 125°C while being purged with nitrogen. Next, 4 g, of bisphenol A and 0.25 g of phosphonium iodide were charged to the flask. The reaction was heated to 145°C. The reaction exothermed to 175°C and was held at this temperature for I hour. The reaction was cooled to 130°C and 82.8 g of melted octadecylamine (equivalent weight of 269) was added to the reaction. The reaction exothermed to 163°C and then cooled to 125°C.

Finally, the reaction was heated at 125-135°C for 1.5 hours. The reaction was cooled to room temperature and 282g of a glassy solid was collected.

Essentially the same emulsification procedure was used as described in the preparation of Hydrocarbon Material H-1.

H-11 - Octadecyl amide of isophorone diamine A three necked 5000 mL flask was equipped with a Dean-Stark trap and an overhead stirrer. 1854 g (6.52 mol) of stearic acid, 1.0 g of IrganoX^{Tm} 245 was added to the reaction flask. The reaction flask was purged with nitrogen for 30 minutes. Next, the flask was slowly heated to 100°C, at which point all of the stearic acid had melted. 554 g (3.26 mol) of isophorone diamine was added to the reaction. The reaction was heated to 190°C for 1 hour. There was 67 mL of water collected in the Dean-Stark trap after 1.5 hours. Next, the reaction was cooled and allowed to stand at room temperature over the weekend. Then the reaction was heated to 2 1 O°C for one hour and then cooled. 2271 g of a white solid was collected, and its identification was confirmed an infrared and I 3C NMR spectra. The melting point was measured to be 85°C.

H-12 - Azelaic diamide of isophorone diamine A three-necked 1000 mL flask was equipped with a Dean-Stark trap and an overhead stirrer. 94 g (0.5 mol) of azelaic acid and 170 g (1.0 mol) of isophorone diamine was added to the reaction flask. Next, the flask was heated to 1900C for 2 hours. At this point, the required amount of water (18 g) had been collected in the Dean-Stark trap. Next, 284 g (1.0 mol) of stearic acid was added to the reaction. The reaction was heated at 2 1 O°C for l hour. The reaction was cooled and 500 g of a glassy solid was collected. Product identification was confirmed by an infrared spectrum.

Essentially the same emulsification procedure was used as described in the preparation of Hydrocarbon Material H- 1.

H-13 - Dytek / Bis-stearamide A three necked 1000 mL flask was equipped with a Dean-Stark trap and an overhead stirrer. 284 g (1.0 mol) of stearic acid, 1.4 g of IrganoXTm 245 (commercially available from Ciba Specialty Chemicals) was added to the reaction flask. The reaction flask was purged with nitrogen for 30 minutes. Next, the flask was slowly heated to 100°C, at which point all of the stearic acid had melted. 63g (0.54 mol) of Dytek Tm A diamine (commercially available from E. 1. duPont de Nemours, Wilmington, Delaware) was added to the reaction and the reaction was heated to 170-180°C. There was 9 mL of water collected in the Dean-Stark trap after 1.5 hours. Next, the reaction was heated to 200°C and placed under vacuum (6 mm torr) for 30 minutes. The reaction was cooled and 260 g of a white solid was collected. Product identification was confirmed by an infra red spectrum, and the melting point was I 10°C.

Essentially the same emulsification procedure was used as described in the preparation of Hydrocarbon Material H-1.

H-14 - Octadecyl urea of VestanatTm T1890 triisocyanate 70.0 g (0.067 eq) of VestanatTm T1890 triisocyanate mixed with 41.6 g of toluene was added in one portion to a stirred solution of 53.8 g (0.20 eq) of ArmeenTM 18D flake (stearylamine, commercially available from Akzo Nobel Corp., Chicago, Illinois) in 40.0 g of toluene heated to 60°C under nitrogen. The temperature of the mixture was increased to 800C and the mixture was stirred for an additional 2.25 hours. The resulting reaction product was poured into an aluminum pan. The yield was 100.9 g (98. 1 % of theoretical).

Essentially the same emulsification procedure was used as described in the preparation of Hydrocarbon Material H-1.

H-15 - Hexadecyl urea of Vestanat^{Tm} T1890 triisocyanate Essentially the same procedure for synthesis and emulsification was used to prepare H- 15 as was used to prepare H- 14, except that 75.0 g (0.071 eq) instead of 70.0 g (0.067 eq) of VestanatTm T 1890 was used and 51.6 g (0. 214 eq) of Armeen TIA 16D flake (cetylamine, commercially available from Akzo Nobel Corp.) was used instead of 53.8 g (0.20 eq) of Armeen TNI 18D flake.

H-17 - Kenamide Tm E-180 - stearyl erucamide, commercially available from Witco Corp.. Memphis, Tennessee.

H-18 - KenamideTm E-221 - erucyl erucamide, commercially available from Witco Corp.. Memphis, Tennessee.

H-19 - Kodak TM carnauba wax flakes - commercially available from Eastman Fine Chemicals, Eastman Kodak Co., Rochester, New York.

H-20 - Vybaem 253 polymer (Pastille) - a highly branched hydrocarbon used as an additive to paraffin wax, commercially available from Petrolite Corp., Polymers Division, Tulsa, Oklahoma.

H-21 - Unirez^{Tm} 221 - polyamide based on dimer acid commercially available from Union Camp Corp., Jacksonville, Florida.

In some cases, the material used in the present invention to impart oil repellency, water repellency and soil resistance to a fibrous substrate can be a hybrid of the fluorochemicals and hydrocarbons previously mentioned. Such materials may be, for example, the reaction product of a fluorochernical with a hydrocarbon material. Again, however, the resulting material must be a hard, glassy, non-tacky material having a glass transition temperature ranging from about 20°C to about 130°C. The following is a nonexhaustive list of hybrid materials:

FH-1 - Urethane Reaction Product of Desmodur N-75 with 75% (mol) of MeFOSE and 25% (mol) of stearyl alcohol 276 g (0.49 eq) of MeFOSE alcohol, 72 g (0.27 eq) of octadecanol and 203 g (0.78 eq) of Desmodur^{Tm} N75 triisocyanate was added along with 449 g of MEBK by funnel to a 2000 mL three-necked round bottom flask fitted with stirrer and condenser. Heat was applied to the mixture using a heat lamp and agitation was started. I g of dibutyltin dilaurate was added resulting a slight exotherm, and the mixture was refluxed for 2.5 hrs. Infrared spectrum analysis of the product showed a small peak at 23 10 cm- 1, indicating the presence of residual NCO in the reaction.

Essentially the same emulsification procedure was followed as was described in the preparation of the emulsion for fluorochemical material F- 18.

The final emulsion weight percent solids was 15.2%.

FH-2 - Urethane Reaction Product of Desmodur^{Tm} N-75 with 50% (mol) of MeFOSE and 50% (mol) of stearyl alcohol Essentially the same procedure for synthesis and emulsification was used to prepare FH-2 as was used to prepare FH-1, except that 184 g (0.33 eq) of MeFOSE alcohol, 144 g (0.53 eq) of octadecanol, 230 g (0.89 eq) of Desmodur TM N75 triisocyanate and 443 g of MI1BK were used. The final emulsion weight percent solids was 15.3%.

FH-3 - Urethane Reaction Product of Desmodur N-75 with 25 % (mol) of MeFOSE and 75% (mol) of stearyl alcohol Essentially the same procedure for synthesis and emulsification was used to prepare FH-3 as was used to prepare FH- 1, except that 92 g (0. 16 eq) of MeFOSE alcohol, 216 g (0.80 eq) of octadecanol, 257 g (0.99 eq) of DesmoduFm N75 triisocyanate and 436 g M1BK were used. The final emulsion weight percent solids was 15.3%.

FH-4 - Urethane Reaction Product of Desmodur N-75 with 10% (mol) of MeFOSE and 90% (mol) of stearyl alcohol Essentially the same procedure for synthesis and emulsification was used to prepare FH-4 as was used to prepare

FH- 1, except that 37 g (0.07 eq) of MeFOSE alcohol, 258 g (0.96 eq) of octadecanol, 273 g (1.05 eq) of Desmodur TM N75 trilsocyanate and 432 g MEBK were used. The final emulsion weight percent solids was 15.3%.

The compositions may further contain a divalent metal salt. The divalent metal salts useful in the present invention include water soluble inorganic and organic salts of metals such as magnesium, barium, calcium, and zinc. Inorganic metal salts include chlorides, sulfates, and nitrates of these metals. Organic metal salts include acetates and formates of these metals. Preferred divalent metal salts are magnesium sulfate, magnesium chloride and magnesium acetate. Mixtures of two or more salts can also be used in this invention. Generally magnesium salts are preferably used to achieve both stain resistance and oil and water repellency. The divalent metal salts are preferably used in an amount of at least 1% sof, more preferably at least 1.5% solids sof, most preferably at least 2% solids. Amounts of the salt in excess of 5% sof generally do not provide any appreciable increase in stain resistance.

Generally the composition of this invention comprises from about 0.01 to 1.0 grams of silsesquioxane (0.000025 to 0.0025 wt %), and about 0.05 to 5 grams of stainblocker (0.0001 to 0.0125 wt.%) dissolved in 400 g of water. This composition may be used to exhaustively treat about 100 g of carpet. Preferably the composition comprises from about 0.05 to 0.5 grams of silsesquioxane, and about 0.1 to 1.0 grams of stainblocker.

EXAMPLES

Unless otherwise specified, all percentages shown in the examples and test methods which follow are percentages by weight.

Glossary

SSQO - To a 3-L 3-necked flask equipped with heater, stirrer and condenser was added 1106.0 g of deionized water and 14.0 g of linear alkylsulfonic acid (available from Alfa Aesar, Johnson Matthey, Ward Hill, MA), believed to be dodecylbenzenesulfonic acid). The resulting mixture was heated to 60°C with stirring until homogeneous, and 280 g of $CH_3Si(OCH_3)_3$ (methyltrimethoxysilane, available from Sigma Aldrich) was slowly added to the mixture over a 4 hour period. The hydrolysis reaction was allowed to continue overnight at 60°C with stirring, the resulting reaction product was filtered, then sufficient 20% aqueous NH_4OH was added to adjust the pH of the mixture to 7. The neutralized mixture was then stripped using a rotovap set at 50°C to produce 530 g of distillate consisting primarily of methanol with a small amount of water. The anionic emulsion of silsesquioxane that had formed was 14% solids and had an average particle diameter of approximately 30 nm, as measured using the Multi Angle Sizing (MAS) option on a Zeta Plus zeta potential analyzer (available from Brookhaven Instruments Corp., Holtsville, NY).

90/10 SSQO - To a 3-L 3-necked flask equipped with heater, stirrer and condenser was added 1972 g of deionized water and 12.5 g of linear alkylsulfonic acid. The resulting mixture was heated to 60°C with stirring until homogeneous, and 450 g of $CH_3Si(OCH_2CH_3)_3$ (methyltriethoxysilane, available from Sigma Aldrich) and 50 g of $Si(OC_2H_5)_4$ (tetraethyl orthosilicate, available from Sigma Aldrich) were each slowly added to the mixture over a 5 hour period. The hydrolysis reaction was allowed to continue for 2 additional hours at 60°C with stirring, after which time the pH of the mixture was 2.2. Sufficient aqueous NH_4OH was then added to adjust the pH of the mixture to 7. 1200 g of the neutralized mixture was then stripped using a rotovap set at 50°C to produce 310 g of distillate consisting primarily of ethanol with a small amount of water. The anionic emulsion of silsesquioxane that had formed was 16.8% solids and had an average particle diameter of approximately 30 nm, as measured using the Multi Angle Sizing (MAS) option on a Zeta Plus zeta potential analyzer.

80/20 SSQO - To a 3-L 3-necked flask equipped with heater, stirrer and condenser was added 1972 g of deionized water and 12.5 g of linear alkylsulfonic acid. The resulting mixture was heated to 60°C with stirring until homogeneous, and 400 g of $CH_3Si(OCH_2CH_3)_3$ and 100 g of $Si(OC_2H_5)_4$ were each slowly added to the mixture over a 5 ½ hour period. The hydrolysis reaction was allowed to continue for 2 ¾ additional hours at 60°C with stirring, then sufficient aqueous NH_4OH was added to adjust the pH of the mixture to 7. The mixture was stirred for an additional 2 hours, after which it was noted that some insoluble material had formed. 1200 g of the neutralized mixture was then stripped using a rotovap set at 50°C to produce 619 g of distillate consisting primarily of ethanol with a small amount of water. The anionic emulsion of silsesquioxane that had formed was cooled to room temperature and was filtered, giving an emulsion containing 13.3% solids and having an average particle diameter of approximately 30 nm, as measured using the Multi Angle Sizing (MAS) option on a Zeta Plus zeta potential analyzer.

TODU (tri-octadecyl urethane of DESMODUR™ N100) - 285 g (1.06 eq) of 1-octadecanol (available from Sigma Aldrich, Milwaukee, WI) and 228 g (1.12 eq) of DESMODUR™ N100 triisocyanate (a biuret isocyanate trimer derived from hexamethylene triisocyanate, commercially available from Mobay Corp., Pittsburgh, PA) was added along with 500 g of methyl ethyl ketone (MEK) by funnel to a 2000 mL three-necked round bottom flask fitted with stirrer and condenser. Heat was applied to the mixture using a heat lamp and agitation was started. 500 mg of dibutyltin dilaurate (available from Sigma Aldrich) was added, resulting in a slight exotherm, and the mixture was refluxed for 2.5 hrs. Infrared spectrum analysis of the resulting urethane reaction product showed a small peak at 2310 cm^{-1}, indicating the presence of a small residual of unreacted isocyanate. The urethane solution was then poured into aluminum trays and the MEK was removed by placing the trays in a vacuum oven at 250°F (121°C). When the solvent had been removed the trays were cooled and the resultant solid urethane was placed into glass bottles.

An emulsion of the urethane in water was then prepared as follows. 100 g of the above solid urethane was added to 250 g of methyl isobutyl ketone (MIBK), and the mixture was heated to approximately 90°C to dissolve the urethane in the solvent. Another mixture consisting of 500 g of water and 5 g of RHODACAL™ DS-10 surfactant (sodium dodecylbenzenesulfonate, available from Rhodia, Inc., Cranbury, NJ) was heated to 70°C to dissolve the surfactant. The two liquids were mixed with stirring and were subjected to 12 minutes of emulsification using a BRANSON SONIFIER™ Ultrasonic Horn 450 (commercially available from VWR Scientific). The solution was stripped of organic solvent on a rotary evaporator. The MIBK was co-distilled with a certain amount of water. When inspection revealed the there was no longer any odor of solvent, the amount of solids was measured and sufficient water was added to bring the final emulsion percent solids to 18%.

FX-661 - 3M™ Stain Release Concentrate FX-661, a stainblocker for carpet comprised of sulfonated phenolic and acrylic resins, available from 3M Company as a 29% solids aqueous emulsion

UPBEAT - UPBEAT™ nylon 6 carpet, light cream color, color no. 45101, style 51145, having a face weight of 26 oz/yd^2 (0.93 kg/m^2), available from Shaw Industries, Dalton, GA.

T-3 - TRANSITION III™ nylon 6,6 carpet, "Blue Moon" color, having a face weight of 36 oz/yd^2 (1.2 kg/m^2), available from Burlington Industries, Greensboro, NC.

Test Methods

Simulated Flex-Nip Application Procedure - The Simulated Flex-Nip Application Procedure described below was used to simulate the flex-nip operations used by carpet mills to apply stainblocking composition to carpet.

In this test, a carpet sample measuring approximately 12 inches by 12 inches (30 cm x 30 cm), typically weighing approximately 125 g, is immersed in deionized water at room temperature until dripping wet. Water is extracted from the wet sample by spinning in a Bock Centrifugal Extractor (available from Bock Engineered Products, Inc., Toledo, OH) until the sample is damp. The damp carpet sample is then steamed for 2 minutes at atmospheric pressure, at a temperature of 90-100°C, and 100% relative humidity in an enclosed steam chamber.

After steaming, the carpet sample is allowed to cool to near room temperature, and the aqueous treating composition is applied by placing the carpet sample, carpet fiber side down, in a glass tray containing the treating composition. The treating composition contains sufficient treating material(s) to give the desired percent solids on fiber (% SOF) and is prepared by dissolving or dispersing the treating materials in deionized water and adjusting the pH of the resulting aqueous treating solution to desired value using 10% aqueous sulfamic acid. The weight of the treating solution present in the glass tray is approximately 4 times the weight of the carpet sample (e.g., 400 g of treating solution for a 100 g carpet sample). The carpet sample absorbs the entire volume of treating solution over a 1 to 2 minute period to give a percent wet pickup of approximately 350%.

Then the wet treated carpet sample is steamed a second time for 2 minutes (using the same conditions and equipment as described above), is immersed briefly in a 5-gallon bucket half full of deionized water, is spun to dampness using the centrifugal extractor, and is cured at 250oF for 25 minutes before testing.

Water Repellency Test - Treated carpet samples were evaluated for water repellency using 3M Water Repellency Test V for Floorcoverings (February 1994), available from Minnesota Mining and Manufacturing Company. In this test, treated carpet samples are challenged to penetrations by blends of deionized water and isopropyl alcohol (IPA). Each blend is assigned a rating number as shown below:

Water Repellency Rating Number	Water/IPA Blend (% by volume)
F	(fails water)
0	100% water
1	90/10 water/IPA
2	80/20 water/IPA
3	70/30 water/IPA
4	60/40 water/IPA
5	50/50 water/IPA
6	40/60 water/IPA
7	30/70 water/IPA
8	20/80 water/IPA
9	10/90 water/IPA
10	100% IPA

In running the Water Repellency Test, a treated carpet sample is placed on a flat, horizontal surface and the carpet pile is hand-brushed in the direction giving the greatest lay to the yarn. Five small drops of water or a water/IPA mixture are gently placed at points at least two inches apart on the carpet sample. If, after observing for ten seconds at a 45° angle, four of the five drops are visible as a sphere or a hemisphere, the carpet is deemed to pass the test. The reported water repellency rating corresponds to the highest numbered water or water/IPA mixture for which the treated carpet sample passes the described test.

Dynamic Water Resistance Test - Dynamic water resistance was determined using the following test procedure. A treated carpet sample (15.2 cm x 15.2 cm) is inclined at an angle of 45° from horizontal and 20-25 g of deionized water is impinged onto the center of the carpet sample through a glass tube with 5 mm inside diameter positioned 45.7 cm above the test sample. The increase in weight (g) of the test sample is measured, with lower weight gains indicating better dynamic water repellency properties.

Stain Resistance Test - Stain resistance was determined using the following test procedure. A treated 10 cm x 10 cm carpet sample is stained for 24 hours by contactingthe carpet sample in an aqueous solution of 0.007% (wt) of Red Dye FD&C #40 in deionized water adjusted to a pH of 2.8 – 3.2 with aqueous acid The treated and stained carpet sample is then immersed briefly in a 5-gallon (19 L) bucket half full of deionized water, followed by rinsing under a stream of deionized water until the wash water runs clear. The wet carpet sample is then extracted to dampness using a Bock Centrifugal Extractor and is air-dried overnight at room temperature.

The degree of staining of the carpet sample is determined numerically by using a 310 CHROMA METER™ compact tristimulus color analyzer (available from Minolta,. The color analyzer measures red stain color autochromatically on the red-green color coordinate as a “delta a” (Δa) value as compared to the color of an unstained and untreated carpet sample. Measurements reported in the tables below are given to one place following the decimal point and represent the average of 3 measurements, unless stated otherwise. A greater Δa value indicates a greater amount of staining from the red dye. Δa values typically vary from 0 (no staining) to 50 (severe staining).

"Walk-On" Soiling Test - The relative soiling potential of each treatment was determined by challenging both treated and untreated (control) carpet samples under defined "walk-on" soiling test conditions and comparing their relative soiling levels. The test is conducted by mounting treated and untreated carpet squares on particle board, placing the samples on the floor of one of two chosen commercial locations, and allowing the samples to be soiled by normal foot traffic. The amount of foot traffic in each of these areas is monitored, and the position of each sample within a given location is changed daily using a pattern designed to minimize the effects of position and orientation upon soiling.

Following a specific soil challenge period, measured in number of cycles where one cycles equals approximately 10,000 foot-traffics, the treated samples are removed and the amount of soil present on a given sample is determined using colorometric measurements, making the assumption that the amount of soil on a given sample is directly proportional to the difference in color between the unsoiled sample and the corresponding sample after soiling. The three CIE L*a*b* color coordinates of the unsoiled and subsequently soiled samples are measured using a 310 CHROMA METER™ color analyzer with a D65 illumination source. The color difference value, ΔE, is calculated using the equation shown below:

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

where: $\Delta L^* = L^*\text{soiled} - L^*\text{unsoiled}$
$\Delta a^* = a^*\text{soiled} - a^*\text{unsoiled}$
$\Delta b^* = b^*\text{soiled} - b^*\text{unsoiled}$

ΔE values calculated from these colorometric measurements have been shown to be qualitatively in agreement with values from older, visual evaluations such as the soiling evaluation suggested by the AATCC, and have the additional advantages of higher precision, being unaffected by evaluation environment or subjective operator differences. The reported ΔE value for each carpet sample is calculated as an average of between five and seven replicates.

Receding Contact Angle Test - The Receding Contact Angle Test provides a quick and precise prediction of the anti-soiling potential of fluorochemical repellent or hydrocarbon repellent candidates. Using this test procedure, receding contact angle values measured with *n*-hexadecane have correlated well with anti-soiling values measured from actual foot traffic using the "Walk-On" Soiling Test.

To run this test, the repellent candidate is applied to nylon film as a solution, emulsion, or suspension (typically at about 3% solids) via dip-coating. The nylon film is prepared as follows. Nylon film is cut into 85 mm x 13 mm rectangular strips. Each strip is cleaned by dipping into methyl alcohol, wiping with a KIMWIPE™ wipe (commercially available from Kimberly Clark Corp., Boswell, GA), taking care not to touch the strip's surface, and allowing the strip to dry for 15 minutes. Then, using a small binder clip to hold one end of the strip, the strip is immersed in the treating solution, and the strip is then withdrawn slowly and smoothly from the solution. The coated film strip is tilted to allow any solution run-off to accumulate at the corner of the strip, and a KIMWIPE™ tissue is touched to the corner to pull away the solution buildup. The coated film strip is allowed to air dry in a protected location for a minimum of 30 minutes and then is cured for 10 minutes at 121°C.

After the coated film strip has dried and cured, a drop of *n*-hexadecane is applied to the strip and the receding contact angle of the drop of is measured using a CAHN Dynamic Contact Angle Analyzer, Model DCA 322 (a Wilhelmy balance apparatus equipped with a computer for control and data processing, commercially available from ATI, Madison, WI). The CAHN Dynamic Contact Angle Analyzer is calibrated using a 500 mg weight. An alligator clip is fastened to a piece of coated film strip about 30 mm long, and the clip and film piece are hung from the stirrup of the balance. A 30 mL glass beaker containing approximately 25 mL of *n*-hexadecane is placed under the balance stirrup, and the beaker is positioned so that the coated film strip is centered over the beaker and its contents but not touching the walls of the beaker. Using the lever on the left side of the apparatus, the platform supporting the beaker is carefully raised until the surface of *n*-hexadecane is 2-3 mm from the lower edge of the film strip. The door to the apparatus is closed, the "Configure" option is chosen from the "Initialize" menu of the computer, the "Automatic" option is chosen from the "Experiment" menu, and the computer program then calculates the time for a total of 3 scans. The result should be a time interval of 1 second and estimated total time of 5 minutes, which are the acceptable settings to show the baseline weight of the sample. The Return Key is then pressed to begin the automatic measurement cycle. 10 readings of the baseline are taken before the scan begins. The apparatus then raises and lowers the liquid so that 3 scans are taken. The "Least Squares" option is then selected from the "Analysis" menu, and the average receding contact angle is calculated from the 3 scans of the film sample. The 95% confidence interval for the average of the 3 scans is typically about ± 1.2°.

Examples 1-4 and Comparative Examples C1-C7

A series of experiments was run to vary the ratio of SSQO silsesquioxane to stainblocker, keeping the total % SOF at 0.8% or 0.3%. In all cases, 1.85 g/L of $MgSO_4 \cdot 7H_20$ was used in the 400 g of treating solution, and the pH was adjusted to either 1.9 or 4. All treating solutions were applied to the carpet using the Simulated Flex-Nip Application Procedure, then the treated carpets were evaluated for performance using the Water Repellency Test (WR), the Stain Resistance Test (SR) (average of two values), and the "Walk-On" Soiling Test (WOS) (one cycle - average of two values).

In Comparative Examples C1-C4, FX-661 stainblocker was applied to TRANSITION III™ nylon 6,6 carpet at either 0.8 or 0.3% SOF at a pH of either 1.9 or 4.)

In Examples C5 and C6, SSQO silsesquioxane at 0.8% was applied to TRANSITION III™ nylon 6,6 carpet SOF at a pH of either 1.9 or 4.

In Examples 1 and 2, a combination of FX-661 stainblocker at 0.5% SOF and SSQO silsesquioxane at 0.3% SOF was applied to TRANSITION III™ nylon 6,6 carpet at a pH of either 1.9 or 4.

In Examples 3 and 4, a combination of FX-661 stainblocker at 0.15% SOF and SSQO silsesquioxane at 0.15% SOF was applied to TRANSITION III™ nylon 6,6 carpet at a pH of either 1.9 or 4.

In Comparative Example C7, no treatment was applied to TRANSITION III™ carpet.

Results are presented in TABLE 1.

TABLE 1

Ex.	FX-661, % SOF	SSQO, % SOF	pH	WR (10 pt. scale)	SR (Δa)	WOS (ΔE)
C1	0.8	---	1.9	F	2.4	2.6
C2	0.8	---	4	F	4.6	2.1
C5	---	0.8	1.9	0	23.4	0.9
C6	---	0.8	4	F	37.2	3.0
1	0.5	0.3	1.9	F	2.6	1.4
2	0.5	0.3	4	0 to F	5.4	1.2
C3	0.3	---	1.9	F	3.7	3.0
C4	0.3	---	4	F	9	2.9
3	0.15	0.15	1.9	F	21.2	1.7
4	0.15	0.15	4	1	21.2	1.9
C7	---	---	---	F	34.2	3.8

The data in TABLE 1 show that, by using a combination of silsesquioxane and stainblocker, improved performance in stain resistance and soil resistance is realized. Best overall performance was achieved in Example 1 with 0.5% SOF stainblocker and 0.3% SOF silsesquioxane, applied at a pH of 1.9.

Examples 5-10 and Comparative Examples C8-C9

A series of experiments was run to vary the ratio of SSQO silsesquioxane to TODU hydrocarbon repellent, keeping the total % SOF at 0.54%. In all cases, the % SOF of FX-661 stainblocker was kept at 1.75%, 1.85 g/L of $MgSO_4 \cdot 7H_20$ was used in each 400 g of treating solution, and the pH was adjusted to 1.9 using aqueous sulfamic acid. All treating solutions were applied to the carpet using the Simulated Flex-Nip Application Procedure, then the treated carpets were evaluated for performance using the Water Repellency Test (WR), the Dynamic Water Resistance (DWR – average of two values), and the "Walk-On" Soiling Test (WOS) (one cycle - average of two values).

In Examples 5-7, treating solutions having ratios of SSQO silsesquioxane to TODU hydrocarbon repellent varying from 1:2 to 2:1 were applied to UPBEAT™ nylon 6 carpet.

In Comparative Example C8, a treating solution containing only SSQO silsesquioxane was applied to the nylon 6 carpet.

In Comparative Example C9, no treatment was applied to the nylon 6 carpet.

In Examples 8-10, treating solutions having ratios of SSQO silsesquioxane to TODU hydrocarbon repellent varying from 1:2 to 2:1 were applied to TRANSITION III™ nylon 6,6 carpet.

In Comparative Example C10, a treating solution containing only SSQO silsesquioxane was applied to the nylon 6,6 carpet.

In Comparative Example C11, no treatment was applied to the nylon 6,6 carpet.

Results are presented in TABLE 2.

TABLE 2

Ex.	SSQO, % SOF	TODU, % SOF	Carpet	WR (10 pt. scale)	DWR (g)	WOS (ΔE)
5	0.18	0.36	nylon 6	1	1.2	1.0
6	0.27	0.27	nylon 6	1	1.6	1.1
7	0.36	0.18	nylon 6	1	2.4	1.3
C8	0.54	-----	nylon 6	0	7.0	1.3
C9	-----	-----	nylon 6	0	20.0	2.0
8	0.18	0.36	nylon 6,6	1	2.8	3.0
9	0.27	0.27	nylon 6,6	F	8.6	3.8
10	0.36	0.18	nylon 6,6	1	3.7	3.1
C10	0.54	-----	nylon 6,6	F to 0	9.2	3.2
C11	-----	-----	nylon 6,6	F	20.0	6.7

The data in TABLE 2 show that treating a nylon carpet with a combination of a silsesquioxane, a stainblocker and a hydrocarbon repellent provides an excellent combination of water repellency and soil resistance to the carpet.

Examples 11-14 and Comparative Examples C12-C16

A series of experiments was run to evaluate silsesquioxane which contains 10% and 20% tetraethylorthosilicate in the silsesquioxane backbone. In all cases 0.1% of either 90/10 SSQO or 80/20 SSQO was applied, and 0.1% SOF of TODU hydrocarbon repellent was co-applied with the silsesquioxanes. FX-661 stainblocker was used in the examples at 0.5% SOF (Examples 11-14) but was omitted from the comparative examples (Comparative Examples C12-C16). 1.85 g/L of $MgSO_4 \cdot 7H_20$ was used in each 400 g of treating solution containing stainblocker. When stainblocker was used, no rinse was done after steaming. In all cases, the pH was adjusted to 2 or 4 using 10% aqueous sulfamic acid. In all cases, the carpet used for evaluation was TRANSITION III™ nylon 6,6 carpet.

All treating solutions were applied to the carpet using the Simulated Flex-Nip Application Procedure, then the treated carpets were evaluated for performance using the

Water Repellency Test (WR), the Stain Resistance Test (SR – average of two values), and the "Walk-On" Soiling Test (WOS) (one cycle - average of two values).

In Comparative Example C16, the carpet was untreated.

Results are presented in TABLE 3.

TABLE 3

Ex.	Silsesquioxane Used	FX-661	pH	WR (10 pt. scale)	SB (Δa)	WOS (ΔE)
11	90/10	Yes	2	F	2.5	2.7
12	90/10	Yes	4	F	7.5	3.5
13	80/20	Yes	2	F	1.7	2.9
14	80/20	Yes	4	F	9.9	2.6
C12	90/10	No	2	F	36.4	2.1
C13	90/10	No	4	F	36.8	3.0
C14	80/20	No	2	F	35.8	3.1
C15	80/20	No	4	F	36.8	3.0
C16	-----	-----	-----	F	39.5	5.7

The data in TABLE 3 show that the 90/10 and 80/20 silsesquioxanes, when co-applied with the FX-661 stainblocker and the TODU hydrocarbon repellent, provide an excellent combination of stain resistance and soil resistance to the carpet.

Claims:

1. A method for treating a fibrous substrate, comprising the steps of: providing a fibrous substrate; applying to the substrate an acidic aqueous composition comprising (a) a stainblocker, and (b) a silsesquioxane.

2. The method of claim 1, wherein the composition further comprises a repellent material selected from the group consisting of (i) fluorochemicals having a receding contact angle to n-hexadecane of at least 45°, and (ii) fluorine-free compositions having at least one hydrocarbon moiety and having a receding contact angle to n-hexadecane of at least about 35°.

3. The method of claim 1, wherein the composition has a pH within the range of about 1.5 to about 5.

4. The method of claim 2, further comprising the step of adjusting the pH of the composition to within the range of about 2 to about 5 through the addition of sulfuric and sulfamic acid.

5. The method of claim 1, wherein said silsesquioxane comprise compounds of the formula $RSiO_{3/2}$ where R is a substituted or unsubstituted alkyl or aryl of up to 7 carbon atoms.

6. The method of claim 1, wherein said silsesquioxane comprise cocondensates of hydrosylates of tetraalkoxysilanes with organotrialkoxysilanes having $RSiO_{3/2}$ or SiO_2 units.

7. The method of claim 1, wherein the composition is applied by means of a flex nip process.

8. The methods of claim 1, further comprising the step of exposing the substrate to steam after it is treated with the composition.

9. The method of claim 1, wherein said composition is applied such that the % solids on fiber of stainblocker is less than about 7%.

10. The method of claim 1, wherein the composition further comprises a polyvalent metal salt selected from the group consisting of sodium sulfate, lithium sulfate, magnesium sulfate, calcium chloride, barium chloride, zinc sulfate, copper sulfate, aluminum sulfate, and chromium sulfate.

11. The method of claim 1, wherein said composition comprises 0.000025 to 0.0025 wt.% silsesquioxane.

12. The method of claim 1 wherein said composition comprises 0.0001 to 0.0125 wt.% stainblocker.