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(54) FLUORINE-EFFICIENT OIL AND WATER REPELLENT COMPOSITIONS

Fluorhaltige Oel- und Wasserabweisende Zusammensetzungen

COMPOSITIONS HYDROPHOBES ET OLEOPHOBES UTILISANT EFFICACEMENT LE FLUOR

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(56) References cited:
EP-A- 0 314 944
EP-A- 0 429 983
FR-A- 2 277 927
US-A- 3 736 177
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Description

Background of the Invention

Technical Field

This invention relates to aqueous compositions containing fluorochemical oil- and water-repellent agents. This invention also relates to agents that improve fluorine efficiency of fluorochemical oil- and water-repellent agents. This invention also relates to processes for providing oil- and water-repellency to fibrous substrate materials.

Description of the Related Art

Water-, oil- and soil-repellent finishes containing fluorochemical agents or compositions are well known. A considerable disadvantage of such finishes, however, is their high price. So-called "extenders" have therefore been developed in order to reduce cost. Modified synthetic resins, waxes, paraffin emulsions, and similar products have been used for this purpose.

U.S. Pat. No. 3,849,521 (Kirimoto et al.) describes oil- and water-repellent compositions containing a polymer containing fluoroalkyl-containing monomer units and an additive copolymer containing monomer units having the formula

$$CR_1R_2=CR_3COOR_4$$

wherein R_1, R_2 and R_3 represents hydrogen atoms or methyl groups, and R_4 represents a C_{1-18} alkyl group; and monomer units having the formula:

$$CH_2=CR_5CONHCH_2OH$$

wherein R_5 represents a hydrogen atom or a methyl group.

U.S. Pat. No. 4,834,784 (Deiner et al.) describes the use of blocked isocyanate compounds as extenders, the isocyanate compound before blocking being diphenylmethane diisocyanate or an isocyanate compound having a molecular weight of at least 450.

Summary of the Invention

This invention provides fluorine-efficient oil- and water-repellent compositions comprising:

(A) a fluorochemical oil- and water-repellent agent;
(B) a copolymer extender comprising

(i) polymerized units derived from a monomer of Formula V:

$$CR_1R_2=CR_3R_4 \quad (V)$$

wherein each of R_1, R_2, R_3 and R_4 independently represents hydrogen, halogen, or an organic group such as alkyl, carboxyl, or acyloxyalkyl (i.e., $-CO_2$alkyl); and
(ii) polymerized units derived from a monomer of Formula VII:

$$CH_2=CR_5X \quad (VII)$$

wherein R_5 represents a hydrogen atom or a methyl group, and X represents a moiety comprising a functional group that can interact with a fibrous substrate; and

(C) a blocked isocyanate extender.

This invention also provides substrates treated with a fluorine-efficient composition as described above, and methods of improving the fluorine-efficiency of a fluorochemical oil- and water-repellent agent, comprising the step of formulating the fluorochemical agent with components (B) and (C) described above.

The compositions of the invention comprise at least one member of each of two classes of extenders. The combination improves the fluorine-efficiency of fluorochemical agents, and thus reduces the cost of fluorochemical treatment, to a greater extent than would be expected based on the properties of each individual class of extenders.

Detailed Description of the Invention

Component (A) in a composition of the invention is a fluorochemical oil- and water-repellent agent generally comprising a plurality of fluoroaliphatic (i.e., R_f) groups. Such agents are well known to those skilled in the art, and many (e.g., SCOTCHGARD™ fabric protector, 3M) are commercially available as ready-made formulations.

In general, fluorochemical agents useful in this invention comprise fluorochemical compounds or polymers containing one or more fluoroaliphatic groups R_f, which are fluorinated, stable, inert, non-polar, preferably saturated, monovalent and both oleophobic and hydrophobic. R_f preferably contains at least about 3 carbon atoms, more preferably 3 to about 20 carbon atoms, and most preferably about 6 to about 14 carbon atoms. R_f can contain straight chain, branched chain, or cyclic fluorinated alkylene groups or combinations thereof or combinations thereof with straight chain, branched chain, or cyclic alkylene groups. R_f is preferably free of polymerizable olefinic unsaturation and can optionally contain catenary heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen. It is preferred that R_f contain about 40% to about 78% fluorine by weight, more preferably about 50% to about 78% fluorine by weight. The terminal portion of the R_f group contains a fully fluorinated terminal group. This terminal group preferably contains at least 7 fluorine atoms, e.g., $CF_3CF_2CF_2$-, $(CF_3)_2CF$-, -CF_2SF_5, or the like. Perfluorinated aliphatic groups (i.e., those of the formula C_nF_{2n+1}) are the most preferred embodiments of R_f.

Examples of fluorochemical agents include, for example, R_f-containing urethanes, ureas, esters, amines (and salts thereof), amides, acids (and salts thereof), carbodiimides, guanidines, allophanates, biurets, and compounds containing two or more of these groups, as well as mixtures and blends thereof.

Useful fluorochemical polymers containing R_f groups include copolymers of fluorochemical acrylate and/or methacrylate monomers with co-polymerizable monomers, including fluorine-containing and fluorine-free monomers, such as methyl methacrylate, butyl acrylate, octadecylmethacrylate, acrylate and methacrylate esters of poly(oxyalkylene) polyol oligomers and polymers, e.g., poly(oxyethylene)glycol dimethacrylate, glycidyl methacrylate, ethylene, vinyl acetate, vinyl chloride, vinylidenechloride, vinylidenefluoride, acrylonitrile, vinylchloroacetate, isoprene, chloroprene, styrene, butadiene, vinylpyridine, vinyl alkyl ethers, vinyl alkyl ketones, acrylic and methacrylic acid, 2-hydroxyethyl acrylate, N-methylolacrylamide, 2-(N,N,N-trimethylammonium)ethyl methacrylate and the like.

Particular fluorochemical agents include those described in Patent Nos. 2,803,615 (Ahlbrecht et al.), 2,934,450 (Brown), 3,068,187 (Bolstad et al.), 3,094,547 (Heine), 3,329,661 (Smith et al.), 3,341,497 (Sherman et al.), 3,398,182 (Guenthner et al.), 3,458,571 (Tokoli), 3,462,296 (Raynolds et al.), 3,574,791 (Sherman et al.), 3,728,151 (Sherman et al.), 3,896,251 (Landucci), 3,916,053 (Sherman et al.), 4,013,627 (Temple), 4,024,178 (Landucci), 4,029,585 (Dettre), 4,034,964 (Sherman et al.), 4,144,367 (Landucci), 4,160,777 (Loudas), 4,165,338 (Katsushima et al.), 4,190,545 (Marshall), 4,215,205 (Landucci), 4,264,484)Patel), 4,325,857 (Champaneria et al.), 4,340,749 (Patel), 4,401,780 (Steel), 4,426,476 (Chang), 4,525,305 (Patel), 4,525,423 (Lynn et al.), 4,529,658 (Schwartz et al.), 4,540,497 (Chang et al.), 4,560,487 (Brinkley), 4,564,366 (Patel), 4,565,641 (Chang et al.), 4,566,981 (Howells), 4,579,924 (Schwartz et al.), 4,582,882 (Lynn et al.), 4,606,737 (Stern), 4,668,406 (Chang), 4,668,726 (Howells), Atty's Docket No. 44348USA6A (commonly assigned and filed of even date), each of which is incorporated herein by reference.

Component (B) in a composition of the invention is a copolymer extender comprising

(i) polymerized units derived from a monomer of Formula V:

$$CR_1R_2=CR_3R_4 \qquad (V)$$

wherein each of R_1, R_2, R_3, and R_4 independently represents hydrogen, halogen, or an organic group; and

(ii) polymerized units derived from a monomer of Formula VII:

$$CH_2=CR_5X \qquad (VII)$$

wherein R_5 is hydrogen or methyl and X is a moiety comprising a functional group that can interact with a fibrous substrate.

Examples of monomers of Formula V include general classes of ethylenic compounds capable of free-radical polymerization, such as lower olefinic hydrocarbons, optionally halogenated, such as ethylene, propylene, isobutene, 3-chloro-2-isobutene, butadiene, isoprene, chloro and dichlorobutadienes, fluoro and difluorobutadienes, 2,5-dimethyl-1,5-hexadiene; vinyl, allyl or vinylidene halides such as vinyl or vinylidene chloride, vinyl or vinylidene fluoride, allyl bromide, allyl chloride, methallyl chloride; styrene and its derivatives such as vinyltoluene, α-methylstyrene, a-cyanomethylstyrene, divinylbenene, N-vinylcarbazole; vinyl esters such as vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl succinate, vinyl stearate, divinylcarbonate; allyl esters such as allyl acetate and allyl heptanoate; alkylvinyl or alkylallyl ethers such as cetyl vinyl ether, dodecyl vinyl ether, isobutyl vinyl ether, ethyl vinyl ether, 2-chloroethyl vinyl ether, tetrallyloxyethane; vinyl alkyl ketones such as vinyl methyl ketone; unsaturated acids such as acrylic, α-chloro

acrylic, α-fluoro acrylic, crotonic, maleic, fumaric, itaconic, and citraconic acids, and anhydrides and esters thereof such as dimethyl maleate, ethyl crotonate, acid methyl maleate, acid butyl itaconate, and vinyl, allyl, methyl, ethyl, butyl, isobutyl, hexyl, 2-ethylhexyl, chlorohexyl, octyl, lauryl, or stearyl acrylates and methacrylates; olefinic silanes such as vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, and methacryloyloxypropyl trimethoxysilane; nitriles such as acrylonitrile, methacrylonitrile, 2-chloroacrylonitrile, 2-cyanoethylacrylate, methylene glutaronitrile, vinylidene cyanide, alkyl cyanoacrylates such as isopropyl cyanoacrylate; (tris)-acryloyl-hexahydro-s-triazine; special acrylates such as butanediol dimethacrylate, dicyclopentenyl acrylate, ethoxylated bisphenol A dimethacrylate, isobornyl acrylate and methacrylate, trimethylopropane triacrylate, allyl methacrylate; acrylamides and methacrylamides; mono or di (meth)acrylates of glycols or polyalkylene glycols such as ethylene glycol dimethacrylate, triethylene glycol acrylate, mono, di, and polyacrylates and methacrylates of methoxypolyethylene glycols and polyethylene glycols of various molecular weights (available as CARBOWAX™), block copolymers of ethylene oxide and propylene oxide endcapped by hydroxy groups (available as PLURONIC™), tetramethyleneoxide glycols (available as TERATHANE™), amino or diamino-terminated polyethers (available as JEFFAMINE™); mono, di, and polyacrylates and methacrylates of siloxane mono-, di-, or polyols such as 1,3-bis(4-hydroxybutyl)tetramethyl disiloxane (Petrarch Systems, Bristol, PA); VP-1610 siloxane diol (Wacker - Germany); Q4-3667 siloxane diol (Dow Corning); Q4-3557 siloxane diol (Dow Corning); acrylamides and methacrylamides of siloxane mono, di, or polyamines such as 1,3-bis(y-aminopropyl)tetramethyl disiloxane (Petrarch Systems); DC-531 siloxane polyamine (Dow Corning); DC-536 siloxane polyamine (Dow Corning); and others described in U.S. Pat. No. 4,728,571 (Clemens et al.), the disclosure of which is incorporated herein by reference.

A particularly preferred class of monomers of Formula V is acrylate monomers of Formula IX

$$CR_6R_7=CR_8COOR_9 \quad (IX)$$

wherein R_6, R_7, and R_8 independently represent a hydrogen atom or a methyl group, and R_9 represents a $C_{1\text{-}18}$, alkyl group.

Preferred among this class are alkyl crotonates, alkyl acrylates and alkyl methacrylates such as methyl acrylate, methyl methactylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, isoamyl acrylate, isoamyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, octyl methacrylate, lauryl acrylate, lauryl methacrylate, cetyl acrylate, or cetyl methacrylate.

The copolymer extender also comprises polymerized units derived from a monomer of Formula VII. Suitable monomers of Formula VII include those comprising a functional group that can interact with a fibrous substrate by, for example, physical entanglement, covalent bonding by way of nucleophilic, electrophilic, ionic, free radical or like reactions between the copolymer and the substrate, or ionic bonding. Wool, leather, paper, cotton, and nylon variously comprise hydroxyl, amino, carboxyl, and carboxamido groups. For the purposes of the instant specification and claims, "a functional group that can interact with a fibrous substrate" designates a group that can interact with a fabric by any of the above-described mechanisms. Such groups can be easily selected by those skilled in the art as a function of the particular fibrous substrate that is intended to be treated with the composition of the invention. Representative groups suitable for interacting with a substrate include polymerizable olefin, olefin that can undergo a hydrosilation reaction, epoxy, amino, hydroxy, halo, haloformyl, aziridino, acid groups such as carboxy, sulfo, sulfino, sulfeno, dihydroxyphosphinyl, and hydroxyphosphinilidene, alkali metal and alkaline-earth metal salts thereof, amine salts thereof, quaternary ammonium salts thereof and the like, or amino and quaternary ammonium groups and salts thereof with, e.g., the above-listed types of acids.

Examples of suitable functionalized monomers include N-methylol acrylamide; N-methylol methacrylamide; aziridinyl acrylate and methacrylate; diacetone acrylamide and methacrylamide; methylolated diacetone acrylamide and methacrylamide; 2-hydroxy-3-chloropropyl acrylate and methacrylate; hydroxy (C_2 to C_4) alkyl acrylates and methacrylates; maleic anhydride; butadiene; isoprene; chloroprene; allyl alcohol; allyl glycolate; isobutenediol; allyloxyethanol; o-allyl phenol; divinyl carbinol; glycerol α-allylether, acrylamide; methacrylamide; maleamide; maleimide; N-cyanoethyl acrylamide; N-isopropyl acrylamide; glyoxal bis-acrylamide; metal salts of acrylic acid and methacrylic acid; vinylsulfonic and styrene p-sulfonic acids and their metal salts; monoallylamine; vinylpyridines; N-vinylpyrrolidone; 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and its salts; vinyl azlactones; glycidyl acrylate and methacrylate; allyl glycidyl ether; acrolein; N,N-dimethylaminoethyl acrylate and methacrylate; N-tert-butylaminoethyl methacrylate; allyl methacrylate; diallyl maleate; vinyltriethoxysilane; vinyltrichlorosilane; and the like.

Preferred functionalized monomers of Formula VII include those of Formula XI:

$$CH_2=CR_5CONHCH_2OH \quad (XI)$$

wherein R_5 represents a hydrogen atom or a methyl group. Copolymers comprising such monomers are described in U.S. Pat. No. 3,849,521 (Kirimoto et al.) incorporated herein by reference. Other suitable copolymers can be prepared by methods well known to those skilled in the art.

Component (C) in a composition of this invention is a blocked isocyanate. Suitable isocyanates for use (before blocking) include aromatic diisocyanates such as 4,4'-methylenediphenylenediisocyanate, 4,6-di-(trifluoromethyl) -1,3-benzene diisocyanate, 2,4-tolunediisocyanate, 2,6-toluene diisocyanate, o, m, and p-xylylene diisocyanate, 4,4,-diisocyanatodiphenylether, 3,3'-dichloro-4,4'-diisocyanatodiphenylmethane, 4,5'-diphenyldiisocyanate, 4,4'-diisocyanatodibenzyl, 3,3,-dimethoxy-4,4,-diisocyanatodiphenyl, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2,-dichloro-5,5,-dimethoxy-4,4'-diisocyanato diphenyl, 1,3-diisocyanatobenzene, 1,2-naphthylene diisocyanate, 4-chloro-1,2-naphthylene diisocyanate, 1,3-naphthylene diisocyanate, and 1,8-dinitro-2,7-naphthylene diisocyanate; alicyclic diisocyanates such as 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate; aliphatic diisocyanates such as methylenediisocyanate, 1,6-hexamethylenediisocyanate, 2,2,4-trimethyl-1,6-hexamethylenediisocyanate, and 1,2-ethylenediisocyanate; aliphatic triisocyanates such as 1,3,6-hexamethylenetriisocyanate; aromatic polyiisocyanates such as polymethylenepolyphenylisocyanate (PAPI); and cyclic diisocyanates such as isophorone diisocyanate (IPDI).

Also useful are isocyanates containing internal isocyanate-derived moieties such as biuret-containing tri-isocyanates such as that available from Mobay as DESMONDUR™ N-100, isocyanurate-containing tri-isocyanates such as that available from Huls AG, Germany, as IPDI-1890, and azetedinedione-containing diisocyanates such as that available from Bayer as DESMONDUR™TT. Also, triisocyanates such as tri-(4-isocyanatophenyl)-methane (available from Bayer as DESMONDUR™R) are suitable.

Another suitable class of isocyanates is isocyanate-functional low molecular weight polyurethanes. These polyurethanes are prepared by reacting a polyfunctional, aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanate, such as, for example, hexamethylene-1,6-diisocyanate, the various isomers of tolulene diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate and the like, with a low molecular weight polyol having at least 2, preferably at least 3 hydroxyl groups. Suitable low molecular weight polyols include trimethylolpropane, 1,3,5-hexanetriol, glycerol, pentaerythritol, propylene glycol, hexylene glycol and diethylene glycol. Also suitable are other low molecular weight polyhydroxy compounds, such as triethanolamine.

These low molecular weight polyurethanes can be prepared by reacting a polyol with an excess of polyisocyanate. The equivalent ratio of hydroxyl to isocyanato groups in the reaction is preferably at least 1:1.3, more preferably 1:1.5 to 2.5.

The above-described isocyanates are used in a composition of the invention in the form of "blocked isocyanates", i.e., the reaction product of an isocyanate and a blocking agent, wherein the blocking agent is removable from the isocyanate under thermal conditions such as those employed during cure of a substrate treated with a compound containing the blocked isocyanato group. Conventional isocyanate blocking agents include arylalcohols (e.g., phenol, cresols, nitrophenols, o- and p-chlorophenol, naphthols, 4-hydroxybiphenyl); C_2 to C_8 alkanone oximes (e.g. acetone oxime, butanone oxime); arylthiols (e.g., thiophenol); organic active hydrogen compounds (e.g.; diethyl malonate, acetylacetone, ethyl acetoacetate, ethyl cyanoacetate, ε-caprolactam); sodium bisulfite; and hydroxylamine. Particularly preferred blocked isocyanates include those blocked with C_2 to C_8 alkanone oximes, particularly butanone oxime. Such blocked isocyanates can be de-blocked at a relatively low temperature, for example during the process of curing a substrate that has been treated with the composition comprising the blocked isocyanate.

Some of the above-described blocked isocyanates are disclosed in U.S. Pat. No. 4,834,764 (Deiner et al.) the disclosure of which is incorporated herein by reference. Others can be prepared by methods well known to those skilled in the art.

A composition of the invention comprises the fluorochemical agent in an amount effective to impart repellent properties to a fibrous substrate treated with the composition. The amount of fluorochemical agent that constitutes an effective amount can be easily determined by those skilled in the art and depends on the particular fluorochemical agent used and on the amounts of the copolymer and blocked isocyanate extenders used.

The copolymer extender and the blocked isocyanate extender are present in a combined amount effective to improve the fluorine efficiency of the fluorochemical agent. Each extender is preferably present in an amount such that the improvement in fluorine efficiency is greater than the improvement provided by either extender alone.

"Improvement in fluorine efficiency" as used herein designates an improvement in the repellent properties imparted by a fluorochemical agent per unit weight of fluorine in a composition comprising the agent, as those repellent properties are measured using the test procedures set forth below. Stated another way, an extender (or combination of extenders) improves the fluorine efficiency of a given fluorochemical agent if performance is improved by including the extender (s) in a composition containing the same or a lesser concentration of the fluorochemical agent.

Generally, the extenders are present in relative amounts between about 1:20 to about 20:1, preferably abut 1:4 to about 4:1, more preferably about 2:1 to abut 1:2, and most preferably about 1:1. Generally, the fluorochemical agent is present in an amount of about 20 to about 2000, preferably 40 to about 900, and most preferably about 100 to about 400, parts by weight based on 100 parts by weight of the copolymer and the blocked isocyanate extenders combined.

When a composition of the invention is applied as a treatment to a fibrous substrate, e.g., a fabric intended for use in a garment, it is preferred that a treated substrate comprises the fluorochemical agent in an amount of abut 0.1% to about 0.6% by weight based on the weight of the untreated substrate. Further, it is preferred that a treated substrate

comprise the fluorochemical agent, the copolymer extender, and the blocked isocyanate extender in a total combined amount of about 0.1% to about 1% by weight based on the weight of the untreated substrate.

Knowing the amount of composition intended to be incorporated on the substrate, the percent pick-up of the substrate, and the mass of the substrate, a composition of the invention can be applied to a substrate by any suitable method. For example, a composition can be prepared in the form of an aqueous dispersion and the substrate treated therewith. A dispersion will generally contain water, an amount of composition effective to provide repellent properties to a substrate treated therewith, and an emulsifier in an amount effective to stablilize the dispersion. Water is preferably present in an amount of about 70 to about 900 parts by weight based on 100 parts by weight of the composition of the invention. The emulsifier is preferably present in an amount of about 1 to about 25 parts by weight, preferably about 5 to about 10 parts by weight, based on 100 parts by weight of the composition of the invention. Conventional cationic, nonionic, anionic, and zwitterionic emulsufiers are suitable.

In order to effect treatment of a substrate, the substrate can be immersed in the dispersion and agitated until it is saturated. The saturated substrate can then be run through a padder/roller to remove excess dispersion, dried in an oven at a relatively low temperature (e.g., 70°C) for a time sufficient to remove the dispersion medium (e.g., water, ethylene glycol, or a mixture thereof), and cured at a temperature and for a time sufficient to provide a cured treated substrate. This curing process can be carried out at temperatures between 40°C and about 200°C depending on the particular composition used. In general, a temperature of about 155°C for period of about 5 minutes is suitable. The cured treated substrate can be cooled to room temperature and used as desired, e.g., incorporated or fashioned into a garment such as rainwear.

In order to improve fixing of a fluorinated compound of the invention to a substrate, it is sometimes advantageous to include in the dispersion certain additives, polymers, thermo-condensable products and catalysts capable of promoting interaction with the substrate. Among these are the condensates or precondensates of urea or melamine with formaldehyde (sometimes referred to herein as resins).

Other auxilliary extenders can be used, either alone or in combination with each other. Suitable auxilliary extenders include paraffin; compositions containing alkylketenes or derivatives thereof; siloxanes; chlorohydrates of stearamidomethylpyridinium; condensates of fatty acids with melamine or urea derivatives (such as the product obtained on reacting stearic acid with hexamethoxymethylmelamine), condensates of fatty acids with polyamides (such as the reaction product of stearic acid with diethylenetriamine) and their epichlorohydrin adducts. It is also possible to use salts of inorganic or organic acids such as aluminum stearate, zirconium acetate, zirconium oxychloride or Werner complexes such as chromium stearatochloride.

If it is desired to improve the softness or "hand" of a substrate treated with a composition of the invention, it is possible to use softeners, such as certain polyethylenes, polydimethylsiloxanes, modified hydrogenalkylpolysiloxanes, or other materials known to those skilled in the art.

In combination with compositions of this invention it is also possible to use auxilliary products such as polyglycols, colloids such as starch, dextrin, casein, sizing agents, fixing or retaining agents, materials to improve stain resistance, cleaning ability, fire proofing or antistatic properties, buffering agents, fungicidal agents, optical bleaching agents, sequestering agents, mineral salts, surface-activity agents, or swelling agents to promote penetration. Particular suitable auxilliary products and amounts thereof can be easily selected by those skilled in the art.

In addition to providing oil- and water-repellent properties to substrates, the compositions of the invention can also be used to provide anti-adhesion properties and to protect substrates against solvents or certain aggresive chemicals. They can also be used for applications such as stain resistance, soil resistance, soil release and stain release on textiles, paper, or leather. Further, they can be used for imparting properties such as antistatic, antipilling, mold release, corrosion inhibition, or anti-fouling properties.

Substrates treated with compositions of the invention were tested by the test methods set forth below.

Water Spray Test (SR)

The resistance of a treated substrate to wetting with water was measured using AATCC Test Method 22-1977, "Water Repellency: Spray Test" as described in American Association of Textile Chemists and Colorists Technical Manual, 1977, 53, 245. Samples are rated on a scale of 0 to 100, with 0 indicating complete wetting of the upper and lower surfaces of the substrate and 100 indicating no wetting.

Oil Repellency Test (OR)

The oil repellency of a substrate treated with a compound of the invention was measured using AATCC Test Method 118-1975, "Oil Repellency: Hydrocarbon Resistance Test" as described in AATCC Technical Manual, 1977, 53, 223. This test measures the resistance of a substrate to wetting by a series of hydrocarbon liquids with a range of surface tensions. The values reported range from 0 (least repellent) to 8 (most repellent).

Laundering Procedure

The procedure set forth below was used to prepare treated substrate samples designated in the examples below as "5x Laundered" or "5 Laund".

A 230 g sample of generally square, 400 cm^2 to about 900 cm^2 sheets of treated substrate was placed in a washing machine along with a ballast sample (1.9 Kg of 8 oz fabric in the form of generally square, hemmed 8100 cm^2 sheets). Conventional detergent ("TIDE", 46 g) is added and the washer is filled to high water level with hot water (49°C ± 3°C). The substrate and ballast load is washed five times using a 12-minute normal wash cycle and the substrate and the ballast are dried together in a conventional clothes dryer set on the "heat" setting for about 45 minutes. The dry substrate is pressed using a hand iron set at the temperature recommended for the particular substrate fabric.

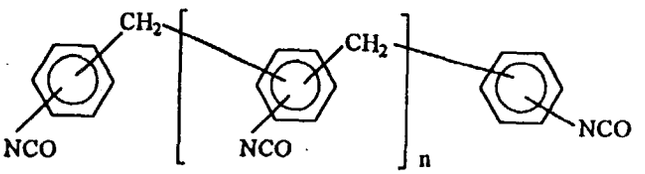
Dry Cleaning Procedure

Substrate samples designated in the examples below as "Dry Cleaned" were treated as set forth in AATCC Test Method 7-1975, note 8.1

The following describes the preparation of extenders and fluorochemical agents used in the Examples that follow. Also described below are several commercially available fluorochemical agents that are used in the Examples.

Intermediate A

2-Butanone oxime (26.1 g, 0.3 mol, available from Servo Company, the Netherlands, as SERVOXIME™ Y-250) was added at room temperature over about 30 minutes to PAPI (40.8 g, 0.3 equivalents, a polyphenylpolyisocyanate, Upjohn, equivalent weight 136 with a chemical structure



wherein average n = 0.7)

The reaction temperature was increased to 60°C and maintained for two hours. The reaction mixture was then diluted to 40% solids in ethyl acetate using about 86 g ethyl acetate. A clear, brown organic solution was obtained.

In a separate flask was placed MARLOWET™ 5401 cationic emulsifier (5.7 g, 10 percent by weight based on total solids, Hüls, Germany), ethylene gylcol (35 g, 60% by weight on total solids) and deionized water (171 g, 300% by weight on total solids). This solution was warmed to about 40°C and under very vigorous mixing added to the organic solution, also at about 40°C. A milky pre-emulsion was obtained, which was passed three times through a MANTON-GAULIN™ emulsifier at about 40°C and 300 bar pressure. The solvent was removed under reduced pressure. A slightly brown dispersion was obtained. This dispersion was diluted to 20% solids and filtered and stored.

Intermediate B

2-Ethylhexyl methacrylate (59,4 g, 0.3 mol), N-methylolacrylamide (1.5 g, 0.014 mol), ETHOQUAD™ 18/25 cationic emulsifier (Akzo, the Netherlands, 3 g, about 5% by weight on total solids), tertiary dodecyl mercaptan (.15 g, about 0.25% by weight on total solids) and V-50™ initiator ([2,2'-azobis[2-methylpropanimidamide]-dihydrochloride, Wako, Japan] 0.12 g, about 0.2% by weight on total solids) and deionized water (140 g) were mixed. The mixture was deaereated and then heated at 75°C for 16 hours. A nearly transparent dispersion was obtained.

Intermediate C

A dispersion was prepared as described in U.S. Pat. No. 3,068,187 (Bolstad et al., Example 5), containing a graft copolymer of a fluorinated monomer and a fluorine-free comonomer.

Intermediate D

A mixture of N-ethyl perfluorooctylsulfonamidoethanol (ETFOSE, 40.8 g, 0.3 equivalents) dry ethyl acetate (100 g) and 4 drops of dibutyltindilaurate was heated at reflux (about 78°C) for 4 hours. 2-Ethylhexanol (13 g, 0.1 mol) was then added and the reation was continued at reflux for another 6 hours. A clear, brown solution was obtained. The

reaction product was emulsified following the procedure described in Intermediate A above. A slightly brown dispersion was obtained, which was further diluted with water to 20% solids filtered, and stored.

Using the same synthetic procedure and emulsification method, Intermediate E was pepared. PAPI (40.8 g, 0.3 equivalent), N-methylperfluoro octylsulfonamidoethanol (44.7 g, 0.1 equivalent), and 2-butanone oxime (17.4 g, 0.2 mol) were reacted to obtain a fluorochemical urethane composition containing blocked isocyanate groups.

Intermediate F

LODYNE™ 921 C (149 g, 0.24 mol, a telomer mercaptan represented by the formula $C_nF_{2n+1}CH_2CH_2SH$ where n = 6, 8, 10, 12, 14 . . . average n is about 10, available from Ciba-Geigy), 2-butyn-1,4-diol (11 g, 0.13 mol) and hexafluoroxylene (100 g) were combined. The mixture was warmed to 62°C and a solution of VAZO™ 52 initiator [(2,2'-azobis-(2,4-dimethylvaleronitrile), 5 g, Du Pont)] in 10 g of dichloromethane was added over a period of 4 hours. The reation was continued for 4 hours at 70°C. A hazy, slightly yellow reaction mixture was formed. Dry ethyl acetate (100 g) and trimethylhexamethylenediisocyanate (22 g, 0.1 mol, TMDI, Bayer) were added and the reaction mixture was heated to 80°C. Dibutyltin dilaureate catalyst (0.2 g) was added. The reaction was continued for 8 hours at 95°C. DDI (51 g, 0.08 mol, dimer diisocyanate, Henkel) and methyldiethanolamine (6 g, 0.05 mol) were added. The reaction was continued at 90°C for 4 hours. A clear, brown solution was obtained. To 200 g of the solution, 101 g butyl acetate, 3.5 g acetic acid and 87 g ethylene glycol were added. The resulting organic solution was warmed to 75°C.

In a separate flask a solution of 5.2 g MARLOWET™ 5401 surfactant (about 5% by weight on total solids) in 463 g deionized water was heated to 75°C. Under vigorous stirring, this aqueous solution was added to the organic solution. The pre-emulsion obtained was passed 5 times through a preheated MANTON-GAULIN™ emulsifier at about 70 to 75°C and 300 bar pressure. A microemulsion was obtained. All solvents were removed (at 50°C and about 5 mm Hg vaccuum) slightly brown dispersion was filtered and stored.

Intermediate G

N-Methylperfluorooctylsulfonamidoethyl acrylate, (61.1 g, 0.1 mol), 2-mercaptoethanol (1.95 g, 0.025 mol), ethyl acetate 40 g and AIBN (0.12 g, 0.2% by weight on total solids) were mixed, deaerated, and heated at reflux (about 80°C) for 16 hours. The reaction mixture was cooled to room temperature. PAPI (10.2 g, 0.075 equivalent) was added together with 2 drops of dibutyltin dilaureate catalyst. The reaction mixture was heated at reflux for 5 hours. The reaction was then cooled to about 60°C and 4.35 g of 2-butanone oxime (0.05 mol) was added. The reaction was continued for 2 hours at 70°C. The reaction product was emulsified at 70°C using the procedure described in Intermediate A. A slightly brown dispersion was obtained, filtered, and stored.

Intermediate H

FC-217, a fluorochemical acrylate copolymer commercially available from 3M Company.

Intermediate I

FC-352, a fluorochemical carbodiimide containing composition commercially available from 3M Company.

Intermediate J

FC-353, a fluorochemical containing ester commercially available from 3M Company.

Intermediate K

N-Allylperfluorooctylsulfonamide (54 g, 0.1 equivalent), a polymethylhydrogensiloxane (12 g, 0.2 equivalents BAY-SILONE-ÖL™ MH15 silicone, Bayer, of the formula

$$(CH_3)_3SiO[(CH_3)(H)SiO]_nSi(CH_3)_3$$

wherein n=40) and butyl acetate (60 g) were combined. The mixture was heated to 110°C and 1 mL of 1% solution of H_2Pt_{116} in 2-butanone is added. After 30 minutes Monylvinylester (2 g, 0.01 mol, VEORA™ 10, Shell) and 0.3 mL of the 1% catalyst solution was added. The reaction was heated at 126°C for 1 hour. A slightly brown solution was obtained. The material was emulsified at 30°C using the procedure, ingredients, and amounts decribed in Intermediate H. A slightly brown dispersion was obtained, the pH was adjusted to 7, and the emulsifion was filtered and stored.

Intermediate L

FC-247, a composition containing a blend of a fluorochemical ester, a fluorochemical urethane, and a fluorochemical acrylate copolymer, commercially available from 3M Company.

Intermediate M

FC-214, a composition containing a blend of a fluorochemical urethane and a fluorochemical copolymer, and commercially available from 3M Company.

Intermediate N

FC-270, a composition containing a blend of a fluorochemical carbodiimide and a fluorochemical acrylate copolymer, commercially available from 3M Company.

Intermediate O

Into a polymerization bottle was placed N-methyl perfluorooctylsulfonamidoethyl acrylate (30.6 g, about 0.050 mol, MeFOSEA), 2-ethylhexyl acrylate (8.1, about 0.044 mol) 2-hydroxyethyl acrylate (0.7 g, about 0.006 mol), 2 g ETHOQUAD™ 18/25 emulsifier. (Akzo, The Netherlands), tertiary dodecylmercaptan (0.2 g, 0.5% by weight on total monomers), V-50™ initiator (2,2'-azobis[2-methylpropanimidamide], 0.08 g, Wako, Japan), acetone (15 g) and deionized water (78 g). The reaction mixture was deaerated and the polymerization bottle was capped and put into a launderometer at 70°C for 16 hours. The resulting nearly transparent dispersion was filtered and stored.

Intermediate P

Following the procedure of Intermediate O, MeFOSEA, octadecyl methacrylate, and polydimethylsiloxane monomethacrylate (molecular weight of about 2000) in a molar ratio 80 to 15 to 5 were reacted. A nearly transparent dispersion was obtained.

Intermediate Q

Hexamethoxymethylmelamine (39 g, 0.1 mol, CYMEL™ 303, American Cyanamid), a fluorochemical mercaptan with general formula C_nF_{2n+1} CH_2CH_2SH (232 g, 0.4 mol, average n is about 10, average molecular weight is about 580, Atochem, France) and para-toluenesulfonic acid (0.42 g) were mixed and heated at 90°C. Methanol was evolved and removed by distillation. Over a 2 hour period the temperature was further raised to 180°C and kept at that temperature for 4 hours. After cooling to about 80°C, hexafluoroxylene solvent was added to make a 40% solids solution (in total, 348 g hexafluoroxylene was used). A dispersion was prepared of this solution according to the procedure set forth in Intermediate F. The dispsersion was filtered and stored.

The above Intermediates were tested, according to the test methods mentioned above, by themselves and in combination with one extender or a combination of two extenders. Formulations were prepared and fabrics treated according to the general procedure set forth below:

Formulation and Treatment Procedure

A fluorochemical agent as described in Intermediates C-Q above is provided and formulated into a treatment bath containing a predetermined amount of each of the appropriate fluorochemical agent, the copolymer extender, and the blocked isocyanate extender such that the treatment can be made by a padding application at the indicated percent solids on fabric. After treatment, the substrate is dried and cured at 150°C for 10 min.

Objects and advantages of this invention are further illustrated by the following examples. The particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Examples 1-24 and Comparative Examples C-1 to C-45

Fluorochemical agents were formulated with single extenders and combinations of extenders to treat a polyester/cotton 50/50 fabric at 0.4% total solids on fabric.

Results are shown in Table I below, wherein FC designates fluorochemical agent and weight percents indicate

percent based on the combined weight of the fluorochemical agent and the extender or extenders.

TABLE I

Ex.	Weight % FC	Weight % Extender 1 (Int. B)	Weight % Extender 2 (Int. A)	Initial OR	Initial SR	5 Laund OR	5 Laund SR	1 Dryclean OR	1 Dryclean SR
			Fluorochemical: Intermediate C						
C-1	100	--	--	5	90	3	60	4	80
C-2	80	20	--	5	100	4	80	5	80
C-3	80	--	20	5	100	3	80	5	80
1	80	10	10	5	100	4	90	5	80
2	70	20	10	5	100	4	90	5	80
			Fluorochemical: Intermediate D						
C-4	100	--	--	5	90	3	50	0	0
C-5	80	20	--	6	90	5	80	0	0
C-6	80	--	20	5	90	4	90	0	0
3	80	10	10	5	100	5	90	0	0
4	70	20	10	5	100	5	90	0	0
			Fluorochemical: Intermediate E						
C-7	100	--	--	2	100	2	80	1	70
C-8	80	20	--	4	100	3	90	3	90
C-9	80	--	20	2	100	3	90	2	90
5	80	10	10	4	100	4	100	3	100

TABLE I (cont.)

Fluorochemical: Intermediate F									
C-10	100	--	--	5	100	4	60	5	80
C-11	80	20	--	5	100	4	70	4	70
C-12	80	--	20	5	100	4	90	4	80
6	80	10	10	6	100	5	100	6	90
7	70	20	10	5	100	4	90	5	90
Fluorochemical: Intermediate G									
C-13	100	--	--	5	100	5	80	5	90
C-14	80	20	--	6	100	5	90	6	90
C-15	80	--	20	6	100	5	90	5	90
8	80	10	10	6	100	5	100	6	100
9	70	20	10	6	100	5	100	6	100
Fluorochemical: Intermediate H									
C-16	100	--	--	5	80	0	0	5	70
C-17	80	20	--	6	100	2	60	6	90
C-18	80	--	20	5	100	3	80	5	90
10	80	10	10	5	100	3	90	6	90
11	70	20	10	5	100	4	90	6	90
Fluorochemical: Intermediate I									
C-19	100	--	--	3	80	2	70	0	0
C-20	80	20	--	3	80	2	80	0	0
C-21	80	--	20	3	80	2	80	1	0
12	80	10	10	3	90	2	80	1	0
13	70	20	10	3	90	2	80	1	0
Fluorochemical: Intermediate J									
C-22	100	--	--	7	50	1	0	0	0
C-23	80	20	--	7	60	2	50	0	0
C-24	80	--	20	7	60	3	50	0	0
14	80	10	10	7	70	6	60	0	0
15	70	20	10	7	80	5	60	0	0
Fluorochemical: Intermediate K									
C-25	100	--	--	4	100	4	80	3	50
C-26	80	20	--	4	100	4	80	3	70
C-27	80	--	20	4	100	4	90	3	70
16	80	10	10	4	100	4	90	3	80

TABLE I (cont.)

Fluorochemical: Intermediate L									
C-28	100	--	--	6	80	3	50	3	0
C-29	80	20	--	6	80	4	60	3	60
C-30	80	--	20	6	90	3	70	3	70
17	80	10	10	6	90	4	70	4	70
Fluorochemical: Intermediate M									
C-31	100	--	--	5	80	4	50	0	0
C-32	80	20	--	5	80	4	60	3	60
C-33	80	--	20	5	90	4	60	3	60
18	80	10	10	5	90	4	80	4	70
Fluorochemical: Intermediate N									
C-34	100	--	--	4	100	3	80	3	90
C-35	80	20	--	5	100	4	90	3	90
C-36	80	--	20	5	100	4	90	4	90
19	80	10	10	5	100	4	90	4	90
Fluorochemical: Intermediate O									
C-37	100	--	--	6	80	0	0	6	6
C-38	80	20	--	7	90	5	60	7	7
C-39	80	--	20	5	100	5	100	5	8
20	80	10	10	6	100	6	100	6	80
21	70	20	10	7	100	7	90	7	80
Fluorochemical: Intermediate P									
C-40	100	--	--	6	80	0	0	0	0
C-41	80	20	--	6	80	4	70	4	80
C-42	80	--	20	6	90	2	60	3	70
22	80	10	10	6	90	5	80	5	90
Fluorochemical: Intermediate Q									
C-43	100	--	--	5	100	3	90	4	70
C-44	80	20	--	6	100	4	90	4	80
C-45	80	--	20	5	100	4	90	4	80
23	80	10	10	6	100	4	100	4	90
24	70	20	10	6	100	4	100	4	80

The results in Table 1 indicate that the compositions of the invention, comprising any of a wide variety of fluoro-

chemical agents in combination with a member of each of the two extender classes, give superior results compared to the compositions of the Comparative Examples comprising only one extender. Superior oil and water repellencies were obtained, and fluorine efficiency was improved relative to the Comparative Examples.

Examples 25-42 and Comparative Examples C-46 to C-72

As described in connection with Examples 1-24 above, formulations were prepared and used to treat 100% cotton fabrics at 0.6% total solids on fabric.

TABLE II

Ex.	Weight % FC	Weight % Extender 1 (Int. B)	Weight % Extender 2 (Int. A)	Initial OR	Initial SR	5 Laund OR	5 Laund SR	1 Dryclean OR	1 Dryclean SR
Fluorochemical: Intermediate C									
C-46	100	--	--	4	80	3	70	4	70
C-47	80	20	--	5	80	4	80	5	70
C-48	80	--	20	5	90	4	80	5	80
25	80	10	10	5	90	4	80	5	80
26	70	20	10	5	100	3	80	5	80
Fluorochemical: Intermediate D									
C-49	100	--	--	5	80	2	50	0	0
C-50	80	20	--	5	80	4	80	0	0
C-51	80	--	20	5	90	4	80	0	0
27	80	10	10	5	90	4	80	0	0
28	80	20	10	5	90	5	90	0	0
Fluorochemical: Intermediate F									
C-52	100	--	--	5	90	4	60	5	60
C-53	80	20	--	5	90	3	70	4	70
C-54	80	--	20	5	100	4	90	4	80
29	80	10	10	6	100	6	90	6	80
30	70	20	10	6	100	5	90	5	80

TABLE II (cont.)

Fluorochemical: Intermediate G									
C-55	100	--	--	6	100	5	80	5	80
C-56	80	20	--	6	100	5	80	6	80
C-57	80	--	20	6	100	5	90	5	90
31	80	10	10	6	100	5	90	6	90
32	70	20	10	6	100	5	90	6	90
Fluorochemical: Intermediate H									
C-58	100	--	--	4	70	0	0	4	0
C-59	80	20	--	5	80	1	60	5	70
C-60	80	--	20	5	90	4	80	5	80
33	80	10	10	5	100	3	80	5	90
34	70	20	10	5	100	4	80	5	90
Fluorochemical: Intermediate I									
C-61	100	--	--	3	80	1	60	0	0
C-62	80	20	--	4	80	2	60	0	50
C-63	80	--	20	3	80	2	80	0	70
35	80	10	10	4	80	2	80	1	70
36	70	20	10	4	80	2	80	0	60
Fluorochemical: Intermediate J									
C-64	100	--	--	7	50	0	0	0	0
C-65	80	20	--	6	60	0	50	0	0
C-66	80	--	20	7	60	5	50	0	0
37	80	10	10	7	70	5	60	0	0
38	70	20	10	7	70	5	60	0	0
Fluorochemical: Intermediate O									
C-67	100	--	--	5	70	0	0	5	70
C-68	80	20	--	6	80	2	60	6	70
C-69	80	--	20	5	90	5	80	5	90
39	80	10	10	6	90	6	80	6	90
40	70	20	10	7	90	6	80	7	80

TABLE II (cont.)

Fluorochemical: Intermediate O

C-70	100	--	--	4	90	3	70	3	70
C-71	80	20	--	5	90	3	80	3	80
C-72	80	--	20	4	100	3	90	3	80
41	80	10	10	5	100	4	90	4	80
42	70	20	10	4	100	4	90	4	80

The results in Table II indicate that some compositions of the invention afford superior results and increased fluorine efficiency compared to the corresponding compositions of the Comparative Examples even on cotton, a fabric known to be difficult to treat effectively.

Claims

1. A fluorine-efficient oil- and water-repellent composition comprising:

(A) a fluorochemical oil- and water-repellent agent;
(B) a copolymer extender comprising:

(i) polymerized units derived from a monomer of the formula:

$$CR_1R_2=CR_3R_4$$

wherein each of R_1, R_2, R_3 and R_4 independently represents hydrogen, halogen, or an organic group; and

(ii) polymerized units derived from a monomer of the formula:

$$CH_2=CR_5X$$

wherein R_5 represents a hydrogen atom or a methyl group, and X represents a moiety comprising a functional group that can interact with a fibrous substrate; and

(C) a blocked isocyanate extender, wherein the fluorochemical agent is present in an amount effective to impart repellent properties to a fibrous substrate treated with the composition, and wherein the copolymer extender and the blocked isocyanate extender are present in a combined amount effective to improve the fluorine efficiency of the fluorochemical agent, and each extender is present in an amount such that the improvement in fluorine efficiency is greater than the improvement provided by either extender alone.

2. A composition according to Claim 1, wherein the copolymer extender comprises:

(i) polymerized units derived from a monomer of the formula:

$$CR_6R_7=CR_8COOR_9$$

wherein R_6, R_7, and R_8 independently represent a hydrogen atom or a methyl groups, and R_9 represents a C_{1-18} alkyl group; and

(ii) polymerized units derived from a monomer of the formula:

$$CH_2=CR_5CONHCH_2OH$$

wherein R_5 represents a hydrogen atom or a methyl group.

3. A composition according to Claim 2, wherein the copolymer extender comprises:

(i) polymerized units derived from a monomer selected from the group consisting of an alkyl crotonate, an alkyl acrylate, and an alkyl methacrylate; and

(ii) polymerized units derived from a monomer of the formula:

$$CH_2=CR_5CONHCH_2OH$$

wherein R_5 represents a hydrogen atom or a methyl group.

4. A composition according to Claim 1, wherein the blocked isocyanate extender is a blocked isocyanate-functional low molecular weight polyurethane.

5. A composition according to Claim 1, wherein the blocked isocyanate extender is a blocked aromatic isocyanate.

6. A composition according to Claim 1, wherein the blocked isocyanate extender is polyphenypolyisocyanate blocked with 2-butanone oxime.

7. A composition according to Claim 1, wherein the copolymer extender comprises polymerized units derived from 2-ethylhexyl methacrylate and polymerized units derived from N-methylol acrylamide.

8. A composition according to Claim 1, wherein the extenders are present in relative amounts between about 1:20 to about 20:1.

9. A composition according to Claim 1, wherein the extenders are present in relative amounts between about 1:4 to about 4:1,

10. A composition according to Claim 1, wherein the extenders are present in relative amounts between about 2:1 to about 1:2.

11. A composition according to Claim 1, wherein the extenders are present in relative amounts of about 1:1.

12. A composition according to Claim 1, wherein the fluorochemical agent is present in an amount of about 20 to about 2000 parts by weight based on 100 parts by weight of the copolymer and the blocked isocyanate extenders combined.

13. A composition according to Claim 1, wherein the fluorochemical agent is present in an amount of about 40 to about 900 parts by weight based on 100 parts by weight of the copolymer and the blocked isocyanate extenders combined.

14. A composition according to Claim 1, wherein the fluorochemical agent is present in an amount of about 100 to about 400 parts by weight based on 100 parts by weight of the copolymer and the blocked isocyanate extenders combined.

15. A substrate with oil- and water-repellent properties comprising a fibrous substrate having on the surface thereof an amount of a composition according to Claim 1 effective to impart oil and water repellent properties thereto.

16. A substrate according to Claim 15, wherein the substrate is paper, non-woven, cotton, a polyester/cotton blend, nylon, or leather.

17. A substrate according to Claim 15, wherein the fluorochemical agent is present in an amount of about 0.1% to about 0.6% by weight based on the weight of the untreated substrate.

18. A substrate according to Claim 15, wherein the fluorochemical agent, the copolymer extender, and the blocked isocyanate extender are present in a total combined amount of about 0.1% to about 1% by weight based on the weight of the untreated substrate.

19. An aqueous dispersion comprising water, an amount of a composition according to Claim 1 effective to provide repellent properties to a substrate treated therewith, and an emulsifier in an amount effective to stabilize the dispersion.

20. An aqueous dispersion according to Claim 19, herein water is present in an amount of about 70 to about 900 parts by weight based on 100 parts by weight of the composition, and the emulsifier is present in an amount of about 1

to about 25 parts by weight, based on 100 parts by weight of the composition.

21. An aqueous dispersion according to Claim 19, wherein water is present in an amount of about 70 to about 900 parts by weight based on 100 parts by weight of the composition, and the emulsifier is present in an amount of about 5 to about 10 parts by weight, based on 100 parts by weight of the composition.

22. A method for imparting oil and water repellent properties to a fibrous substrate material, comprising the steps of:

(1) applying to the surface of the fibrous substrate material an amount of a composition according to Claim 1 effective to impart oil and water repellent properties to the substrate; and
(2) heating the treated substrate from step (1) at a temperature and for a time sufficient to cure the treated substrate.

23. A method of improving the fluorine efficiency of a fluorochemical agent comprising the step of formulating the fluorochemical agent with:

(a) a copolymer extender comprising:

(i) polymerized units derived from a monomer of the formula:

$$CR_1R_2=CR_3R_4$$

wherein each of R_1, R_2, R_3 and R_4 independently represents hydrogen, halogen, or an organic group; and

(ii) polymerized units derived from a monomer of the formula:

$$CH_2=CR_5X$$

wherein R_5 represents a hydrogen atom or a methyl group, and X represents a moiety comprising a functional group that can interact with a fibrous substrate; and

(b) a blocked isocyanate extender.

Patentansprüche

1. Öl- und wasserabweisende Zusammensetzung mit Fluor-Wirksamkeit, umfassend:

(A) ein fluorchemisches öl- und wasserabweisendes Mittel;
(B) ein Copolymer-Streckmittel, umfassend:

(i) polymerisierte Einheiten, deriviert von einem Monomer der Formel:

$$CR_1R_2=CR_3R_4$$

worin jedes R_1, R_2, R_3 oder R_4 unabhängig Wasserstoff, Halogen oder eine organische Gruppe darstellen; sowie
(ii) polymerisierte Einheiten, deriviert von einem Monomer der Formel:

$$CH_2=CR_5X$$

worin R_5 ein Wasserstoffatom oder eine Methylgruppe darstellt und X einen Teil darstellt, umfassend eine funktionelle Gruppe, die mit einem Fasersubstrat in Wechselwirkung treten kann; sowie

(C) ein geblocktes Isocyanat-Streckmittel, worin das fluorchemische Mittel in einer wirksamen Menge vorliegt, um einem mit der Zusammensetzung behandelten Fasersubstrat abweisende Eigenschaften zu verleihen, wobei das Copolymer-Streckmittel und das geblockte Isocyanat-Streckmittel in einer wirksamen vereinigten Menge vorliegen, um die Fluor-Wirksamkeit des fluorchemischen Mittels zu verbessern, und wobei jedes Streckmittel in einer solchen Menge vorliegt, daß die Verbesserung der Fluor-Wirksamkeit größer ist als die durch eines der Streckmittel allein vermittelte Verbesserung.

2. Zusammensetzung nach Anspruch 1, bei welcher das Copolymer-Streckmittel aufweist:

(i) polymerisierte Einheiten, deriviert von einem Monomer der Formel:

$$CR_6R_7=CR_8COOR_9$$

worin R_6, R_7 und R_8 unabhängig ein Wasserstoffatom oder eine Methylgruppe darstellen und R_9 eine $C_{1...18}$-Alkylgruppe darstellt; sowie
(ii) polymerisierte Einheiten, deriviert von einem Monomer der Formel:

$$CH_2=CR_5CONHCH_2OH$$

worin R_5 ein Wasserstoffatom oder eine Methylgruppe darstellt.

3. Zusammensetzung nach Anspruch 2, bei welcher das Copolymer-Streckmittel aufweist:

(i) polymerisierte Einheiten, deriviert von einem Monomer, ausgewählt aus der Gruppe, bestehend aus einem Alkylcrotonat, einem Alkylacrylat und einem Alkylmethacrylat; sowie
(ii) polymerisierte Einheiten, deriviert von einem Monomer der Formel

$$CH_2=CR_5CONHCH_2OH$$

worin R_5 ein Wasserstoffatom oder eine Methylgruppe darstellt.

4. Zusammensetzung nach Anspruch 1, bei welcher das geblockte Isocyanat-Streckmittel ein geblocktes, Isocyanatfunktionelles, niedermolekulares Polyurethan ist.

5. Zusammensetzung nach Anspruch 1, bei welcher das geblockte Isocyanat-Streckmittel ein geblocktes aromatisches Isocyanat ist.

6. Zusammensetzung nach Anspruch 1, bei welcher das geblockte Isocyanat-Streckmittel Polyphenylpolyisocyanat ist, geblockt mit 2-Butanonoxim.

7. Zusammensetzung nach Anspruch 1, bei welcher das Copolymer-Streckmittel polymerisierte Einheiten umfaßt, deriviert von 2-Ethylhexylmethacrylat, sowie polymerisierte Einheiten, deriviert von N-Methylolacrylamid.

8. Zusammensetzung nach Anspruch 1, bei welcher die Streckmittel in relativen Mengen zwischen etwa 1:20 bis etwa 20:1 vorliegen.

9. Zusammensetzung nach Anspruch 1, bei welcher die Streckmittel in relativen Mengen zwischen etwa 1:4 bis etwa 4:1 vorliegen.

10. Zusammensetzung nach Anspruch 1, bei welcher die Streckmittel in relativen Mengen zwischen etwa 2:1 bis etwa 1:2 vorliegen.

11. Zusammensetzung nach Anspruch 1, bei welcher die Streckmittel in relativen Mengen von etwa 1:1 vorliegen.

12. Zusammensetzung nach Anspruch 1, bei welcher das fluorchemische Mittel in einer Menge von etwa 20 bis etwa 2.000 Gewichtsteilen bezogen auf 100 Gewichtsteile der vereinigten Copolymer- und geblockten Isocyanat-Streckmittel vorliegt.

13. Zusammensetzung nach Anspruch 1, bei welcher das fluorchemische Mittel in einer Menge von etwa 40 bis etwa 900 Gewichtsteilen bezogen auf 100 Gewichtsteile der vereinigten Copolymer- und geblockten Isocyanat-Streckmittel vorliegt.

14. Zusammensetzung nach Anspruch 1, bei welcher das fluorchemische Mittel in einer Menge von etwa 100 bis etwa 400 Gewichtsteilen bezogen auf 100 Gewichtsteile der vereinigten Copolymer- und geblockten Isocyanat-Streckmittel vorliegt.

15. Substrat mit öl- und wasserabweisenden Eigenschaften, umfassend ein Fasersubstrat, welches auf einer seiner Oberflächen eine Menge einer Zusammensetzung nach Anspruch 1 aufweist, und zwar mit Wirksamkeit zum Verleihen von öl- und wasserabweisenden Eigenschaften.

16. Substrat nach Anspruch 15, umfassend Papier, Vliesstoff, Baumwolle, ein Polyester/Baumwoll-Gemisch, Nylon oder Leder.

17. Substrat nach Anspruch 15, bei welchem das fluorchemische Mittel in einer Menge von etwa 0,1 % bis etwa 0,6 Gewichtsprozent bezogen auf die Masse des unbehandelten Substrats vorliegt.

18. Substrat nach Anspruch 15, bei welchem das fluorchemische Mittel, das Copolymer-Streckmittel und das geblockte Isocyanat-Streckmittel in einer vereinigten Gesamtmenge von etwa 0,1 % bis etwa 1 Gewichtsprozent bezogen auf die Masse des unbehandelten Substrats vorliegen.

19. Wäßrige Dispersion, umfassend Wasser, eine Menge einer Zusammensetzung nach Anspruch 1, die wirksam ist, um einem damit behandelten Substrat abweisende Eigenschaften zu verleihen, sowie ein Emulgiermittel in einer zum Stabilisieren der Dispersion wirksamen Menge.

20. Wäßrige Dispersion nach Anspruch 19, in der Wasser in einer Menge von etwa 70 bis etwa 900 Gewichtsteilen bezogen auf 100 Gewichtsteile der Zusammensetzung vorliegt und das Emulgiermittel in einer Menge von etwa 1 bis etwa 25 Gewichtsteilen bezogen auf 100 Gewichtsteile der Zusammensetzung vorliegt.

21. Wäßrige Dispersion nach Anspruch 19, in der Wasser in einer Menge von etwa 70 bis etwa 900 Gewichtsteilen bezogen auf 100 Gewichtsteile der Zusammensetzung vorliegt und das Emulgiermittel in einer Menge von etwa 5 bis etwa 10 Gewichtsteilen bezogen auf 100 Gewichtsteile der Zusammensetzung vorliegt.

22. Verfahren, um einem faserigen Substratmaterial öl- und wasserabweisende Eigenschaften zu verleihen, umfassend die Schritte:

(1) Aufbringen einer wirksamen Menge einer Zusammensetzung nach Anspruch 1 auf die Oberfläche des faserigen Substratmaterials, um dem Substrat öl- und wasserabweisende Eigenschaften zu verleihen; und
(2) Erhitzen des behandelten Substrats von Schritt (1) auf eine Temperatur und für eine Dauer, ausreichend zum Härten des behandelten Substrats.

23. Verfahren zum Verbessern der Fluorwirksamkeit eines fluorchemischen Mittels, umfassend den Schritt der Zubereitung des fluorchemischen Mittels mit:

(a) einem Copolymer-Streckmittel, umfassend

(i) polymerisiete Einheiten, deriviert von einem Monomer der Formel:

$$CR_1R_2=CR_3R_4$$

worin jedes R_1, R_2, R_3 und R_4 unabhängig Wasserstoff, Halogen oder eine organische Gruppe darstellen; sowie
(ii) polymerisierte Einheiten, deriviert von einem Monomer der Formel:

$$CH_2=CR_5X$$

worin R_5 ein Wasserstoffatom oder eine Methylgruppe darstellt und X einen Teil darstellt, umfassend eine funktionelle Gruppe, die mit dem Fasersubstrat in Wechselwirkung treten kann; sowie

(b) einem geblockten Isocyanat-Streckmittel.

Revendications

1. Composition oléofuge et hydrofuge utilisant efficacement le fluor, comprenant:

(A) un agent chimique fluoré oléofuge et hydrofuge;
(B) un diluant copolymère comprenant:

(i) des motifs polymérisés dérivés d'un monomère de formule:

$$CR_1R_2=CR_3R_4$$

dans laquelle chacun des radicaux R_1, R_2, R_3 et R_4 représente indépendamment un atome d'hydrogène, un atome d'halogène, ou un groupe organique; et

(ii) des motifs polymérisés dérivés d'un monomère de formule:

$$CH_2=CR_5X$$

dans laquelle R_5 représente un atome d'hydrogène ou un groupe méthyle, et X représente un groupement comprenant un groupe fonctionnel pouvant interagir avec un substrat fibreux; et

(C) un diluant isocyanate bloqué,

dans laquelle l'agent chimique fluoré est présent dans une proportion efficace pour conférer des propriétés repoussantes à un substrat fibreux traité avec la composition, et dans laquelle le diluant copolymère et le diluant isocyanate bloqué sont présents dans une proportion combinée efficace pour améliorer l'efficacité en fluor de l'agent chimique fluoré, et chaque diluant est présent dans une proportion telle que l'amélioration de l'efficacité en fluor soit plus grande que l'amélioration apportée par l'un ou l'autre des diluants seul.

2. Composition selon la revendication 1, dans laquelle le diluant copolymère comprend:

(i) des motifs polymérisés dérivés d'un monomère de formule:

$$CR_6R_7=CR_8COOR_9$$

dans laquelle R_6, R_7 et R_8 représentent indépendamment un atome d'hydrogène ou un groupe méthyle, et R_9 représente un groupe alkyle en C_1-C_{18}; et

(ii) des motifs polymérisés dérivés d'un monomère de formule:

$$CH_2=CR_5CONHCH_2OH$$

dans laquelle R_5 représente un atome d'hydrogène ou un groupe méthyle.

3. Composition selon la revendication 1, dans laquelle le diluant copolymère comprend:

(i) des motifs polymérisés dérivés d'un monomère choisi dans le groupe constitué par un crotonate d'alkyle, un acrylate d'alkyle et un méthacrylate d'alkyle; et

(ii) des motifs polymérisés dérivés d'un monomère de formule:

$$CH_2=CR_5CONHCH_2OH$$

dans laquelle R_5 représente un atome d'hydrogène ou un groupe méthyle.

4. Composition selon la revendication 1, dans laquelle le diluant isocyanate bloqué est un polyuréthane de faible masse moléculaire à fonction isocyanate bloquée.

5. Composition selon la revendication 1, dans laquelle le diluant isocyanate bloqué est un isocyanate aromatique bloqué.

6. Composition selon la revendication 1, dans laquelle le diluant isocyanate bloqué est un polyphénylpolyisocyanate bloqué par un 2-butanone-oxime.

7. Composition selon la revendication 1, dans laquelle le diluant copolymère comprend des motifs polymérisés dérivés du méthacrylate de 2-éthylhexyle et des motifs polymérisés dérivés du N-méthylolacrylamide.

8. Composition selon la revendication 1, dans laquelle les diluants sont présents en proportions relatives comprises entre environ 1:20 et environ 20:1.

9. Composition selon la revendication 1, dans laquelle les diluants sont présents en proportions relatives comprises entre environ 1:4 et environ 4:1.

10. Composition selon la revendication 1, dans laquelle les diluants sont présents en proportions relatives comprises entre environ 2:1 et environ 1:2.

11. Composition selon la revendication 1, dans laquelle les diluants sont présents en proportions relatives d'environ 1:1.

12. Composition selon la revendication 1, dans laquelle l'agent chimique fluoré est présent dans une proportion d'environ 20 à environ 2 000 parties en poids, pour 100 parties en poids du diluant copolymère et du diluant isocyanate bloqué combinés.

13. Composition selon la revendication 1, dans laquelle l'agent chimique fluoré est présent dans une proportion d'environ 40 à environ 900 parties en poids, pour 100 parties en poids du diluant copolymère et du diluant isocyanate bloqué combinés.

14. Composition selon la revendication 1, dans laquelle l'agent chimique fluoré est présent dans une proportion d'environ 100 à environ 400 parties en poids, pour 100 parties en poids du diluant copolymère et du diluant isocyanate bloqué combinés.

15. Substrat ayant des propriétés oléofuges et hydrofuges, comprenant un substrat fibreux dont la surface comporte une quantité de composition selon la revendication 1 efficace pour lui conférer des propriétés oléofuges et hydrofuges.

16. Substrat selon la revendication 15, dans lequel le substrat est du papier, un non tissé, du coton, un mélange polyester/coton, du nylon ou du cuir.

17. Substrat selon la revendication 15, dans lequel l'agent chimique fluoré est présent dans une proportion d'environ 0,1% à environ 0,6% en poids, rapportée au poids du substrat non traité.

18. Substrat selon la revendication 15, dans lequel l'agent chimique fluoré, le diluant copolymère et le diluant isocyanate bloqué sont présents dans une proportion totale combinée d'environ 0,1% à environ 1% en poids, rapportée au poids du substrat non traité.

19. Dispersion aqueuse comprenant de l'eau, une quantité d'une composition selon la revendication 1, efficace pour procurer des propriétés repoussantes à un substrat traité avec cette dernière, et un émulsifiant dans une proportion efficace pour stabiliser la dispersion.

20. Dispersion aqueuse selon la revendication 19, dans laquelle l'eau est présente dans une proportion d'environ 70 à environ 900 parties en poids, pour 100 parties en poids de la composition, et l'émulsifiant est présent dans une proportion d'environ 1 à environ 25 parties en poids, pour 100 parties en poids de la composition.

21. Dispersion aqueuse selon la revendication 19, dans laquelle l'eau est présente dans une proportion d'environ 70 à environ 900 parties en poids, pour 100 parties en poids de la composition, et l'émulsifiant est présent dans une proportion d'environ 5 à environ 10 parties en poids, pour 100 parties en poids de la composition.

22. Procédé pour conférer des propriétés oléofuges et hydrofuges à une matière de substrat fibreuse, comprenant les étapes consistant à:

(1) appliquer sur la surface de la matière de substrat fibreuse une quantité d'une composition selon la revendication 1, efficace pour procurer des propriétés oléofuges et hydrofuges au substrat; et
(2) chauffer le substrat traité de l'étape (1) à une température et pendant une durée suffisantes pour durcir le substrat traité.

23. Procédé pour améliorer l'efficacité en fluor d'un agent chimique fluoré, comprenant l'étape consistant à formuler l'agent chimique fluoré avec;

(a) un diluant copolymère comprenant:

(i) des motifs polymérisés dérivés d'un monomère de formule:

$$CR_1R_2=CR_3R_4$$

dans laquelle chacun des radicaux R_1, R_2, R_3 et R_4 représente indépendamment un atome d'hydrogène,

un atome d'halogène, ou un groupe organique; et
(ii) des motifs polymérisés dérivés d'un monomère de formule:

$$CH_2=CR_5X$$

dans laquelle R_5 représente un atome d'hydrogène ou un groupe méthyle, et X représente un groupement comprenant un groupe fonctionnel pouvant interagir avec un substrat fibreux; et

(C) un diluant isocyanate bloqué.