

1

2

3,503,915  
**FABRIC TREATING COMPOSITION AND TREATED FABRIC**

Richard L. Peterson, Hudson, Wis., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 575,572, Aug. 29, 1966. This application Sept. 5, 1967, Ser. No. 665,253

Int. Cl. D06m 15/32, 15/36, 15/72

U.S. Cl. 260—29.2 10 Claims

**ABSTRACT OF THE DISCLOSURE**

A composition for treatment of washable fabrics to render same oil repellent comprising an admixture of an oleophobic fluorine containing polymer having limited affinity for hydrocarbon and a water insoluble, fluorine free, hydrophilic, polar organic polymer.

This application is a continuation-in-part of my prior and copending application SN 575,572, filed Aug. 29, 1966, now abandoned.

This invention relates to the treatment of washable natural and synthetic fabrics to render such fabrics stain resistant. In one aspect, this invention relates to the treatment of permanent press fabrics to render the fabrics oil repellent and to aid in the removal of organic water insoluble stains therefrom.

Today most textile fabrics are treated or finished with various finishing agents to impart improved properties to the fabric. For example, although the synthetic fabrics including the "blends" have good strength, resistance to abrasion, and thermoplasticity allowing shape retention, they are usually treated with finishing agents such as softeners to give them a better "hand" or feel. The natural fabrics such as cotton have good "hand" properties but are usually treated to give the fabrics increased stiffness and wear resistance properties. Both types of fabrics are often treated with thermosetting organic resins to give them "wash and wear" and permanent press characteristics, particularly the cotton fabrics which without such treatment wrinkle badly upon wearing and as the result of laundering.

Fabrics treated with thermosetting resins, cured and then cut into garments provide "wash and wear" characteristics; if the cure is deferred until after cutting of the garment, "permanent press" fabrics are obtained. While the mechanism of providing crease resistance is not completely understood, it appears to be characterized by a permanent crosslinking of the individual fibers by the thermosetting resin; typical of the resins used are aminoplasts, reaction products of formaldehyde and polyamino compounds, such as dimethylol dihydroxy ethylene urea, dimethylol propylene urea, dimethylol ethylene urea, urea derivatives, carbamates, triazones, melamines, sulfones, acrolein derivatives, acetals and epoxy derivatives.

In addition to the thermosetting resin, catalysts to promote the crosslinking reaction are required, and as above indicated various modifying additives or finishing agents such as softeners, stiffeners, etc. are also usually used in addition to the thermosetting resin to provide a suitable commercial fabric.

This combination of treating or finishing agents results in a fabric with good wearing characteristics. However, the tendency of the fiber to accept stains, oil borne or water borne, is somewhat increased and the ability of the material to release such stains upon laundering is markedly reduced. Well-known fluorochemical treating agents to improve the resistance to staining, such as oil

repellency and water repellency, are available. Such fluorochemical treating agents characteristically further inhibit the ability of the material to release stains, particularly oil stains, which occur despite the treatment usually when pressure and prolonged contact force the stain into the fabric. The most serious defect presently observed in wash and wear and permanent press fabrics is the "permanently stained" nature of such garments after a few wearings. Such stains can be removed by dry cleaning but this, for most garments such as shirts, children's clothing, and slacks is impractical and undesirable. It is the purpose of this invention to provide a composition which increases the stain resistance of the fabric per se, in other words, renders the fabric oil repellent, and also aids in removal of the stain from the fabric by water washing, without serious harm to the hand, water absorption and the crease resistance of the treated fabric.

An object of this invention is to provide a new fabric treating composition useful to provide a treated fabric which is stain resistant and has the minimum stain retention.

Still another object of this invention is to provide an aqueous composition for treating washable fabrics to render such fabrics stain resistant.

Yet another object is to treat fabrics for permanent press properties while simultaneously rendering the treated fabric permanently stain resistant and of improved stain removal properties.

Various other objects and advantages will become apparent to those skilled in the art from the accompanying description and disclosure.

In accordance with this invention, a composition for rendering washable fabrics stain resistant and capable of being water washed to remove the strains (cleanable) is provided which comprises an admixture of a fluorine-containing oleophobic polymer and a hydrophilic fluorine free thermoplastic polar polymer, which mixture has a contact angle with water under laundering conditions of less than 90°.

The fabric to be finished is treated with this mixture and then dried, and heat cured if desired. Treatment may be done by padding or spraying the fabric with the composition of this invention. In another embodiment of the present invention, separate emulsions or solutions of the fluorine-containing oleophobic polymer and the hydrophilic polar polymer are separately applied to the fabric with low temperature drying between applications followed by a curing step. The hydrophilic polar polymer on the fabric provides the ease of stain removal by washing with water. The particular fluorine polymer of this invention provides the characteristic of stain resistance by rendering a fabric both oil and/or water repellent and yet does not interfere with the stain removal properties imparted by the hydrophilic polar polymer. The above active ingredients of the composition are usually dispersed or dissolved in a suitable liquid vehicle or diluent which can be either water or organic solvent. The treating liquid usually contains from about 0.1 to about 10 weight percent of the above active polymers and may contain in addition certain other treating resins, such as stabilizing resins (wash and wear resins and permanent press resins), for example, dimethylol dihydroxy ethylene urea and hand modifiers, for example, partially saponified polyvinyl acetate which do not interfere with the stain removal properties imparted to the fabric. The treated fabric should contain between about 0.01 and 0.1 gram of polar polymer per gram of fabric and between about 0.001 and about 0.01 gram of fluorine-containing polymer per gram of fabric (based on dry weight of fabric).

The problem of oily stain retention in fabrics is most pronounced with the synthetic noncellulosic fabrics which

3

may be a pure synthetic fabric or a blend of synthetic fibers with natural fibers such as cotton and wool. Generally, when blends are used, the natural fibers are present in an amount not more than about 80 percent by weight. The present invention applies most particularly to those synthetic noncellulosic fabrics made of fibers of synthetic resins such as polyesters, polyamides, and polymers and copolymers derived from acrylonitrile, vinylchloride and vinylacetate. These synthetic fibers are known in the art and are available on the market under various trade names, such as rayon, Dacron, nylon, Kodol, Fortrel, Acrilan, etc.

The fluorine-containing oleophobic polymer component of the present invention may be a homopolymer of a fluorinated monomer or a copolymer of a fluorinated monomer and a nonfluorinated monomer. Even with relatively low fluorine content, for example, below 20 percent, such polymers will exhibit oil repellency. However, such polymers may contain an oil solubilizing portion, and if the oil solubilizing portion of the homopolymer or copolymer is too high, oily stains will tend to dissolve therein and be difficult to remove in normal laundering. A convenient measure of the oil solubilizing property of the polymer is obtained by exposing the polymer to an atmosphere of hydrocarbon as described in Example V hereinafter. It has been found that if more than about 25 percent by weight of cyclohexane is absorbed from the saturated vapor at room temperature, the corresponding polymer will provide treatment which is not cleanable under normal laundering conditions. In other words, the fabric is still considerably stained after laundering.

The fluorine-containing polymer component of the present composition is a fluorinated polymer containing appendant perfluorocarbon tails in the form of terminal portions or side chains in the polymer. The perfluorocarbon tail is a monovalent perfluorocarbon radical of at least 3 and not more than about 20 carbon atoms in which all the substituents are fluorine or a completely or highly fluorinated saturated organic radical. Preferably, the perfluorocarbon tail is an aliphatic radical, either acyclic or alicyclic, which may contain oxygen, nitrogen, sulfur or other atoms in the chain without departing from the scope of this invention. The perfluorocarbon radical may be straight chain, branched or cyclic. The fluorine of the perfluorocarbon tail of the fluorine-containing polymer should represent at least about 20 percent, preferably at least 30 percent, by weight of the polymer in order to permit removal of oil stains by water washing the fabric. The backbone of the polymer usually contains methylene groups and also the side chains may contain methylene groups. These methylene groups in the backbone and side chains of the polymer should be less than 30 percent by weight of the polymer. Also the side chains which contain methylene groups should preferably be terminated by a perfluorocarbon radical as above. These fluorine-containing polymers are generally solid, high molecular weight resins, including vinyl polymers and condensation polymers. The term polymer as used herein includes adducts of two or more of the same or different monomeric units, such as dimers and trimers, without departing from the scope of this invention. Usually, the fluorine-containing polymer is linear and may be a homopolymer of a fluorine monomer or a copolymer of a fluorinated monomer and a fluorine free organic monomer. Preferably, the copolymer is a random copolymer. Generally, these fluorinated polymers which are useful in accordance with the present invention are prepared from fluorinated organic precursors having the perfluorocarbon tail or radical at one end of the molecule and a reactive functional group at the other end of the molecule and may be represented by the following typical formula:  $R_fQ(CH_2)_nX$  in which  $R_f$  is the perfluorocarbon radical as previously defined of at least 3 carbon atoms,  $Q$  is a divalent linking radical such as a sulfonoamido radical, carbonamido radical, monosubstituted nitrogen, an ester

4

radical, an unsubstituted alkylene radical, a halogen (chlorine or fluorine) substituted alkylene radical, an aryene radical, a ketone radical or oxygen,  $n$  of the above formula is from 0 to 14 and  $X$  is a reactive functional group such as a carbinol group, a carboxyl group, an amine group, a mercaptan group or halogen, such as chlorine, bromine or iodine. The above fluorinated precursor compound may be reacted with another compound having functional groups reactable therewith to form directly the adduct or polymer such as with an organic diisocyanate. The fluorine-containing precursor compound may alternatively be reacted with an ethylenically unsaturated organic compound containing a functional group reactable therewith to produce a vinyl monomer, such as an acrylate or methacrylate, which acrylate or methacrylate is then polymerized by vinyl addition to produce the ultimate polymer. The processes of producing such fluorine-containing polymers and such polymers are known in the art, for example, U.S. Patent No. 2,642,416, U.S. Patent No. 2,803,615 and British Patent No. 999,795. Illustrative types of these fluorine-containing polymers are those obtained by the homopolymerization of the acrylate, methacrylate and  $\alpha$ -chloro acrylate esters of N-alkanol perfluoroalkane sulfonamides or carbonamides, N-alkanol perfluoro(morpholinoalkane) sulfonamides or carbonamides, 1,1-dihydroperfluoroalkanols, omega-perfluoroalkyl alkanols and 1,1,3-trihydroperfluoroalkanols, 1,1-dihydroperfluoroalkyl acrylamides, 1,1-dihydroperfluoroalkyl vinyl ethers, vinyl perfluoroalkyl ketones, allyl perfluoroalkyl ketones, 1-perfluoro alkanes, perfluoroalkyl alkenes, 1,1-dihydroperfluoro alkene-1, perfluoroalkyl substituted styrenes, and vinyl and allyl esters of perfluoroalkanoic acids.

Copolymers may be prepared by coreacting the above fluorinated monomer with various nonfluorinated ethylenically unsaturated organic monomers, including ethylene, vinyl acetate, acrylonitrile, acrylamide, acrylyl chloride, glycidyl methacrylate, hydroxypropyl methacrylate, styrene, acrylic and methacrylic acid and alkyl esters thereof, vinyl alkyl ketones, butadiene, chloroprene and isoprene. Also, these polymers may be prepared from the reaction of perfluoroalkyl sulfonamido or carbonamido alkanols, amines or mercaptans with the aromatic diisocyanates such as toluene diisocyanate as disclosed in British Patent No. 999,795.

The hydrophilic fluorine free polar thermoplastic polymers used in the composition of this invention generally have an interfacial tension with water below 5 dynes per centimeter when deposited on a pure polyester fabric. The polar polymer is usually insoluble in water, the solubility of the polar polymer in water being less than about one weight percent at 25° C. The hydrophilic property of the polar polymer is measured by its equilibrium contact angle with water which should be below 80°. Examples of such polar polymers include polyvinyl pyrrolidone ethyl acrylate copolymers, partially hydrolyzed polyvinylacetate, polyethylene oxide-polypropylene oxide copolymers and polyesters, relatively low molecular weight polytetramethylene oxide polymers, condensation products of polyethylene oxide, formaldehyde and melamine, and polyethylene oxide acrylate and methacrylate polymers. A particularly useful polar polymer is a polyethylene oxide (600 M.W.)-terephthalic acid copolymer having hydroxy termination in the form of an emulsion of 15 percent solids by weight, sold under the trade name Cirrasol PT. The water insolubility of both the polar polymer and the fluorinated polymer aid in obtaining a permanent or durable treatment to the fabric which is not readily removed by water washing.

The visual ratings for cleanability shown in the following examples are run as described herein. An apparatus is set up as described in the 1964 Technical Manual of the AATCC, vol. 40, page B-95, Howes Publishing Co., 44 E. 23rd Street, New York, with the overhead lighting arrangement shown in FIG. 2.

Fabrics were stained and washed as described in the examples. The samples to be tested are placed on black table top directly in front of viewing board. The samples are rated for cleanability according to the following rating scale, in accordance with the nomenclature suggested on page B-52 of the above reference.

Significance	Rating
Negligible or no staining (excellent cleanability)	5
Slightly stained (good cleanability) -----	4
Noticeably stained (fair cleanability) -----	3
Considerably stained (poor cleanability) -----	2
Heavily stained (very poor cleanability) -----	1

#### Example I

Beige or tan fabrics of 50/50 polyester cotton (Pepperell's "Starbuck") were treated with aqueous pad baths consisting of the following in which percents are by weight:

- Lot 1—Untreated.
- Lot 2—25% Valrez H-17 (dimethylol dihydroxy ethylene urea, permanent press resin, 45% solids by wt.) 5% Valcat 1700 (zinc nitrate, catalyst, 50% solids by wt.).
- Lot 3—Same as Lot 2, plus 20% Cirrasol PT (polyethylene oxide-terephthalic acid polymer latex, 15% solids by wt.).
- Lot 4—Same as Lot 2, plus 4% Moropol A-164 (polyethylene latex, 50% solids by wt.).
- Lot 5—Same as Lot 3, plus 0.3% (solids) fluorinated urethane (an emulsified reaction product of two moles of N-ethyl perfluorooctane sulfonamido ethyl alcohol and one mole of toluene diisocyanate).
- Lot 6—Same as Lot 3, plus 0.3% (solids) fluorinated copolymer (a cationic latex copolymer of 93.5:6.5% N-ethyl perfluorooctane sulfonamido ethyl methacrylate and isoprene).
- Lot 7—Same as Lot 3, plus 0.15% (solids) of fluorinated urethane of Lot 5 plus 0.15% (solids) of fluorinated copolymer of Lot 6.
- Lot 8—Same as Lot 3, plus 0.6% (solids) fluorinated copolymer (a cationic latex polymer 50:50% N-ethyl perfluorooctane sulfonamido ethyl methacrylate and chloroprene).
- Lot 9—Same as Lot 2, plus 0.3% (solids) of fluorinated urethane of Lot 5.
- Lot 10—Same as Lot 3, plus 0.3% (solids) poly 1,1-dihydroperfluorooctyl methacrylate.
- Lot 11—Same as Lot 4, plus 0.3% (solids) urethane of Lot 5.
- Lot 12—Same as Lot 3, plus 0.3% (solids) fluorinated urethane (2 moles of N-ethyl perfluorodecyl sulfonamido ethyl alcohol and 1 mol toluene diisocyanate).
- Lot 13—Same as Lot 2, plus 0.3% (solids) fluorinated homopolymer (homopolymer of N-ethyl perfluorooctane sulfonamido ethyl methacrylate).
- Lot 14—Same as Lot 3, plus 0.3% (solids) of poly N-butyl perfluorooctane sulfonamido ethyl acrylate.
- Lot 15—Same as Lot 3, plus 0.3% (solids) of poly N-propyl perfluorooctane sulfonamido ethyl acrylate.
- Lot 16—Same as Lot 3, plus 0.3% (solids) of poly N-ethyl perfluorooctane sulfonamido ethyl acrylate.
- Lot 17—Same as Lot 3, plus 0.3% (solids) of poly N-ethyl perfluorooctane sulfonamido ethyl methacrylate.
- Lot 18—Same as Lot 3, plus 0.6% (solids) of fluorinated copolymer (a cationic latex copolymer 50:50% N-ethyl perfluorooctane sulfonamido ethyl methacrylate and isoprene).
- Lot 19—Same as Lot 3, plus 0.3% (solids) of poly omega (N-methyl perfluorooctane sulfonamido) undecyl acrylate.
- Lot 20—Same as Lot 3, plus 0.3% (solids) of poly 1,1-dihydroperfluorooctyl methacrylate.
- Lot 21—Same as Lot 3, plus 0.3% (solids) of a fluorinated urethane (an emulsified reaction product of two

moles of N-ethyl perfluorobutane sulfonamido ethyl alcohol and one mole of toluene diisocyanate).

- Lot 22—Same as Lot 6, plus 0.05% of polyisoprene.
- Lot 23—Same as Lot 6, plus 0.3% of polyisoprene.
- Lot 24—Same as Lot 6, plus 0.3% of polychloroprene.
- Lot 25—Same as Lot 3, plus 0.33% (solids) of fluorinated copolymer (a cationic latex copolymer 90:10% N-ethyl perfluorooctane sulfonamido ethyl methacrylate and isoprene).
- Lot 26—Same as Lot 3, plus 0.38% (solids) of fluorinated copolymer (a cationic latex copolymer 80:20% N-ethyl perfluorooctane sulfonamido ethyl methacrylate and isoprene).
- Lot 27—Same as Lot 3, plus 0.43% (solids) of fluorinated copolymer (a cationic latex copolymer 70:30% N-ethyl perfluorooctane sulfonamido ethyl methacrylate and isoprene).
- Lot 28—Same as Lot 3, plus 0.4% (solids) fluorinated urethane (an emulsified reaction product of one mole of N-ethyl perfluorooctane sulfonamido ethyl alcohol and one mole of dimethylamino ethanol and one mole of toluene diisocyanate).
- Lot 29—Same as Lot 3, plus 0.3% (solids) of poly N-butyl perfluorooctane sulfonamido ethyl acrylate.
- Lot 30—Same as Lot 3, plus 0.35% (solids) of fluorinated copolymer (a cationic latex copolymer 85:15% N-methyl perfluorooctane sulfonamido ethyl acrylate and isoprene).

The fabrics were padded, run through a wringer having a 40 pound nip pressure and dried and cured for 10 minutes at 160° C., followed by a post-cure of 30 seconds at 190° C.

On each of the fabrics were placed 20 drops of Mazola oil. The oil was rubbed with a metal spoon with a circular motion until it was rubbed into the fabric. This left a severe oily stain of about 1 inch to 2 inches in diameter on the fabric. At this stage all lots looked similar in the severity of staining. The samples were washed in a home-style laundering machine, agitator type, with 2 pounds of cotton fabric as ballast. The water temperature was approximately 140° F. The water level was set for one-half load and 100 ml. of "Tide" detergent was used.

The samples were then rated for stain as shown in Table I, using the following scale of measurement in which  $\Delta K/S$  values below about  $0.10 \pm 0.03$  indicate acceptable stain removal and values below 0.03 indicate no appreciable visible stain retention and the higher the values the greater the stain retention. Above 0.20 values indicate unacceptable stain retention.

TABLE I

Lot No.	$\Delta K/S$
1	0.05
2	0.10
3	0.03
4	0.51
5	0.00
6	0.06
7	0.00
8	0.32
9	0.11
10	0.09
11	0.33
12	0.00
13	0.13
14	0.05
15	0.05
16	0.01
17	0.12
18	0.34
19	0.02
20	0.09
21	0.00
22	0.08
23	0.24

TABLE I—Continued

Lot No.	$\Delta K/S$
24	0.08
25	0.06
26	0.15
27	0.31
28	0.09
29	0.12
30	0.17

The extent of soiling ( $\Delta K/S$ ) was calculated from the reflectance values measured with a Hunter Reflectometer. The  $K/S$  values were calculated using the Kubelka-Munk equation,  $K/S = (1-R)^2/2R$  where  $R$  is the observed reflectance,  $K$  is the coefficient of reflectivity, and  $S$  is the coefficient of light scattering.  $K/S$  is nearly the linear function of the amount of oil present on the fabric.  $\Delta K/S$  is the difference between the  $K/S$  of the soiled fabric and original fabric ( $\Delta K/S = K/S[\text{soiled}] - K/S[\text{original}]$ ).

The absolute value of  $\Delta K/S$  is somewhat dependent upon the color and texture of the test fabric. A beige or tan colored fabric is most sensitive, and will, therefore, give the highest apparent values, since the high reflectance of white smooth fabrics and the low reflectance of dark or rough fabrics tends to minimize differences between stained and unstained portions; difference in cleanability (of the latter fabrics) are frequently more apparent visually than indicated by the instrument readings.

In addition to the low stain retention exhibited by Lots 5, 6, 7, 9, 10 and 12-17, 19-22, 24-26 and 28-30, the fabric treated with these lots exhibited excellent oil repellancy (an oil repellancy rating above 80). Other wash and wear fabrics showed similar results when treated with the composition of this invention.

The fabric may be treated by successively applying the polar polymer and the fluorinated polymer from separate solutions or dispersions with air drying between applications followed by curing.

#### Example II

This example shows the evaluation of the hydrophilic property of the polar polymer by measurement of the contact angle. Those polar polymers having an equilibrium contact angle with water below 80° work well in the composition of this invention as shown in Example I and of the  $\Delta K/S$  of Table II below. The polymer to be tested is dissolved or dispersed in a liquid such as water or toluene. Film is cast from the liquid on a glass microscope slide; the film is air-dried, then heated for 10 minutes at

TABLE II

Polar polymer	Contact angle (deg.)	$\Delta K/S$
(1) Polyethylene oxide-terephthalic acid polymer, av. M.W. 600	30	0.00
(2) Polytetramethylene oxide hydroxy terminated, av. M.W. 1,128	30	0.00
(3) Polytetramethylene oxide hydroxy terminated, av. M.W. 15,000	90+	0.44
(4) Adduct from: 1 mol octadecylamine, 2 mol Carbowax 350, <sup>2</sup> 1 mol bis-(phenyl isocyanato methyl) phenyl isocyanate	50	0.03
(5) Oxidize 1 polyethylene	90+	0.30
(6) 50/50 (weight) Carbowax <sup>2</sup> acrylatemethylmethacrylate copolymer	35	0.07
(7) Adduct from: 0.75 mol Carbowax, <sup>2</sup> 0.125 mol dipropylene glycol, 1.0 mol toluene diisocyanate	30	0.00
(8) Adduct from: 1 mol polypropylene glycol (M.W. 2,000) and 1 mol of toluene monoisocyanate	30	0.09
(9) Polymer of 1 mol polypropylene glycol (M.W. 1,000) and 1 mol of toluene diisocyanate	90+	0.20
(10) Polyvinyl pyrrolidone, ethyl acrylate copolymer	50	0.02
(11) Diethylene glycol sebacate polymer	45	0.05

<sup>1</sup>  $\Delta K/S$  of the treatment with Lot 9 of Example I plus 3 wt. percent polar polymer in Table II.

<sup>2</sup> Carbowax 350 is  $\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ , where  $n$  is approximately 7.

#### Example III

The following example illustrates the durability to laundering of the composition of this invention. A fabric was treated with aqueous pad-bath containing:

	Wt. percent in bath
Dimethylol dihydroxy ethylene urea (permanent press resin)	12.5
Zinc nitrate	2.5
Fluorochemical polymer	0.3
Polymer of polyethylene glycol (600 M.W.) and terephthalic acid	3.0
Water	81.7

The fabric was a 50:50 polyester:cotton fiber blend, twill, 100 x 50 count, 1.65 yards per pound, 44 inch width, dyed beige, ready for finishing. The fabric was padded as 8 inch by 8 inch samples, nipped at 40 p.s.i., dried in air and cured 10 minutes at 160° C., post-cured 30 seconds at 190° C. The material was stained with a pool of 20 drops Mazola (corn oil), fabric placed on two folds of cheesecloth, spot covered by a 5 pound weight with circular area of about 12 inches square (i.e.—0.5 pound/in.<sup>2</sup>) for 5 minutes at 25° C. The fabric was laundered in the standard cycle of Example I and retested, laundered four more times, tested for oil repellancy, restained as above, relaundered and retested for  $\Delta K/S$ :

TABLE III

Polymer	Initial		$\Delta K/S$	1 Laundering oil <sup>1</sup>	5 Launderings	
	Oil <sup>1</sup>	Spray <sup>2</sup>			Oil <sup>1</sup>	$\Delta K/S$
(A) Lot 6 copolymer of N-ethyl perfluorooctane sulfonamido ethyl methacrylate:isoprene-93.5:6.5 by wt.	120	50	0.04	80	50	0.03
(B) Blend of A:adduct of 2 mols N-ethyl perfluorooctane sulfonamido ethanol, 1 mol toluene diisocyanate 90:10 by wt.	120	50	0.06	90	60	0.02
(C) Blend of A:adduct of B, 70:30 by wt.	120	50	0.04	90	60	0.03
(D) Blend of A:adduct of B, 50:50 by wt.	120	50	0.03	100	60	0.03

<sup>1</sup> For oil repellancy tests, see Textiles Res. Journal 32, pp. 321-331 (1962).

<sup>2</sup> For Spray rating tests, see British Pat. No. 999,795.

160° C. in a circulating air oven. The slide is cooled to about 25° C., drops of distilled water placed on it, and the contact angle (internal angle) measured with a goniometer. Because of some irregularities in the film, four drops are placed on the film, and the highest value obtained is recorded.

#### Example IV

The fabric treating composition of this invention when applied to the fabric must be oil repellent (oleophobic) but at the same time when the treated fabric is immersed in water during laundering it must be preferentially wetted by water so that the water will displace

the oil stain. In other words, the treated cloth must have an oil repellency rating above 50, preferably above 80, and have a contact angle with water below 90°, preferably below 80°, under laundering conditions of time and temperature. Table IV below shows oil repellency ratings and contact angle for representative composition of Example I. The contact angle shown in Table IV for the respective compositions was determined in accordance with the method of Example II.

TABLE IV

	Contact angle (deg.)		Oil rating
Lot 5.....	50		110
Lot 6.....	75		110
Lot 8.....	90+		110

Example V

To show the effect of utilizing more nonfluorinated monomer (oil receptive component) in the polymer, a comparison is shown in Table V below of a treatment with compositions including a fluorinated copolymer containing varying amounts of nonfluorinated comonomer. The tests were carried out with a composition and in a manner similar to the preceding Examples, i.e. repellency and cleanability. To more clearly make a comparison of the effect of the oil receptive component of the fluorinated copolymer, the table also shows the weight percent gain (swelling) of the fluorinated copolymer (oleophobic copolymer) alone (absent other ingredients of lot) when a film of the copolymer was exposed to a saturated atmosphere of vapor of cyclohexane for 24 hours at 75° F. in the absence of air and inert gases.

TABLE V

Copolymer (wt. per cent isoprene)	Repellency		Cleanability visual	Percent gain in cyclohexane, 24 hours
	Oil	Spray		
0 (Lot 17).....	90	50	3	4.6
6.5 (Lot 6).....	100	50	4	7.2
10 (Lot 25).....	105	50	4	11.6
20 (Lot 26).....	100	50	3	19.1
30 (Lot 27).....	100	50	2	47
50 (Lot 18).....	70	50	2	120

The samples with less than 30% isoprene are good, while the samples with 30% or more are poor.

Example VI

The same comparison as described and shown in Example V was carried out with another set of fluorinated polymers and mixtures thereof. The results are shown in Table VI below.

TABLE VI

Polymer	Repellency		Cleanability visual	Vapor percent gain in cyclohexane, 24 hours
	Oil	Spray		
Lot No. 8.....	100	50	2	48
Lot No. 19.....	130	50	4	0
Lot No. 5.....	110	50	5	0
Lot No. 28.....	90	50	4	0
Lot No. 29.....	80	50	3	7.8
Lot No. 30.....	100	50	3	0

Having described my invention, I claim:

1. An oil repellent fabric-treating composition for enhancing stain-resistance of washable fabric and aiding in

the removal of stains when the fabric is washed in water, comprising an admixture of (A) from about 1 to about 10 parts of a fluorine-containing oleophobic polymer having affinity for hydrocarbon limited to not more than about 25% by weight uptake from saturated cyclohexane vapors at 75° F. for 24 hours and containing a perfluorocarbon radical of at least 3 carbon atoms, the fluorine atoms of the perfluorocarbon radical constituting at least 20% by weight of the polymer, and (B) from about 10 to about 100 parts of a water-insoluble substantially fluorine free, thermoplastic, hydrophilic polar organic polymer having a contact angle with water of less than 80°, said composition being characterized by having a contact angle with water of less than 90° under laundering conditions.

2. The composition of claim 1 in the form of an aqueous dispersion containing from about 0.1 to about 10 weight percent of the said composition.

3. A fabric treated with the composition of claim 1. 4. The fabric of claim 3 which is a cotton polyester fabric blend.

5. The composition of claim 1 in which said fluorinated polymer is a fluorocarbon-diisocyanate adduct.

6. The composition of claim 1 in which said polar polymer is a polyester polymer.

7. An oil repellent fabric-treating composition according to claim 1 wherein the fluorine-containing oleophobic polymer has an affinity for hydrocarbon limited to not more than about 25% by weight uptake from saturated cyclohexane vapors at 75° F. for 24 hours and contains at least 30% by weight of fluorine.

8. A fabric according to claim 3 additionally treated with thermosetting crease-resistant resin finish.

9. A fabric according to claim 3 wherein there is about 0.001 to about 0.01 gram of fluorine-containing polymer and from about 0.01 to about 0.1 gram of hydrophilic polymer per gram (dry weight) of fabric.

10. An oil repellent fabric-treating composition according to claim 1 containing thermoplastic hydrophilic polar organic polymer having a contact angle with water of up to 50°.

References Cited

UNITED STATES PATENTS

3,407,026	10/1968	Mauloin .....	117—139.5
3,081,274	3/1963	Heine .....	260—900
3,242,117	3/1966	Cohen.	
3,252,932	5/1966	Bolstad et al.	
3,341,497	9/1967	Sherman et al. ....	260—873
3,380,943	4/1968	Enders et al. ....	260—29.2
3,385,812	5/1968	Brachman .....	260—859

OTHER REFERENCES

Peper et al.: Relation Between Surface Properties of Cotton Finishes and Wet Soiling, American Dyestuff Reporter. Vol. 54, No. 21, pp. 36—42, Oct. 11, 1965.

SAMUEL H. BLECH, Primary Examiner

JOHN C. BLEUTGE, Assistant Examiner

U.S. Cl. X.R.

8—115.6, 116.3; 117—121, 137.8, 138.8, 161; 260—29.4, 29.6, 29.7, 849, 850, 851, 852, 858, 859, 860, 873, 895, 900