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LAUNDERABLY REMOVEABLE, SOIL AND STAIN RESISTANT FABRIC TREATMENT

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13 Claims

ABSTRACT OF THE DISCLOSURE

A non-durable treating composition for frequently laundered fabrics which renders the surface of fabrics treated therewith soil and stain resistant. The treating composition is removed from the fabric surface by laundering. The treating composition comprises an aqueous suspension of a water insoluble fluorocarbon compound containing a hydrophobic and oleophobic perfluoroalkyl group of at least 3 carbon atoms adsorbed on a water soluble organic film-forming fabric sizing agent, said suspension having a maximum solids content of about 25 weight percent. A method of treating fabrics and treated fabrics are also disclosed.

This application is a continuation-in-part of application Ser. No. 489,070, filed Sept. 21, 1965, now abandoned.

The present invention relates to a fabric treating composition and to treated fabrics. More particularly it relates to a composition comprising a sizing ingredient and a fluorocarbon compound which will impart temporary oil and water repellent properties to fabrics, especially washable fabrics, treated with the composition.

The use of fluorocarbon compounds to impart oil and water repellent properties to a variety of materials is, of course, well known. However, washable fabrics treated with a fluorocarbon compound present a unique problem of soil removal which is encountered in the laundering process.

Soiling of fabrics and garments normally occurs in three ways. The first occurs during normal use and wearing of a garment and is usually referred to as dry soiling. Here, soiling occurs on the surface of the garment and results from environmental surfaces and conditions. A second source of soiling results from the spilling of stain producing materials such as foodstuffs, greases and oils and inks onto the surface of the garment, resulting in a garment which may be severely soiled (stained) in several small areas. The last category of soiling involves wet soiling or the re-deposition of dispersed soil from the wash water onto the fabric surface during the laundering process. In this instance, soil which is removed from the treated garment itself or from other garments during laundering is suspended in the aqueous medium and has a tendency to be re-deposited on the garment.

As previously noted, the use of fluorocarbon compounds to impart oil and water repellency to fabrics and garments is not new nor is the fact that they are excellent for inhibiting dry soiling and spillage soiling of fabrics and garments so treated. However, such treatment of fabrics and garments with fluorocarbon compounds generally does not assist in inhibiting the re-deposition of dispersed soil from the wash water onto the fabric or garment but, in fact, aggravates and contributes to soiling in this manner. It has been shown that the wet soiling or the re-deposition of soil upon a fabric or garment during laundering is related to a considerable degree upon the finish of the fabric. Those normally permanent fabric finishing

agents exhibiting strong repellency characteristics to dry soiling such as the fluorocarbon compounds have affinity for the same type of soil when placed in an aqueous system. Among the explanations given for this "wet soiling" of fluorocarbon treated surfaces, perhaps the most easily understandable relates to analysis of the surface energies involved. For example, see the article entitled Wet Soiling of Cotton, part IV Surface Energies of Cotton Finishing Chemicals, Julian Berch and Henry Peper, Textile Research Journal, March 1965, vol. 35, number 3, page 252. An untreated cotton surface exhibits a strong affinity for oily soils in an air environment due to its high surface energy. When wet, however, the same cotton surface exhibits excellent resistance to the same oily soiling media due to the now low surface energy involved at the water-fabric interface. Under the same circumstances, the fluorocarbon surfaces possess low surface energies in air which account for their oil repellency characteristic. Once submerged in an aqueous media, this situation reverses and the fluorocarbon-water interface forms a high energy surface which can be wet by oily soils. In addition, once soil is deposited on such surfaces it becomes highly resistant to removal by laundering. Obviously, this phenomenon is a serious handicap to the utilization of fluorocarbon compound treatments for everyday use garments such as shirts and blouses where frequent laundering is required.

It is accordingly an object of the present invention to provide a fabric treating composition for washable fabrics and garments which will greatly lessen or eliminate the chances of a fabric or garment becoming soiled from all three of the aforementioned sources of soiling.

A further object of the invention resides in the provision of a facile method of treating fabrics and garments with the treating composition.

Another object of the invention is to provide a washable fabric having a treatment applied thereto which imparts temporary oleophobic and hydrophobic properties to the fabric surface.

A further object is to provide a treating composition for frequently laundered fabrics in such a form that the treating composition can be easily and selectively applied to the fabric surface.

It has been discovered that an effective, temporary oil and water repellent fabric treating composition could be developed through the inclusion of a water soluble or dispersible organic film-forming sizing agent with a fluorocarbon compound.

The resulting composition imparts soil resistance to fabric and garment surfaces during use and wear and more importantly, eliminates the problem of soil re-deposition on the fabric surface during laundering, by causing the fluorocarbon compound to be removed from the fabric leaving an untreated surface which has little attraction for the dispersed soil in the wash water. This surprising result is achieved by using fluorocarbon-size formulations in which the sizing agent is present in sufficient quantities to allow for removal of the fluorocarbon compound. The mixture of the two has as its only prerequisite that the sizing agent maintain contact with the fluorocarbon compound after application so as to insure that the fluorocarbon compound is removed along with the sizing component during laundering. In the case of cationic fluorocarbon lattices, this is quite easy due to the electrostatic combining of the two oppositely charged ingredients prior to application. This reaction prevents the fluorocarbon compound from attaching itself to the cotton and enables the sizing ingredient to carry the fluorocarbon compound along with it during its removal in laundering. In the case of anionic and neutral fluorocarbon lattices, electrostatic attraction is not involved. Instead, a film of sizing agent containing dispersed fluorocarbon compound particles is formed. While this film imparts excellent oil and water

repellency properties to the fabric surface due to the presence of the fluorocarbon compound, the removal of the fluorocarbon compound together with the sizing agent during laundering (water washing), substantially destroys these oleophobic and hydrophobic properties. Thus, again, the prerequisite of having a strippable (removable) fluorocarbon treated surface is fulfilled.

The fabric treating composition of the present invention comprises an aqueous emulsion of a water insoluble fluorocarbon compound exhibiting oil and water repellent properties and water soluble or dispersible organic film-forming fabric sizing agent. The fluorocarbon component of the composition can be any one or combinations of the compounds comprising a large family of organic compounds containing a perfluoroalkyl radical of at least 3 carbon atoms, preferably 3 to 18 and generally 4 to 12 carbon atoms, which has sufficient mobility to allow it to orient outwardly from the surface and thereby impart oleophobic and hydrophobic characteristics to the surface upon which it is applied. The fluorocarbon compound acts as a soil barrier due to its nonwettable characteristics. Thus, the class of useful fluorocarbon compounds is not limited to those that are employed in other arts for the durable coating or sizing of materials that are subjected to mechanical wearing, or cleaning, or to weathering. The fluorocarbon compound of the present invention need not provide a polymeric coating on the treated surface.

The only essential requirements of the hydrophobic and oleophobic fluorocarbon compound are that it supply hydrophobic and oleophobic fluorocarbon radicals and that it be compatible with the fabric sizing agent and permit of making up dilute aqueous emulsions thereof. Compatibility means that degradation or undue coagulation, etc. of the fabric sizing agent, thereby reducing its effectiveness as a fabric size, is avoided.

A wide variety of hydrophobic and oleophobic fluorocarbon compounds useful in the present invention are already well known in the art. Included in this category are the water insoluble homopolymers of fluorine-containing monomers having the general structural formula R_fX where R_f is a monovalent fluorinated aliphatic radical containing 3 to 18 (preferably 4 to 12) carbon atoms. The aliphatic chain may be straight, branched, or, if sufficiently large, cyclic and may include oxygen or trivalent nitrogen atoms bonded only to carbon atoms. A fully fluorinated radical is preferred, but hydrogen or chlorine atoms may be present as substituents provided that not more than one atom of either is present for every two carbon atoms, and, preferably, the radical contains at least a terminal perfluoromethyl group such as the acrylate, methacrylate and alpha-chloro acrylate esters of N-alkanol perfluoroalkane sulfonamides, 1,1-dihydroperfluoroalkanol, omega-perfluoroalkyl alkanols and 1,1,3-trihydroperfluoroalkanol, 1,1-dihydroperfluoroalkyl acrylamides, 1,1-dihydroperfluoroalkyl vinyl ethers, vinyl perfluoroalkyl ketones, alkyl perfluoroalkyl ketones, 1-perfluoroalkenes, 2-perfluoroalkyl ethylenes, 1,1-dihydroperfluoroalkene-1, perfluoroalkyl substituted styrenes, and vinyl alkyl esters of perfluoroalkanoic acids; and copolymers thereof with polymerizable ethylenically unsaturated monomers such as ethylene, vinyl acetate, vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, vinyl chloroacetate, acrylonitrile, vinylidene cyanide, styrene, alkylated styrenes, sulfonated styrenes, halogenated styrenes, acrylic acid and alkyl esters thereof, methacrylic acid and alkyl esters thereof, alpha-chloro acrylic acid and alkyl esters thereof, methacrylonitrile, acrylamide, methacrylamide, vinyl carbazole, vinyl pyrrolidone, vinyl pyridine, vinyl alkyl ethers, vinyl alkyl ketones, butadiene, chloroprene, fluoroprene and isoprene.

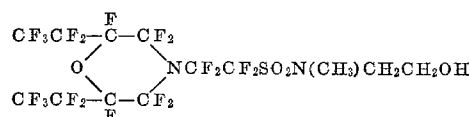
Of particular interest are the adducts prepared most conveniently by reaction of an alcohol containing a perfluoroalkyl group with an organic isocyanate or polyisocyanate compound.

The isocyanate compound may be either monoisocyanate or polyisocyanate such as a diisocyanate represented by the formula $R(NCO)_{n+(p-1)}$ in which R is an organic radical having 2 to about 30 carbon atoms for each —NCO group and about hydrocarbon radicals adjacent the valence bonds in the connecting chain, such as a hydrocarbon radical, an alkoxy (up to 6 carbon atoms) substituted or normally gaseous halogen substituted hydrocarbon radical, a hydrocarbon ether radical, and a radical derivable from the reaction product of a hydrocarbon isocyanate or alkoxy (up to 6 carbon atoms) substituted or normally gaseous halogen substituted hydrocarbon isocyanate with a hydrocarbyl alcohol, mercaptan, phenol, thiophenol, carboxylic acid or amine; n is an integer from 1 to 3 and p is an integer from 1 to 6, preferably 1 to 3, and the sum of $n+(p-1)$ is from 2 to 6. The adducts, containing one or more urethane linking groups can also be prepared, for example, by reaction of a perfluoroalkyl group-containing chlorocarbonate with an organic amine (or polyamine) or by reaction of perfluoroalkyl group-containing alcohol with a carbamoyl chloride.

Such adducts, in contrast to the vinyl polymers and copolymers described above, are characteristically low melting (e.g., below about 250° C. and preferably below about 175° C.) and are poor film formers. Accordingly, a higher ratio of fluorocarbon compound to sizing agent can be tolerated than in the case of the good film-forming polymers without danger of retaining a fluorocarbon fabric surface during and after laundering. This higher fluorocarbon radical content enhances the size properties and also acts as a lubricant thus making ironing easier. In addition, it appears to contribute to the elimination of such starch disadvantages as flaking and buildup.

As indicated previously, the structure of the alcohol is unimportant, providing only that it contains both an aliphatic hydroxyl group and a terminal perfluorocarbon group of at least 3 to about 18, preferably 4 to 12, carbon atoms. The intervening structure may comprise one or more linking radicals such as alkylene, arylene, oxa, imino, sulfonamido, carbonamido, and the like. Included in the contemplated alcohols are:

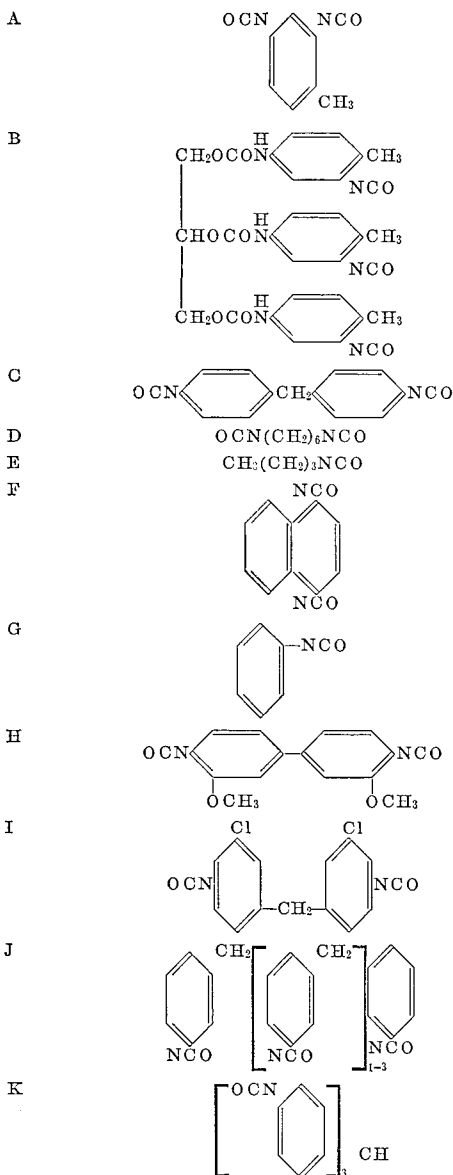
- (1) $CF_3(CF_2)_7SO_2N(CH_3)CH_2CH_2OH$
- (2) $CF_3(CF_2)_8SO_2N(CH_3)CH(CH_3)CH_2OH$
- (3) $CF_3(CF_2)_3SO_2N(CH_2CH_3)CH_2CH_2OH$
- (4) $CF_3(CF_2)_3SO_2N(CH_3)CH_2CH(CH_3)OH$
- (5) $CF_3(CF_2)_7SO_2N(CH_2CH_3)CH_2CH_2OH$
- (6) $CF_3(CF_2)_9SO_2N(CH_2CH_2CH_3)CH_2CH_2OH$
- (7) $CF_3(CF_2)_7SO_2N(CH_2CH_2CH_3)CH_2CH_2OH$
- (8) $CF_3(CF_2)_7SO_2N(C_2H_5)(CH_2)_6OH$
- (9) $CF_3(CF_2)_7SO_2N(C_2H_5)(CH_2)_{11}OH$
- (10) $CF_3(CF_2)_7SO_2N(C_4H_9)(CH_2)_4OH$
- (11) $CF_3(CF_2)_7SO_2N(CH_3)(CH_2)_4OH$
- (12) $CF_3C_6F_{10}C_2F_4SO_2N(CH_3)CH_2CH_2OH$
- (13) $C_2F_5O(C_2F_4O)_3CF_2CONHC_2H_4OH$
- (14) $CF_3(CF_2)_7SO_2N(C_3H_7)CH_2OCH_2CH_2CH_2OH$



- (16) $CF_3CF(CF_2Cl)(CF_2CF_2)_6CF_2CON(CH_3)CH_2CH_2OH$
- (17) $CF_3(CF_2)_6SO_2CH_2CH_2OH$
- (18) $CF_3(CF_2)_6COCH_2CH_2OH$
- (19) $C_7F_{15}CON(C_2H_5)C_2H_4OH$
- (20) $C_4F_9SO_2N(C_2H_5)CH_2CHOHCH_2OH$

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The organic isocyanate compound may include one, two, or more isocyanate groups. Suitable isocyanate compounds include



Because of their low cost and ready availability, the aliphatic or aromatic mono- and diisocyanates containing two to about 30 carbon atoms are preferred.

The primary requirements for the fabric sizing agent are that it be film-forming, water soluble or dispersible and thus readily removed from the fabric surface and can be combined with the fluorocarbon component. In the combination of these ingredients, the electrical charge on the fluorocarbon latex, if any, should be taken into consideration. With the cationic fluorocarbon latices, it is desirable that the sizing materials, such as many of the starches, be highly electro-negative. This factor tends to insure that the cationic fluorocarbon latex attach itself to the size and in addition provides an excellent base from which the perfluoroalkyl radicals can orient themselves to yield maximum oil and water repellent properties. Included in the category of sizing agents suitable for utilization in this invention are the natural starches, most of which are polymeric compounds of glucose having the empirical formula $(C_6H_{10}O_5)_n$. The many modified starches are also suitable and include those produced through acid conversion oxidation, enzyme conversion, dextrinization and those pregelatinized varieties manufactured by rupturing

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the starch granules. In addition, other water soluble gums of vegetable and synthetic origin are suitable. Here should be included the carbohydrates, glues, salts of complex organic acids such as gum Arabic as well as synthetic gums such as carboxy methyl cellulose, hydroxyl ethyl cellulose, methyl cellulose and a host of other cellulose esters and ethers. Other factors which should be considered in selecting the proper sizing agent are the amount of stiffening desired, ease of formulation with water, final appearance of the garment from a luster and color standpoint and ease of application to the garment.

The present invention does not pertain to the chemistry of the specific compounds utilized, nor is novelty asserted as to the more general principle of fabric sizing. This invention deals with the specific novel idea of the herein described fabric treating composition, and with the discovery that new and improved results can thereby be obtained for everyday use garments requiring frequent laundering. The term laundering or water washing refers to the normal process of immersing garments or fabrics in an ample quantity of water with suitable agitation so that the deposited soil on the garment or fabrics is removed and floated away. Usually either a soap or detergent is used for assisting in soil removal; however, the presence of either is desirable but not a necessity. The temperature of the water is not critical although a normal range of 70–160° F. would be expected.

Since the fabric treating composition of the present invention is primarily intended for utilization on everyday use garments such as shirts and blouses where frequent laundering is required, a simple and convenient method for applying the composition to such garments after each laundering is required. Of course, the normal method for the application of an aqueous fabric sizing solution wherein the article to be treated is immersed in the sizing solution and then dried could be utilized. In many cases, however, the housewife would not want to size the entire garment. This is particularly true for men's shirts where only the areas of greatest soiling, i.e., the collar and sleeve cuffs, would be sized.

Thus, a method whereby the fabric treating composition could be selectively applied to such frequently laundered items would be exceedingly useful. Such a method is realized with an aerosol or self-pressurized package which permits the composition to be dispensed in spray form. This not only allows for efficient dispensing of the fabric treating composition onto the desired areas of treatment, but, in addition, offers the convenience and the ability to dampen the garments for ironing simultaneously with the sizing operation.

The use of the self-pressurized package as the preferred form of packaging, of course, necessitates and permits several modifications of the formulation to adapt it to a self-pressurized system. Common corrosion inhibitors such as sodium borate, monoethanol amine or ammonia would normally be added. Also, if desired, a brightening agent can be added to provide the necessary whiteness to convey the appearance of a cleaner garment. Typical brighteners which have been found useful are the organic fluorescent materials such as Calcofluor ST, Calcofluor CBP, Tinopal 2BA and Emkatint C.

In addition, items such as starch plasticizers can be incorporated to achieve a finer textured finish and provide better hand-appeal to the user. These plasticizers can include the sulfonated castor oils or the monocrystalline or paraffin waxes. Ironing aids such as silicones, glycols and waxes can also be used to impart good glide characteristics to the iron during ironing of the treated garment. Better freeze-thaw stability can be built into the formulation with the inclusion of various salts such as sodium chloride or sodium tetraborate. The utilization of a light perfume can add further aesthetic qualities to the composition. If natural sizes are used, a bacteriostat preservative such as formaldehyde and the short chain ester of parahydroxy benzoic acid can be included.

It will be apparent from the foregoing that the treating composition of the present invention must be an aqueous based system. However, the intrinsic oil and water resistant properties of the fluorocarbon compounds presented the perplexing problem of stabilizing the fluorocarbon compound in an aqueous system free of organic solvents. It was discovered that the fluorocarbon compound could be stabilized, e.g., in emulsion form, in an aqueous system by the proper selection of processing aids and process conditions and provided the particle dimensions of the fluorocarbon compound were of the order of about .01 to 1 micron. In particular, the selection of surfactants to properly emulsify the fluorocarbon compound requires a careful balance of the hydrophilic-oleophilic properties and electrical charge characteristics in order to obtain a stable sub-micron particle size emulsion, as is well known in the art.

Some attention must be given to proper formulation since it is important that the proportion of sizing agent to fluorocarbon compound be high enough to allow for removal of the fluorocarbon compound during laundering and yet not mask its oil and water repellent properties. The ratios of fluorocarbon compound to sizing agent will depend upon the specific ingredients used and it has been found that they can vary from about 1:1 to as high as about 1:50, preferably about 1:5 to about 1:30. It has been found that with many of the fluorocarbon polymers which were emulsion polymerized with cationic surfactants, the positively charged micelle would be attracted to the negatively charged sizing agent. This results in a high degree of orientation of the fluorocarbon compound yielding excellent repellent properties when the combined system is applied to the fabric surface. Due to this inter-reaction, it becomes possible to use far lower amounts of fluorocarbon compound than with formulations containing neutral or anionic materials. At times this factor is offset by the film-forming characteristics of the fluorocarbon compound. If the compound used is an excellent film former then it may be necessary to increase the amount of sizing agent to insure removal. This becomes nothing more than a physical mixture of the two with the fluorocarbon compound contained as "aggregate" and allows for water removal of the size film together with the fluorocarbon compound. The following formulations illustrate the compositions and range of blending possible in accordance with this invention:

Nonionic perfluoro acrylic latex polymer
(good film former)

0.5% a segmented copolymer of the methacrylate ester of N-ethyl, N-ethanol, perfluorooctane sulfonamide and chloroprene which had been prepared with a $C_8F_{17}SO_2NH(CH_2)_3N(CH_3)_2HCl$ emulsifier
6.0% natural corn starch
1.0% auxiliaries (corrosion inhibitors, brighteners, etc.)
92.4% water

Nonionic perfluoro urethane compound
(poor film former)

1.0% a 2:1 diurethane adduct of a $C_8F_{17}SO_2N(C_2H_5)_2C_2H_4OH$
and toluene diisocyanate
3.0% natural corn starch
1.0% auxiliaries (corrosion inhibitors, brighteners, etc.)
95.0% water

Cationic perfluoro acrylic latex polymer

0.3% a segmented copolymer of the methacrylate ester of N-ethyl, N-ethanol, perfluorooctane sulfonamide and chloroprene which had been prepared with a $C_8F_{17}SO_2NH(CH_2)_3N^+(CH_3)_3Cl^-$ emulsifier

7.0% natural corn starch
1.0% auxiliaries (corrosion inhibitors, brighteners, etc.)
91.7% water

Anionic perfluoro acrylic latex polymer

0.6% a homopolymer of the acrylate ester of N-propyl, N-ethanol, perfluorooctane sulfonamide
7.0% natural corn starch
1.0% auxiliaries (corrosion inhibitors, brighteners, etc.)
93.4% water

Nonionic perfluoro acrylic latex polymer

0.6% a homopolymer of the methacrylate ester of 1,1,2,2-tetrahydro perfluorooctanol
15.0% natural corn starch
1.0% auxiliaries (corrosion inhibitors, brighteners, etc.)
83.4% water

As an example of the effect of varying concentrations (percent by weight) of size when formulated with a fixed level of fluorocarbon, the following chart is presented. This chart illustrates the repellency features before and after laundering relative to each size and fluorocarbon concentration. The repellency features were judged by placing drops of a light oil and water on the fabric surface for one minute and then removing these by blotting. When both materials penetrated the fabric the repellency properties were assumed to be destroyed and that the fabric had an ineffective level of fluorocarbon present on the surface. By the term destroyed it is meant that the oleophobic and hydrophobic properties which had been exhibited by the treated fabric prior to laundering were no longer in evidence. While trace amounts of fluorocarbon compound may remain on the fabric surface, the level is not high enough to impart oleophobic and hydrophobic characteristics. The size used was a thin boiling acid converted corn starch. The fluorocarbon compound used was a nonionic perfluoro aliphatic alcohol acrylate polymer supplied in emulsion form. The formulations were made up by incorporating the size and fluorocarbon into a water solution. No auxiliaries were used. The fluorocarbon compound was an excellent film former. The fabric tested was an untreated bleached 80 x 80 cotton. The formulation was applied by immersing the fabric into the solution and then wringing out the excess. The samples were then dried by ironing before evaluating. Laundering was accomplished by immersing the fabric into an aqueous 0.5% soap solution with agitation for a two minute period followed by rinsing in warm water.

Solids concentration		Oil and water repellency	
FC	Size	Before laundering	After laundering
A.. 0.3	0.6	Yes.....	Yes.
B.. 0.3	1.0	Yes.....	Yes.
C.. 0.3	3.0	Yes.....	Yes.
D.. 0.3	6.0	Yes.....	Slight.
E.. 0.3	7.0	Yes.....	No.
F.. 0.3	8.0	Slight.....	No.
G.. 0.3	9.0	Very slight..	No.

From this data it is obvious that the formulation in Sample E is the most suitable for utilization in a product for application to washable fabrics. This choice was made since the formulation affords initial oil and water repellency to the fabric and still allows for removal of the fluorocarbon compound during laundering as is evidenced by the subsequent lack of oil and water repellency.

It is thus seen that the fluorocarbon compounds should constitute from about 0.1 to about 5%, preferably about 0.4 to about 1.5%, by weight of the total fabric treatment composition in order to realize the desirable hydrophobic and oleophobic properties characteristic of fluorocarbon compounds and still retain the ability of being removable from the fabric during laundering by the sizing agent. Similarly the fabric sizing agent should constitute from about 0.5 to about 20%, preferably about 2 to about 7% by weight of the total fabric treating composition.

Other sprayable starch-fluorochemical mixtures were prepared as follows:

To a strongly agitated solution of 6.67 grams of fluorochemical urethane and 1.6 grams of polyoxyethylene sorbitan monooleate dissolved in 45 grams of ethyl acetate and heated to 50° C. was added a solution of 0.4 gram of alkyl-arylsulfonate dissolved in 68 grams of water and heated to 50° C., and the mixture passed twice through a colloid mill to form an emulsion; 10 grams of the above emulsion was added to 50 milliliters of water in which was dispersed 1.9 grams of soluble starch, to form a spray solution containing approximately 1% fluorochemical. Shown in the table below are the results obtained from a variety of fluoroaliphatic urethanes.

FC compound	Before washing		After washing		Mustard stain	Nujol oil stain	Grapejuice stain
	Oil repellency	Water repellency	Oil repellency	Water repellency			
(C ₄ F ₉ SO ₂ N(C ₂ H ₅)CH ₂ CH ₂ O ₂ CNH) ₂ C ₇ H ₅ -----	80	Some	None	None	Almost completely removed.	Completely removed.	Completely removed.
(C ₇ F ₁₅ CH ₂ CH ₂ O ₂ CNH) ₂ C ₇ H ₅ -----	100	do	70	do	do	do	Do.
C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)CH ₂ CH ₂ O ₂ CNHC ₇ H ₅ NECO ₂ C ₁₈ H ₃₇ -----	100	Very good.	None	do	do	do	Do.
(C ₇ F ₁₅ CH ₂ O ₂ CNH) ₂ C ₇ H ₅ -----	80	Almost none.	8	do	do	do	Do.
(C ₇ F ₁₅ CONHC ₂ H ₄ O ₂ CNH) ₂ C ₆ H ₇ -----	100	Good	70	do	do	do	Do.
(C—C ₈ F ₁₃ SO ₂ N(C ₂ H ₅)CH ₂ CH ₂ O ₂ CNH) ₂ C ₆ H ₇ -----	90	do	None	do	do	do	Do.
Control—No starch, no F.C.-----	None	None	None	do	Significant residual stain.	do	Do

In a typical embodiment of the invention, a 2:1 diurethane adduct of a C₈F₁₇SO₂N(C₂H₅)C₂H₄OH and toluene diisocyanate was dissolved in n-butyl acetate with a non-ionic polyoxyethylene sorbitan monooleate surfactant (Tween 80) and an anionic alkyl aryl sulfonate surfactant (G-3300). These ingredients were combined in the following proportions (parts by weight):

Fluorocarbon compound	Parts
n-Butyl acetate	100
Tween 80	8
G-3300	2

The mixture was heated and held at 175–190° F. while 290 parts of deionized water was added. A homogeneous mixture resulted which, however, was not stable since the mixture tended to stratify upon aging; it could be easily reincorporated, however. The mixture was then passed through a Manton-Gaulin homogenizer where it was subjected to high internal shear (8000 p.s.i.g.) to produce sub-micron micelles. The homogenized mixture was diluted with an equal amount of deionized water and the n-butyl acetate was then steam distilled from the mixture resulting in an emulsion having the following composition:

Fluorocarbon compound	Parts
Tween 80	8
G-3300	2
Deionized water	624
n-Butyl acetate	<1.83

The emulsion is then compounded into a sizing formulation in the following proportions, all parts being by weight percent:

	Percent
5 Corn starch (National 1135) -----	2.82
Emulsified Fluorocarbon compound (15% fluorocarbon compound) -----	3.76
Ethyl Parasept preservative -----	0.094
Freshol #74/Tween 80 (98:2) -----	0.057
10 Calcofluor CBP brightener -----	0.112
Ammonia -----	0.094
Deionized water -----	87.063
Isobutane propellant -----	6.00

15 National 1135 starch is a 100% amylopectin Amoka Corn starch derived by an acetylation process and requires cooking to achieve solution.

Ethyl parasept preservative is ethyl ester parahydroxy benzoic acid.

20 Freshol #74 is a perfume.

Calcofluor CBP brightener is an organic fluorescent material.

It will be understood that similar processing steps and conditions will be followed in formulating fabric treating compositions with other fluorocarbon compounds and

sizing agents, particularly those earlier compositions and formulations discussed herein.

The treating composition thus obtained was tested to determine its effectiveness in resistance to the aforementioned three sources of soiling. Five sample swatches of 80 x 80 cotton cloth were prepared with the following surface treatments:

50 Sample 1 was aerosol sprayed with the composition of the present invention;

Sample 2 was aerosol sprayed with the same fluorocarbon compound used in formulating the treating composition of the present invention and then sized with starch in the usual manner;

55 Sample 3 was first sized with starch and subsequently aerosol sprayed with the fluorocarbon compound utilized in Sample 2.

Sample 4 was sized with starch; and

60 Sample 5 was aerosol sprayed with the fluorocarbon compound used to treat Samples 2 and 3.

The samples were then subjected to soiling by having staining media of water, mineral oil, clay and prepared mustard applied directly to the surfaces. The resistance to soiling of the samples was observed and recorded in the following table. The excess staining media were removed from the samples and the samples washed in hot soapy water and dried. The degree of permanent staining, if any, was then observed and recorded in the table. The dried samples were also checked for wet soiling, i.e., re-deposition of soil from the wash water. As earlier stated, wet soiling of fabrics is, to a large degree, determined by the oil and water repellency characteristics of the fabrics. Hence, resistance to wet soiling as reported in the table reflects the oil and water repellency properties of the fabric after laundering.

TABLE

Sample	Resistance to dry soiling ¹	Resistance to permanent staining ²	Resistance to wet soiling ³
1	Excellent	Excellent	Excellent
2	do.	do.	Poor
3	Fair	Fair	Excellent
4	Poor	Poor	Do.
5	Excellent	Excellent	Poor

¹ The ability of the fabric to resist soiling caused by environmental surfaces and conditions.

² The ability of the fabric to resist soiling from the spillage of stain producing materials.

³ The ability of the fabric to resist soiling by re-deposition of soil from the wash water.

The foregoing table clearly establishes the efficacy of the treating composition of the present invention in imparting soil resistance to garment surfaces during their wear and eliminating the problem of soil re-deposition during laundering by causing the fluorocarbon compound to be removed from the fabric leaving an untreated surface which has little attraction for wet soils.

While dry soiling can also be retarded by placing a layer of a fluorocarbon compound over a layer of starch (Sample 3), it will be seen that permanent staining of a garment due to spillage soiling is noticeably increased through the utilization of consecutive starch and fluorocarbon compound treatment. In addition, a combined treatment procedure offers the easily recognized economic and time-saving advantages to a housewife over a two-step operation. The treating composition of the present invention thus makes it possible to achieve the excellent oil and water repellent characteristics obtained by treatment with fluorocarbon compounds and still avoid the objectionable wet soiling characteristics of such fluorocarbon compound treatment.

Various modifications and embodiments will be apparent from the above disclosure without departing from the scope of this invention.

What is claimed is:

1. A launderably removable fabric treating composition for frequently laundered fabrics capable of rendering the surface of said fabrics non-durably oleophobic and hydrophobic when applied thereto comprising an aqueous suspension of a water soluble organic film-forming fabric sizing agent having adsorbed thereon a water insoluble fluorocarbon compound containing a hydrophobic and oleophobic perfluoroalkyl group of at least 3 carbon atoms and having particle dimensions of about .01 to about 1 micron, the ratio of fluorocarbon compound to film-forming sizing agent in said suspension between about 1:1 and about 1:50 such that substantially all of said fluorocarbon compound is adsorbed onto said sizing agent so that the oleophobic and hydrophobic properties of said fabric surface due to the fluorocarbon compound are substantially destroyed by removal of said fluorochemically treated sizing agent from said fabric surface by water washing the fabric, said suspension having a maximum solids content of about 25 percent by weight.

2. A composition according to claim 1 wherein the fluorocarbon compound comprises from about 0.1 percent to about 5 percent of the composition and the film-forming sizing agent comprises from about 0.5 percent to about 20 percent of the composition by weight.

3. A composition according to claim 2 wherein the film-forming sizing agent is a starch and comprises about 2 percent to about 7 percent of the composition by weight.

4. A composition according to claim 3 wherein the fluorocarbon compound is the reaction product of an organic isocyanate and an alcohol containing at least one aliphatic hydroxyl group and a terminal perfluoroalkyl radical, said alcohol being otherwise free of further isocyanate reactive groups.

5. A composition according to claim 4 wherein the fluorocarbon compound is the reaction product of an isocyanate represented by the formula $R(NCO)_{n+(p-1)}$ in which R is an organic radical having 2 to about 30 carbon atoms for each $-NCO$ group and containing hydrocarbon radicals adjacent the valence bonds in the connecting chain, n is an integer from 1 to 3, p is an integer from 1 to 6 and the sum of $n+(p-1)$ is from 1 to 6 with an alcohol containing at least one aliphatic hydroxyl group and a terminal perfluoroalkyl group, said alcohol being otherwise free of further isocyanate reactive groups, the hydroxyl:isocyanate ratio being essentially one, said product having a melting point below about 250° C.

6. A composition according to claim 5 wherein the fluorocarbon compound is a 2:1 diurethane adduct of a $C_8F_{17}SO_2N(C_2H_5)C_2H_4OH$ and toluene diisocyanate and comprises about 0.4 percent to about 1.5 percent of the composition by weight.

7. A composition according to claim 3 wherein the fluorocarbon compound is a segmented copolymer of the methacrylate ester of N-ethyl, N-ethanol, perfluorooctane sulfonamide and chloroprene which has been prepared with a $C_8F_{17}SO_2NH(CH_2)_3N(CH_3)_2HCl$ emulsifier and comprises about 0.3 percent to about 2 percent of the composition by weight.

8. A composition according to claim 3 wherein the fluorocarbon compound is a segmented copolymer of the methacrylate ester of N-ethyl, N-ethanol, perfluorooctane sulfonamide and chloroprene which has been prepared with a $C_8F_{17}SO_2NH(CH_2)_3N^+(CH_3)_3Cl^-$ emulsifier and comprises about 0.3 percent to about 2 percent of the composition by weight.

9. A composition according to claim 3 wherein the fluorocarbon compound is a homopolymer of the acrylate ester of N-propyl, N-ethanol, perfluorooctane sulfonamide and comprises about 0.4 percent to about 2 percent of the composition weight.

10. A composition according to claim 3 wherein the fluorocarbon compound is a homopolymer of the methacrylate ester of 1,1,2,2-tetrahydro perfluorooctanol and comprises about 0.3 percent to about 2 percent of the composition by weight.

11. Fabrics sized with a launderably removable composition comprising an aqueous suspension of a water soluble organic film-forming fabric sizing agent having adsorbed thereon a water insoluble fluorocarbon compound containing a hydrophobic and oleophobic perfluoroalkyl group of at least 3 carbon atoms and having particle dimensions of about .01 to about 1 micron said fluorocarbon compound being adsorbed on a film of said sizing agent with its hydrophobic and oleophobic group outwardly oriented so as to render the fabric both water repellent and oil repellent until said fluorochemically treated sizing agent is removed from the fabric surface by laundering.

12. A method of treating frequently laundered fabrics in order to render the surface of said fabrics non-durably oleophobic and hydrophobic which comprises applying an aqueous suspension of a water soluble organic film-forming fabric sizing agent having adsorbed thereon a water phobic and oleophobic perfluoroalkyl group of at least 3 carbon atoms and having particle dimensions of about .01 to about 1 micron, the ratio of fluorocarbon compound to film-forming sizing agent in said suspension being between about 1:1 and about 1:50 such that substantially all of said fluorocarbon compound is adsorbed on said sizing agent so that the oleophobic and hydrophobic properties of said fabric surface due to the fluorocarbon compound are substantially destroyed by removal of said fluorochemically treated sizing agent from said fabric surface

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by water washing the fabric, said suspension having a maximum solids content of 25 percent by weight and being in aerosol form.

13. A fabric treating composition for frequently laundered fabrics capable of rendering the surface of said fabrics non-durably oleophobic and hydrophobic when applied thereto and until said fabric treating composition is removed from the fabric surface by laundering, said composition comprising an admixture of a propellant and an aqueous suspension of a water insoluble 2:1 diurethane adduct of a $C_8F_{17}SO_2N(C_2H_5)C_2H_4OH$ and toluene diisocyanate adsorbed on a film-forming starch, the diurethane adduct comprising 0.5 percent of the composition by weight and the starch comprising 3 percent of the composition by weight, said composition capable of being applied in aerosol form.

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