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METHOD OF TREATING TEXTILE ARTICLES WHICH ARE USUALLY LAUNDERED

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U.S. Cl. 117—66 **15 Claims**

ABSTRACT OF THE DISCLOSURE

A method for laundering and treating articles with mixture comprising a quaternary ammonium compound and fluorocarbon containing composition. The mixture is used in a laundering operation for imparting water and oil repellency and resistance to soiling to laundered textile articles.

The present invention relates to a novel method of treating household articles. More particularly, the invention relates to a method for providing household and apparel articles with water and oil repellency, resistance to water and oil-borne stains and resistance to soiling by particulate soils in a home laundering operation.

The laundering of clothes to clean them is centuries old. However, in the past such laundering methods have merely cleaned the articles. The laundering of household articles may be carried out wholly by hand, in semi-automatic washing machines or in completely automatic washing machines. By the term articles as used herein is meant household fabrics such as sheets, pillow cases, shirts, blouses, dresses, skirts, socks, shorts, playsuits, slipcovers, curtains, draperies, napkins, tablecloths, towels, wash cloths and in short a myriad of objects of different sizes, shapes and different physical characteristics.

In the laundering operation, the household articles to be laundered are thoroughly wetted with water and detergent. The water and detergent are then at least partially extracted from the articles to complete the washing cycle. The articles are then rinsed one or more times with water substantially free of detergent and the water is extracted therefrom after each rinsing. When laundering white goods, it is not unusual to add a bluing compound to the last rinse. The laundered articles are then air dried or dried in a clothes dryer and often ironed after being at least partially dried.

In addition to conventional laundering as hereinbefore described to provide clean household articles, it is desirable in many cases to provide such household fabrics with other properties such as water and oil repellency, resistance to water and oil-borne stains, resistance to soiling by particulate soils and ease of maintenance.

While chemical composition have been available to provide some or all of these properties to fabrics, such compositions have only been available for industrial use in treating fabrics in the textile mills. Furthermore, such compositions are used in the textile mills only on virgin fabrics of known fiber, dye and finish composition.

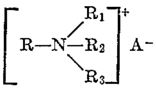
Generally, the compositions employed in the textile finishing plants will contain treating materials which do not exhaust onto the fabric. By the term exhaust is meant that the chemical in the bath has a selective affinity for the fiber being treated, e.g. a composition which preferentially leaves the aqueous bath and migrates into the fiber. It is generally undesirable in continuous textile treating processes to employ chemical agents which exhaust onto the fiber being treated in the padding bath. Such conditions cause a continual reduction in concentration of treating chemical in the bath which results in the deposition of continually decreasing amounts of the chemical on the fiber substrate. This phenomena is known in the textile art as "tailing." Textiles so produced show an extreme variation of treating agent applied between the beginning and end of the textile piece. Accordingly, it is desired in continuous industrial textile treatment to employ non-exhausting treating compositions which do not change in concentration in the treating bath during processing. In order to provide extreme durability to multiple launderings, the textile finishers have resorted to use of high concentrations of treating composition; e.g. concentrations of 18 to 25% being not at all unusual.

It has now been unexpectedly discovered that the desired properties of water repellency, oil repellency, resistance to water-borne stains, resistance to oil-borne stains, resistance to soiling by particulate soils and greater ease of subsequent laundering, ironing and wear life may be easily and conveniently imparted to household and apparel articles in the home by laundering such articles while treating with a dilute solution of a quaternary ammonium compound and a fluorocarbon-containing composition which exhausts onto the article being treated and then curing the treated articles.

In contrast to the relatively inflexible industrial methods of high speed production of thousands of yards of fabric per hour, the methods which are used in the present invention are significantly different. In conventional household laundering, which is the method employed in the present invention, the method is flexible so that close control of time, temperature, quantities of materials, special instrumentation and specially trained operators are not needed. Furthermore, the method does not utilize compositions which are corrosive to metal, cloth and skin, toxic or give off obnoxious odors.

While it is well-known in the usual textile mill applications of water and oil repellent agents that the fabrics being treated must be absolutely free of detergents, salts, wetting agents and any loosely bound hydrophilic materials, it has been unexpectedly found in the method of the present invention that by treatment with quaternary ammonium compounds and fluorocarbon compounds, household articles containing normal carry-over of detergents, salts, wetting agents and loosely bound hydrophilic material in the laundering process can be provided with a high degree of water and oil repellency, resistance to oil and water-borne stains and soiling by particulate soils.

The quaternary ammonium compounds employed may be those having a composition corresponding to the formula:



$$\left[R{-}N\begin{matrix} R_1 \\ {-}R_2 \\ R_3 \end{matrix} \right]^+ A^-$$

where R is a C_6–C_{22} and preferably a C_{12}–C_{18} alkyl or aryl radical; R_1 is a C_1–C_{22} and preferably a C_{18} alkyl radical, R_2 is the same as R_1 or a polyoxyalkalene radical; R_3 is H or an alkyl or aryl radical of from C_1–C_{22} carbon atoms which may also contain side substituents; and A^- is an ion selected from the group consisting of halogens, acetate, formate, lactate, ethosulfate and other monovalent anions. Typical compounds having such formulae are distearyl dimethyl ammonium chloride, cetyl stearyl dimethyl ammonium chloride, distearyl dimethyl ammonium ethosulfate, di(hydroxyisopropyl) methyl hydrogenated tallow ammonium chloride, octylphenoxy ethoxybutyl dimethyl ammonium chloride, octyl phenoxy ethoxy methyl benzyl dimethyl ammonium chloride, dilauryl dimethyl ammonium bromide, cetyl pyridinium bromide, octadecyl trimethyl ammonium chloride, hexadecyl dimethyl ammonium sulfate and like cationic surfactants. It has been found that the above quaternary amonium compounds when used in combination with fluorocarbon containing compositions provide synergistic results which are superior to those obtained by the use of either alone. Thus, the use of the quaternary ammonium compounds permits the exhaustion onto the articles being treated of fluorocarbon compounds which ordinarily could not be employed in such a laundering method or with far greater effectiveness than employed alone.

The quaternary ammonium compound may be employed at a level of 1 to 10×10^{-4} mole percent by weight of the articles being treated and preferably 3 to 6×10^{-4} mole percent. More preferably the quaternary ammonium compound will be employed at a level of 0.05 to 0.5% by weight of the articles being treated.

It is essential that the fluorocarbon-containing compositions be capable of being used in low concentrations to obtain the desired results of the present invention. Low concentrations permit complete exhaustion of the composition form the bath onto the household article leaving a bath which is essentially free of the treating composition. The treating compositions must be capable of being used on a wide variety of household articles made from diverse natural and man-made fibers and blends thereof which may have been subjected to other prior chemical treatments whether such articles are laundered individually or together. It will be seen that compositions having such properties provide the following:

(1) The use of relatively dilute, inexpensive solutions;

(2) Exhaustion of the composition from the bath onto the fabric when a quaternary ammonium compound is present;

(3) The use of conventional home laundering methods to impart to household articles the desired properties of water repellency, oil repellency, resistance to water-borne stains, resistance to oil-borne stains, resistance to soiling by particulate soils and greater ease of subsequent laundering, ironing and wear life.

The fluorocarbon containing compositions referred to herein are compositions containing a fluorocarbon radical which in the presence of a quaternary ammonium compound will exhaust during treatment onto the articles being treated. The fluorocarbon radical must be derived from a compound having a reactive functional group and the compounds used as starting raw materials for their preparation may be selected from fluoroacids, alcohols, aldehydes, ketones, esters, chlorides, isocyanates, ketenes, amines and amides. The fluorocarbon radicals must also have a chain length of at least four carbon atoms and preferably more than six carbon atoms. Substantially all, and preferably at least 70% of the hydrogen atoms must have been replaced by fluorine atoms.

One class of fluorocarbon compounds useful in preparing the fluorocarbon compounds of the present invention are the highly fluorinated carboxylic acids which have the formula [Z] COOH where Z is a fluorocarbon radical containing at least 3 carbon atoms and preferably 7 to 17 carbon atoms wherein substantially all and preferably at least 70% of the hydrogen atoms have been replaced by fluorine atoms and the carbon radical does not contain hydrophilic groups. Some substantially fluorinated acids are known in the art and generally have a long aliphatic saturated chain within the range of 6 to 18 and preferably 8 to 12 carbon atoms wherein at least the major amount and preferably at least 70% of the replaceable hydrogen atoms attached to carbon have been replaced by fluorine atoms and the terminal carbon is CHF_2 and preferably CF_3.

Most preferably, the fluoroacids employed are those which have the formula $F(CF_2)_n$ COOH wherein *n* is an integer in the range of 3 to 17 and preferably 7 to 11. Examples thereof are perfluoro octanoic, caprylic, capric, lauric, myristic, tridecanoic, palmitic and stearic acids. These perfluoro materials may contain mixtures of variable chain length depending upon their method of manufacture and the use of such mixtures is usually economical and within the scope of the invention.

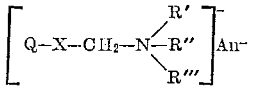
The fluorinated acids of corresponding chain length having a minor number of hydrogen atoms attached to carbons may be employed also and are known in the art. Examples are the fluorinated acids wherein one or two hydrogen atoms are attached to carbon atoms, such as on the alpha, beta or gamma carbon atoms, or the terminal carbon from the carboxylic group. Included therein are compounds having the formula $H(CF_2)_n$ COOH such as 7-hydro perfluoro heptanoic acid, 9-hydro perfluoro nonanoic, 11-hydro perfluoro undecylinic acid and similar acids as described above. Examples of the fluoro acids having hydrogens intermediate on the chain are 1, 2 or 3 hydro perfluoro hexanoic, octanoic, nonanoic and decanoic acids; 1,1 di-hydro perfluoro octanoic and decanoic acids; and 1,2 di-hydro perfluoro hexanoic, octanoic and decanoic acids. The fluorinated aliphatic chain may have substituted thereon other substituents which are inert or do not substantially adversely affect the desired properties and in particular the oil, water and soil repellency.

Further materials useful in the preparation of the substantive fluorocarbon compositions are the perfluoro acids having a minor amount of chlorine substituted thereon such as on the alpha, beta, intermediate or terminal carbon atoms. Examples are the same acids described above wherein the minor amount of the hydrogen substituents are replaced by chlorine atoms, e.g., 8-chloro perfluoro octanoic and 7-chloro perfluoro heptanoic acids; 1, 2 or 3 chloro perfluoro octanoic, 1,1 dichloro or 1,2 dichloro perfluoro octanoic and decanoic acids and the like. In addition to the known prior art fluorinated acids which may be employed, it is also possible to employ fluorinated carboxylic acids containing aromatic substituents. Typical of such acids are perfluoro benzoic acid and para pentadecyl fluoro octa-benzoic acid.

While the above description has referred specifically to the carboxylic functionality of certain compounds, it is to be understood that analogous fluorochemical radicals may be attached to other reactive groups such as alcohols, aldehydes, ketones, esters, chlorides, isocyanates, ketenes, amines and amides.

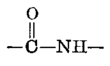
Some of the fluorocarbon compounds or compositions which may be used in the present invention are:

(1) Water-soluble perfluoroalkanamidomethyl quaternary ammonium compounds as disclosed and claimed in co-pending application S.N. 301,628, filed August 12, 1963, now abandoned, having a composition corresponding to the formula:



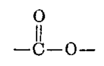
$$\left[Q\text{–}X\text{–}CH_2\text{–}N\begin{matrix}\diagup R' \\ \text{—}R'' \\ \diagdown R'''\end{matrix}\right]^+ An^-$$

where X is



$$\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—NH—}$$

—O—, —S—, and



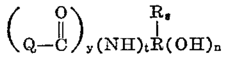
$$\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—O—}$$

R′, R″ and R‴ are alkyl groups having 1 to 6 carbon atoms of which 2 adjacent carbon atoms form with nitrogen a heterocyclic group having 5 or 6 carbon atoms or R′, R″ and R‴ can be aromatic groups. R′, R″ and R‴ can be the same or different alkyl or aromatic groups or two of R′, R″ and R‴ can be alkyl or cycloalkyl groups and the other can be an aromatic group; and Q is an aliphatic radical having three to twenty-one carbon atoms and 7 to 43 hydrogen atoms of which hydrogen atoms at least 70 percent is replaced by fluorine atoms and the terminal carbon group is CHF_2 or CF_3.

(2) Methylol perfluoroalkanamides such as water-insoluble, alcohol-soluble, waxy solids as disclosed and claimed in co-pending application S.N. 301,597, filed

Aug. 12, 1963, now Patent No. 3,210,048 comprising at least one methylol derivative of perfluoroalkanamide, the perfluoro moiety of the perfluoroalkanamide having three to twenty-one carbon atoms, and the terminal groups of said perfluoro moiety being selected from CHF_2 and CF_3.

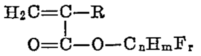
(3) Hydroxymethylated, fluoracylated aminohydroxy aromatic compounds as disclosed and claimed in co-pending application S.N. 301,622, filed Aug. 12, 1963 such as a perfluoroacylaminohydroxy aromatic compound having a composition corresponding to the formula:



$$\left(Q-\overset{\overset{O}{\|}}{C}\right)_y(NH)_t\overset{\overset{R_s}{|}}{R}(OH)_n$$

where R is the nucleus of an aminohydroxy aromatic compound having a single ring, two fused rings or three fused rings, and at least two active hydrogens; R′ is hydrogen or alkyl having one to five carbon atoms; Q is an alkyl group having three to twenty-one carbon atoms in which at least 70 percent of the 5 to 81 hydrogen atoms has been replaced with fluorine atoms; *n* is 1 or 2; *t* is 1 or 2; *x* is the same as *t*; *s* is an integer 6, 8 or 10 minus $(n+t)$.

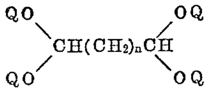
(4) Thermoplastic fluorocarbon polymers or copolymers as disclosed in co-pending application S.N. 295,506, filed July 16, 1963 such as a copolymer of at least one perfluoroalkylacrylate monomer and at least one monomer copolymerizable with the perfluoroalkylacrylate wherein the perfluoroalkylacrylate monomer has a composition corresponding to the formula:



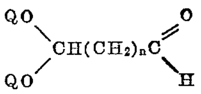
$$\begin{array}{l}H_2C=C-R\\ \quad\;\; |\\ O=C-O-C_nH_mF_r\end{array}$$

where F is fluorine, *n* is 4 to 22, *m* is 0.1 *n* to 0.25 *n*, *r* is 0.9 *n* to 0.75 *n*, and the terminal group of $C_nH_mF_r$ is CHF_2 or CF_3 and R is H or CH_3.

(5) Fluoroalkylacetals of dialdehydes such as perfluoroalkylacetals of dialdehydes as disclosed in co-pending application S.N. 295,507, filed July 16, 1963, now abandoned having a composition corresponding to the formulae:



and



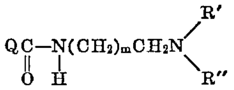
where Q is an alkyl group having 3 to 22 carbon atoms, having a terminal CH_2-group or a terminal CF_2-group, having at least 70 percent of the hydrogen atoms of the alkyl group of the parent alcohol replaced by fluorine atoms, and the alkyl chain is straight or branched and *n* is zero to 22.

(6) Silicate and titanate orthoesters such as waxy solids as disclosed in co-pending application S.N. 308,639, filed Sept. 13, 1963, now Patent No. 3,342,630 having a composition corresponding to the formula:

$$(RO)_n-X-(OQ)_m$$

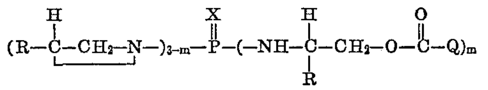
where R is an alkyl group having one to six carbon atoms, Q is the fluorinated alkyl group of an aliphatic alcohol having one to twenty-two carbon atoms and three to forty-five hydrogen atoms of which at least 70 percent has been replaced by fluorine and the terminal group is selected from CHF_2 and CF_3; *n* is 0 to 3; *m* is 4 to 1; and *x* is Si or Ti.

(7) Quaternary ammonium derivatives of highly fluorinated carboxylic acids such as aminoalkylamido derivatives of highly fluorinated aliphatic carboxylic acids as disclosed in co-pending application S.N. 308,631, filed Sept. 13, 1963, now Patent No. 3,350,218 having compositions corresponding to the formula:



where Q is a hydrocarbon radical having three to twenty-one carbon atoms and seven to forty-three hydrogen atoms of which hydrogen atoms at least 70 percent to 100 percent has been replaced with fluorine atoms and at least two fluorine atoms are attached to the terminal carbon atom; R′ and R″ are the same or different alkyl groups having one to six carbon atoms.

(8) Fluoroacid derivatives of trisaziridinyl phosphine oxides and sulfides such as perfluoroalkanoic acid derivatives of aziridinyl phosphine oxide and sulfide as disclosed and claimed in copending application S.N. 288,490, filed June 17, 1963, now abandoned having a composition corresponding to the formula:



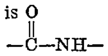
where R is hydrogen or CH_3, N is nitrogen, P is phosphorous, X is oxygen or sulfur, *m* is 1, 2 or 3, Q is the alkyl group of an alkanoic acid having 4 to 22 carbon atoms having a terminal CF_3 group and having about 75 to about 100 percent of the hydrogens other than the carboxyl hydrogen replaced with fluorine atoms.

9. Fluoroalkyl derivatives of amino-aldehyde compounds such as heterocyclic nitrogen bases as disclosed in copending application S.N. 312,291, filed Sept. 20, 1963, now Patent No. 3,296,264 having compositions corresponding to the formula:

$$(Q-X-CH_2)_n-R-(CH_2OR')_m$$

where Q is a fluoroalkyl group having four to twelve (inclusive) carbon atoms in which at least 70 percent to 100 percent of the $(2n+1)$ hydrogen atoms (*n* is 4 to 12) has been replaced by fluorine atoms and at least two and preferably three fluorine atoms are attached to the terminal or omega carbon atoms;

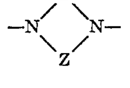
X is



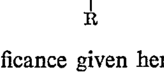
$$-\overset{\overset{O}{\|}}{C}-NH-$$

or —O—, R′ is hydrogen, CH_3—, CH_2H_5—, C_3H_7—; *m* is one to five dependent upon the functionality of the amido residue; *n* is at least 1; $(m+n)$ is two to six inclusive, R is a divalent radical selected from the group

Monocyclic ureas



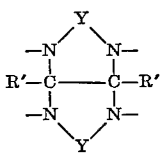
where Y is C=O, C—NH, C=S and Z is $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,



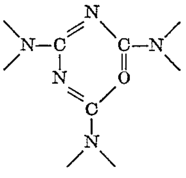
$$-CH_2-\underset{\underset{R}{|}}{N}-CH_2$$

and R′ has the significance given hereinbefore,

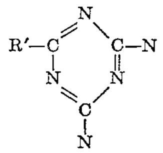
Diheterocyclic ureas



where Y and R′ have the significance given hereinbefore, Triazines

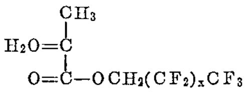


Guanamines



and ethylene urea, propylene urea, uron, triazones, acetylene diurea, dimethylacetylene diurea, melamine and acetoguanamine.

(10) Omega-fluoro methacrylic acid esters as disclosed in co-pending application S.N. 288,442, filed June 17, 1963 having a composition corresponding to the formula:

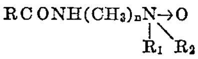


$$H_2O=\overset{\overset{\displaystyle CH_3}{|}}{C}\underset{O=\overset{|}{C}-OCH_2(CF_2)_xCF_3}{}$$

where F is fluorine and x is 1 to 20.

In carrying out the present invention, the fluorocarbon chemical compositions employed are generally employed at a level of 0.01 to 5% and preferably about 0.1 to 1% by weight of the articles being treated. In the present invention levels greater than 5% by weight of the articles are undesirable as such levels provide no additional beneficial effect and merely increase the cost to the consumer. At levels lower than 0.01% by weight of the articles being treated, the desired properties are not obtained to a degree sufficient to provide acceptable results. The above levels employed in the present invention correspond to about 0.005% to 0.25% by weight of the treating solution, i.e., usually about 17 gallons.

Where it is desired to use the quaternary ammonium compound with fluorochemical emulsions having an anionic charge to treat the articles in a single treating step, it has been found advantageous to use them in a mixture containing an amine oxide which provides a stable emulsion. Typical of the amine oxides which may be employed are those having long chain alkyl radicals of about 10 to 18 carbon atoms such as decyl, tetradecyl lauryl, cetyl, oleyl, hexadecyl and stearyl. In place of either or both of the methyl radicals, there may be used an ethyl, propyl, hydroxyethyl, hydroxyethoxyethyl or hydroxy polyethoxyethyl radical. The long chain hydrophobic radical attached to the nitrogen of the amine oxide need not be only a hydrocarbon radical. It may, for example, contain other groups, such as carbonamide groups, such as in amine oxides of the formula



$$RCONH(CH_3)_n\underset{R_1\ \ R_2}{N}\rightarrow O$$

in which RCO is a long chain alkanoyl radical, n is a small whole number, and R_1 and R_2 are lower aliphatic groups; a specific example being the compound in which RCO is the acyl radical of cocofatty acids, n is 2 and R_1 and R_2 are methyl.

The proportions of amine oxide which may be employed in the present invention are in the range of about 1 to 4 times the weight of quaternary ammonium compound and preferably 2 to 4 times the weight of the quaternary ammonium compound. It has further been found that the ratio of amine oxide to anionic fluorocarbon compound to quaternary ammonium compound should be in the range of about 1:10:1–4:10:1.

The compositions used in the present invention can be used in baths which also contain one or more of other adjuncts such as fabric softeners, antistatic agents, starches and other customary laundering aids provided they do not interfere with the attainment of the desired properties.

The laundering method of the present invention preferably consists of a washing cycle wherein the household articles are wetted, agitated in the presence of a detergent composition and dewatered and at least one rinse cycle using water substantially free of detergent wherein a fluorocarbon containing composition which exhausts onto the articles is present during at least part of the laundering process and preferably in the rinse. Optionally, in the case of white household articles, bleaching may be employed in the conventional manner.

The detergent compositions which may be employed in the present invention are any of the common, well-known household anionic and non-ionic detergent compositions usually containing various builders and other adjuvant materials. Thus, anionic detergents such as sodium or potassium salts of one or more fatty acids, i.e., the traditional bar soap or soap flakes or liquid soap or the more modern detergent mixtures comprising sulfated and/or sulfonated synthetic detergents with or without builders, water softeners, anti-soil redeposition agents, optical brighteners, builders or extenders, perfume and the like may be used. These anionic detergents generally have about 8 to about 26, usually about 12 to about 22 carbon atoms in the molecule. In addition, the soaps are generally the water soluble salts of higher fatty acids or rosin acids and are usually derived from fats, oils, and waxes of animal, vegetable or marine origin, e.g. tallow, coconut oil, tall oil, etc., though of course, these carboxy acids may also be prepared synthetically such as by oxidation of suitable hydrocarbons.

The sulfated and sulfonated detersive compounds which may be employed are well-known in the art and may be prepared from suitable organic materials which are applicable to sulfonation ("true sulfonation and/or sulfation"), including fatty oils, unsaturated fatty acids, mineral oils, partial fatty acid esters of alcoholic compounds, aromatic and alkylated aromatic compounds, alcohols, olefins, etc. Of the vast variety of sulfates and sulfonates suitable as active ingredients in detergent compositions, it is preferred to use the aliphatic sulfates and sulfonates of about 8 to 22 carbon atoms and the alkyl aromatic sulfonates.

The alkyl aromatic sulfonate detergents referred to may be mononuclear or polynuclear in structure. More particularly, the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresols, phenol ethers, naphthalene, derivatives of phenanthrene nuclei, etc. It has also been found that the alkyl group may vary similarly. Thus, for example, the alkyl group may be straight or branch chained and may consist in such radicals as dodecyl, hexyl, octyl, nonyl decyl, keryl, mixed alkyls derived from fatty materials, cracked paraffin wax olefins, and polymers of lower mono olefins, etc. While the number of sulfonic acid groups present on the nucleus may vary, it is usual to have only one such group present in order to preserve as much as possible a balance between hydrophilic and hydrophobic portions of the molecule.

Within the scope of the terms "surface-active sulfated" or "sulfonated aliphatic compounds" are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g., coconut oil monoglyceride monosulfate, tallow diglyceride monosulfate; the long chain pure or mixed alkyl sulfates, e.g., lauryl sulfate, cetyl sulfate; the hydroxy sulfonated higher fatty acid esters, e.g., higher fatty acid esters of low molecular weight alkylol sulfonic acids, e.g. oleic acid ester of isethionic acid; the fatty acid ethanolamide sulfates; the fatty acid amides of amino alkyl sulfonic acids, e.g. lauric amide of taurine and the like.

The non-ionic agents are also well-known in the art including the polyoxyethylene ethers of alkyl aromatic hydroxy bodies (e.g. the alkylated polyoxyethylene phenols) and the polyoxyethylene ethers of long chain aliphatic alcohols.

The anionic surface-active agents are commonly used in the form of their water-soluble salts. For the synthetic anionic compounds, the alkali metal (i.e. sodium, potassium) and ammonium salts are preferred, though other salts such as amine, alkylolamine, alkaline earth metals (e.g. calcium, magnesium) salts may be used if desired.

The concentration of these active ingredients and mixtures thereof in the detergent compositions vary widely according to the contemplated field of application. Thus, with regard to household soaps in particulate form, the composition may consist of practically pure soap with little if any builder whereas other types of soap powders may contain a substantial quantity of builders such as soda ash, phosphates, borax, etc., together with soap. The synthetic detergents designed for household and industrial cleaning generally contain at least about 5% and preferably about 10% of active ingredient by weight of total solids. The remainder of the composition generally comprises inorganic salts such as sodium sulfate, sodium chloride, phosphates, carbonates, etc.

If desired, compatible adjuvant laundry aids such as starches, bluing compositions, softeners and optical brighteners may be used in the present invention to provide other benefits.

While the treated articles may be used after laundering and drying, it has been found that generally with most of the compositions employed, improved results are obtained if after drying the treated articles are cured as by ironing or heat treatment for a short period of time. As it is intended that the present invention be used primarily in the home, ironing with a hand iron is the prefered method of curing. Curing temperatures should be preferably in the order of 300° F. to 400° F. Time of curing when using a hand iron will be in the order of about 50 to 100 seconds/ft.^{2}. If other curing means are employed, curing times giving results equivalent to those for hand ironing are practical, e.g., 5–10 minutes at 350° F. As most articles which would be treated in order to provide the desired results of the present invention are ordinarily ironed after laundering, the preferred curing method in most cases would result in no additional work for the user.

A number of evaluations were made on fabrics treated with compositions typical of those described hereinbefore. Typical of the evaluations made and results obtained are the following examples.

Example I

The polymer of 1H,1H,7H-dodecafluoroheptylmethacrylate was applied as an anionic emulsion to 80 x 80 cotton print cloth swatches. Part of the swatches were first treated with a quaternary ammonium salt and part were not.

Sixty grams of 80 x 80 cotton print cloth were washed in a "Tergotometer" in 1200 cc. of 0.15 percent concentration of a nonionic detergent, "Tergitol NPX" (Union Carbide Corporation, New York, N.Y.). The washed swatches were rinsed once in clear water and then those to be treated with a quaternary ammonium salt were immersed in 1194 cubic centimeters of a 0.01 percent solution of di(hydroxyisopropyl) methylhydrogenated tallow ammonium methyl sulfate (a cationic quaternary ammonium salt). The swatches were stirred for one minute and 5.36 grams of the anionic polymer emulsion of 1H,1H,7H-dodecafluoroheptylmethacrylate (prepared as described hereinafter) were then added slowly to the bath and agitation was continued for ten minutes. The cotton swatches were extracted in the spin cycle of a washing machine and dried in an electric clothes dryer. The swatches were then ironed with a steam iron at 350° F. The swatches free of quaternary ammonium salt were treated in the same manner as above except that the quaternary ammonium salt was omitted from the bath. The results are set forth in Table I.

The 1H,1H,7H-dodecafluoroheptylmethacrylate monomer was polymerized by standard emulsion-polymerization technique to yield an anionic emulsion containing 22.4 percent of polymer solids, having a pH of 9.06. The polymer had an inherent viscosity of 1.64 using 1,3-bis (trifluoromethyl) benzene as the solvent.

TABLE I

Addition to Rinse Cycle			Dry Soil Value (1)		Static Stain Value (2)			
					Repellency		Launderability	
Quaternary ammonium salt (a) percent wt.	Polymer solids(b) percent wt.	percent polymer on fabric (analysis)	Repellency	Launderability	Water borne	Oil borne	Water borne	Oil borne
None	None	------------	28	72	1.8	1.8	5.4	5.4
Do	0.1	0.21	37	71	2.2	1.6	5.5	4.0
0.02	0.1	1.68	44	74	4.8	4.0	7.6	5.1

[a] Di(hydroxyisopropyl)methylhydrogenated tallow ammonium methyl sulfate.
[b] 1H,1H,7H-dodecafluoroheptylmethacrylate.

(1) No official test has been recognized for the purpose of testing the effect of particulate household articles and the effect of various treatments in resisting such a soil but it has been found that the following procedure employing a standardized synthetic soil provides reproducible results.

The standardized soil was prepared by the method described by Salisbury et al. "Soil Resistant Treatment of Fabric" American Dyestuff Reporter, March 26, 1956, page 199. The test using the standardized soils is as follows:

Locate the tumbling device[a] in a conditioning room. Use 4 replicates per treatment (usually four) and 3 each for Washed and Untreated Control cotton washed with commercially available detergent "Fab." * Randomize by tumbling in unheated dryer. A total of twenty-two (22) conditioned specimens (5" x 7" 80 x 80 cotton) are tumbled 1,320 revolutions with Synthetic Soil ** (10% O.W.F.). The end-over-end tumbling is carried out in a 6" diameter by 12" long cylindrical stainless steel jar rotating at 43 r.p.m.[a]. Six (6) No. 8 Neoprene rubber stoppers (average weight 41.5±0.5 grams) are distributed evenly with the soil among the specimens. After tumbling, the specimens are removed and each shaken 15 times by hand to remove free soil by holding one corner 8 times and the diagonally opposite corner 7 times. Each swatch is cut in half after repellency reflectance readings to produce two 5" x 3½" pieces (22 pairs total). Twenty-two swatches, one from each pair, are washed in an automatic washer[b] using 50 grams of "Fab" in the cotton cycle with 5 pounds additional dummy load and then dried 5 minutes in an automatic dryer at the high setting and lightly hand ironed.

The degree of soil before and after washing is determined with the Photovolt Reflectance Meter[c]. The meter is standardized by placing the probe head on a block of $MgCO_3$ (freshly ground against an identical block); then readings are taken on a porcelain plate used as a secondary standard. Readings using the Model 610Y probe with tri-blue filter and the Model 610D probe with tri-green filter have proved comparable with synthetic soil. Eight readings are taken with small probe or 6 readings with the large probe (610D) and the average value is reported.

COMPOSITION OF SYNTHETIC SOIL

Ingredient	Percentage	Supplier
Peat Moss	38	Michigan Peat, Inc., Capac, Michigan.
Cement	17	Portland Cement.
Kaolin Clay, Peerless	17	R.T. Vanderbilt Co., Park Ave., N. Y.
Silica (200 mesh)	17	Davidson Chem. Corp., Baltimore, Md.
Molacco Furnace Black	1.75	Columbia and Carbon, 380 Madison Ave., N.Y.
Red Iron Oxide N-1860	0.50	C. K. Williams Co., Easton, Pennsylvania.
Mineral Oil (Nujol)	8.75	Standard Oil Co. of New Jersey, Elizabeth, N.J.

[a] Tumble Jar Dynamic Absorption Tester, See AATCC Test Method (tentative). 70B-1961T; Andrew Technical Supply Co.; 2540 East Wood, Evanston, Illinois.

[b] Kelvinator Home Automatic Washer.

[c] Photovolt Corp., 1115 Broadway, New York, New York.

[d] Cyanamid Textile Resin Dept. Textile Finishing Bulletin No. 150.

* Colgate-Palmolive Company, New York, New York.

** Synthetic soil prepared by the method described by Salisbury et al., "Soil Resistant Treatment of Fabric" Amer. Dyestuff Reporter, March 26, 1956, Page 199.

The peat moss is dried two (2) hours at 105° C. in a forced draft convection oven, weighed, and then blended with the other ingredients in a ball mill (without ceramic balls) for 2 hours. After drying the blend on a large pan 8 hours at 50° C. in the forced draft convection oven, the dried blend is ball milled with ceramic balls for 25 hours. The soil is stored in a tight jar.

(2) Resistance to common household staining materials was tested by the following method:

(a) The fabrics were stretched lightly on 12" x 31" frames. All or part of the frame area was used depending on the amount of fabric available. The frames were supported at both ends with the fabric about 8" above a bench-top surface. The fabric touched nothing.

(b) 3" medicine droppers were used to draw the stains from their containers. A 1 cc. calibration was established and marked on the exterior of the droppers. The stains were squeezed vertically downward from a height 2" above the cloth.

(c) After 5 minutes the unabsorbed stain was wiped off the fabric with 2 sweeps of facial tissue (Kleenex) and the stains rated as follows.

Stain Ratings

Degree of Stain:	Numerical Ratings
Heavy stain over large area	1
Heavy stain over medium sized area	2
Heavy stain over small area	3
Medium stain over large area	4
Medium stain over medium area	5
Medium stain over small area	6
Light stain over large area	7
Light stain over small area	8
Very slight visible stain	9
No visible stain	10

(d) Stain used:

Water-borne Stains:
1. Instant Tea, Tetley.[a]
2. Sheaffer's 232 Blue-Black Skrip.
3. A & P Concord Grape Juice.
4. Ann Page Salad Mustard.
5. Bosco Chocolate Syrup.

Oil-borne Stains:
6. Wesson Oil.
7. Gulf Supreme Motor Oil 20/20.
8. Oleomargarine, Nutley's.[b]
9. La Rosa Tomato Sauce.
10. Jergen's Lotion.

These stains were applied in two lines in the above order with the water and oil stains kept separate.

In reporting the relative staining resistance and ease of stain removal in laundering the values from the water-borne and oil-borne stains were averaged and reported separately. In all cases the stains were allowed to dry on the fabrics for 24 hours before laundering.

The data in Table I clearly establish that (A) the presence of cationic material increased the amount of anionic polymer deposited on the treated textile; (B) the dry soil repellency is improved considerably; (C) resistance to staining by water- and oil-borne stains is increased appreciably; and (D) launderability is also improved.

Example II

A 5 gram portion of a 10% by weight solution of lauryl dimethyl amine oxide was added to 3.51 grams of a 34.2% solids emulsion of 1H,1H,7H dodecafluoroheptylmethacrylate polymer that had been diluted to 10 grams with water. The polymer emulsion was anionic in character by virtue of the emulsion polymerization surfactant being sodium lauryl sulfate. Ten grams of a 1% solution of n-methyl di-(hydroxyisopropyl) hydrogenated tallow ammonium methyl sulfate (Propoquad HT-12) was then added. Normally, the addition of the latter material, a cationic surfactant, to the anionic emulsion would have been sufficient to coagulate the emulsified particles and cause precipitation of the polymer. However, the protective action of the amine oxide prevented this precipitation and a stable pH 6.30 emulsion remained. This preparation was further diluted to 52 grams and added to 1150 cc. of water and 60 grams of 80 x 80 cotton swatches in a rinse cycle addition of a Tergotometer wash. Three similar preparations were also evaluated to demonstrate the effect of amine oxide in stabilization and ultimate antisoiling performance.

The swatches were removed from the Tergotometer rinse after ten minutes agitation, extracted by hand and dried in a home laundry electric clothes dryer. They were then ironed with a hand iron and tested by the methods described. Analysis was also carried out to determine the amount of polymer deposited on swatches through measurement of the amount of elemental fluorine.

Data shown in Table II exemplify the utility of combining the cationic Propaquad with the anionic polymer in the presence of amine oxide to give a one-step "single package" product for rinse cycle application. A, B, C and D represent four preparations and E is an untreated control. Preparations C and D show that levels of amine oxide greater than 2 to 4 times the level of quaternary ammonium compound, provide less desirable results.

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[a] 8 cc. dry powder/200 cc. water applied at 160° F.

[b] Melted and applied at 160° F.

TABLE II

Rinse solution percent by weight			Percent polymer on fabric theoret.	F analysis	Spray rating[3]	Dry Soil Value[4]		Static Stain Value[5]			
								Water Borne		Oil Borne	
Polymer[1]	Amine oxide	Quat. ammonium salt[2]				Repellency	Launderability	Before	After	Before	After
A, 0.1	0.008	0.01	2.0	1.34	80	39	72	4.2	9.0	3.4	6.6
B, 0.1	0.042	0.01	2.0	[6] 1.30	50	42	75	5.8	7.8	3.4	7.0
C, 0.1	0.083	0.01	2.0	[6] 1.15	70	38	67	3.0	7.6	3.4	7.0
D, 0.1	0.250	0.01	2.0	1.10	70	37	66	3.0	7.6	3.4	5.5
E, 0.0	0.000	0.00	0.0	0.00	0	30	78	1.8	5.4	2.4	6.2

[1] 1H,1H,7H-dodecafluoroheptylmethacrylate.

[2] n-Methyl di(hydroxyisopropyl)hydrogenated tallow ammonium methyl sulfate.

[3] The test used for water repellency was Standard Test Method 22–1961 described in the 1962 Technical Manual of the American Association of Textile Chemists and Colorists.

[4] Method is the same as footnote 1 of Table I.

[5] Method is the same as footnote 2 of Table I.

[6] Estimated.

Example III

The emulsion of a terpolymer consisting of 97.5% 1,1,2,2-tetrahydro perfluoroheptylmethacrylate, 2.0% n-butyl acrylate and 0.5% n-methanol acrylamide, hereinafter called "the polymer" is cationic by virtue of the fact that the emulsion polymerization surfactant is dimethyloctadecyl amine acetate.

TABLE III

Polymer percent by (1) by wt.*	Quat. ammonium salt percent by wt.* (2)	Percent FP by analysis*	Spray rating (3)	Oleophobic rating (4)	Stain Test (5)											
					Static Staining						Dynamic Staining					
					Repellency			Launderability			Repellency			Launderability		
					W.B.**	O.B.***	Total	W.B.	O.B.	Total	W.B.	O.B.	Total	W.B.	O.B.	Total
0.5	0.3	0.35	50	3	18	16	34	27	14	41	0	−3	−3	22	8	30
0.5		0.35	0	0	4	5	9	4	4	8	−3	−3	−6	17	3	20
	0.3	0	0	0	3	5	8	3	5	8	−2	−3	−5	23	3	26

**W.B.=Water-borne.

***O.B.=Oil-borne.

*=Percent by wt. of fabric.

(1) 1H,1H,7H-dodecafluoroheptylmethacrylate.

(2) n-methyl di(hydroxyisopropyl)hydrogenated tallow ammonium methyl sulfate.

(3) Method is the same as that in footnote (b) of Table II.

(4) Rating system described in Example III.

(5) A revised stain test method was used in place of the method in footnote (2), Table I. The revised method was been found to be more quantitative and reproducible than the original. The 6 actual staining materials have been determined to be statistically representative of a very large group of stains in work done by Collins, et al., American Dyestuff Reporter, December 1962. The method is the subject of a detailed research report published by the author.

One and one-half cc. of each of the six representative stains is applied to the treated fabric and allowed to stand for two minutes. The excess soil is then removed by vacuum. The size and intensity of the residual stained area is then rated against a visual standard in a graduated scale from one (worst stain) to ten (no stain). The total of all six stains is then compiled. The maximum rating (most resistant) is 60 and the minimum rating is 6.

The method can be used for stains applied in either a static or dynamic (abraded) manner and for measuring launderability as well as repellency. No quantitative rating system can be used for Dynamic Stain Repellency but a modification can give qualitative information about the resistance of the finished fabric to abraded stains. A value of 0 is given to each stain whose spread remains confined to a 1" diameter area. A value of +1 is assigned when a stain fails to wet a 1" circular area with 15 seconds' rubbing and a value of −1 is assigned for each stain which spreads outside a 1" circle.

Thus, one would expect that the polymer would exhaust onto cotton from rinse solutions. This in indeed the case, as shown in Table III but, as in Example I, the data indicate that combinations of the polymer and a cationic surfactant (n-methyl di(hydroxyisopropyl)hydrogenated tallow ammonium methyl sulfate) are considerably better than application of either of these materials alone. The oleophobic ratings in Table III were obtained by a method similar to that described in the Minnesota Mining and Manufacturing Company Textile Chemicals Bulletin, Appendix A (Test Methods), page 1, except that different hydrocarbons were used. Drops of the hydrocarbons were placed on the fabric surface without impact. The extent of surface wetting is determined visually. The results obtained are a measure of the interfacial tension between a fabric surface and liquid hydrocarbons of different surface tensions. The hydrocarbons used and their ratings were:

Hydrocarbon:	Oleophobic Rating Number[1]
n-Heptane	9
n-Octane	8
n-Decane	7
N-dodecane	6
n-Tetradecane	5
50 ml. "Nujol" +50 ml. n-hexadecane	4
75 ml. "Nujol" +25 ml. n-hexadecane	3
"Nujol"	2
("Nujol" wets)	2

[1] Hydrocarbon with the highest rating number that does not "wet" the fabric.

The Oleophobic Rating Number may be combined with AATCC Spray Test ratings to give a combination water and oil repellency; e.g. 106 is combination of a 100 Spray Test rating and a 6 oleophobic rating.

Example IV

To test the practical application and limitations of the inventions, a rinse cycle application to some clothing and household items was carried out in a standard washing machine.

A 136 gram portion of the polymer emulsion of Example III containing 22% (or 30 grams) solids was blended with a 11.5 gram portion of a 78% solution of Propoquad HT–12 that had been previously diluted to 30 cc. The mixture was further diluted to 250 cc. This would give 1% of the polymer, 0.3% Propoquad HT–12 on 3000 grams of fabric described below. Ten pillowcases, 10-T-shirts and 10 terry hand towels totaling approximately 3000 grams of new fabric were washed in a Kenmore Automatic washing machine at 130° F. wash cycle temperature using 1 cup (80 grams) of FAB laundry detergent. The complete automatic cycle of wash and rinses was allowed to finish, then the machine was reset to deliver 110° F. waater for a second cycle. After the machine was filled, however, the above described finishing mixture was added to the laundry and allowed to agitate for ten minutes. The machine setting was then advanced to the "final spin" and extraction was allowed to take place. The fabric was then dried in a Kenmore electric dryer. The pillowcases were ironed twice on a hand ironer, at its hottest setting. The T-shirts were also ironed in this way. This, in essence, was the desired curing step for the fabrics. The hand towels were not cured since their normal practical use does not include such a step.

During the use of the items, the pillowcases were ironed after every use and laundering, the T-shirts were not ironed and the towels, of course, were also not ironed. A total of ten use-wash cycles were carried out with these items and untreated but otherwise identical counterparts. After the ten cycles, the items were examined by a panel of ten people who indicated their visual preference for the cleanliness of the items. The panel results are shown on Table IV.

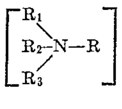
TABLE IV.—VISUAL PREFERENCE OF TREATED ITEMS
[Rating by a panel of 10, 10 treated items versus 10 untreated in each class]

Items	Treatment	Percent prefer treated	Percent prefer untreated	Percent no preference
Pillowcases	Cured after application of finish, ironed after every wash.	74	9	17
T-shirts	Cured after application of finish, not ironed after washing.	40	25	35
Hand towels	Not ironed after application of finish, not ironed after washing.	45	41	14

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made, and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

What is claimed is:

1. A method of treating textile articles to provide them with water and oil repellency, resistance to water and oil-borne stains and resistance to soiling by particulate soils while providing greater ease of subsequent laundering, ironing and wear-life which comprises laundering and treating said articles with from 1 to 10×10^{-4} mole percent based on the weight of said articles of a quaternary ammonium compound and at least 0.01% by weight based on the weight of said articles of a fluorocarbon containing composition which exhausts onto the articles being treated, said fluorocarbon being selected from the class consisting of fluoroacids, alcohols, aldehydes, ketones, esters, chlorides, isocyanates, ketenes, amines and amides and having a general length of at least 4 carbon atoms with at least 70% of the hydrogen atoms replaced by fluorine atoms, and said quaternary ammonium compound having as its cation formula:



$$\left[\begin{matrix} R_1 \\ R_2{-}N{-}R \\ R_3 \end{matrix} \right]$$

where

R is a C_6 to C_{22} alkyl or aryl radical,

R_1 is C_1 to C_{22} alkyl,

R_2 is R_1 or polyoxyalkylene, and

R_3 is H or C_1 to C_{22} alkyl or aryl.

2. The method of claim **1** wherein the treatment comprises laundering said articles in a laundering process which includes at least one wash and one rinse cycle while concurrently treating said articles during the rinse cycle with the composition containing the quaternary ammonium compound and the fluorocarbon containing composition which exhausts onto the articles being treated and drying and curing said treated articles.

3. The method of claim **2** wherein the quaternary ammonium compound is employed at a level of 1 to 10×10^{-4} mole percent by weight of the treated articles and the fluorocarbon containing composition at a level of 0.01 to 5.0% by weight of the treated articles.

4. The method of claim **2** wherein the quaternary ammonium compound is employed at a level of 3 to 6×10^{-4} mole percent by weight of the treated articles, the fluorocarbon containing composition at a level of 0.1 to 1.0% by weight of the treated articles.

5. The method of claim **2** wherein the quaternary ammonium compound is employed at a level of 0.05 to 0.5% by weight of the treated articles, the fluorocarbon containing composition at a level of 0.1 to 1.0% by weight of the treated articles.

6. The method of claim **2** wherein the quaternary ammonium compound is employed at a level of 0.3% by weight of the treated articles, the fluorocarbon containing composition at a level of 0.5% to 1.0% by weight of the treated articles.

7. The method of claim **1** wherein the treatment comprises laundering said articles in a laundering process which includes at least one wash and one rinse cycle, treating said articles with the quaternary ammonium compound during the rinse cycle, then treating said articles with the fluorocarbon containing composition which exhausts onto the article being treated during the rinse cycle, and drying and curing said treated articles.

8. The method of claim **7** wherein the quaternary ammonium compound is employed at a level of 1 to 10×10^{-4} mole percent by weight of the treated articles and the fluorocarbon containing composition at a level of 0.01 to 5.0% by weight of the treated articles.

9. The method of claim **7** wherein the quaternary ammonium compound is employed at a level of 3 to 6×10^{-4} mole percent by weight of the treated articles and the fluorocarbon containing composition at a level of 0.1 to 1.0% by weight of the treated articles.

10. The method of claim **7** wherein the quaternary ammonium compound is employed at a level of 0.3% by weight of the treated articles and the fluorocarbon containing composition at a level of 0.5 to 1.0% by weight of the treated articles.

11. The method of claim **1** wherein the treatment comprises laundering said articles in a laundering process which includes at least one wash and one rinse cycle with the composition containing the quaternary ammonium compound, the fluorocarbon containing composition which exhausts onto the article being treated and an amine oxide containing at least one 10 to 18 carbon alkyl radical and drying and curing said treated articles.

12. The method of claim **11** wherein the quaternary ammonium compound is employed at a level of 1 to 10×10^{-4} mole percent by weight of the treated articles, the fluorocarbon containing composition at a level of 0.01 to 5.0% by weight of the treated articles and the amine oxide at a level of 1 to 4 times the weight of the quaternary ammonium compound.

13. The method of claim **11** wherein the quaternary ammonium compound is employed at a level of 3 to 6×10^{-4} mole percent by weight of the treated articles, the fluorocarbon containing composition at a level of 0.1 to 1.0% by weight of the treated articles and the amine oxide at a level of 2 to 4 times the weight of the quaternary ammonium compound.

14. The method of claim **11** wherein the quaternary ammonium compound is employed at a level of 0.3 to 0.5% by weight of the treated articles, the fluorocarbon containing composition at a level of 0.1 to 1.0% by weight of the treated articles and the amine oxide at a level of 2 to 4 times the weight of the quaternary ammonium compound.

15. The method of claim **11** wherein the quaternary ammonium compound is employed at a level of 0.3% by weight of the treated articles, the fluorocarbon containing composition at a level of 0.5% to 1.0% by weight of the treated articles and the amine oxide at a level of 2 to 4 times the weight of the quaternary ammonium compound.

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