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FLUOROCARBON DERIVATIVES

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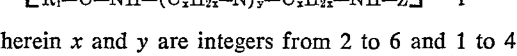
U.S. Cl. 260—294.8 F **14 Claims**

ABSTRACT OF THE DISCLOSURE

Fluorinated quarternary ammonium salts having the formula



$$\left[R_f-\overset{\overset{\large O}{\|}}{C}-NH-(C_xH_{2x}-\overset{\overset{Z'}{|}}{N})_y-C_xH_{2x}-NH-Z\right]^{q\oplus}\cdot\frac{q}{r}X^{r\ominus}$$

wherein *x* and *y* are integers from 2 to 6 and 1 to 4, respectively; R_f is a perfluoroalkyl or a fluorinated isoalkoxyalkyl radical; Z is H, a fluorinated acyl radical R_fCO— wherein R_f is as described above, a vinyl sulfone radical or a sulfone-tertiary amine adduct radical; Z′ is H, a fluorinated acyl radical R_fCO— wherein R_f is as described above, a vinyl sulfone radical, a sulfone-tertiary amine adduct radical, or a —C_xH_{2x}—NHZ radical wherein *x* and Z have the above meaning, there being at least one fluorinated acyl radical and one sulfone-tertiary amine adduct radical in the molecule represented by Z and Z′; X is an anion of a salt-forming acid; *q* is an integer corresponding to the number of sulfone-tertiary amine adduct radicals in the molecule; and *r* is an integer corresponding to the valency of X. These salts are water- and/or oil repellency agents for materials such as textiles and paper.

BACKGROUND OF THE INVENTION

This invention is directed to a new class of fluorocarbon derivatives and to their application to textiles, paper, and like fibrous materials to produce oil- and water-repellent products.

Various fluorochemicals have heretofore been employed in the treatment of textiles and paper to impart thereto oil- and water-repellency properties. In general, these fluorochemicals are composed of a fluorinated alkyl chain affixed to an active functional group. The oleophobic and hydrophobic properties of the fluorochemicals are attributed, at least in part, to the inherent low surface energy of the fluorinated surface provided by the fluorinated alkyl chain. The portion of the molecule to which the fluorinated alkyl chain is affixed provides the physical and chemical bond between the fluorinated alkyl chain and the substrate surface. The bond not only influences the degree of orientation and packing of the fluorinated groups of the fluorinated alkyl chain, and hence, the oil- and water-repellency properties of the fluorochemical, but also determines the durability of the oleophobic and hydrophobic properties when the treated substrate surface is exposed to repeated laundering and dry cleaning treatments. A high degree of durability of oleophobic and hydrophobic properties is highly desirable for obvious reasons.

Also, the portion of the molecule to which the fluorinated alkyl chain is affixed determines, in part, the solubility characteristics of these fluorochemicals. In commercial practice, oil- and water repellency agents are applied to the substrate in diluted form from a liquid medium which, for reasons of economy, is preferably an aqueous medium. Most known fluorochemical repellency agents, however, are insoluble in water, and for that reason cannot be applied from an aqueous solution, but must be applied from aqueous emulsions. Such emulsions,

however, have a tendency to coagulate when subjected to shearing action. This can be extremely troublesome when these repellents are applied to textiles in a padding bath wherein the shearing action of the squeeze rolls can cause coagulation of the repellent. Coagulated repellent sticks to the rolls and eventually is picked up by the fabric, causing streaks and spots. This, of course, cannot happen when the repellent is soluble or dispersible in water. For these and other reasons water solubiilty or water dispersibility is a highly desirable property in repellency agents.

Further, the portion of the molecule to which the fluorinated alkyl chain is affixed determines, at least in part the type of catalyst, e.g. acid or base catalyst, if any, that may suitably be employed to effect bonding of the repellent to the substrates, particularly cellulosic substrates. Cellulosic fabrics, in addition to repellency treatment, are often subjected to various other treatments enhancing their properties, such as permanent press treatments and wrinkle-resistance treatments. These other treatments commonly involve use of acidic or basic catalysts and/or reagents. Fluorochemical repellents which are responsive to both acidic ac well as basic catalysts provide for flexibiilty in application in that they are compatible with other treatments involving both acidic or basic conditions. For these and other reasons favorable response to both acidic as well as basic catalysts is a highly desirable property in repellency agents.

Accordingly, one object of the present invention is the provision of novel fluorocarbon derivatives.

It is another object of the present invention to provide water soluble or water dispersible repellency agents suitable for treating textiles, paper and like fibrous materials, in particular cellulosic materials, to impart thereto hydrophobic and/or oleophobic properties.

A further object is the provision of water soluble or water dispersible repellency agents suitable for bonding to cellulosic materials, using both acidic and basic catalysts to impart thereto hydrophobic and/or oleophobic properties.

A still further object is the provision of textile and paper materials treated with the fluorocarbon derivatives of the present invention.

An additional object is the provision of cellulosic materials chemically modified with the novel fluorocarbon derivatives of the present invention.

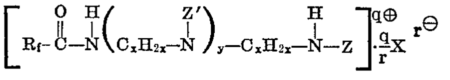
These and other objects will become apparent from the following description.

SUMMARY OF THE INVENTION

In accordance with the present invention we have discovered a new class of fluorinated quaternary ammonium salts which are valuable oil- and water repellency agents for textiles, paper and like fibrous materials capable of imparting durable oil-repellent properties. These fluorinated quaternary ammonium salts are water soluble or water dispersible and can be bonded to cellulosic substrates, if desired, using both acidic as well as basic catalysts.

DESCRIPTION OF THE INVENTION

The novel fluorinated quaternary ammonium salts of the present invention have the formula

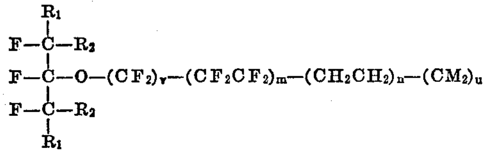


$$\left[R_f-\overset{\overset{\large O}{\|}}{C}-\overset{\overset{H}{|}}{N}\left(C_xH_{2x}-\overset{\overset{Z'}{|}}{N}\right)_y-C_xH_{2x}-\overset{\overset{H}{|}}{N}-Z\right]^{q\oplus}\cdot\frac{q}{r}X^{r\ominus} \qquad (I)$$

wherein

(1) R_f is a radical selected from the group consisting of
  (a) perfluoroalkyl having from 3 to 17 carbon atoms, and

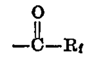
(b) a radical having the formula



$$\begin{array}{l} \quad R_1 \\ \quad | \\ F-C-R_2 \\ \quad | \\ F-C-O-(CF_2)_v-(CF_2CF_2)_m-(CH_2CH_2)_n-(CM_2)_u \\ \quad | \\ F-C-R_2 \\ \quad | \\ \quad R_1 \end{array}$$

wherein
- (i) R_1 and R_2 are fluorine or are fluoroalkyl groups, or when taken together, are fluoroalkylene groups forming a cycloaliphatic structure, which R_1 and R_2 groups may each have from 1 to 9 carbon atoms, provided that not more than three of the R_1 and R_2 groups may be fluoroalkyl groups,
- (ii) *m* and *n* are each integers of from 0 to 20, with the proviso that the sum of *m* and *n* is from 0 to 20, and provided further that when *v* is 0, *m* is at least 1,
- (iii) *m* is selected from the group consisting of hydrogen and fluorine, with the proviso that when *n* is greater than 0, then X is always hydrogen,
- (iv) *u* is 0 or 1,
- (v) *v* is 0 or 1, with the proviso that when the sum of *m, n* and *u* is greater than 0, then 1 is always 0,

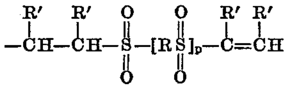
(2) *x* is an integer from 2 to 6,
(3) *y* is an integer from 1 to 4,
(4) Z is a member selected from the group consisting of
- (a) hydrogen,
- (b) an acyl radical having the formula



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

wherein R_f has the afore-stated meaning,

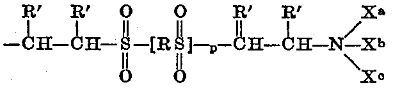
- (c) a vinyl sulfone radical having the formula



$$-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-[R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}]_p-\overset{R'}{\overset{|}{C}}=\overset{R'}{\overset{|}{C}}H$$

wherein
- (i) *p* is 0 or 1,
- (ii) R is an alkylene, aryl or aralkyl radical, and
- (iii) R′ is hydrogen, an alkyl, an aryl or a substituted aryl radical, and

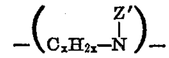
- (d) a sulfone-tertiary amine adduct radical having the formula



$$-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-[R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}]-_p-\overset{R'}{\overset{\|}{C}}H-\overset{R'}{\overset{|}{C}}H-N\!\begin{array}{l}\diagup X^a \\ -X^b \\ \diagdown X^c\end{array}$$

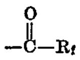
wherein *p*, R and R′ have the afore-stated meanings and wherein X^a, X^b and X^c collectively represent the residue of the pyridine, methyl-substituted pyridine or quinoline ring systems,

(5) Z′, which may be the same or different in different



$$-\left(C_xH_{2x}-\overset{\overset{Z'}{|}}{N}\right)-$$

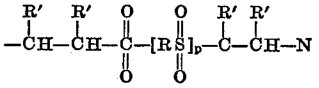
groups, is a member selected from the group consisting of
- (a) hydrogen,
- (b) an acyl radical having the formula



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

wherein R_f has the afore-stated meaning,

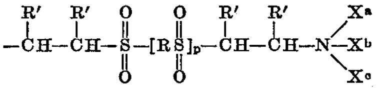
- (c) a vinyl sulfone radical having the formula



$$-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-[R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}]_p-\overset{R'}{\overset{|}{C}}-\overset{R'}{\overset{|}{C}}H-N$$

wherein R, R′ and *p* have the afore-stated meanings,

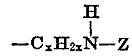
- (d) a sulfone-tertiary amine adduct radical having the formula



$$-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-[R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}]_p-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-N\!\begin{array}{l}\diagup X^a \\ -X^b \\ \diagdown X^c\end{array}$$

wherein *p*, R, R′, X^a, X^b and X^c have the afore-stated meanings, and

- (e) a radical having the formula

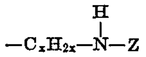


$$-C_xH_{2x}\overset{\overset{H}{|}}{N}-Z$$

wherein X and Z have the afore-stated meanings,

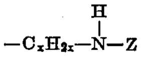
(6) X is a negatively charged ion selected from the group consisting of a halide ion, a sulfate anion, an acid sulfate anion, a phosphate anion and an acid phosphate anion,
(7) *q* is a whole number from 1 to 4 corresponding to the number of sulfone-tertiary amine adduct radicals present in the molecule,
(8) *r* is a whole number from 1 to 3 corresponding to the valency of the negatively charged ion,

with the proviso that at least one of Z and Z′ is an acyl radical or Z′ is a radical having the formula



$$-C_xH_{2x}-\overset{\overset{H}{|}}{N}-Z$$

wherein Z is an acyl radical and at least one of Z and Z′ is a sulfone-tertiary amine adduct radical or Z′ is a radical having the formula



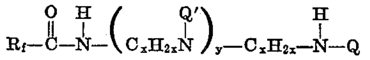
$$-C_xH_{2x}-\overset{\overset{H}{|}}{N}-Z$$

wherein Z is a sulfone-tertiary amine adduct radical, said acyl and sulfone-tertiary amine adduct radicals having the afore-stated formulas.

In the above formulas, the alkylene $-C_xH_{2x})-$ linkage may be a straight-chain or branched-chain group, preferably containing from 2 to 4 carbon atoms. R may be a straight-chain or branched-chain alkylene radical containing from 1 to 4 carbon atoms; an aryl radical such as phenyl or naphthyl; or an aralkyl radical such as benzyl, phenethyl or xylyl. R′ moy be an alkyl radical containing from 1 to 6 carbon atoms including methyl, ethyl, propyl, hexyl as well as various isomeric forms thereof; or an aryl radical such as phenyl, naphthyl and substituted derivatives thereof, including ortho-, meta- or para-tolyl; ortho-, meta- or para-chlorophenyl and paranitrophenyl.

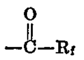
The fluorinated quaternary ammonium salts of the present invention may be prepared by reacting a corresponding divinyl sulfone adduct reactant with a heterocyclic tertiary amine salt of a salt-forming acid.

The divinyl sulfone adduct reactant has the formula



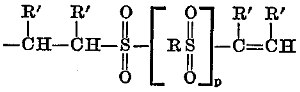
$$R_f-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-\left(C_xH_{2x}\overset{\overset{Q'}{|}}{N}\right)_y-C_xH_{2x}-\overset{\overset{H}{|}}{N}-Q \qquad \text{(II)}$$

wherein R_f, *x* and *y* have the afore-stated meanings, wherein Q is a member selected from the group consisting of hydrogen, an acyl radical having the formula



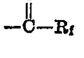
$$-\overset{\overset{O}{\|}}{C}-R_f$$

wherein R_f has the afore-stated meaning, and a vinyl sulfone radical having the formula



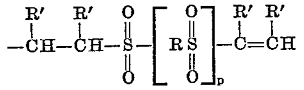
$$-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\left[R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\right]_p-\overset{R'}{\overset{|}{C}}=\overset{R'}{\overset{|}{C}}H$$

wherein R, R′ and *p* have the afore-stated meanings, and Q′ is a member selected from the group consisting of hydrogen, an acyl radical having the formula



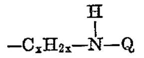
$$-\overset{\overset{O}{\|}}{C}-R_f$$

wherein R_f has the afore-stated meanings, a vinyl sulfone radical having the formula



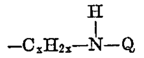
$$-\overset{R'}{\overset{|}{C}}H-\overset{R'}{\overset{|}{C}}H-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-\left[R\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\right]_p-\overset{R'}{\overset{|}{C}}=\overset{R'}{\overset{|}{C}}H$$

wherein R, R' and p have the afore-stated meanings and a radical having the formula



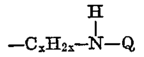
$$-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Q$$

wherein x and Q have the afore-stated meanings, with the proviso that at least one of Q and Q' is an acyl radical or Q' is a radical having the formula



$$-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Q$$

wherein Q is an acyl radical and at least one of Q and Q' is a vinyl sulfone radical or Q' is a radical having the formula



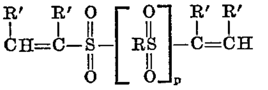
$$-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Q$$

wherein Q is a vinyl sulfone radical, said acyl and vinyl sulfone radicals having the afore-stated formulas.

The heterocyclic amine salts of salt-forming acids suitable for reaction with the above-described divinyl sulfone adduct reactants to yield the novel fluorinated quaternary ammonium salts of the present invention are the halides, i.e. fluorides, chlorides, bromides, iodides, the sulfates or the phosphates of pyridine, the methyl-substituted pyridines, i.e. the picolines, lutidines and the collidines, and quinoline.

The divinyl sulfone adduct reactants of Formula II, above, may be prepared by reacting a corresponding fluorinated polyamide reactant with a vinyl sulfone reactant.

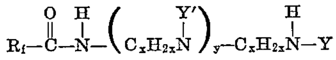
The vinyl sulfone reactant employed in the preparation of the divinyl sulfone adduct reactant of Formula II, above, may be substituted or unsubstituted and, when substituted, has only one substituent on each vinyl group. Illustratively, the vinyl sulfone reactant is represented by the formula



$$\overset{R'}{\overset{|}{C}}H=\overset{R'}{\overset{|}{C}}-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-\left[R\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\right]_p-\overset{R'}{\overset{|}{C}}=\overset{R'}{\overset{|}{C}}H \qquad \text{(III)}$$

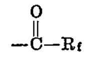
wherein R, R' and p are as previously defined. Specific examples of vinyl sulfone reactants include divinyl sulfone; dipropenyl sulfone; diisopropenyl sulfone; distyryl sulfone; bis(1-hexenyl) sulfone; bis(alpha-ethylvinyl) sulfone; bis(alpha-n-butylvinyl) sulfone; bis(alpha-phenylvinyl) sulfone; 1,2-bis(vinylsulfonyl) ethane; 1,2-bis (styryl sulfonyl) ethane; 1,4-bis(alpha-ethylvinyl sulfonyl) butane; and 1,4-bis(vinyl sulfonyl) benzene and the like.

The fluorinated polyamide reactant suitable for reaction with the vinyl sulfone reactant of Formula III, above, to prepare the divinyl sulfone adduct reactants of Formula II, above, is characterized by the structural formula



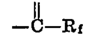
$$R_f-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\left(C_xH_{2x}\overset{Y'}{\overset{|}{N}}\right)_y-C_xH_{2x}\overset{H}{\overset{|}{N}}-Y \qquad \text{(IV)}$$

wherein R_f, x and y have the above-stated meanings, Y is a member selected from the group consisting of hydrogen and an acyl radical having the formula



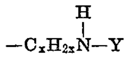
$$-\overset{O}{\overset{\|}{C}}-R_f$$

in which R_f has the afore-stated meaning and Y 'is a member selected from the group consisting of hydrogen, an acyl radical having the formula



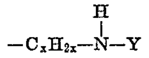
$$-\overset{O}{\overset{\|}{C}}-R_f$$

in which R_f has the afore-stated meaning and a radical having the formula



$$-C_xH_{2x}\overset{H}{\overset{|}{N}}-Y$$

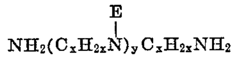
in which x and Y have the afore-stated meanings, provided that at least one of Y and Y' is an acyl radical or Y' is a radical having the formula



$$-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Y$$

in which Y is an acyl radical, said acyl radical having the afore-stated formula, and at least one of Y and Y' is hydrogen.

The fluorinated polyamide reactant of Formula IV, above, is prepared by reaction of a fluorine-containing carboxylic acid having the formula R_fCOOH, wherein R_f has the afore-stated meaning, or a derivate thereof such as an ester, anhydride or acid halide thereof with a polyalkylene polyamine corresponding to the formula



$$NH_2(C_xH_{2x}\overset{E}{\overset{|}{N}})_yC_xH_{2x}NH_2 \qquad \text{(V)}$$

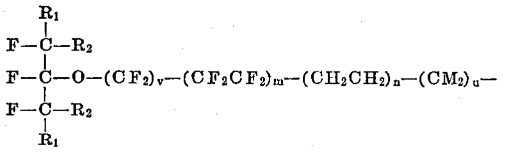
wherein x and y have the afore-stated meanings and E is hydrogen or an aminoalkyl radical having the formula $-C_xH_{2x}NH_2$ wherein x has the afore-stated meaning.

The polyalklylene polyamine reactants employed in the preparation of the fluorinated polyamide reactants of Formula IV, above, are known compounds. These reactants may be straight-chain or branched-chain compounds and may be used in the form of a single compound, as a mixture of isomers or as a mixture of polyamines containing from 3 to 6 nitrogen atoms in the molecule. Specific examples of polyaklene polyamines include diethylene triamine, di-n-propylene triamine, di-i-butylene triamine, di-n-hexylene triamine, triethylene tetramine, tri-i-propylene tetramine, tri-n-hexylene tetramine, 4-(2-aminoethyl)-1,4,7 - triazaheptane, tetraethylene pentamine, tetra-n-propylene pentamine, tetra-n-butylene pentamine, 4 - (2-aminoethyl)-1,4,7 - tetraazadecane, tetra-n-hexylene pentamine and pentaethylene hexamine.

Fluorine-containing carboxylic acid reactants, above described, wherein R_f is perfluoroalkyl, suitable for the preparation of fluorinated polyamide reactants of Formula IV, above, comprise perfluorocarboxylic acids, esters, anhydrides or acid halides thereof. Perfluorocarboxylic acid reactants suitable for reaction with the above polyalkylene polyamine reactants are saturated straight-chain or branched-chain monocarboxylic acids or stated derivatives thereof containing from 4 to 18, preferably from 6 to 14, carbon atoms in the acid portion of the molecule. Discrete molecular species of the perfluorocarboxylic acid reactants may be used or mixtures of these reactants in various proportions having the indicated carbon chain length may be employed. Illustrative perfluorocarboxylic acid reactants include perfluorobutyric, perfluorocaproic, perfluorocaprylic, perfluorolauric, perfluoromyristic, perfluoropalmitic, and perfluorostearic acids, as well as various isomeric forms thereof.

Perfluorocarboxylic acid reactants herein contemplated containing up to about ten carbon atoms are readily prepared by the electrochemical fluorination of alkanoic acids in anhydrous hydrogen fluoride with subsequent hydrolysis of the resulting fluorinated acid fluorides, as disclosed in U.S. Pat. 2,567,011, issued Sept. 4, 1951. Longer chain perfluorocarboxylic acid reactants, i.e. those containing from about 11 to 18 carbon atoms, may be obtained by reaction of perfluoroalkyl iodides with oleum containing about 15% to 45% sulfur trioxide at elevated temperatures followed by hydrolysis of the resulting perfluorocarboxylic acid fluoride, as disclosed in French Pat. 1,343,601 of Oct. 14, 1963.

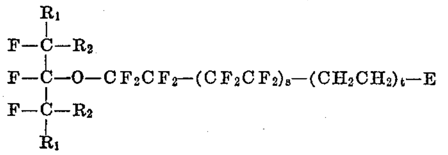
Fluorine-containing carboxylic acid reactants, above described, wherein R_f is a radical having the formula



$$\begin{array}{l} \quad R_1 \\ \quad | \\ F-C-R_2 \\ \quad | \\ F-C-O-(CF_2)_v-(CF_2CF_2)_m-(CH_2CH_2)_n-(CM_2)_u- \\ \quad | \\ F-C-R_2 \\ \quad | \\ \quad R_1 \end{array} \qquad \text{(VI)}$$

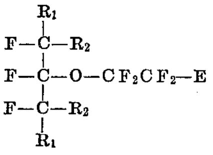
wherein R_1, R_2, M, *v*, *n*, *m* and *u* have the afore-stated meanings may be prepared by various hereinafter described methods.

Fluorine-containing carboxylic acids of the formula R_fCOOH wherein R_f has the Formula VI, above, wherein *v* is 0, *m* is at least 1 and the sum of *n* and *u* is at least 1, can be prepared from telomers having the general formula



$$\begin{array}{l} \quad R_1 \\ \quad | \\ F-C-R_2 \\ \quad | \\ F-C-O-CF_2CF_2-(CF_2CF_2)_s-(CH_2CH_2)_t-E \\ \quad | \\ F-C-R_2 \\ \quad | \\ \quad R_1 \end{array} \qquad \text{(VII)}$$

wherein R_1 and R_2 have the afore-stated meanings, wherein *s* and *t* are each integers from 0 to 20, the sum of *s* and *t* being at least 1, and wherein E is a halogen selected from the group consisting of Br and I. Telomers of that type and their preparation are described in commonly assigned copending application of Anello et al. entitled, "Telomers and Process for the Preparation Thereof," Ser. No. 633,359, filed Apr. 25, 1967, the pertinent subject matter of which is hereby incorporated by reference. By way of general description, these telomers are prepared by radical addition reactions of polyfluoroisoalkoxyalkyl halide telogens of the formula



$$\begin{array}{l} \quad R_1 \\ \quad | \\ F-C-R_2 \\ \quad | \\ F-C-O-CF_2CF_2-E \\ \quad | \\ F-C-R_2 \\ \quad | \\ \quad R_1 \end{array} \qquad \text{(VIII)}$$

wherein R_1, and R_2 and E have the afore-stated meanings, with telomerizable unsaturated compounds. The telomerization reaction may be initiated by heat or by means of a free radical initiating catalyst. The polyfluoroisoalkoxyalkyl halide telogen starting materials may be prepared by reacting a corresponding fluorinated ketone with an ionizable fluoride salt, e.g. CsF, to form a fluorinated organic salt and then reacting the organic salt with a halogen other than fluorine or chlorine and tetrafluoroethylene. Preparation of the telogen starting materials is described in detail in copending applications of Litt et al., "Fluorinated Ethers," U.S. Ser. Nos. 492,276 and 513,574, filed Oct. 1, 1965, and Dec. 13, 1965 respectively, the pertinent subject matter of which applications is hereby incorporated by reference.

Fluorine-containing carboxylic acids of the formula R_fCOOH wherein R_f has the formula VI, above, wherein *v*, *n* and *u* are all 0 and wherein *m* is at least 2 may be prepared by reacting the corresponding telomer represented by general Formula VII, above, wherein *t* is 0 with ICN or $(CN)_2$ to form the nitrile, followed by hydrolysis of the nitrile in known manner to form the free acid. The reaction between the telomer and the ICN or $(CN)_2$ to form the nitrile is carried out under superatmospheric pressure above about 20 to 200 atmospheres or more at temperatures in excess of about 300° C., preferably using an excess of the ICN or $(CN)_2$ reactant. Hydrolysis of the nitrile to form the free acid can be effected by treatment with aqueous mineral acid, such as hydrochloric, phosphoric, or sulfuric acid, at temperatures between about 60° and about 125°.

Fluorine-containing carboxylic acids of the formula R_fCOOH wherein R_f has the Formula VI, above, wherein *m* is at least 1, *v* and *u* are both 0 and *n* is greater than 0 may be prepared by reacting the corresponding telomer represented by Formula VII, above, wherein *t* is greater than 0 with an alkali metal cyanide to form the nitrile, followed by hydrolysis of the nitrile to form the free acid, as described above. The reaction between the telomer and the alkali metal cyanide is preferably carried out in aqueous alcoholic solution at temperature between about 60° and about 100° C.

Fluorine-containing carboxylic acids of the formula R_fCOOH wherein R_f has the Formula VI, above, wherein *m* is at least 1, *v* is 0, *u* is 1 and M is hydrogen can be prepared by reacting the corresponding telomer represented by general Formula VII, above, wherein *t* is at least 1 with SO_3 to form the corresponding pyrosulfate, or with oleum to form the corresponding hydrosulfate, hydrolysis of the pyrosulfate or the hydrosulfate with aqueous acid to form the corresponding alcohol, followed by oxidation of the alcohol with dichromate, permanganate or strong nitric acid to form the free acid.

Fluorine-containing carboxylic acids of the formula R_fCOOH wherein R_f has the Formula VI, above, wherein *m* is at least 1, *v* and *n* are both 0, *u* is 1 and M is fluorine can be prepared by reacting a corresponding telomer represented by Formula VII, above, wherein *t* is 0 with SO_3 to form corresponding acid halides and fluoropyrosulfates, and hydrolyzing the acid halides and fluoropyrosulfates by refluxing with water to obtain the corresponding free acids. Fluorine-containing carboxylic acids of the formula R_fCOOH wherein R_f has the Formula VI, above, wherein *v* is 1 and *m*, *n* and *u* are all 0 can be prepared by the same method from polyfluoroisoalkoxyalkyl halide compounds of Formula VIII above.

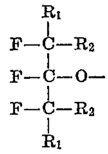
Fluorine-containing carboxylic acids of the Formula R_fCOOH wherein R_f has the Formula VI, above, wherein *m* is 1 and *v*, *n* and *u* are all 0 can be prepared from polyfluoroisoalkoxyalkyl halide compounds of Formula VIII, above, by reacting them with a Grignard reagent to form a magnesium halide adduct, reacting this adduct with CO_2 to form a magnesium halide salt, and then acidifying the salt to obtain the desired acid. The reactions involving the Grignard reagent and the carbon dioxide proceed very rapidly and can be conducted at temperatures considerably below 0° C. Preparation of these acids is described in detail in commonly assigned co-pending application of Litt et al., "Fluorinated Ethers," U.S. Ser. No. 492,276, filed Oct. 1, 1965, referred to above.

The esters and acid halides of the above-described acids may be prepared from the acids by conventional procedures.

While the telomers of Formula VII, above, and the fluorine-containing carboxylic acid reactants derived therefrom, may be prepared as discrete compounds, they are generally obtained as mixtures of compounds of varying chain length. It is to be understood that both, the individual discrete fluorine-containing carboxylic acid reactants as well as their mixtures of compounds of varying chain length are suitable for the preparation of the fluorinated polyamide compounds employed in the preparation of the compounds of the present invention.

Preparation of above-described acids wherein R_f has the Formula VI, above, is described in more detail in commonly assigned copending applications of Anello et al., U.S. Ser. Nos. 721,115 and 721,117, both filed Apr. 12, 1968, respectively entitled "Fluorocarbon Acids and Derivatives" and "Fluorocarbon Compounds," the pertinent subject matter of which application is hereby incorporated by reference.

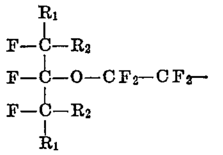
When the R_f group is a fluorinated isoalkoxyalkl group represented by Formula VI, above then, in the



$$\begin{array}{l} \quad R_1\\ \quad | \\ F-C-R_2 \\ \quad | \\ F-C-O- \\ \quad | \\ F-C-R_2 \\ \quad | \\ \quad R_1\end{array}$$

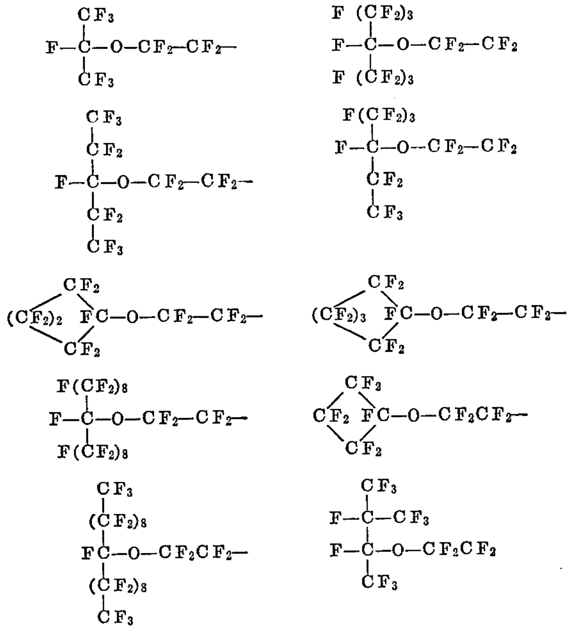
moiety, R_1 and R_2 are preferable fluorine or perfluoroalkyl groups. When perfluoroalkyl groups, R_1 and R_2 preferably contain 1–2 carbon atoms. When the R_1 and R_2 groups contain hydrogen substitution, the atomic ratio of fluorine to hydrogen is at least 1:1.

In preferred embodiments integer *m* in the R_f radical of Formula VI, above, is at least 1, and the sum of *m* and *n* is preferably from 1 to 10. Specific examples of preferred embodiments of the preferred



$$\begin{array}{l} \quad R_1\\ \quad | \\ F-C-R_2 \\ \quad | \\ F-C-O-CF_2-CF_2- \\ \quad | \\ F-C-R_2 \\ \quad | \\ \quad R_1\end{array}$$

moiety of the R_f radical of Formula VI, above, include the following:



$$\begin{array}{l} \quad CF_3 \\ \quad | \\ F-C-O-CF_2-CF_2- \\ \quad | \\ \quad CF_3 \end{array} \qquad \begin{array}{l} F\ (CF_2)_3 \\ \quad | \\ F-C-O-CF_2-CF_2 \\ \quad | \\ F\ (CF_2)_3 \end{array}$$

$$\begin{array}{l} \quad CF_3 \\ \quad | \\ \quad CF_2 \\ \quad | \\ F-C-O-CF_2-CF_2- \\ \quad | \\ \quad CF_2 \\ \quad | \\ \quad CF_3 \end{array} \qquad \begin{array}{l} F(CF_2)_3 \\ \quad | \\ F-C-O-CF_2-CF_2 \\ \quad | \\ \quad CF_2 \\ \quad | \\ \quad CF_3 \end{array}$$

$$\begin{array}{l} F(CF_2)_8 \\ \quad | \\ F-C-O-CF_2-CF_2- \\ \quad | \\ F(CF_2)_8 \end{array}$$

$$\begin{array}{l} \quad CF_3 \\ \quad | \\ \ (CF_2)_8 \\ \quad | \\ FC-O-CF_2CF_2- \\ \quad | \\ \ (CF_2)_8 \\ \quad | \\ \quad CF_3 \end{array} \qquad \begin{array}{l} \quad CF_3 \\ \quad | \\ F-C-CF_3 \\ \quad | \\ F-C-O-CF_2CF_2 \\ \quad | \\ \quad CF_3 \end{array}$$

The fluorinated polyamide reactant of Formula IV, above, may be prepared by simply mixing the fluorine-containing carboxylic acid reactant with the polyalkylene polyamine reactant. These reactants may be charged in a molar proportion of 1 mol of polyalkylene polyamine reactant to about 0.5 to 7 mols of fluorine-containing carboxylic acid reactant. If desired, the reaction may be carried out in the presence of a suitable inert organic solvent. Suitable reaction temperatures range between about 0° C. to about 200° C. Upon conclusion of the reaction, the desired fluorinated polyamide may be recovered from the reaction mixture by methods known to those skilled in the art.

The fluorinated polyamide obtained as a result of the reaction of the fluorine-containing carboxylic acid reactant with the polyalkylene polyamine reactant above described, may comprise a single compound conforming to Formula IV, above, a mixture of isomers thereof or a reaction mass composed of amide products containing two or more amide functions. The resulting fluorinated polyamide is suitable without further purification for reaction with the vinyl sulfone reactant of Formula III, above, to yield the divinyl sulfone adduct reactant of Formula II, above. However, if desired, the fluorinated polyamide may be further purified prior to reaction with the vinyl sulfone reactant as by distillation or recrystallization.

The divinyl sulfone adduct reactant of Formula II above, may be prepared by heating a mixture of the sulfone reactant of Formula III above, with the fluorinated polyamide above-described. These reactants may be charged in a mol proportion of 1 mol of fluorinated polyamide to about 1 to 10 mols of sulfone reactant. The reaction temperature and time are dependent upon the particular fluorinated polyamide and sulfone reactants involved. The temperature ranges from about 25° C. to 160° C., and the time ranges from about ½ to 4 hours. If desired, the reaction may be conducted in the presence of an inert organic solvent. The resulting divinyl sulfone adduct may be recovered from the reaction mixture by conventional methods.

The novel fluorinated quaternary ammonium salts of the present invention may be prepared by simply mixing the divinyl sulfone adduct reactant with the heterocyclic tertiary amine salt of a salt-forming acid, or alternatively, by mixing the divinyl sulfone adduct reactant with the heterocyclic tertiary amine and the salt-forming acid. These reactions are preferably carried out in the presence of a suitable inert organic solvent. These reactants may be charged in a molar proportion of 1 mol of divinyl sulfone adduct reactant to about 1 to 15, preferably about 5 to 10 mols of heterocyclic tertiary amine salt reactant. When the heterocyclic tertiary amine and the salt-forming acid are charged separately, then it is preferred to employ a slight excess of the heterocyclic tertiary amine, say between about 1.1 to 1.8 mols of heterocyclic tertiary amine per mol of salt-forming acid. The reaction temperature and time are dependent upon the particular divinyl sulfone and heterocyclic tertiary amine salt reactants involved. The temperature varies from about 25° C. to 100° C., preferably about 50° C. to 75° C., and the time ranges from about 5 minutes to about 24 hours.

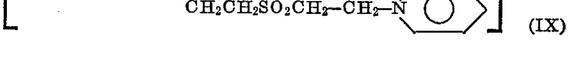
The reaction is preferably conducted in the presence of an inert organic solvent or solvent mixture. The lower aliphatic ketones and alcohols are exemplary of suitable inert organic solvents. When a solvent is employed, the maximum temperature is limited only by the reflux temperature of the reaction mixture. Although the reaction may be conducted at superatmospheric pressure, it is preferred to conduct the reaction at atmospheric pressure.

If desired, the reaction may be carried out in the presence of a tertiary aliphatic amine catalyst. Exemplary suitable tertiary aliphatic amine catalysts are triethylamine, tripropylamine, tributylamine, and the like. Triethylamine is a preferred catalyst. The tertiary aliphatic amine catalyst, if one is employed, is used in amount of between about 0.1% and about 1.0% of the combined weight of the reaction mixture.

Upon completion of the reaction, the sought-for fluorinated quaternary ammonium salt product may be recovered from the reaction mixture by evaporation of solvent therefrom to obtain the crude product as the residue, or by cooling the mixture to precipitate the product which may then be recovered by filtration.

The product thus obtained is suitable for use as oil- and water-repellency agent without further purification. However, if desired, the fluorinated quaternary ammonium salt so produced may be further purified prior to use, as by recrystallization using any commonly employed inert organic solvent, such as acetonitrile, ethanol or isopropanol.

Preferred fluorinated quaternary ammonium salts of the present invention correspond to the general formula



$$\left[R_f-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(C_xH_{2x}N)_y-C_xH_{2x}-\underset{CH_2CH_2SO_2CH_2-CH_2-N^{+}C_5H_5}{\overset{H}{\overset{|}{N}}}-\overset{O}{\overset{\|}{C}}-R_f\right]^{y\oplus} \cdot yX^{\ominus} \quad \text{(IX)}$$

wherein R_f, x and y have the aforestated meanings and wherein X represents a halide ion, most preferable a chloride ion.

A specific class of preferred embodiments of the present invention are fluorinated quaternary ammonium salts according to Formula IX, above, wherein the R_f radical has the formula

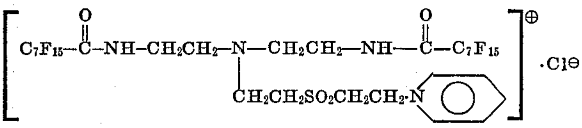
$$(CF_3)_2CFO—(CF_2CF_2)_m—(CH_2CH_2)_n—(CM_2)_u—$$

wherein m is an integer from 1 to 10, n is an integer from 0 to 10, with the proviso that the sum of m and n is from 1 to 10, and wherein M and u have the aforestated meanings.

The following examples relate to the preparation of representative fluorinated quaternary ammonium salts of the present invention but are not intended to be limiting on the scope thereof.

EXAMPLE 1

To a solution of 15.18 g. (0.015 mol) of 1,7-bis(perfluorooctanoyl) - 4 - (2 - vinylsulfonylethyl) - 1,4,7 - triazaheptane in 50 ml. of acetone are added 5 drops of triethylamine (as catalyst). Into this solution is dropped a mixture of 8.28 g. (0.1 mol) of pyridine, 5.04 ml. of 12 N hydrochloric acid and 10 ml. of ethanol. The mixture thus obtained is stirred and refluxed for a period of 3 hours. The mixture is then cooled for 1 hour in an ice-bath to precipitate the crude 1,7 - bis(perfluorooctanoyl) - 4 - [2 - (2 - pyridiniumethylsulfonyl)ethyl]-1,4,7-triazaheptane chloride product. The crude product (18 g.) is separated from the reaction mixture by filtration, is washed with ethyl ether, and is recrystallized from acetonitrile. There is thus recovered 10 g. of purified product having the formula



M.P. 172–174° C. in 64 percent yield. The product is dispersible in water. Analysis of an analytical sample of the product compares with calculated analysis for $C_{29}H_{23}N_4O_4SClF_3$ as follows:

Calculated (percent): C, 30.8; H, 2.06; N, 4.96; F, 51.0; S, 2.84; Cl, 3.14. Analysis (percent): C, 30.59; H, 1.88; N, 4.95; F, 49.69; S, 2.94; Cl, 3.49.

The infrared spectrum of the product (KBr) shows bands at approximately 3.0μ (medium), 3.45μ (weak), 5.9μ (strong), 6.11μ (weak), 6.5μ (medium), 7.55μ (weak), 7.75μ (medium), and an envelope of strong bands at about 8.1 to 8.9μ.

The 1,7 - bis(perfluorooctanoyl) - 4 - (2-vinylsulfonylethyl)-1,4,7-triazaheptane reactant is prepared as follows:

Solid 1,7 - bis(perfluorooctanoyl) - 1,4,7-triazaheptane (2.4 g.) is heated at 130° C. to 140° C. in 15 ml. of dimethylformamide until all of the solid dissolves. To this solution is added 2 ml. of divinyl sulfone, and the resulting reaction mixture is heated to 140° C. for 3 hours. The reaction product is cooled to room temperature and is transferred to a separatory funnel. Thereafter, 25 ml. of water is added and a yellow water-insoluble oil layer is formed. The oily product is extracted with two 25 ml. portions of diethyl ether, the ether extracts are combined, washed with two 25 ml. portions of water and dried over anhydrous magnesium sulfate. The ether is evaporated under vacuum, and the resulting yellow solid residue is recrystallized from carbon tetrachloride. The product thus obtained is a solid melting at 93°–94° C. It is represented by the following structural formula

$$C_7F_{15}—\overset{\overset{\displaystyle O}{\|}}{C}—NHCH_2CH_2\underset{\underset{\displaystyle CH_2CH_2SO_2CH=CH_2}{|}}{N}CH_2CH_2NH—\overset{\overset{\displaystyle O}{\|}}{C}—C_7F_{15}$$

The perfluoroalkyl diamide reactant employed in the preparation of the above divinyl sulfone adduct is prepared in the following manner:

A solution of 49 g. (0.475 mol) of diethylene triamine in 60 ml. of diethyl ether is placed in a reaction vessel equipped with a dropping funnel, condenser, magnetic stirrer and a calcium chloride drying tube. After chilling the vessel in an ice water bath for a period of about 20 minutes, 34.2 g. (0.079 mol) of n-perfluorooctanoyl chloride is added with stirring to the contents of the vessel during a 30 minute period. After the addition of the n-perfluorooctanoyl chloride reactant is complete, the ice water bath is removed and the stirring is continued at room temperature for a period of 20 minutes. Thereafter, 100 ml. of an 8% aqueous sodium hydroxide solution is added to the reaction mixture and the stirring is continued for an additional 15 minutes. The resulting gelatinous precipitate is filtered at reduced pressure and washed with water. After air drying the precipitate, a yield of about 31 g. of 1,7-bis(perfluorooctanoyl)-1,4,7-triazaheptane, a white solid (melting point 94–97° C.), having the following structural formula is obtained:

$$C_7F15—\overset{\overset{\displaystyle O}{\|}}{C}—NHCH_2CH_2NHCH_2CH_2NH—\overset{\overset{\displaystyle O}{\|}}{C}—C_7F_{15}$$

The 1,7 - bis(perfluorooctanoyl) - 4 - [2 - (2 - pyridiniumethylsulfonyl)ethyl] - 1,4,7 - triazaheptane chloride product exhibits unusually high surface active properties and may be used in the manner in which surfactants are conventionally employed, such as in the preparation of emulsions and to increase wettability, such as in the dyeing of textile fabrics. The effect of that product on the surface tension of water is determined by measuring the surface tensions of a series of aqueous solutions with a tensiometer in accordance with ASTM Test D–1590. The results are as follows:

Concentration of compound in water (wt. percent):	Surface tension (dyne/cm.)
1.0	19.3
0.5	20.1
0.1	23.5

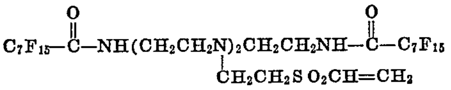
When the above product is applied to a glass microscope slide by evaporation of a dilute acetone solution, a drop of water placed on the surface so treated exhibits a contact angle of 75°, and a drop of mineral oil ("Nujol," Saybolt viscosity 360/390 at 100° F., sp. gr. 0.880/0.900 at 60° F.) exhibits a contact angle of 85°. A drop of the same mineral oil applied to a slide treated with acetone alone exhibits a contact angle of about 25.5°.

EXAMPLE 2

To a solution of 31.95 g. (0.03 mol) of 1,10-bis(perfluorooctanoyl) - 4,7 - bis(2 - vinylsulfonylethyl) - 1,4,7,10-tetraazadecane in 135 ml. of acetone are added 8 drops of triethylamine (as catalyst). Into this solution is dropped a mixture of 31.64 g. (0.4 mol) of pyridine, 19.3 ml. of 12 N hydrochloric acid and 20 ml. of ethanol. The mixture thus obtained is stirred and refluxed for a period of 3 hours. The mixture is then cooled for 1 hour in an ice-bath to precipitate the crude 1,10-bis(perfluorooctanoyl) - 4,7 - bis[2 - (2 - pyridiniumethylsulfonyl) ethyl] - 1,4,7,10 - tetraazadecane dichloride product. The crude product is recovered by filtration and is recrystallized from acetonitrile to yield 15 g. of product, M.P. 160°–165° C. Upon further recrystallization (twice) from acetonitrile, the product has a melting point of 170°–175° C. The product is soluble in water.

The 1,10 - bis(perfluorooctanoyl) - 4,7 - bis(2 - vinylsulfonylethyl) - 1,4,7,10 - tetraazadecane reactant is prepared as follows:

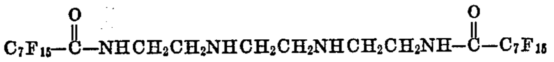
Six grams of 1,10 - bis(perfluorooctanoyl) - 1,4,7,10-tetraazadecane are dissolved in 20 ml. of dimethylformamide by heating to 80° C. for a few minutes. To this solution there are added 3 ml. of divinyl sulfone and the mixture is heated to 90° C. for a period of 3 hours. To the reaction product is added 20 ml. of water and a white solid is formed. The solid is washed with water and air dried to yield 1,10-bis(perfluorooctanoyl)-4,7-bis(2 - vinylsulfonylethyl) - 1,4,7,10 - tetraazadecane (melting point 118–121° C.) having the following structural formula



$$C_7F_{15}-\overset{O}{\overset{\|}{C}}-NH(CH_2CH_2\underset{CH_2CH_2SO_2CH=CH_2}{\underset{|}{N}})_2CH_2CH_2NH-\overset{O}{\overset{\|}{C}}-C_7F_{15}$$

The perfluoroalkyl diamide reactant is prepared in the following manner:

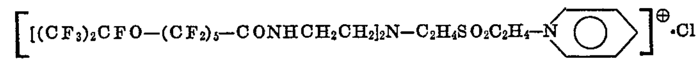
To a solution of 20 g. (0.0467 mol) of methyl-n-perfluorooctanoate in 25 ml. of diethylether, there is added 3.4 g. (0.0233 mol) of triethylene tetramine. The resulting solution is heated under reflux temperature for a period of 24 hours. After removal of the solvent under reduced pressure, 20 g. of a white sticky solid is obtained which is subsequently recrystallized from acetonitrile. The product of this reaction is 1,10 - bis(perfluorooctanoyl)-1,4,7,10-tetraazadecane, a white powder (melting point 89–92° C.) having the following structural formula



$$C_7F_{15}-\overset{O}{\overset{\|}{C}}-NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH-\overset{O}{\overset{\|}{C}}-C_7F_{15}$$

EXAMPLE 3

Following the procedure set forth in Example 1 there is reacted 1,7 - bis[perfluoro(7 - oxa - 8 - methylnonanoyl)] - 4 - (2 - vinylsulfonylethyl) - 1,4,7 - triazaheptane with pyridine hydrochloride to obtain as product the water soluble compound



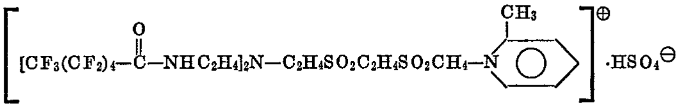
The 1,7 - bis[perfluoro(7 - oxa - 8 - methylnonanoyl)]-4 - (2 - vinylsulfonylethyl) - 1,4,7 - triazaheptane reactant is prepared as follows:

A solution of 5.0 g. (0.0049 mol) of 1,7-bis[perfluoro (7 - oxa - 8 - methylnonanoyl)] - 1,4,7 - triazaheptane and 5.8 g. (0.049 mol) of divinyl sulfone in 35 ml. of dimethylformamide is stirred and maintained at a temperature of 75° C. for a period of 4 hours. The reaction mixture is then cooled to ambient temperature and is diluted with 70 ml. of cold water to precipitate about 3.6 g. of the crude product. The crude product, recrystallized thrice from acetonitrile, yields about 2 g. of purified product, M.P. 94.5°–95.5° C. having the structure

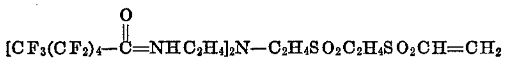
$$[(CF_3)_2CFO—(CF_2)_5CONHC_2H_4]_2N—C_2H_4SO_2CH=CH_2$$

EXAMPLES 4–24

In manner analogous to that described in the above examples, other compounds illustrative of the present invention may be prepared as follows:

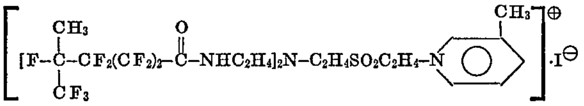


by reaction of

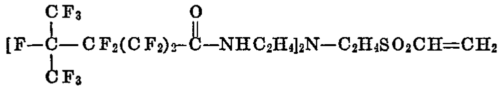


$$[CF_3(CF_2)_4-\overset{O}{\overset{\|}{C}}=NHC_2H_4]_2N-C_2H_4SO_2C_2H_4SO_2CH=CH_2$$

with 2-methylpyridine hydrogen sulfate.

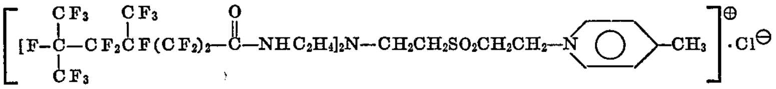


by reaction of



$$[F-\overset{CF_3}{\underset{CF_3}{C}}-CF_2(CF_2)_2-\overset{O}{\overset{\|}{C}}-NHC_2H_4]_2N-C_2H_4SO_2CH=CH_2$$

with 3-methylpyridine hydroiodide.



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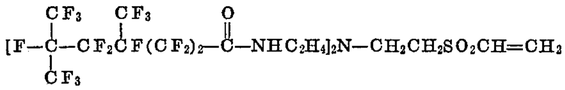
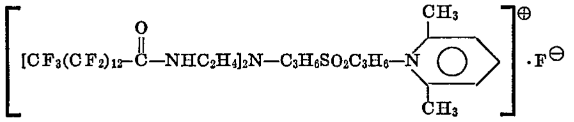
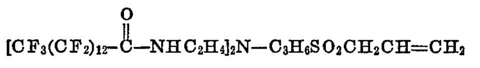


$$[F-\overset{CF_3}{\underset{CF_3}{C}}-CF_2\overset{CF_3}{C}F(CF_2)_2-\overset{O}{\overset{\|}{C}}-NHC_2H_4]_2N-CH_2CH_2SO_2CH=CH_2$$

with 4-methylpyridine hydrochloride.

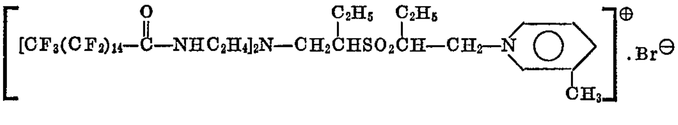


by reaction of



$$[CF_3(CF_2)_{12}-\overset{O}{\overset{\|}{C}}-NHC_2H_4]_2N-C_3H_6SO_2CH_2CH=CH_2$$

with 2,6-dimethylpyridine hydrofluoride.



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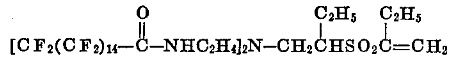
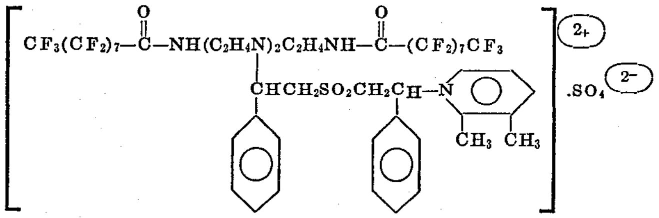


$$[CF_2(CF_2)_{14}-\overset{O}{\overset{\|}{C}}-NHC_2H_4]_2N-CH_2\overset{C_2H_5}{C}HSO_2\overset{C_2H_5}{C}=CH_2$$

with 3,5-dimethylpyridine hydrobromide.



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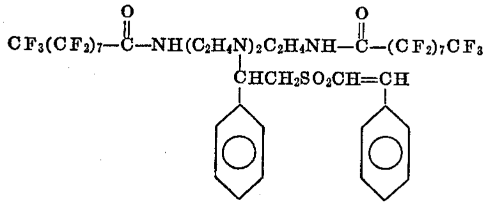
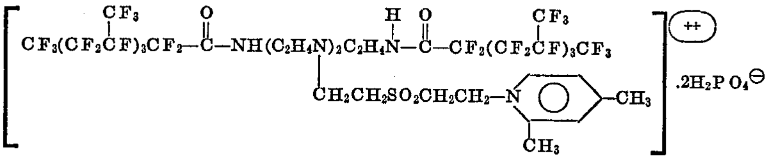


with 2,3-dimethylpyridine sulfate.



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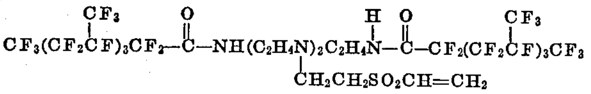
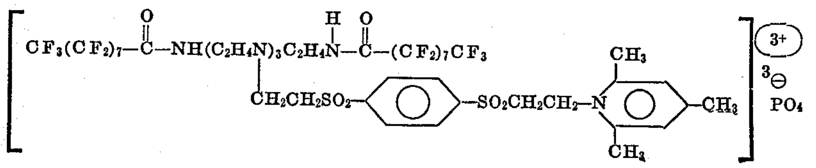
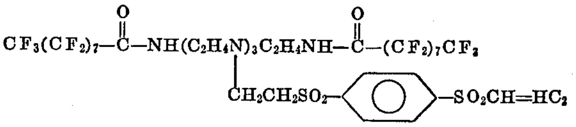


$$CF_3(CF_2\overset{CF_3}{C}F)_3CF_2-\overset{O}{\overset{\|}{C}}-NH(C_2H_4\underset{CH_2CH_2SO_2CH=CH_2}{N})_2C_2H_4\overset{H}{N}-\overset{O}{\overset{\|}{C}}-CF_2(CF_2\overset{CF_3}{C}F)_3CF_3$$

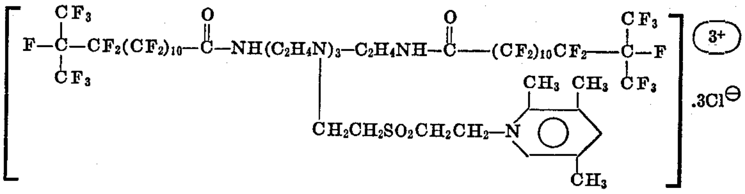
with 2,4-dimethylpyridine dihydrogen phosphate.



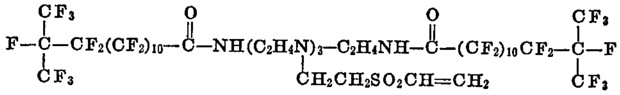
by reaction of



with 2,4,6-trimethylpyridine phosphate.

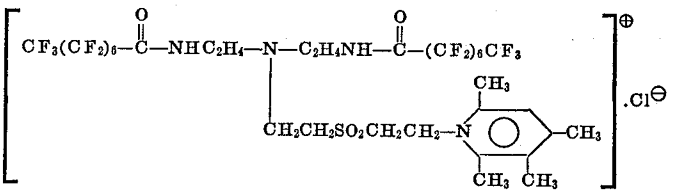


by reaction of

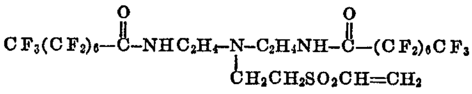


$$F-\underset{CF_3}{\overset{CF_3}{C}}-CF_2(CF_2)_{10}-\overset{O}{\overset{\|}{C}}-NH(C_2H_4\underset{CH_2CH_2SO_2CH=CH_2}{N})_3-C_2H_4NH-\overset{O}{\overset{\|}{C}}-(CF_2)_{10}CF_2-\underset{CF_3}{\overset{CF_3}{C}}-F$$

with 2,3,5-trimethylpyridine hydrochloride.

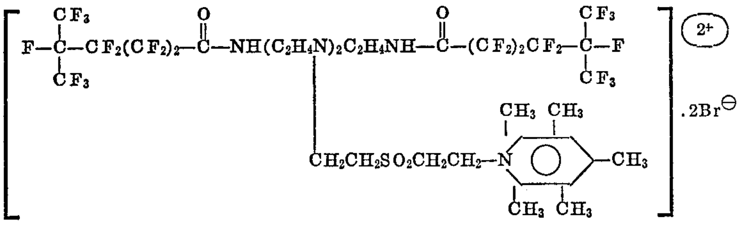


by reaction of

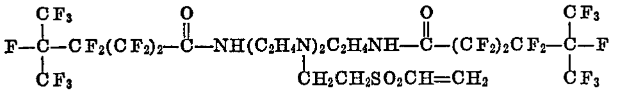


$$CF_3(CF_2)_6-\overset{O}{\overset{\|}{C}}-NHC_2H_4-\underset{CH_2CH_2SO_2CH=CH_2}{N}-C_2H_4NH-\overset{O}{\overset{\|}{C}}-(CF_2)_6CF_3$$

with 2,3,4,6-tetramethylpyridine hydrochloride.

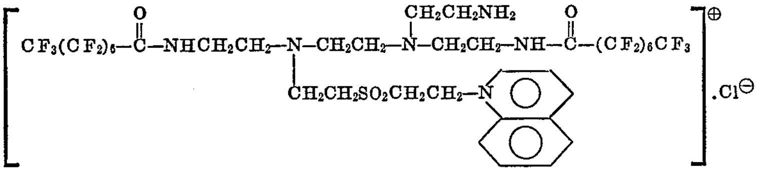


by reaction of

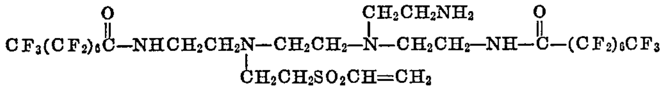


$$\mathrm{F{-}\overset{CF_3}{\underset{CF_3}{C}}{-}CF_2(CF_2)_2{-}\overset{O}{\overset{\|}{C}}{-}NH(C_2H_4\underset{CH_2CH_2SO_2CH=CH_2}{N})_2C_2H_4NH{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_2CF_2{-}\overset{CF_3}{\underset{CF_3}{C}}{-}F}$$

with 2,3,4,5,6-pentamethylpyridine hydrobromide.

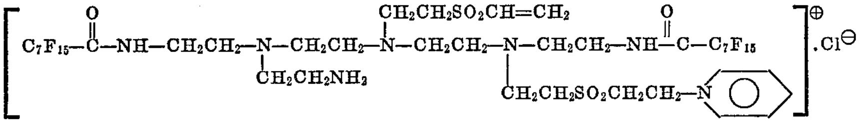


by reaction of

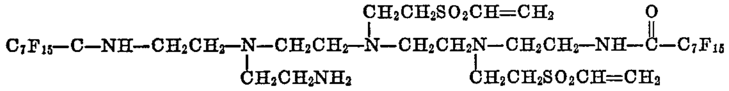


$$\mathrm{CF_3(CF_2)_6\overset{O}{\overset{\|}{C}}{-}NHCH_2CH_2\underset{CH_2CH_2SO_2CH=CH_2}{N}{-}CH_2CH_2{-}\overset{CH_2CH_2NH_2}{N}{-}CH_2CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_6CF_3}$$

with quinoline hydrochloride.

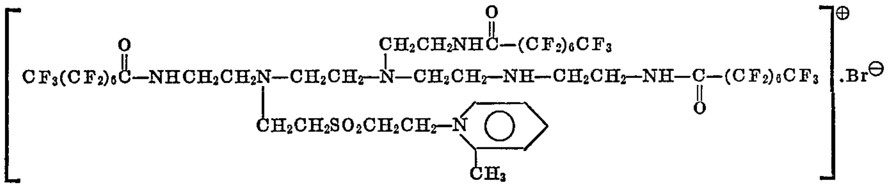


by reaction of

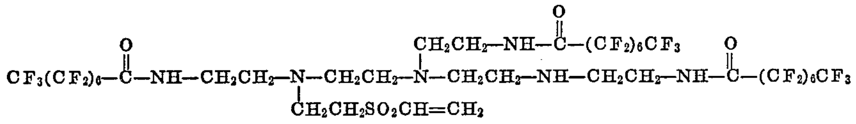


$$\mathrm{C_7F_{15}{-}C{-}NH{-}CH_2CH_2{-}\underset{CH_2CH_2NH_2}{N}{-}CH_2CH_2{-}\overset{CH_2CH_2SO_2CH=CH_2}{N}{-}CH_2CH_2\underset{CH_2CH_2SO_2CH=CH_2}{N}{-}CH_2CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}C_7F_{15}}$$

with pyridine hydrochloride.

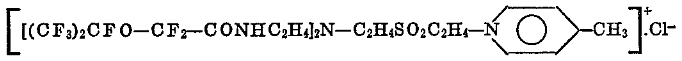


by reaction of



$$\mathrm{CF_3(CF_2)_6{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2CH_2{-}\underset{CH_2CH_2SO_2CH=CH_2}{N}{-}CH_2CH_2{-}\overset{CH_2CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_6CF_3}{N}{-}CH_2CH_2{-}NH{-}CH_2CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_6CF_3}$$

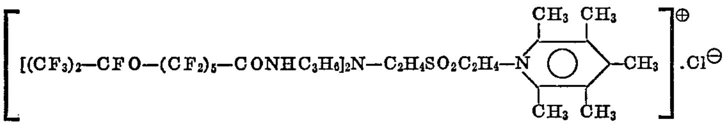
with 2-methylpyridine hydrobromide.



by reaction of

$[(CF_3)_2CFO{-}CF_2{-}CONHC_2H_4]_2N{-}C_2H_4SO_2CH{=}CH_2$

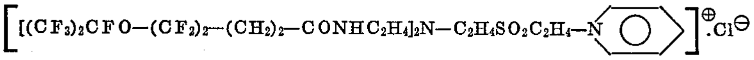
with 4-methylpyridine hydrochloride.



by reaction of

$[(CF_3)_2CFO{-}(CF_2)_5{-}CONHC_3H_6]_2N{-}C_2H_4SO_2CH{=}CH_2$

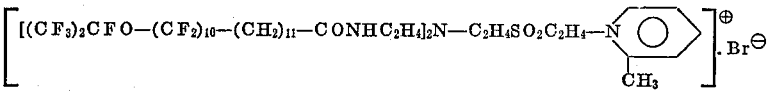
with 2,3,4,5,6-pentamethylpyridine hydrochloride.



by reaction of

$[(CF_3)_2CFO{-}(CF_2)_2{-}(CH_2)_2{-}CONHC_2H_4]_2N{-}C_2H_4SO_2CH{=}CH_2$

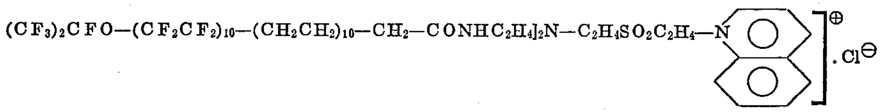
with pyridine hydrochloride.



by reaction of

$[(CF_3)_2CFO{-}(CF_2)_{10}{-}(CH_2)_{11}{-}CONHC_2H_4]_2N{-}C_2H_4SO_2CH{=}CH_2$

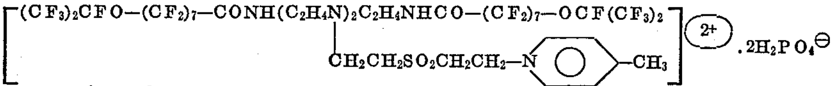
with 2-methylpyridine hydrobromide.



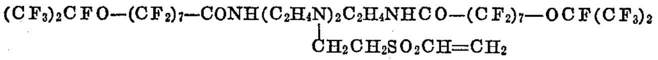
by reaction of

$[(CF_3)_2CFO{-}(CF_2CF_2)_{10}{-}(CH_2CH_2)_{10}{-}CH_2{-}CONHC_2H_4]_2{-}N{-}C_2H_4SO_2CH{=}CH_2$

with quinoline hydrochloride.

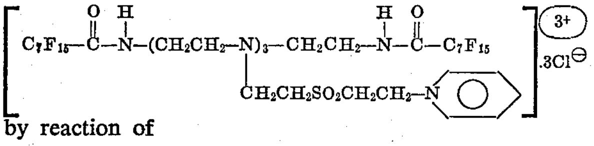


by reaction of



$$\mathrm{(CF_3)_2CFO{-}(CF_2)_7{-}CONH(C_2H_4\underset{\underset{CH_2CH_2SO_2CH=CH_2}{|}}{N})_2C_2H_4NHCO{-}(CF_2)_7{-}OCF(CF_3)_2}$$

with 4-methylpyridine dihydrogen phosphate.



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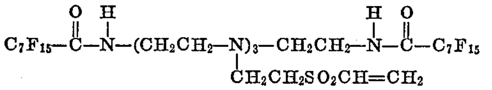
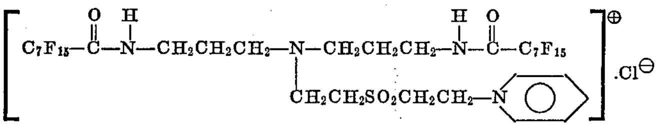
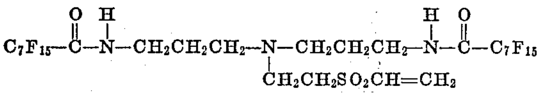


$$\mathrm{C_7F_{15}{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}(CH_2CH_2{-}N)_3{-}\underset{\underset{CH_2CH_2SO_2CH=CH_2}{|}}{CH_2CH_2}{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}C_7F_{15}}$$

with pyridine hydrochloride.

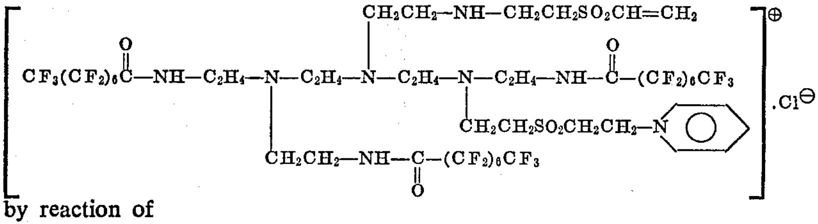


by reaction of



$$\mathrm{C_7F_{15}{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}CH_2CH_2CH_2{-}\underset{\underset{CH_2CH_2SO_2CH=CH_2}{|}}{N}{-}CH_2CH_2CH_2{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}C_7F_{15}}$$

with pyridine hydrochloride.



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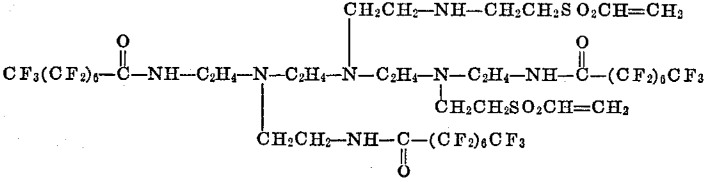


$$\mathrm{CF_3(CF_2)_6{-}\overset{\overset{O}{\|}}{C}{-}NH{-}C_2H_4{-}\underset{\underset{CH_2CH_2{-}NH{-}\underset{\underset{O}{\|}}{C}{-}(CF_2)_6CF_3}{|}}{N}{-}C_2H_4{-}\overset{\overset{CH_2CH_2{-}NH{-}CH_2CH_2SO_2CH=CH_2}{|}}{N}{-}C_2H_4{-}\underset{\underset{CH_2CH_2SO_2CH=CH_2}{|}}{N}{-}C_2H_4{-}NH{-}\overset{\overset{O}{\|}}{C}{-}(CF_2)_6CF_3}$$

with pyridine hydrochloride.

The oil- and water-repellent compounds of the invention are useful in treating paper as well as textiles (fabrics and fibers) comprised of natural or synthetic fibers including cotton, nylon, wool, polyethylene terephthalate and polyacrylonitrile. The fluorinated quaternary ammonium salts of the invention are especially useful in the treatment of fabrics and fibers comprised of cellulosic and certain cellulosic derivatives which contain cellulosic hydroxyl groups such as cotton, linen, viscose, cupra ammonium rayon, saponified celulose acetate and salts of cellulose xanthate. The invention is also applicable to the treatment of blends of natural and/or synthetic fibers in cloth, for example, blends containing polyethylene terephthalate, polyacrylonitrile, nylon, cotton and wool. If desired, auxiliary agents such as those imparting crease resistance, permanent press properties and softening properties may be applied in conjunction with the fluorinated quaternary ammonium salts of the invention. In addition, other materials such as the surfaces of wood, plastics, glass and metals may be treated with solutions or dispersions containing the fluorinated quaternary ammonium salts of the invention to render the same oil- and water-repellent.

The fluorinated quaternary ammonium salts of the present invention may be applied to the article to be rendered oil-repellent by treating the same with a solution or dispersion of the repellent and evaporating the solvent or dispersant. If desired, the treated article may then be cured at an elevated temperature. The concentration of the oil- and water-repellent compound on the treated article generally may vary from about 0.5% to 20%, preferably 1.0% to 10.0%, based on the weight of the article. Since the fluorinated quaternary ammonium salts of the present invention are soluble or dispersible in water, they are preferably applied from an aqueous solution or an aqueous dispersion, although, if desired, any organic liquid inert to the article to be treated and capable of dissolving or dispersing the requisite amount of oil- and water-repellency agent may be employed. Acetone, methyl ethyl ketone, acetonitrile and dimethylformamide are illustrative organic liquids which may be used in preparing oil- and water-repellent compositions comprising fluorinated quaternary ammonium salts of the present invention.

The solvent or dispersant may be evaporated by air drying at room temperature. If it is desired to cure the treated articles the solvent or dispersant may be evaporated prior to curing or during curing of the oil- and water-repellent chemical onto the articles. Preferably, the article treated with a solution or dispersion of the fluorinated quaternary ammonium salt is air dried prior to curing for a time sufficient to evaporate essentially all of the solvent or dispersant. Thereafter, the article having on its surface the oil- and water-repellent chemical is cured or "heat-set" at a temperature of about 100° C. to 160° C. for a time period varying inversely with the temperature, ranging from about 1 second to 5 minutes.

When cellulosic textile materials are to be rendered oil- and water-repellent, the fluorinated quaternary ammonium salts of the present invention are preferably applied thereto from an aqueous solution or an aqueous dispersion and in the presence of a catalyst of the type commonly used as crosslinking catalyst for crosslinking resins with cellulose materials. The fluorinated quaternary ammonium salts of the present invention respond well to both basic and acidic catalysts, thus offer the decided advantage that their application is compatible with permanent press treatment of textiles, which treatment commonly employs acidic reactants and/or catalysts. The cellulosic textile material is moistened with an aqueous solution of the catalyst, air dried to remove residual water and then impregnated with an aqueous solution or dispersion of the fluorinated quaternary ammonium salt of the invention for a time, normally 30 seconds to about 30 minutes, sufficient to retain on the cellulosic textile material about 1 to 20%, preferably 2 to 8% of the oil- and water-repellency agent, based on the weight of the cellulosic textile material. The thusly impregnated cellulosic textile material is then heated at a temperature of 100° C. to 165° C. for a time period varying inversely with the temperature ranging from about 15 minutes to 30 seconds. After the reaction of the fluorinated quaternary ammonium salt with the cellulosic textile material is complete, the chemically modified cellulosic textile material is washed free of excess catalyst with water and dried.

Various modifications of the above-described treatment may also be employed without departing from the spirit of the invention. For example, the cellulosic textile material may be first impregnated with an aqueous solution or dispersion of the fluorinated quaternary ammonium salt, then treated with an aqueous solution of the catalyst, air dried and finally heated to effect reaction of the fluorinated quaternary ammonium salt with the cellulosic material. Another modification of the above-described procedure involves premixing the aqueous solution or dispersion of the fluorinated quaternary ammonium salt together with the catalyst prior to impregnation of the cellulosic textile material.

Chemical modification of cellulosic material under anhydrous conditions, as in the presence of solvents capable of penetrating cellulosic fibers such as benzene, chloroform, dioxane and acetone, constitutes still another variation of the afore-described procedures.

In general, suitable basic catalyst should have a dissociation constant in water of at least 1.8×10^{-5} at 25° C. Phosphates, carbonates and hydroxides of alkali metals such as sodium phosphate, sodium carbonate, sodium hydroxide and potassium hydroxide; alkaline-earth metal hydroxides including calcium hydroxide and magnesium hydroxide; and quaternary ammonium hydroxides such as tetraethyl ammonium hydroxide and benzyl trimethyl ammonium hydroxide are illustrative of preferred effective basic catalysts. Suitable acid catalysts are the mineral acids and strong organic acids, as well as the ammonium salts, amine salts and metal salts of strong acids. The salts of strong acids are preferred acid catalyst, ammonium chloride, magnesium chloride, zinc nitrate and zinc chloride being specific examples of preferred acid catalysts. The catalyst concentration is normally dependent upon the strength of the acid or base selected, speed of reaction desired and the nature of the cellulosic material to be treated. In general, catalyst concentrations of about 1 to 20%, preferably 2 to 5%, based on the weight of the solution are satisfactory.

Results of tests relating to the evaluation of a typical fluorocarbon derivative compositions of the present invention as oil- and water-repllency agent on textiles are shown below.

The procedure employed in determining the oil-repellency ratings on textiles is described, for example, on pages 323–4 of the April 1962 edition of the Textile Research Journal. This procedure involves gently placing on the treated fabric drops of mixtures of mineral oil ("Nujol") and n-heptane in varying proportions. The drops are allowed to stand on the treated fabric undisturbed for 3 minutes. After the 3 minute time period the wetting and penetration of the fabric is visually observed. Referring to following Table I, the number corresponding to the mixture containing the highest percentage of heptane which does not penetrate or wet the fabric is considered to be the oil-repllency rating of the treated fabric.

TABLE I

Oil-repellency rating	Percent mineral oil [a]	Percent n-heptane [b]
150	0	100
140	10	90
130	20	80
120	30	70
110	40	60
100	50	50
90	60	40
80	70	30
70	80	20
60	90	10
50	100	0
0	No holdout to mineral oil	

[a] "Nujol" Saybolt viscosity 360/390 at 100° F. Specific gravity 0.880/0.900 at 60° F. Percent by volume at 20° C.

[b] Heptane B.P. 98–99° C. Percent by volume at 20° C.

When typical oily staining materials are dropped onto treated fabrics and subsequently blotted off, those fabrics with an oil-repllency rating of 50–70 will exhibit only fair resistance to staining; those fabrics with an oil-repellency rating of 80–90 will have good resistance to staining; and those with an oil-repellency rating of 100 and up will give excellent resistance.

Hydrophobic properties of the treated cloth were determined by Method 22–1961 of the American Association of Textile Chemists and Colorists which is described, for example, on pages 152–153 of the Technical Manual and Yearbook of that association for the year 1961. It is to be noted that this method provides for no interpolation of results which are reported as one of the Standard Spray Test ratings which are the six ratings 0, 50, 70, 80, 90 and 100.

Wash fastness of the treated cloth was determined by subjecting the cloth to repeated launderings in hot water in a household automatic washing machine using a heavy duty detergent, followed by drying in an automatic household drier. The material was ironed prior to testing.

The results obtained are set forth in Table II below.

TABLE II

Specimen	Loading (wt. percent)	Catalyst	Oil repellency after launderings								Water repellency after launderings							
			0	1	2	3	4	5	6	7	0	1	2	3	4	5	6	7
a	16.0	NaOH	130	110	110	110	110	110	110	110	70	50	50	50	50	50	50	50
b	4.5	$MgCl_2$	140	110	110	110	110	110	110	110								
c	7.0	CH_3COONa	140	110	110	110	110	110	110	110								

NOTE.—1,7-bis(perfluorooctanoyl)-4[2-(2-pyridiniumethylsulfonyl)ethyl]1,4,7-triazaheptane chloride was dissolved in water in amount calculated to give a 4% aqueous solution. The solution remained cloudy even upon warming to 60° C. Weighed specimens of 80 x 80 count cotton print cloth, pre-conditioned at 50% R.H. were totally immersed for three minutes in aqueous catalyst solutions consisting of 5% sodium hydroxide (specimen a), 5% magnesium chloride (specimen b), and 5% sodium acetate (specimen c). The specimens were wrung and dried at 85° C. for 10 minutes. The specimens were then impregnated by total immersion for 10 minutes in individual portions of the 4% aqueous repellency agent solution, described above, were dried at 85° C. for 10 minutes and were then cured at 150° C. for a 5 minute period. The specimens were then gently rinsed in cold water, redried at 85° C. for 10 minutes, ironed, and conditioned at 50% R.H. The specimens were weighed to determine loading and were then subjected to the initial oil- and water-repellency tests. After each laundering and before each subsequent repellency test, the specimens were again ironed and conditioned at 50% R.H.

In the treatment of paper to render the same oil- and water-repellent, the fluorinated quaternary ammonium salts of the present invention may be applied thereto either externally, as by treating the paper with a solution or dispersion of the repellent and evaporating the solvent or dispersant in the manner described above, or the repellent may be applied thereto internally, as by adding the repellent to the furnish from which the paper is to be formed, and then forming the paper in the usual manner. When paper is to be rendered oil- and water-repellent by internal treatment, the fluorinated quaternary ammonium salts of the present invention are suitably added to the furnish in amount of between about .2% and about 4%, dry weight basis, preferably between about .5% and about 2%, dry weight basis. The repellent may be added to the furnish neat or in form of its solution or suspension in water or one of the above-described solvents or dispersants.

If desired, the repellent may be added to the furnish together with any of the usual additives, such as fillers, e.g. kaolin, China clay, calcium carbonate, titanium dioxide; sizes, e.g. rosin, hydrocarbon and natural waxes, natural gums, starches, casein, asphalt emulsions, synthetic resins, cellulose derivatives; coloring matter, e.g. dyes and pigments; and alum.

Preparation of the paper from the furnish to which the repellent has been added, as described above, follows conventional paper making procedure.

Oil-repellency tests on paper specimens rendered oil-repellent by both external and internal treatment with an illustrative fluorinated quaternary ammonium salt of the present invention are described below.

The procedure employed in determining the oil-repellency ratings on paper is described, for example, in a Technical Bulletin issued by the Minnesota Mining and Manufacturing Company entitled, "Paper Chemical FC-805—IV. Properties of Treated Paper—C. Oil Resistance—2. Comparative Kit Test." This procedure involves gently placing on treated paper drops of mixtures of castor oil, toluene and heptane in varying proportions. The drops are allowed to stand on the treated paper undisturbed for 15 seconds. After the 15-second period, the wetting and penetration of the paper is visually observed. Failure is detected by pronounced darkening caused by penetration. The darkening of even a small portion of the area under the drop is considered failure. The number corresponding to the mixture containing the highest percentage of heptane which does not penetrate or wet the paper is the "Kit Number" of the paper and is considered to be the oil-repellency rating of the treated paper. Table III below shows the compositions of the oil mixtures and corresponding "Kit Numbers."

TABLE III

	Volume		
	Castor oil	Toluene	Heptane
Kit No.:			
1	200	0	0
2	180	10	10
3	160	20	20
4	140	30	30
5	120	40	40
6	100	50	50
7	80	60	60
8	60	70	70
9	40	80	80
10	20	90	90
11	0	100	100
12	0	90	110

Papers having a "Kit Number" of about 5–6 or below will exhibit only fair oil-repellency; those papers having a "Kit Number" of 8–10 will have good oil-repellency; and those having a "Kit Number" of 10 or above will have excellent oil-repellency.

Handsheets of unsized 50/50 hardwood/softwood pulp beaten to 400 ml. Canadian Standard freeness were impregnated with 1,7-bis(perfluorooctanoyl) - 4 - [2-(2-pyridiniumethylsulfonyl)ethyl] - 1,4,7-triazaheptane repellent by total immersion for a period of 60 seconds in a 0.4% by weight aqueous solution of the repellent. After the 60-second period, the handsheets were removed from the repellent solution, excess repellent solution was removed by blotting with blotting paper, and the sheets were dried on a laboratory handsheet drier at 115° C. for a period of 1½ minutes. The handsheets were then conditioned at 50% R.H. at 72° C. for a period of 72 hours and were then subjected to the oil-repellency test, above described. The handsheets had a "Kit Number" of 9–10, indicating excellent oil-repellency.

Twelve grams of a 50/50 mixture hardwood/softwood bleached kraft pulp, beaten to 70 seconds Williams freeness were dispersed in 500 ml. water using a "Waring" (T.M.) blender, 5 seconds at low speed followed by 15 seconds at high speed, to form a homogeneous slurry. This slurry was diluted to 0.40% consistency, the 1,7-bis (perfluorooctanoyl) - 4 - [2-(2-pyridiniumethylsulfonyl) ethyl]-1,4,7-triazaheptane repellent was added in form of its aqueous solution in predetermined amounts, the slurry was agitated by slow stirring to evenly distribute the repellent solution in the slurry, and the slurry was divided into three equal portions. Each of these portions was then diluted to 0.05% consistency, and each portion so diluted was fed to a Williams handsheet mold to form 7½ x 7½ in. handsheets. The sheets so formed were then pressed to a consistency of about 32% using a Noble and Wood handsheet press, and were then dried at 115° C. for a 1½ minute period using a Noble and Wood rotary handsheet drier. Oil-repellency of the sheets so formed was determined immediately after drying and again after these sheets were aged for 24 hours at 50% R.H. at 72° C. Results of the oil-repellency tests are summarized in Table IV below.

TABLE IV

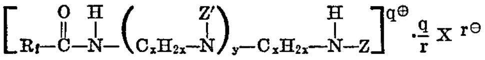
Amount of repellent added to slurry (percent dry wt. basis)	"Kit Number"	
	Off the drier	Aged 24 hours
0.1	2	3
0.2	5	5
0.3	6	7
0.5	8	
0.6		12
0.7	9	
0.9	10	
1.1	10	

When textiles and paper materials are treated with other fluorinated quaternary ammonium salts of the present invention in the manner described above, similar results are obtained, that is to say, good oil-repellency is imparted to the materials so treated.

Since various changes and modifications may be made in the invention without departing from the spirit or essential characteristics, it is intended that all matter contained in the above description shall be interpreted as illustrative and not restrictive, the invention being solely limited by the scope of the appended claims.

We claim:

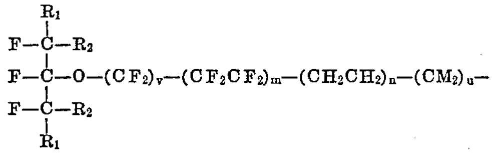
1. Compounds having the structural formula



$$\left[R_f-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\left(C_xH_{2x}-\overset{Z'}{\overset{|}{N}}\right)_y-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Z\right]^{q\oplus}\cdot\frac{q}{r}X^{r\ominus}$$

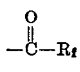
wherein

(1) R_f is a radical selected from the group consisting of
  (a) perfluoroalkyl having from 3 to 17 carbon atoms, and
  (b) a radical having the formula



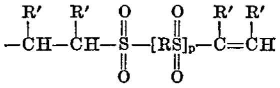
  wherein
    (i) R_1 and R_2 are fluorine or are fluoroalkyl groups, or when taken together, are fluoroalkylene groups forming a cycloaliphatic structure, which R_1 and R_2 groups may each have from 1 to 9 carbon atoms, provided that not more than three of the R_1 and R_2 groups may be fluoroalkyl groups,
    (ii) *m* and *n* are each integers of from 0 to 20, with the proviso that the sum of *m* and *n* is from 0 to 20, and provided further that when *v* is 0, *m* is at least 1,
    (iii) M is selected from the group consisting of hydrogen and fluorine, with the proviso that when *n* is greater than 0, then M is always hydrogen,
    (iv) *u* is 0 or 1,
    (v) *v* is 0 or 1, with the proviso that when the sum of *m*, *n* and *u* is greater than 0, then *v* is always 0,

(2) *x* is an integer from 2 to 6,
(3) *y* is an integer from 1 to 4,
(4) Z is a member selected from the group consisting of
  (a) hydrogen,
  (b) an acyl radical having the formula



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

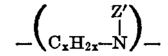
  wherein R_f has the afore-stated meaning, and
  (c) a vinyl sulfone radical having the formula



$$-\overset{R'}{\overset{|}{C}H}-\overset{R'}{\overset{|}{C}H}-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-[R\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}]_p-\overset{R'}{\overset{|}{C}}=\overset{R'}{\overset{|}{C}H}$$

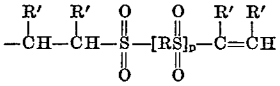
  wherein
    (i) *p* is 0 or 1,
    (ii) R is an alkylene, aryl or aralkyl radical, and
    (iii) R′ is hydrogen, an alkyl, an aryl or a substituted aryl radical,

(5) Z′, which may be the same or different in different



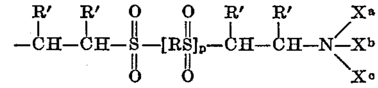
$$-\left(C_xH_{2x}-\overset{Z'}{\overset{|}{N}}\right)-$$

groups, is a member selected from the group consisting of
  (a) hydrogen,
  (b) a vinyl sulfone radical having the formula

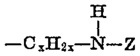


$$-\overset{R'}{\overset{|}{C}H}-\overset{R'}{\overset{|}{C}H}-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-[R\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}]_p-\overset{R'}{\overset{|}{C}}=\overset{R'}{\overset{|}{C}H}$$

  wherein R, R′ and *p* have the afore-stated meanings,
  (c) a sulfone-tertiary amine adduct radical having the formula



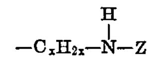
  wherein *p*, R, R′ have the afore-stated meanings, and X^a, X^b and X^c collectively represent the residue of the pyridine, methyl-substituted pyridine or quinoline ring systems and,
  (d) a radical having the formula



$$-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Z$$

  wherein *x* and Z have the afore-stated meanings,

(6) X is a negatively charged ion selected from the group consisting of a halide ion, a sulfate anion, an acid sulfate anion, a phosphate anion, and an acid phosphate anion,
(7) *q* is a whole number from 1 to 4 corresponding to the number of sulfone-tertiary amine adduct radicals present in the molecule,
(8) *r* is a whole number from 1 to 3 corresponding to the valency of the negatively charged ion, with the proviso that Z is an acyl radical or Z′ is a radical having the formula



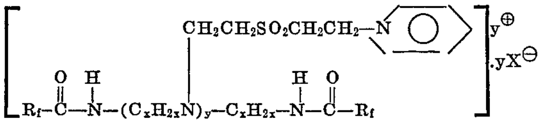
$$-C_xH_{2x}-\overset{H}{\overset{|}{N}}-Z$$

wherein Z is an acyl radical and in at least one occurrence Z′ is a sulfone-tertiary amine adduct radical,

$$-C_xH_{2x}-N-Z$$

said acyl and sulfone-tertiary amine adduct radicals having the afore-stated formulas.

2. Compounds according to claim 1 having the structural formula

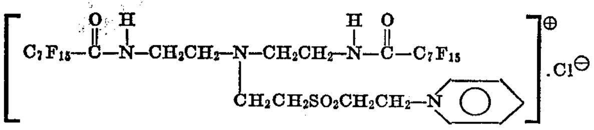


wherein R_f, *x* and *y* have the afore-stated meanings and wherein X represents a halide ion.

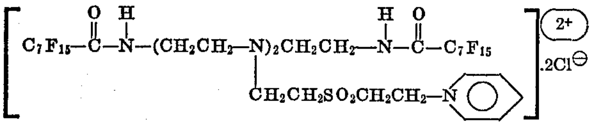
3. Compounds according to claim 2 wherein R_f is a perfluoroalkyl radical containing from 6 to 14 carbon atoms, *x* is an integer from 2 to 4 and *y* is an integer from 1 to 4.

4. Compounds according to claim **3** wherein X is a chloride ion.

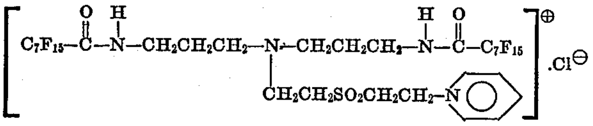
5. A compound according to claim **4** having the structural formula



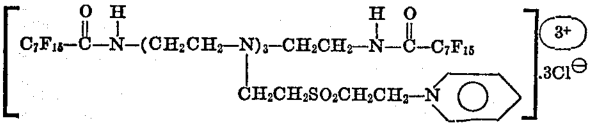
6. A compound according to claim **4** having the structural formula



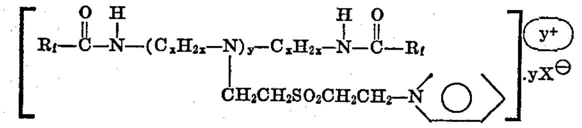
7. A compound according to claim **4** having the structural formula



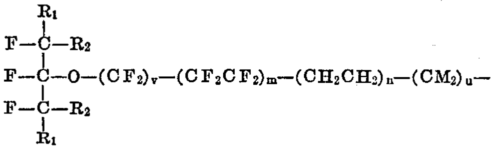
8. A compound according to claim **4** having the structural formula



9. Compounds according to claim **1** having the structural formula



wherein *x* and *y* have the meanings given in claim **1**, X represents a halide ion, and R_f is a radical having the formula



wherein R_1, R_2, M, *v*, *m*, *n* and *u* have the meanings given in claim **1**.

10. Compounds according to claim **9** wherein the R_f radical has the formula

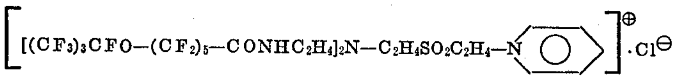
$$(CF_3)_2CFO—(CF_2CF_2)_m—(CH_2CH_2)_n—(CM_2)_u—$$

wherein *m* is an integer from 1 to 10, *n* is an integer from 0 to 10, with the proviso that the sum of *m* and *n* is from 1 to 10, and wherein M and *u* have the meanings stated in claim **9**.

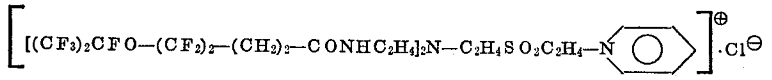
11. Compounds according to claim **10** wherein *x* is an integer from 2 to 4.

12. Compounds according to claim **11** wherein X is a chloride ion.

13. A compound according to claim **12** having the structural formula



14. A compound according to claim **12** having the structural formula



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