United States Patent Office 3,446,570 Patented May 27, 1969

3,446,570

NOVEL FLUOROCARBON DERIVATIVES

Richard F. Sweeney, Dover, and Koei-Liang Liauw, Morristown, N.J., assignors to Allied Chemical Corporation, New York, N.Y., a corporation of New York

No Drawing. Filed Aug. 25, 1965, Ser. No. 482,597
Int. Cl. D06m 13/08
U.S. Cl. 8—116.2 9 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to a new class of fluorocarbon derivatives and to their application to textile materials to produce oil- and water-repellent products. More particularly, this invention relates to reaction products of perfluoroalkyl polyamide compounds with vinyl sulfone compounds, to treatment of textile materials therewith to render the same oleophobic and hydrophobic, and to textile products treated therewith so as to have been rendered oil- and water-repellent.

Various fluorochemicals have heretofore been employed in the treatment of textiles to impart thereto oil- and water-repellency properties. In general, these fluorochemicals are composed of a perfluoroalkyl 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 prefluoroalkyl chain. The portion of the molecule to which tht perfluoroalkyl chain is affixed provides the physical and chemical bond between the perfluoroalkyl chain and the substrate surface. This bond not only influences the degree of orientation and packing of the perfluoro groups of the perfluoroalkyl chain, and hence, the oil- and water-repellency properties of the fluorochemical, but in particular, determines the durability of the oleophobic and hydrophobic properties obtained. Although some of the prior art fluorochemicals have obtained acceptable levels of oil- and water-repellency, prolonged oil- and water-repellency effects have not been realized using these prior art chemicals. For example, when these chemicals are used for the coating and sizing of textile fabrics and fibers, they are readily removed in laundering and dry cleaning treatments. Apparently, the bonds formed by the active functional group of the fluorochemicals with the treated substrate surface are unstable when the substrate surface is exposed to repeated laundering and dry cleaning treatments. There is, therefore, a great need for oil- and water-repellency agents not only capable of obtaining high levels of oil- and water-repellency but also capable of maintaining oleophobic and hydrophobic properties of substrate surfaces treated therewith after their repeated exposure to laundering and dry cleaning treatments.

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

Another object is to provide oil- and water-repellent compositions of said fluorocarbon derivatives suitable for treating textiles, in particular, cellulosic materials, to impart thereto oleophobic and hydrophobic properties.

A still further object is to provide methods for the treatment of textiles employing said fluorocarbon derivatives.

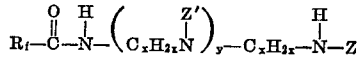
A further object is to provide textile materials treated with the fluorocarbon derivatives of the present invention.

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

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

In accordance with the invention, reaction products of perfluoroalkyl polyamide compounds with vinyl sulfone compounds have been found to impart to textile materials oil- and water-repellency properties which properties not only are superior than those characteristic of commercially available oil- and water-repellent agents but which are also more durable when cellulosic materials, in particular, treated with the novel reaction products, are exposed to repeated laundering and dry cleaning treatments. In addition, certain of the fluorocarbon derivatives of this invention, namely, those containing more than one vinyl sulfone radical hereinbelow identified, also may exhibit crease- and muss-resistance properties not possessed by the oil- and water-repellent agents of the prior art.

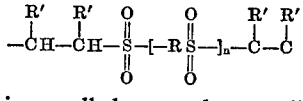
The compounds proposed for use as oil- and water-repellency agents conform to the general formula:



wherein R_f is a perfluoroalkyl radical containing of from 3 to 17 carbon atoms, x is an integer of from 2 to 6, y is an integer of from 1 to 4, Z is a member selected from the group consisting of hydrogen, an acyl radical having the formula



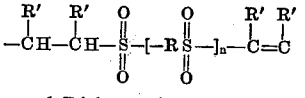
in which R_f has the afore-stated meaning and a vinyl sulfone radical having the formula



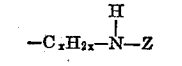
in which R is an alkylene, aryl or aralkyl radical, n is 0 to 1 and R' is hydrogen, an alkyl, an aryl or a substituted aryl radical and Z' is a member selected from the group consisting of hydrogen, an acyl radical having the formula



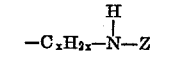
in which R_f has the afore-stated meaning, a vinyl sulfone radical having the formula



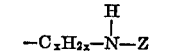
in which R, n and R' have the afore-stated meaning and a radical having the formula



in which x and Z have the afore-stated meaning, with the proviso that at least one of Z and Z' is an acyl radical or a radical having the formula



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

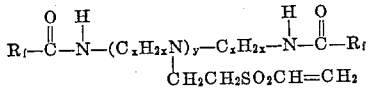


wherein Z is a vinyl sulfone radical, said acyl and vinyl sulfone radicals having the afore-stated formulas.

In the above formulas, R_f represents the same or a different saturated straight-chain or branched-chain perfluoroalkyl group, preferably containing from 6 to 14

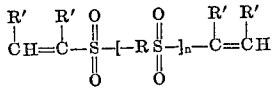
carbon atoms. The alkylene (C_xH_{2x}) linkage may be a straight-chain or branched-chain group, preferably containing from 2 to 4 carbon atoms. R may be a straight-chain or branched-chain alkylene radical containing from 1 to 4 carbon atoms; an aryl radical such as phenyl or naphthyl; or an aralkyl radical such as benzyl, phenethyl or xylyl. R′ may 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 para-nitrophenyl.

Compounds corresponding to the general formula:



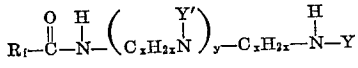
wherein R_f, x and y have the afore-stated meanings constitute preferred embodiments of the present invention.

The vinyl sulfone reactant employed in the preparation of the novel fluorocarbons of the present invention 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:

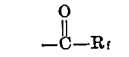


wherein R, R′ and n are as previously defined. Specific examples of vinyl sulfone reactants employable herein include divinyl sulfone; dipropenyl sulfone; di-isopropenyl sulfone; distyryl sulfone; bis(1-hexenyl) sulfone; bis-(alpha-ethylvinyl) sulfone; dis(alpha-n-butylvinyl) sulfone; bis(alpha-phenylvinyl) 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. If desired, the sulfone reactant may comprise a compound capable of forming a vinyl sulfone in situ at reaction conditions at which the textile material is treated with the fluorocarbon derivatives of the invention. Typical compounds exhibiting these properties are the bis(β-hydroxyethyl) sulfones, the lower alkanoic carboxylic acid esters thereof and compounds of the class described for example, in the U.S.P. 3,000,762 of Sept. 19, 1961.

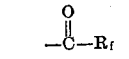
The perfluoroalkyl polyamide reactant suitable for reaction with the above sulfone compounds is characterized by the structural formula:



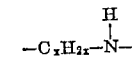
wherein R_f, x and y have the above-stated meanings, Y is a member selected from the group consisting of hydrogen and an acyl radical having the formula



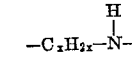
in which R_f has the afore-stated meaning and Y′ is a member selected from the group consisting of hydrogen, an acyl radical having the formula



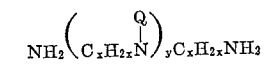
in which R_1 has the afore-stated meaning and a radical having the formula



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



in which Y is an acyl radical, said acyl radical having the stated formula, and at least one of Y and Y′ is hydrogen. The perfluoroalkyl polyamide reactant herein contemplated is prepared by reaction of a perfluorocarboxylic acid or derivative thereof such as an ester, anhydride or acid halide thereof with a polyalkylene polyamine corresponding to the formula:



wherein x and y have the afore-stated meaning and Q is hydrogen or an aminoalkyl radical having the formula $-C_xH_{2x}NH_2$ in which x has the afore-stated meaning, as described and claimed in our copending application Ser. No. 482,599 filed of even date. The reaction product, obtained as a result of the reaction of the perfluorocarboxylic acid and polyalkylene polyamine reactants above described, may comprise a single compound conforming to the above-stated structural formula, a mixture of isomers thereof or a reaction mass composed of amide products containing two or more amide functions. The resulting perfluoroalkyl polyamide is suitable without further purification for direct use as an intermediate in the preparation of the fluorocarbon derivatives of the present invention. However, if desired, the perfluoroalkyl polyamide may be further purified prior to reaction with the vinyl sulfone reactant, as by distillation or recrystallization using any commonly employed inert organic solvent such as acetonitrile or chloroform.

The novel fluorocarbon derivatives of this invention are prepared by heating a mixture of the sulfone reactant with the perfluoroalkyl polyamide starting material, above described. These reactants may be charged in a mol proportion of 1 mol of perfluoroalkyl polyamide to about 1 to 10, preferably about 2 to 4, mols of sulfone reactant. The reaction temperature and time are dependent upon the particular perfluoroalkyl polyamide and sulfone reactants involved. The temperature ranges from about 25° C. to 160° C., preferably about 40° C. to 90° 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 and, when present, the maximum temperature employable is limited only by the reflux temperature of the mixture. Although the reaction may be effected at superatmospheric pressure, it is preferred to conduct the reaction at atmospheric pressure.

At the conclusion of the reaction, the reaction mixture is cooled to ambient conditions and treated with water to effect insolubilization of the fluorocarbon derivative of the present invention. When a discrete molecular species of perfluoroalkyl polyamide is subjected to reaction with the vinyl sulfone reactant, the desired product is obtained as a solid and may be recovered by conventional means, as by filtration. However, when mixtures of perfluoroalkyl polyamides are employed as a starting material in the process, the desired fluorocarbon derivative is obtained as a liquid and may be recovered as the distilland by distillation of the reaction mass.

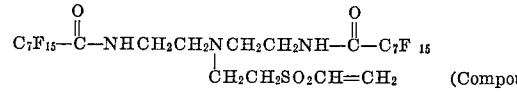
The resulting solid or liquid fluorocarbon product of the reaction is suitable for direct application as an oil- and water-repellency agent without further purification. However, if desired, the fluorocarbon product may be further purified prior to treatment therewith of the textile material, as by distillation or recrystallization from any inert organic solvent such as carbon tetrachloride or acetonitrile.

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

EXAMPLE 1

Solid 1,7 - di - n - perfluorooctanoyl - 1,4,7 - triazaheptane (2.4 grams) was heated at 130 to 140° C. in 15 ml. of dimethylformamide until all of the solid dissolved. To this solution was added 2 ml. of divinyl sulfone, and the

resulting reaction mixture was heated to 140° C. for 3 hours. The reaction product was cooled to room temperature and transferred to a separatory funnel. Thereafter, 25 ml. of water was added and a yellow water-insoluble oil layer was formed. The oily product was extracted with two 25 ml. portions of diethyl ether, the ether extracts were combined, washed with two 25 ml. portions of water and dried over anhydrous magnesium sulfate. The ether was evaporated under vacuum, and the resulting yellow solid residue was recrystallized from carbon tetrachloride. The product of the reaction, 1,7-di-n-perfluorooctanoyl - 4- (β - vinylsulfonyl) - ethyl - 1,4,7 - triazaheptane, was a solid melting at 93–94° C. It is represented by the following structural formula:

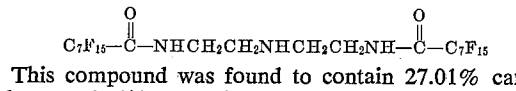


(Compound I)

This compound was found to contain 28.4% carbon (theory 28.5%), 1.6% hydrogen (theory 1.69%), 4.0% nitrogen (theory 4.16%) and 2.83% sulfur (theory 3.17%).

The perfluoroalkyl diamide reactant was prepared in the following manner:

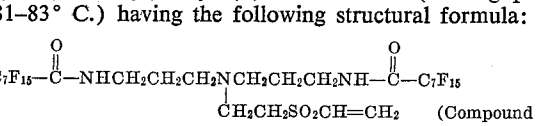
A solution of 49 grams (0.475 mol) of diethylene triamine in 60 ml. of diethyl ether was placed in a reaction vessel equipped with a dropping funnel, condenser, magnetic stirrer and a calcium chloride drying tube. After chilling the vessel in an ice water bath for a period of about 20 minutes, 34.2 grams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



This compound was found to contain 27.01% carbon (theory 26.8%), 1.45% hydrogen (theory 1.23%) and 4.74% nitrogen (theory 4.71%).

EXAMPLE 2

Ten grams of 1,9-di-n-perfluorooctanoyl-1,5,9-triazanonane were heated to 80° C. in 30 ml. of dimethylformamide for a few minutes to effect solution. To this solution 5 ml. of divinyl sulfone were added and the reaction mixture was heated to 90° C. for a period of about 3 hours. The reaction mixture was cooled to room temperature and transferred to a separatory funnel. A total of 30 ml. of water was added to the reaction mixture and a yellow water-insoluble oil layer was formed. The oily layer was extracted with two 25 ml. portions of diethyl ether and the combined ether extract was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether, a pale yellow oil remained which formed a gel on standing. The gel was recrystallized from carbon tetrachloride to yield 1,9-di-n-perfluorooctanoyl-5-(β-vinylsulfonyl)-ethyl-1,5,9-triazanonane (melting point 81–83° C.) having the following structural formula:

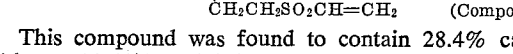


(Compound II)

This compound was found to contain 29.6% carbon (theory 30.0%), 1.92% hydrogen (theory 2.02%), 3.7% nitrogen (theory 4.03%) and 55.8% fluorine (theory 54.8%).

The prefluoroalkyl diamide reactant was prepared in the following manner:

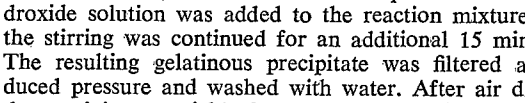
To a solution of 20 grams (0.0467 mol) of methyl-n-perfluorooctanoate in 25 ml. of diethyl ether, there was added 3.07 grams (0.0235 mol) of di-n-propylene triamine. The resulting solution was heated under reflux temperature for a period of 24 hours. After removal of the solvent under reduced pressure, 16.6 grams of a light yellow oil which solidified in about 30 minutes to give a white sticky solid were obtained. The white sticky solid was recrystallized from acetonitrile to yield 1,9-di-n-perfluorooctanoyl-1,5,9-triazanonane (a white powder melting at 84–85° C.) having the following structural formula:



This compound was found to contain 28.63% carbon (theory 28.58%), 59.56% fluorine (theory 61.66%), 1.57% hydrogen (theory 1.63%) and 4.77% nitrogen (theory 4.55%).

EXAMPLE 3

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

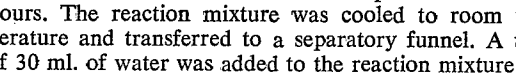


(Compound III)

This compound was found to contain 30.6% carbon (theory 30.7%), 5.46% sulfur (theory 5.48%), 4.99% nitrogen (theory 4.78%) and 48.4% fluorine (theory 48.7%).

The perfluoroalkyl diamide reactant was prepared in the following manner:

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

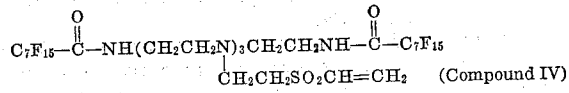


This compound was found to contain 28.51% carbon (theory 28.15%), 62.50% fluorine (theory 60.74%), 1.86% hydrogen (theory 1.72%) and 6.41% nitrogen (theory 5.97%).

EXAMPLE 4

To a solution of 16 grams (0.037 mol) of methyl perfluorooctanoate in 20 ml. of diethyl ether there was added 3.5 grams (0.018 mol) of tetraethylenepentamine. The resulting solution was heated to reflux temperature for a period of 3 hours. After removal of the diethyl ether solvent under reduced pressure there remained a viscous yellow oil which did not solidify on standing. This oil was dissolved in 15 ml. of dimethylformamide by heating to 85° C. for a few minutes. To this solution 6 ml. of divinyl sulfone was added and the mixture was heated

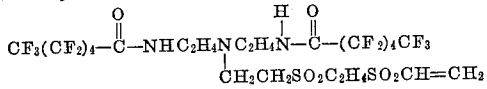
to 85° C. for a period of 3 hours. Thereafter the reaction mixture was cooled and 20 ml. of water were added thereto. A water-insoluble oil layer was formed which was extracted with two 25 ml. portions of diethyl ether and the combined ether extracts were dried over magnesium sulfate. After removal of the ether solvent by evaporation under reduced pressure, a viscous yellow oil was obtained. When the product oil was subjected to distillation, it began to decompose at 180–190° C. and 2–3 millimeters pressure. The product oil, 1,13-di-n-perfluorooctanoyl-4,7,10-tri(β-vinylsulfonyl) - ethyl - 1,4,7,10,13-pentaazatridecane, having the following structural formula:



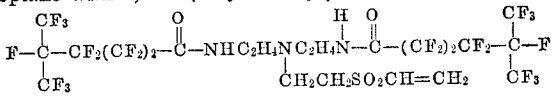
(Compound IV)

was soluble in acetone and acetonitrile.

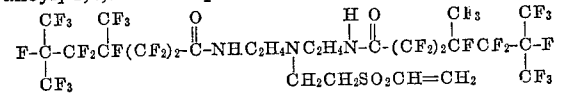
In a manner analogous to that described in the above examples, other compounds illustrative of the present invention may be prepared as follows:



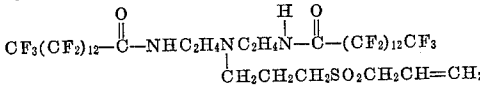
by reaction of 1,7-di-n-perfluorohexanoyl-1,4,7-triazaheptane with 1,2-bis(vinylsulfonyl) ethane



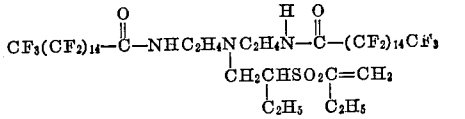
by reaction of 1,7-di-[(5-trifluoromethyl) perfluorohexanoyl]-1,4,7-triazaheptane with divinyl sulfone.



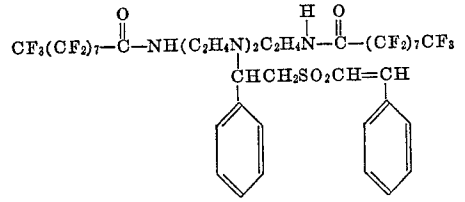
by reaction of 1,7-di-[(4,6-di-trifluoromethyl) perfluoroheptanoyl]-1,4,7-triazaheptane with divinyl sulfone.



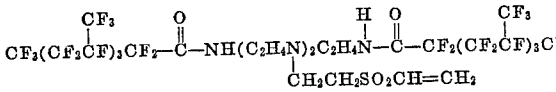
by reaction of 1,7-di-n-perfluorotetradecanoyl-1,4,7-triazaheptane with dipropenyl sulfone.



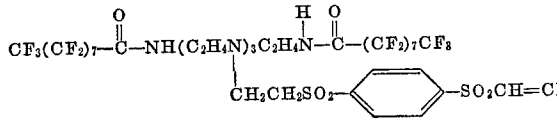
by reaction of 1,7-di-n-perfluorohexadecanoyl-1,4,7-triazaheptane with bis(alpha-ethylvinyl) sulfone.



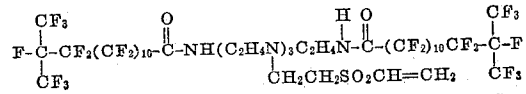
by reaction of 1,10-di-n-perfluorononanoyl-1,4,7,10-tetraazadecane with distyryl sulfone.



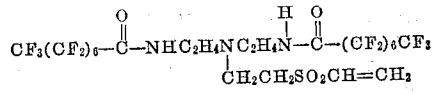
by reaction of 1,10-di-[(3,5,7-tri-trifluoromethyl) perfluorononanoyl]-1,4,7,10-tetraazadecane with divinyl sulfone.



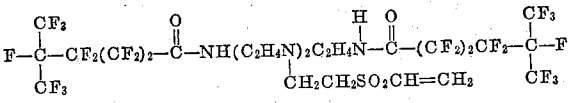
by reaction of 1,13-di-n-perfluorononanoyl-1,4,7,10,13-pentaazatridecane with 1,4-bis(vinylsulfonyl) benzene.



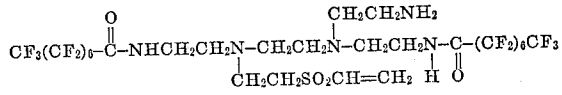
by reaction of 1,13-di-[(13-trifluoromethyl) perfluorotetradecanoyl] - 1,4,7,10,13 - pentaazatridecane with divinyl sulfone.



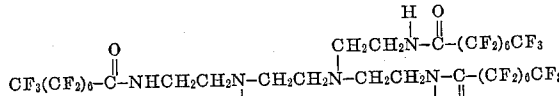
by reaction of 1,11-di-n-perfluorooctanoyl-1,6,11-triazaundecane with divinyl sulfone.



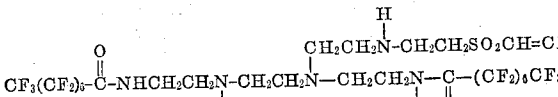
by reaction of 1,13 - di - [(5 - trifluoromethyl) perfluoroheptanoyl] - 1,5,9,13 - tetraazatridecane with divinyl sulfone.



by reaction of 1,10-n-diperfluorooctanoyl-7-(2-aminoethyl)-1,4,7,10-tetraazadecane with divinyl sulfone.



by reaction of 1,10-n-diperfluorooctanoyl-7-(2-n-perfluorooctanamidoethyl) - 1,4,7,10 - tetraazadecane with divinyl sulfone.



by reaction of 1,10 - n - diperfluorooctanoyl-7-(2-aminoethyl)-1,4,7,10-tetraazadecane with divinyl sulfone.

The oil- and water-repellent compounds of the invention are useful in treating textiles (fabrics and fibers) comprised of natural or synthetic fibers including cotton, nylon, wool, polyethylene terephthalate and polyacrylonitrile. The fluorocarbon derivatives 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 cellulose 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 water repellency, crease resistance and softening properties may be applied in conjunction with the fluorocarbon chemicals of the invention. In addition, other materials such as the surfaces of wood, plastics, glass, paper and metals may be treated with solutions containing the fluorocarbon derivatives of the invention to render the same oil- and water-repellent.

The fluorocarbon derivatives of the present invention may be applied to the article to be rendered oil-repellent by treating the same with a solution of the repellent and evaporating the solvent. If desired, the treated article may then be cured at an elevated temperature. The concentration of the fluorocarbon derivative on the treated

article generally may vary from about 0.5% to 10%, preferably 1.0% to 4.0%, based on the weight of the article. Since the solvent used in formulating the oil- and water-repellent composition functions essentialy as a carrier for the fluorocarbon derivative, any organic liquid inert to the article to be treated and capable of dissolution of the requisite amount of oil- and water-repellency agent may be employed. Acetone, methyl ethyl ketone, acetonitrile and dimethylformamide are illustrative solvents which may be used in preparing the oil- and water-repellent compositions. Alternatively, aqueous emulsions of the oil- and water-repellent may be applied onto the articles to be treated by conventional aqueous application methods.

The solvent may be evaporated by air drying at room temperature. If it is desired to cure the treated articles the solvent may be evaporated prior to curing or during curing of the oil- and water-repellent chemical onto the article. Preferably, the article treated with a solution of the fluorocarbon derivative is air dried prior to curing for a time sufficient to evaporate essentially all of the solvent. 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 materials are to be rendered oil- and water-repellent, the fluorocarbon derivatives of the present invention are preferably applied thereto from an aqueous solution or an aqueous emulsion and in the presence of a basic catalyst. The cellulosic material is moistened with an aqueous solution of the basic catalyst, air dried to remove residual water and then impregnated with an aqueous solution or emulsion of the fluorocarbon derivative of the invention for a time, normally 30 seconds to about 30 minutes, sufficient to retain on the cellulosic material about 1 to 10%, preferably 2 to 4% of the fluorocarbon derivative, based on the weight of the cellulosic material. The thusly impregnated cellulosic 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 fluorocarbon derivative with the cellulosic material is complete, the chemically modified cellulosic 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 material may be first impregnated with an aqueous solution or emulsion of the fluorocarbon derivative, then treated with an aqueous solution of the basic catalyst, air dried and finally heated to effect reaction of the fluorocarbon derivative with the cellulosic material. Another modification of the above-described procedure involves premixing the aqueous solution or emulsion of the fluorocarbon derivative together with the basic catalyst prior to impregnation of the cellulosic material. Chemical modification of the 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.

Any strong alkaline material which is inert to the sulfone reactant is suitable as a catalyst in effecting the chemical modification of the cellulosic material. In general, the 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 quarternary ammonium hydroxides such as tetraethyl ammonium hydroxide and benzyl trimethyl ammonium hydroxide are illustrative of preferred effective basic catalysts. The catalyst concentration is normally dependent upon the strength of the 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.

Tests relating to the evaluation of typical fluorocarbon derivative compositions of the present invention as oil- and water-repellency agents were conducted. In addition, oil- and water-repellency durabilities of textile test specimens treated with fluorocarbon derivative compositions of this invention were compared with oil- and water-repellency durabilities of textile test specimens treated with commercially available oil- and water-repellent fluorocarbon derivative compositions.

The procedure employed in determining the oil-repellency ratings 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-repellency rating of the treated fabric.

TABLE I

Oil-repellency rating	Percent mineral oil [1]	Percent n-heptane [2]
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	

[1] "Nujol" Saybolt viscosity 360/390 at 100° F. Specific gravity 0.880/0.900 at 60° F. Percent by volume at 20° C.
[2] 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-repellency 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 Method 61–1961 (Test II A) of the American Association of Textile Chemists and Colorists which method is described on pages 105–106 of the Technical Manual and Yearbook of that association for the year 1961. Conditions employed in this test give results which correlate with the results of five average, careful hand launderings at a temperature of 120° F.

The effect of repeated dry cleaning of the treated cloth was determined by Method 85–1060T of the American Association of Textile Chemists and Colorists which method is described on pages 87–88 of the Technical Manual and Yearbook of that association for the year 1961. This test is based on an extensive series of interlaboratory tests which showed there is good correlation between the test and 3 commercial dry cleanings in a 4% charged system using perchloroethylene solvent.

The results obtained are set forth in Tables II and III below:

TABLE II

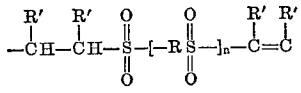
Fluorocarbon derivative	Treated textile	Loading (percent by weight)	Oil-repellency rating	Water-repellency rating
I	Wool [1]	4.8	90	70
I	Dacron [2]	5.0	120	50
I	Nylon [2]	3.3	100	50

[1] Test pieces of the textile cloth (worsted flannel), conditioned ai 50% R.H., were impregnated by total immersion in a 4% acetone solution of the fluorocarbon derivative, blotted on paper toweling after removal from the sample solution and air dried overnight. The impregnated cloths were then heated for 5 minutes in an oven at 155° C. Thereafter the test pieces were conditioned at 50% R.H., weighed to determine the loading (amount of fluorocarbon derivative retained on the cloth), ironed and tested for oil- and water-repellency.

[2] Test pieces of the textile cloth (sheer dacron and nylon taffeta), conditioned at 50% R.H., were dipped in acetone for 4 minutes, air dried for 8 minutes and weighed. The weighed cloths were then impregnated by total immersion in a 4% acetone solution of the fluorocarbon derivative, air dried for 8 minutes at 50% R.H. and weighed to determine the loading (amount of fluorocarbon derivative retained on the cloth). The thusly treated test pieces were then ironed and tested for oil- and water-repellency.

6, y is an integer of from 1 to 4, Z is a member selected from the group consisting of hydrogen, an acyl radical having the formula

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



in which R is an alkylene, an aryl or an aralkyl radical, n is 0 to 1 and R′ is hydrogen, an alkyl, or substituted aryl radical and Z′ is a member selected from the group consisting of hydrogen, an acyl radical having the formula



TABLE III

Fluorocarbon derivative	Loading (Percent by weight)	Oil-repellency rating	Water-repellency rating	Oil-repellency rating (after laundering)	Water-repellency rating (after laundering)	Oil-repellency rating (after dry cleaning)	Water-repellency rating (after dry cleaning)
I	4.0	[2] 130	[2] 70	[5] 130	[5] 70	[7] 100	[7] 50
I	2.6	[2] 130	[2] 70				
I	6.3	[3] 140	[3] 70	[6] 130	[6] 50	[7] 130	[7] 50
I	6.8	[3] 140	[3] 70				
II	2.7	[2] 130	[2] 50	[5] 120	[5] 50	[8] 110	[8] 50
II	2.9	[2] 130	[2] 50				
III	4.8	[2] 130	[2] 70	[5] 110	[5] 70	[8] 120	[8] 70
III	5.5	[2] 130	[2] 70				
IV	4.3	[2] 130	[2] 70	[5] 120	[5] 70	[8] 110	[8] 70
IV	5.5	[2] 130	[2] 70				
Zepel [1]		[4] 140	[4] 100	[9] 0	[5] 50	[7] 100	[7] 50
Do		[4] 140	[4] 100				
Scotchguard [1]		[4] 110	[4] 70	[6] 0	[5] 50	[10] 0	[7] 50
Do		[4] 110	[4] 70				

[1] A commercially available oil- and water-repellent.

[2] Pieces of white cotton print cloth (80 x 80 count), conditioned at 50% R.H., were dipped in a 5% aqueous sodium hydroxide solution for 5 minutes and then air dried for a period of 30 to 45 minutes. The air dried cloths were impregnated by total immersion in a 4% by weight acetone solution of the fluorocarbon, and then blotted on paper toweling after removal from the sample solution. The impregnated cloths were then heated at a temperature of 150–160°C. for a period of about 5 minutes in an oven. The test pieces were rinsed with water, blotted with paper toweling and heated for 5 minutes at 150–160°C. Thereafter the test specimens were conditioned at 50% R.H., weighed to determine the loading (amount of fluorocarbon derivative retained on the cloth) and were ironed. The oil- and water-repellency ratings of the thusly treated cloths were then determined before and after subjection of the treated cloths to standard laundering and dry cleaning treatments.

[3] Pieces of white cotton print cloth (80 x 80 count), conditioned at 50% R.H., were impregnated by total immersion in a 4% by weight acetone solution of the fluorocarbon. The test pieces were blotted with paper toweling, then heated at 150°C. for 5 minutes in an oven. The test pieces were dipped in a 5% aqueous sodium hydroxide solution for 5 minutes, air dried for 30 minutes, and then heated at 150°C. for 5 minutes in an oven. The test pieces were rinsed with water, blotted with paper toweling and heated for 5 minutes at 150°C. Thereafter the test pieces were conditioned at 50% R.H., weighed to determine the loading (amount of fluorocarbon derivative retained on the cloth) and were ironed. The oil- and water-repellency ratings of the thusly treated cloths were then determined before and after subjection of the treated cloths to standard laundering and dry cleaning treatments.

[4] Oleophobic and hydrophobic properties of pieces of white cotton print cloth, commercially finished with the fluorocarbon derivative indicated, were determined before and after subjection of the commercially finished cloths to standard laundering and dry cleaning treatments; in these tests, the loading (amount of fluorocarbon derivative retained on the cloth) was unknown.

[5] Rating recorded after washing equivalent to 30 home launderings.

[6] Rating recorded after washing equivalent to 20 home launderings.

[7] Rating recorded after dry cleaning equivalent to 18 commercial dry cleanings.

[8] Rating recorded after dry cleaning equivalent to 12 commercial dry cleanings.

[9] Rating recorded after washing equivalent to 15 home launderings.

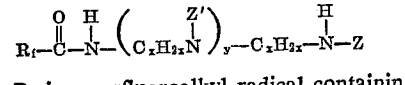
[10] Rating recorded after dry cleaning equivalent to 6 commercial dry cleanings.

From the foregoing it is apparent that we have discovered a series of novel and valuable compounds which are not only more effective than commercially available oil- and water-repellent compositions but also provide maintenance of oleophobic and hydrophobic properties of substrate surfaces treated therewith after their repeated exposure to laundering and dry cleaning treatments.

Since various changes and modifications may be made in the invention without departing from the spirit thereof, it is intended that all matter contained in the above descripion shall be interpreted as illustrative and not in a limiting sense.

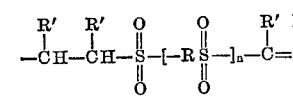
We claim:

1. A textile treated with a compound having the structural formula:

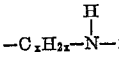


wherein R_f is a perfluoroalkyl radical containing from 3 to 17 carbon atoms, x is an integer of from 2 to

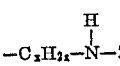
in which R_f has the afore-stated meaning, a vinyl sulfone radical having the formula



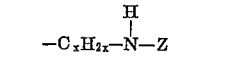
in which R, n and R′ have the afore-stated meaning and a radical having the formula



in which x and Z have the afore-stated meaning, with the proviso that at least one of Z and Z′ is an acyl radical or a radical having the formula

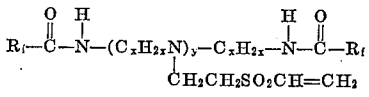


wherein Z is an acyl radical and at least one of Z and Z' is a vinyl sulfone radical or a radical having the formula



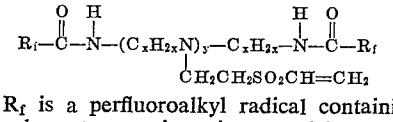
wherein Z is a vinyl sulfone radical, said acyl and vinyl sulfone radicals having the afore-stated formulas.

2. A textile treated with a compound having the structural formula:



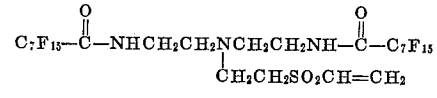
wherein R_f is a perfluoroalkyl radical containing from 3 to 17 carbon atoms, x is an integer of from 2 to 6 and y is an integer of from 1 to 4.

3. A textile treated with a compound having the structural formula:

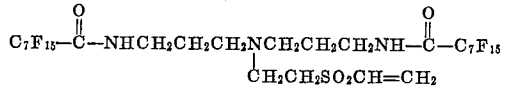


wherein R_f is a perfluoroalkyl radical containing from 6 to 14 carbon atoms, x is an integer of from 2 to 4 and y is an integer of from 1 to 4.

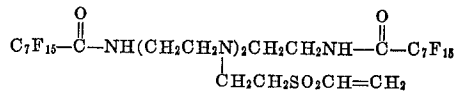
4. A textile treated with a compound having the structural formula:



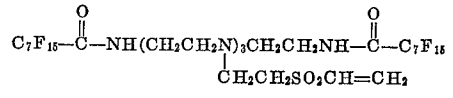
5. A textile treated with a compound having the structural formula:



6. A textile treated with a compound having the structural formula:



7. A textile treated with a compound having the structural formula:



8. A process for rendering a textile material oil- and water-repellent which comprises treating said textile material with a solution of a compound as defined in claim **1**.

9. A process for rendering a cellulosic textile material oil- and water-repellent which comprises treating said cellulosic textile material with a solution of a compound as defined in claim **1** and heat curing the resulting treated material under alkaline conditions.

References Cited

UNITED STATES PATENTS

3,128,272	4/1964	Wear.
3,274,244	9/1966	Mackenzie.
3,238,204	3/1966	Hauptschein.
3,352,625	11/1967	Gagliari.

NORMAN G. TORCHIN, *Primary Examiner.*

J. E. CALLAGHAN, *Assistant Examiner.*

U.S. Cl. X.R.

8—120; 260—561