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(54) Fluorinated paper sizes.

(57) Cellulosic products, paper and other non-woven articles are effectively sized to provide oil and water repellency thereto by the application of a treatment composition containing an acid or salt thereof which contains a fluoroaliphatic radical in the absence of any cationic resin coadditive.

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This invention relates to a method of rendering cellulosic products, paper or non-woven article oil and water repellent by applying thereto an effective amount of a stable aqueous fluorochemical solution or emulsion as a size in the absence of any cationic resin coadditive, said fluorochemical being comprised of selected multiple perfluoroalkyl terminated acids, salts or oligomers, optionally in the presence of starch or modified starch.

Conventional fluorochemical phosphate sizing agents are described in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd. Ed. Vol. 16, pp. 812-813 (1981); and in United States Patent Nos. 3,112,241; 3,492,374; 3,919,361 and 3,953,283.

Other fluorochemical sizing agents for paper are described in U.S. Patent Nos. 2,809,990; 3,382,097; 3,409,647; 3,901,864; 4,239,915; 4,302,366 and 4,426,466.

The instant method differs from that of the prior art, as exemplified by U.S. Patent No. 4,426,466, by requiring no cationic resin coadditive in order to achieve the desired level of oil and water repellency on the sized substrate.

Object of the Invention

The object of this invention is to provide a method for treating cellulosic products, paper or non-woven articles to impart oil and water repellency thereto by applying thereto an aqueous solution or emulsion of a perfluoroalkyl substituted acid, salt or oligomer in the absence of any cationic polymer retention aid.

Detailed Disclosure

The instant invention pertains to a method for treating a cellulosic product, paper or non-woven article to impart oil and water repellency thereto, which method comprises applying from an aqueous solution or emulsion to said product, paper or non-woven article an effective amount of a fluorochemical compound of formula I

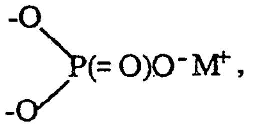
$$(R_f)_p\text{-}G\text{-}(L)_q \quad \text{(I)}$$

wherein

R_f is independently a straight or branched chain hydrophobic, oleophobic fluoroaliphatic group of 1 to 20 carbon atoms or pefluoroalkyl of 2 to 12 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms, or an oligo(hexafluoropropene oxide) terminal group,

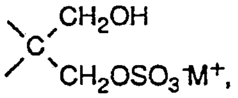
L is a moiety selected from the group consisting of

$$\text{-COO}^-M^+,\ \text{-OSO}_3^-M^+,\ \text{-SO}_3^-M^+,\ \text{-OPO(O}^-M^+)_2,$$

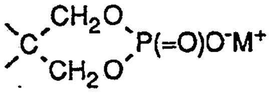


$$\genfrac{}{}{0pt}{}{\text{-O}}{\text{-O}}\!>\!P(=O)O^-M^+,\quad \text{-N}^+R_1R_2R_3Q^-,\quad \text{-[}T_1]_r\text{-[}T_2]_t\text{-H},$$

$$\text{-N}^+R_1R_2\text{-}G_1\text{-}Q_1^-,$$

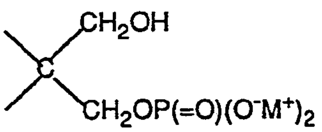


$$>C(CH_2OH)(CH_2OSO_3^-M^+),$$



$$>C\genfrac{}{}{0pt}{}{CH_2O}{CH_2O}\!>\!P(=O)O^-M^+$$

and



$$>C(CH_2OH)(CH_2OP(=O)(O^-M^+)_2)$$

wherein

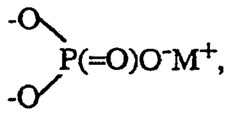
M is hydrogen, an alkali metal, ammonium or organoammonium ion;

R_1, R_2 and R_3 are independently hydrogen, alkyl of 1 to 4 carbon atoms or said alkyl substituted by hydroxyl;

Q is a halide or an anion derived from an inorganic or organic acid;
Q_1 is an anion of an inorganic or organic acid,
G_1 is a divalent radical of 1 to 6 carbon atoms, or said radical substituted by hydroxy;
T_1 is a monomer unit derived from a hydrophilic vinyl monomer or salt thereof;
T_2 is a monomer unit derived from a hydrophobic vinyl monomer;
r is 1 to 500 with the proviso that the ratio of r to t is > 0,8, t is 0 to 499 and the sum of r plus t is 1 to 500;
p is 2 to 6;
q is 1 to 6; and
G is a (p+q)-valent linking group;
when p plus q is 3, G is alkanetriyl of 4 to 24 carbon atoms, or said alkanetriyl interrupted or terminated by one or more groups selected from the group consisting of -O-, -S-, -N<, -CO-, $-NR_4-$, $-CONR_4-$, -CON<, $-SO_2NR_4-$, $-SO_2N<$, $-SO_2-$, -CH=CH-, $-C(=CH_2)CH_2-$, $-OC_2H_4-$, $-C_6H_4-$, $-C_6H_3<$, $>C_6H_2<$, $-C_6H_3Cl-$, $-C_6Cl_4-$, heteroaromatic radicals, cycloaliphatic radicals, norbornylene and combinations thereof; wherein R_4 is hydrogen or alkyl of 1 to 4 carbon atoms, and n is 1 to 20;

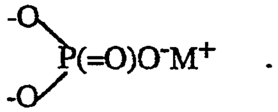
when p plus q is 4 to 12, G is alkanetetrayl, alkanepentayl, alkanehexayl, alkaneheptayl, alkaneoctayl, alkanenonayl, alkanedecayl, alkaneundecayl or alkanedodecayl of 4 to 24 carbon atoms or said alkanepoly-yl interrupted or terminated by one or more groups selected from the group consisting of -O-, -S-, -N<, -CO-, $-NR_4-$, $-CONR_4-$, -CON<, $-SO_2NR_4-$, $-SO_2N<$, $-SO_2-$, -CH=CH-, $-C(=CH_2)CH_2-$, $-OC_2H_4-$, $-C_6H_4-$, $-C_6H_3<$, $>C_6H_2<$, $-C_6H_3Cl-$, $-C_6Cl_4-$, heteroaromatic radicals, cycloaliphatic radicals, norbornylene, and combinations thereof;

with the proviso that when p is 2 and q is 1, L is not $-COO^-M^+$, $-OPO(O^-M^+)_2$ or



$$\genfrac{}{}{0pt}{}{-O}{-O}\!>P(=O)O^-M^+,$$

and that when p is 4 and q is 1, L is not



$$\genfrac{}{}{0pt}{}{-O}{-O}\!>P(=O)O^-M^+ \quad .$$

The fluorochemical sizes of the instant invention are acids, salts or oligomers which contain one or more fluoroaliphatic radicals R_f. Each R_f radical can be the same or different from the other R_f radicals in the fluorochemical compound used as the sizing agent. R_f is a monovalent, fluorinated, aliphatic, preferably saturated, organic radical having at least three fully fluorinated carbon atoms, Preferably, R_f contains not more than 20 carbon atoms since such a large radical results in the inefficient use of the fluorine content. The skeletal chain of R_f can be straight, branched or, if sufficiently large, cyclic and can include catenary divalent oxygen atoms or trivalent nitrogen atoms bonded only to carbon atoms. Preferably, R_f is fully fluorinated, but carbon-bonded hydrogen or chlorine atoms can be present as substituents on the skeletal chain of R_f provided that not more than one atom of either hydrogen or chlorine is present for every two carbon atoms in the skeletal chain of R_f and further provided that R_f contains at least a terminal perfluoromethyl group or perfluoroisopropyl moiety. Preferably R_f has an average of about 6 to 12 carbon atoms.

It is understood that the R_f group usually represents a mixture of perfluoroalkyl moieties. When the R_f group is identified as having a certain number of carbon atoms, said R_f group also usually concomitantly contains a small fraction of perfluoroalkyl groups with a higher number of carbon atoms. Commonly, the perfluoroalkyl group is preferably a mixture of C_4F_9-, $C_6F_{13}-$, $C_8F_{17}-$, $C_{10}F_{21}-$, $C_{12}F_{25}-$ and $C_{14}F_{29}-$.

Preferably R_f is independently a straight or branched chain hydrophobic, oleophobic fluoroaliphatic group of 1 to 20 carbon atoms or perfluoroalkyl of 2 to 12 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms, or an oligo(hexafluoropropene oxide) terminal group.

It is noted that G as an alkanepoly-yl group is a straight or branched chain moiety, usually branched.

Preferably, the instant compounds of formula I are represented by formula II or III

$$\overset{+-}{[MO_2C]_m}\text{-}Y\text{-}(CO)_k\text{-}O\text{-}[CH_2C(CH_2X\text{-}E\text{-}R_f)_2CH_2O]_n\text{-}(OC)_k\text{-}Y\text{-}\overset{-+}{[CO_2M]_m} \qquad (II)$$

$$\overset{+-}{[MO_2C]_m}\text{-}Y\text{-}(CO)_k\text{-}O\text{-}[CH_2C(CH_2X\text{-}R_f)_2CH_2O]_n\text{-}(OC)_k\text{-}Y\text{-}\overset{-+}{[CO_2M]_m} \qquad (III)$$

wherein R_f is a straight or branched chain perfluoroalkyl of 1 to 18 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms, E is branched or straight chain alkylene of 1 to 10 carbon atoms or said alkylene interrupted by one to three groups selected from the group consisting of -NR-, -O-, -S-, $-SO_2-$, -COO-, -OOC-, -CONR-, -NRCO-, $-SO_2NR-$ and $NRSO_2-$ or terminated at the R_f end with -CONR- or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, and for formula I, X is -S- -O-, SO_2-, or -NR-, and for formula II, X is -CONR- or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom,
k is independently 0 or 1,
when k is 0 and m is 0, Y is hydrogen,
when k is 0 and m is 1, 2 or 3, Y is a straight or branched chain alkanediyl, alkanetriyl or alkanetetrayl of 2 to 10 carbon atoms, a straight or branched chain alkenylene of 2 to 8 carbon atoms, $-C(=CH_2)CH_2-$, or benzylene,
when k is 1 and m is 1, 2 or 3, Y is a straight or branched chain alkanediyl, alkanetriyl or alkanetetrayl of 2 to 10 carbon atoms, benzenediyl, benzenetriyl or benzenetetrayl, alkylene of 2 to 8 carbon atoms substituted by one or two halogen atoms or by phenyl, a straight or branched chain alkenylene of 2 to 8 carbon atoms or said alkylene substituted by one or two halogen atoms, $-C(=CH_2)CH_2-$, xylylene, benzylene, cyclohexylene, norbornylene, benzenediyl substituted by nitro, pyridin-2,3-diyl, anilino-N,2-diyl or 4-haloanilino-N,2-diyl,
R is independently hydrogen, alkyl or hydroxyalkyl of 1 to 6 carbon atoms;
n is an integer from 1 to 3; m is independently 0, 1, 2, or 3 with the proviso that m cannot be 0 in both instances;
M is independently hydrogen, an alkali metal, ammonium or organoammonium ion.

Preferably the instant compounds of formula II are those where R_f is perfluoroalkyl of 2 to 14 carbon atoms or perfluoroalkyl of 2 to 6 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms, E is alkylene of 2 to 6 carbon atoms, $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $CH_2CH_2SO_2NCH_2CH_2-$ or $SO_2NCH_2CH_2-$, X is -S- or $-SO_2-$, and m is 1 or 2, M is an organoammonium ion.

R_f is preferably perfluoroalkyl of 6 to 14 carbon atoms, more preferably perfluoroalkyl of 6 to 12 carbon atoms.

E is preferably a branched or straight chain alkylene of 2-6 carbon atoms, or said alkylene interrupted by one group selected from the group consisting of -NR-, -O-, -S-, SO_2-, $-O_2C-$, -CONR-, and $-SO_2NR-$. Most preferably E is ethylene.

Preferably X is -S-, $-SO_2-$, or -O-; most preferably -S-, or $-SO_2-$.

Y is preferably independently hydrogen, a straight or branched chain alkylene of 1 to 4 carbon atoms, -CH=CH-, $-C(=CH_2)CH_2-$, phenylene or benzenetriyl.

R is independently hydrogen, alkyl or hydroxyalkyl of 1 to 7 carbon atoms. Preferred alkyl groups are those containing 1-6 carbon atoms such as methyl, ethyl and the like; more preferably methyl. Preferred hydroxyalkyl groups are those containing 1-3 carbon atoms, most preferably 2-hydroxyethyl.

Preferably n is 1 or 2 and m is independently 1-3, most preferably 1-2.

M is independently hydrogen, an alkali metal, ammonium or organoammonium ion. Suitable alkali metals include sodium, potassium or lithium. Sodium or potassium is the preferred alkali metal. Suitable organoammonium ions include diethanolammonium, triethanolammonium, triethylammonium and the like, preferably triethanolammonium. Preferably M is an organoammonium ion.

Preferred are compounds where R_f is perfluoroalkyl of 6 to 14 carbon atoms, E is an alkylene link of up to 10 carbon atoms, X is sulfur, and Y is alkylene of 2 to 4 carbon atoms, k is 1, and M is an organoammonium ion. i.e.

$MO_2CC_2H_4CO_2CH_2C(CH_2SCH_2CH_2R_f)_2CH_2O_2CC_2H_4CO_2M$

Most preferred are compounds where R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene, X is $-SO_2-$, Y is alkylene of 2 to 4 carbon atoms, k is 0, m is 1, and M is an organoammonium ion. i.e.

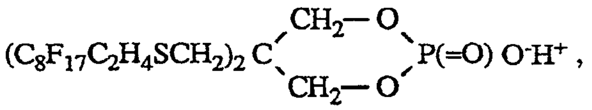
$MO_2CCH_2O[CH_2SO_2CH_2CH_2R_f)_2CH_2O]_2CH_2CO_2M$

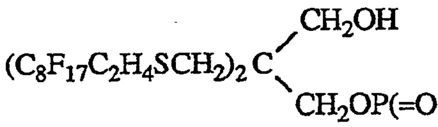
Other preferred compounds are those wherein said R_f is perfluoroalkyl of 2 to 14 carbon atoms or perfluoroalkyl of 2 to 6 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms, E is alkylene of 2 to 6 carbon atoms, $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $CH_2CH_2SO_2NCH_2CH_2-$ or $SO_2NCH_2CH_2-$, X is

-S- or -SO_2-, k is 0 or 1, m is 1 or 2, and M is an organoammonium ion.

Representative compounds of formula 1 include:

$[C_8F_{17}C_2H_4SCH(COONH_4)\text{-}]_2$,

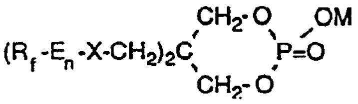




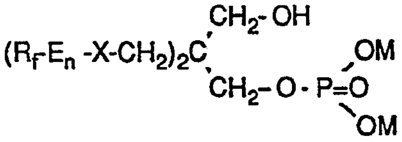
$$(C_8F_{17}C_2H_4SCH_2)_2C\begin{cases}CH_2OH\\CH_2OP(=O)(O^-M^+)_2\end{cases},$$

$(C_8F_{17}C_2H_4SCH_2)_2C(CH_2OP(=O)O^-M^+)_2$,
$(C_8F_{17}C_2H_4SCH_2)_2C(CH_2OCH_2COOH)_2$,
$(C_8F_{17}C_2H_4SCH_2)_2C(CH_2OH)CH_2OSO_3^-M^+$,
$[C_8F_{17}CH_2CH_2SO_2N(CH_2COOH)CH_2\text{-}]_2$,
$(C_8F_{17}CH_2CH_2SCH_2)C(CH_2OH)CH_2S[CH_2CH(CONH_2)]_{20}\text{-}H$,
$(C_9F_{19}CF{=}CHCH_2)_2N^+(CH_3)_2Q^-$,
$[R_fCH(OH)CH_2]_2NCH_2CH_2N^+(CH_3)_2CH_2COO^-$.

Still other preferred embodiments of the instant compounds are the R_f-neopentyl phosphorus derivatives of formula IV, V or VI

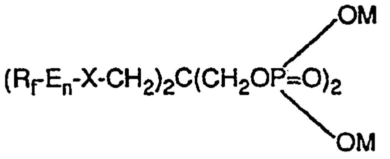


(IV)



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{cases}CH_2\text{-}OH\\CH_2\text{-}O\text{-}P(=O)(OM)_2\end{cases}$$

(V)



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C(CH_2OP(=O)(OM)_2)_2$$

(VI)

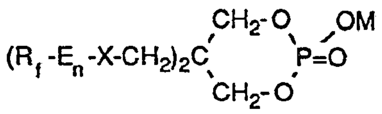
wherein R_f is a straight or branched chain perfluoroalkyl of 2 to 12 carbon atoms or perfluoroalkyl of 2 to 6 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms,

n = 1 or 0, and when n = 1,

E is a branched or straight chain alkylene of 2 to 10 carbon atoms or said alkylene interrupted by one to three groups selected from the group consisting of -NR-, -O-, -S-, SO_2-, -COO-, -OOC-, -CONR-, -NRCO-, -SO_2NR-, and -NRSO_2-, or terminated at the R_f end with -CONR- or -SO_2NR-, where R_f is attached to the carbon or sulfur atom, and X is -S-, -O-, -SO_2-, or -NR-, and when n = 0, X is a direct bond, -CONR- or -SO_2NR-, where R_f is attached to the carbon or sulfur atom, and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms, and M is independently hydrogen, lower alkyl, an alkyl- or mixed polyalkyl- substituted aromatic group, or represents an ammonium, organoammonium, alkali metal or alkaline earth metal salt of the respective phosphate group.

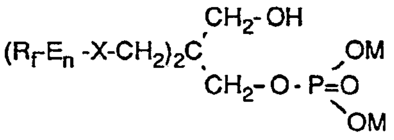
Preferably the instant compounds are those where R_f is perfluoroalkyl of 2 to 12 carbon atoms, E is alkylene of 2 to 6 carbon atoms, $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $-CH_2CH_2SO_2NHCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2-$, or $-SO_2NHCH_2CH_2-$, and X is -S-, -SO_2- or -O-.

Most preferred are compounds of the formulae



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{array}{l} CH_2\text{-}O \\ CH_2\text{-}O \end{array}\!\!\!\!\!\!\!\!\begin{array}{l} \quad\searrow \quad OM \\ \quad\ \ P{=}O \\ \quad\nearrow \end{array}$$

(IVa)



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{array}{l} CH_2\text{-}OH \\ CH_2\text{-}O\text{-}P(=O)(OM)_2 \end{array}$$

(Va)

where R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene, and X is S and M is an organo ammonium ion. The most preferred compound is 5,5-bis(1,1,2,2-perfluorodecylthiomethyl)-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane, triethanolamine salt.

The compounds of formula I wherein L is $-[T_1]_r-[T_2]_t-H$ are prepared by opening the R_f substituted oxetanes described in copending patent application Serial No. 444,073 with thiourea followed by treatment with base to form an R_f-substituted mercaptan.

The oligomerization of selected hydrophilic and hydrophobic vinyl monomers in the presence of a free radical initiator such as 2,2′-azobis(isobutyronitrile) and the R_f-substituted mercaptan forms oligomeric products of formula I where L is $-[T_1]_r-[T_2]_t-H$ where T_1,T_2,r and t have the above meaning given in formula I.

Suitable hydrophilic monomers include, without limitation, hydroxy substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, C_1-C_2-lower alkyl acrylamide and methacrylamide, ethoxylated acrylates and methacrylates, hydroxy substituted lower alkyl acrylamide and methacrylamide, hydroxy substituted lower alkyl vinyl ethers, sodium ethylene sulfonate, sodium styrene sulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinyl succinimide, N-vinyl-2-pyrrolidone, 2- and 4-vinylpyridine, acrylic acid, methacrylic acid, amino (including quaternary ammonium) substituted lower alkyl acrylates and methacrylates.

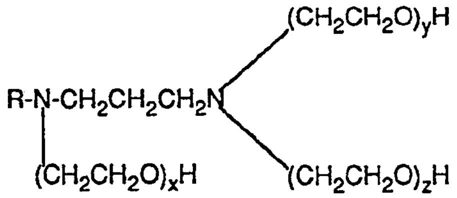
Preferably the hydrophilic vinyl monomers include 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, acrylamide, methacrylamide, N,N-dimethylacrylamide, N-vinyl-2-pyrrolidone, acrylic acid and methacrylic acid.

Suitable hydrophobic vinyl monomers include, without limitation, C_1-C_{18}-alkyl acrylates and methacrylates, acrylonitrile, styrene, vinyl alkanoates, vinyl alkyl ethers, alkenes and haloalkenes.

Preferably the hydrophobic vinyl monomers include methyl methacrylate and vinyl acetate.

Prior-art di-perfluoroalkyl group containing acids as described in U.S. 4,239,915; 4,419,298; 4,426,466; 3,478,116, and 3,578,701 are disclosed as useful, inter alia, for textile treating or as chromium complexes which are useful as grease or oil repellents for paper. Unfortunately, these acids possess, in general, very limited water solubility and therefore require an organic solvent, or the like, for the application of the di-perfluoroalkyl group containing acids to the cellulose, synthetic or natural polyamide substrate in order to obtain the desired oil and water repellent properties. Such organic solvent containing solutions are often undesirable due to odor, toxicity and flammability hazards. Furthermore, such organic solvent containing systems tend to be inefficient.

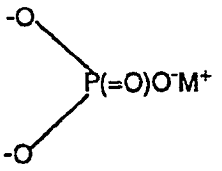
It is an object of the present invention to avoid such problems by utilizing the ammonium and amine salts of the present invention prepared by reacting the corresponding di-perfluoroalkyl group containing acids with ammonia or the amine in a diluent substantially inert to the acid and ammonia or amine reactants. The reaction can be produced at temperatures between 0° and 100°C, preferably at ambient temperature conditions. Where the amine is introduced in gaseous forms, such as anhydrous ammonia or methyl amine, it can be bubbled through the acid in the liquid diluent medium. As the reaction tends to be exothermic, cooling of the reaction vessel may be advantageously employed. Where the inert diluent is organic in nature, such as a lower alkanol, for example methanol, diethylene glycol dimethyl ether or the like, the ammonium or amine salts reaction product can be recovered by precipitation, or evaporation of the diluent. The ammonium or amine salt need not be separated from the solvent media. The amines should be water soluble mono- or polyamines having a water solubility of at least 2 % by weight. Suitable amines are aminomethane, aminoethane, 1-aminopropane, 2-aminopropane, 1-aminobutane, -amino-2-methyl-propane, 1,1-dimethylethylamine, 1-aminopentane, isoamylamine, tert-amylamine, allylamine, dimethylamine, diethylamine, diisopropylamine, trimethylamine, triethylamine, tri-n-butylamine, ethylenediamine, 1,2-propanediamine, trimethylenediamine, 1,3-diaminobutane, 1,4-diaminobutane, hexamethylene diamine, diethylenetriamine, triethylenetriamine, tetraethylenepentamine, polyethyleneimine having an average of about 20, 80, 120 or 200 units, diethylaminopropylamine, ethanolamine, diethanolamine, triethanolamine, ethylenediaminetetraacetic acid, nitrilotrisacetic acid, N-(hydroxyethyl)-ethylenediamine, N,N"-bis-(hydroxyethyl)-diethylenetriamine, N,N,N′-tetrakis-(2-hydroxypropyl)-ethylendiamine, N-(2-hydroxypropyl)-ethylenediamine, cyclohexylamine, dicyclohexylamine, 1,8-diamino-p-methane, and



where R is tallow fatty alkyl and x+y+z is 3, 10 or 15, fatty diethanolamines, mono-, di, and tri-isopropanolamines, polyoxyethyleneamines.

Alternately, quaternary ammonium salts can be obtained from tetraalkylammonium bases by neutralization.

Many bis-perfluoroalkyl phosphates of formula



have been used as paper sizes, as described in U.S. 3,083,249. Variant structures, many of which may be similarly useful, are described in U.S. Patent Nos. 3,094,547; 3,112,241; 3,492,374; 3,810,772; 3,812,217; 3,817,958; 3,911,056; 3,919,361; 3,976,698; and EP 280, 115, 288,933; and 299,307.

These products have been used for over twenty years and are the most commonly used sizing agents, in part because they are approved by the FDA for indirect food-contact packaging. The products are sold as 33 wt. % solids solutions in water with either isopropanol or 2-butoxyethanol as the cosolvent. As external sizes, they have inferior performances to the subject acid salts, particularly at low add-ons. As internal sizes, they can only be retained efficiently with cationic retention aids.

Phosphate products such as SCOTCHBAN FC-807 (3M Co.) and ZONYL RP (DUPONT CO.) contain single-tailed perfluoroalkyl impurities that detract from the product effectiveness. These impurities are volatile, and act as surfactants allowing water wetting and penetration. In fact these by-products are themselves sold as surfactants - namely, ZONYLS FSE, FSP, FSJ, and UR. Preferred products of phosphate, carboxylate or other type acid functionalities should consist of 98 % or greater of multiple R_f-tailed products to minimize volatility and wetting.

Novel, and entirely twin-tailed, bis-perfluoroalkyl phosphates useful for paper sizing are the subject of a copending U.S. Patent application Serial No. 513,356.

Multiply perfluoroalkyl terminated acid salts, and oligomers are useful to coat paper surfaces because they have a low free surface energy that provides oil and water repellency. Compounds containing a single R_f-function are much more readily available, but do not provide nearly the same degree of repellency to preformed paper especially when applied from solution or emulsion. Further, they do not have sufficient thermal stability.

Prior-art bis-perfluoroalkyl terminated monocarboxylic acid salts are not sufficiently soluble as concentrates or in the pad bath media. It is necessary for an external size that it be applied from homogeneous solution, without the concurrent use of emulsifiers or surfactants, since they detract from oil and water repellency. This is accomplished, according to this invention, by designing the effective molecule with an increased hydrophilic/lipophilic balance (HLB) to insure solubility.

Whereas many multiple tailed acids or salts have been reported, few have been made that have adequate hydrolytic stability to function satisfactorily as paper sizes. Fluorochemicals containing ester functions lack the requisite aqueous stability to provide a product with extended shelf life, since the product realistically has to withstand hydrolysis at ambient temperatures approaching 40°C for extended periods of time. It is appreciably more difficult to synthesize hydrolytically stable structures.

The acids also must be thermally stable with regard to bond fragmentation and/or volatility to at least 200°C, for 1-2 hours, in order to be acceptable for baking applications. One feature that affects volatility is that the molecule generally has to have a molecular weight of greater than 1000. The need for such a high molecular weight is not expected, but must be due at least in part to the high surface area exhibited by a good paper size. This generally precludes the use of single-tail R_f chemicals. Features affecting thermal stability vary with each candidate structure, but can be quantified by high temperature baking studies, thermal gravimetric analyses, and differential scanning calorimetry.

Monomeric or low molecular weight products are preferred for optimum surface coverage at low application levels since they can more freely orient themselves when compared with high molecular weight polymers that have fixed bond distances. Fluorochemical polyurethanes, for example, perform inadequately at low application levels.

Further, the structure must be at least 1 % soluble in water so that it can be pre-diluted in the pad bath before application. This factor is quite important and can generally be predetermined by consideration of the hydrophobic/lipophobic balance (HLB) of the molecule under consideration. It is critical that the sizing agent retain good solubility. Practical performance criteria can only be determined by actual testing and are quantified Certain useful long chain bis-perfluoroalkyl terminated carboxylic acids and salts thereof are the subjects of copending U.S. Patent applications Serial Nos. 444,073 and EP-A-O 376 882 include

$(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)SCH(CO_2H)CHCH_2CO_2H$,
$(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OCH_2CO_2H)$, and
$(C_8F_{17}CH_2CH_2SO_2CH_2)_2C(CH_2OCH_2CO_2H)_2$

Other suitable carboxylic acids or salts thereof, that have been described for various applications, but not as external paper sizes, include-

$(R_fCH_2CH_2)_2C(COOH)_2$; U.S. Pat. No. 3,578,701
$[(CF_3)_2CFO(CF_2)_4(CH_2)_9CH(COOH)]_2$-S; U.S. Pat. No. 3,828,098
$[CF_3(CF_2)_5O(CF_2)_2CH_2CH(CF_2CF_2COOH)]_2$-; U.S. Pat. No. 4,083,756
$[(R_fCH_2CH_2S)CH(COOH)]_2$-; U.S. Pat. 4,426,466
$[C_8F_{17}SO_2N(CH_2CO_2H)CH_2]_2$-; E.P. 0319942
$[C_7F_{15}CON(CH_2CH_2CO_2H)CH_2]$- E.P. 0319942

Additional compounds with acceptable hydrophilic functionalities for this invention include-

1. $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2S(CH_2CHCONH_2)_{20}$-H
2. $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2S(CH_2CHCOOH)_7$-H
3. $[C_8F_{17}CH_2CH_2SO_2N(CH_2CO_2H)CH_2]_2$-
4. $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2OSO_3^-M^+$

4. $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2OSO_3^-M^+$

Compounds 1. and 2. are prepared by the oligomerization of $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2SH$ and acrylamide and acrylic acid respectively. The mercaptan is prepared from the bromohydrin described in copending U. S. Patent application Serial No. 444,073.

Compound 3. is prepared analogously to other diacids cited in EP 0319942.

Compound 4. is prepared by sulfation of the diol described in U.S. Patent No. 4,898,981.

Compounds with other possibly suitable functionalities that have been reported, but have not been suggested as external paper sizes, are

$(R_fCONH)_2$-C_6H_3-$NHCONHCH_2CH_2SSO_3Na$; Ger. Offen. 2115139
$(C_9F_{19}CF{=}CHCH_2)_2N^+(CH_3)_2X^-$; J.P. 63- 154608
$(R_fO)2$-C_6H_3-SO_3H; J.P. 55-079454
$(R_fCH(OH)CH_2)_2NCH_2CH_2N^+(CH_3)_2CH_2CO_2^-$; GB 2018759

The subject multiple perfluoroalkyl terminated acid salts, and oligomers of formula (I) are used by dissolving them in an alkaline aqueous application formulation. Alternately, a concentrate is prepared containing 5 to 80 % by weight of the neutralized acid, optionally in the presence of excess base. The perfluorochemical is applied from water or from a solvent soluble in water to at least 0.1 %.

For topical application, suitable aqueous dilutions advantageously contain 0.005 % to 5 %, preferably 0.005 % to 0.2 % by weight of the fluorochemical at use dilution. Conventional adjuvants such as water repellent assistants, bacteriostats, coloring agents, surface conditioners and the like, may be included in an amount between about 0.01 % and 10 % by weight in the solution. Optionally, sizing agents, may be present in the amounts of 0.01 % to 10 % by weight.

The sizing agent may be a natural sizing agent such as animal glue, asphalt emulsions, wax emulsions, rosins, starches; a semi-synthetic sizing agent such as a fatty acid salt or complex, a fortified rosin, e.g., trisodium maleoprimaric acid salt, sodium alginate or sodium carboxymethyl-cellulose; or a synthetic sizing agent such as an alkylketene dimer, alkylsuccinic anhydrides, polyvinyl alcohol, styrene-maleic anhydride polymers, and the like. Also, mixtures thereof may be used.

Thus, suitable dilutions for topical application contain the following:

(a) 0.005 to 5 % by weight of the fluorochemical;
(b) 0 to 5 % water repellent assistant, filler, bacteriostat, coloring agent or surface conditioner adjuvant;
(c) 0 to 10 % sizing agent, and
(d) the remainder water.

These formulations are applied to the surface of the cellulosic, natural or synthetic material by conventional techniques, including padding, spraying, coating, washing, and brushing. After application, the treated surface is dried, with or without an intermediate washing stage. The resulting surface is now water and oil resistant.

Suitable cellulosic and natural substrates for topical application include paper, non-woven fabrics, textiles, paperboard, wood, wood fiber products such as plywood, hair, including wool, hides, leather, and feathers.

While the instant formulations are suitable for rendering a variety of materials oil and water repellent, they are particularly advantageous in rendering paper articles, both oleophobic and hydrophobic.

No cationic agent is necessary, in contrast to the teaching of U.S. Patent No. 4,426,466 that claims sizing treatment compositions, comprising fluoroaliphatic carboxylic acids, and water-soluble epoxidic resins. Such compositions are strictly for internal sizes. The use of cationic retention aids is not applicable to external sizes, only to internal sizes.

In the process of external sizing it is common to use non-charged additives such as starch, polyvinyl alcohol, protein, cellulose based thickeners and latex systems.

However, even the cations in hard water may cause precipitation, and it is common to use a chelating agent to soften the water. Cationic binding agents would interfere with the pad bath stability, and serve no useful purpose. Although they are unlikely to effect performance, the use of small quantities as auxiliaries would be considered to be within the scope of this invention.

If desired, an oxidized or cationically modified starch can be used. The use of a cationic starch to improve the performance of the subject multiple perfluoroalkyl terminated acids, salts, and oligomers of formula (I) has not previously been reported. Starches are often used as paper additives for performance and economic reasons. They effect the strength and finish of the paper, by increasing its flexibility. They also prevent dusting and linting, and promote barrier properties, by restricting the penetration of fluids, inks, and coatings into the sheet.

Suitable cationic agents, may include cationic modified starches, such as INTERBOND C, LOK-SIZE 30, CATO 2, CATO 15 and CATO 17 from Hercules Inc.

Cationic agents, conventionally used to treat cellulose materials such as paper pulp, include conventional cationic modified starches, such as INTERBOND C, LOK-SIZE 30, CATO 2, CATO 15 and CATO 17 cationic modified aminoplast resins such as KYMENE 557H from Hercules Inc.; cationic polymers such as HYPO WB-4000 with W.R. Grace Inc.

Jointly with the perfluoroalkyl group containing chemicals of the invention, one or more of a wide choice of water proofing sizing agents selected from classes such as alkyl anhydrides, e.g., FIBRON 68; alkyl ketene dimers, e.g., AQUAPEL 360 XC or HERCON 40; polyurethane emulsions, e.g., GRAPHSIZE C; acrylic resins, e.g., CARBOSET; stearyl amine surfactants, e.g., ETHOMEEN 18/25 complexed with a fatty acid, e.g., stearic acid; NEOFAT 14, NEOFAT 47 or HYSTRENE 9718, can also be added.

Suitable hydrophobic sizing agents are described by Davis, et al., TAPPI, 39 (1) pp. 21-23 (1956) and in U.S. Patent Nos. 4,243,481 and 4,279,794.

The following examples are intended for illustrative purposes only, and are not intended to restrict the scope of the invention in any way. All parts are by weight unless otherwise specified.

SAMPLE PREPARATION AND TESTING

Pad Application of Fluorochemicals as an External Size

Samples of fluorochemicals are diluted to the test application levels with distilled water. The solutions are added to a 4 % aqueous solution of papermaker's starch and then applied to unsized paper by padding (paper dipped through starch solution, and passed through single nip rollers). The resulting sheets are dried at ambient conditions for 15 minutes, then 3 minutes at 200°F (93°C) in an "Emerson Speed Drier" (heated metal plate with canvas cover).

Internal Size Application and Testing

Six grams of dry pulp are diluted in 289 ml distilled water and thoroughly dispersed in a blender. To this pulp slurry is added a 1 % dilution (as is) of the test dispersion in distilled water. This is mixed in for 5 minutes, then 6 ml of a 1 % aqueous solution of cooked cationic starch is added. This is mixed together for an additional

5 minutes. To this, 24 ml of a 50 % (on solids) dilution of a water repellent adjuvant is added. This is mixed in for another 10 minutes. The resulting slurry is diluted with an additional 500 ml of dist. water and mixed again. This mixture is then poured over a 100 mesh wire screen, with a vacuum applied from below which pulled the water from the pulp mixture to form a sheet on the screen. The wet sheet is removed from the screen and dried between another screen and hard surface at a pressure of approximately 0.4 lb/in^2 at 110°C for 1 1/2 hours. One ml of hot (110°C) corn oil is placed on the paper and the time is noted for penetrations to occur (20 min. max). Similarly, 1 ml of hot (80°C) water containing 0.5 % of Triton X-165 wetting agent (from Rohm & Haas) placed on the paper is tested. Paper made in the same manner, including the cationic starch and water repellant adjuvant but without a fluorochemical demonstrated as oil kit number of < 1, and held the hot corn oil and hot water/Triton X-165 solution for less than one minute (began to penetrate as soon as applied).

Grease Resistance Test

Creased test papers are placed over a grid sheet imprinted with 100 squares. Five grams of sand are placed in the center of the crease. A mixture of synthetic oil and a dye for visualization is pipetted onto the sand and the samples are maintained at 60°C for 24 hours. Evaluation is determined by the percentage of the grid that stains.

Another aspect of this invention describes to a substrate containing 0.005 to 5 % by weight of a fluorine-containing composition, at least part of said fluorine being provided by one or more units derived from the subject R_f-chemicals.

AATCC Oil Test

The AATCC Oil Rating was determined according to Standard Test method 118-1983 of the American Association of Textile Chemists and Colorists. Ratings are given from 0 (minimum) to 8 (maximum). A commonly accepted level of repellency for oil repellent fabrics in the United States is an oil repellency of 4.

All mentioned AATCC Tests are listed in the Technical manual of the American Association of Textile Chemists and Colorists, Volume 61, edition 1986.

Hydrolysis Test

The compound is dissolved, generally in the form of its salt, at 20 % Actives and the aqueous concentrate is heated at 60°C for two weeks. The concentrate is observed for changes in turbidity, pH, and composition. Changes of greater than 10 % in any criteria constitute failure.

Thermal Stability Test

The compound is applied to paper as an external size at 0.2 % Actives and then treated at 200°C for 1 hour. The samples are evaluated based on the Grease Resistance Test and the AATCC Oil Test. Oil penetration and/or an Oil Kit Rating below 3 indicates failure.

Solubility Test

The compound must exhibit a solubility of at least 20 % in the concentrate and 1 % in the pad bath.

Baking Test

A sample is internally sized and heated to 204°C for 30 minutes. The sample is then tested for Oil Kit, and hold-out on hot, 110°C, Corn Oil and hot, 80°C, Triton X-165 solution.

Temperatures in the Examples are given in °C unless otherwise stated.

In the following examples, where M^+ is shown, triethanolammonium salts of the subject acids are used in the evaluations.

EXAMPLE 1

This example describes comparative external size performance of certain carboxylic acid salts and a sulfate salt.

Compound A $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OCH_2CO_2^-M^+)_2$

Compound B $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2SCH(CO_2^-M^+)CH_2CO_2^-M^+$
Compound C $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2OSO_3^-M^+)$

Tests are run against the competitive commercial paper size - SCOTCHBAN FC-807 (3M Co.), a bis-pefluoroalkyl phosphate ester, ammonium salt. The performance of a twin tailed monocarboxylic-type size, described in U.S. 4,419,298, Example 59, is also compared. The products are applied to paper by pad application and tested for Oil Kit Rating and the Grease Resistance Test.

	Fluorine (Found). on Wt. of Paper	Oil Kit Number	Grease Resistance Test
Compound A	0.036	3	fail
	0.042	4	pass
Compound B	0.031	2-3	fail
	0.036	3-4	pass
Compound C	0.035	4	pass
SCOTCHBAN	0.060	6	fail
FC-807	0.066	7	pass
Example 59	0.079	6-7	fail
of U.S.	0.087	7	pass
4,419,298			

The results show that the carboxylate and sulfate salts have superior performance compared to the prior-art phosphate size at much lower application levels, as measured by the Grease Resistance Test. Further, the novel salts pass the Grease Resistance Test at lower Kit Numbers. This allows their application to products requiring better adhesive bonding, better label adhesion, and lessens problems with printing.

EXAMPLE 2

This example describes comparative external size performance of the subject 5,5-bis(1,1,2,2-tetrahydroperfluoroalkylthio-methyl)-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane, (Compound D); its mixture with the acyclic acid ester, 2,2-bis(1,1,2,2-tetrahydroperfluoroalkylthiomethyl)-3-hydroxy-1-propyl dihydrogen phosphate (Compound E), both as triethanolammonium salts, and SCOTCHBAN FC-807 (3M). The products are applied to paper by pad application and tested for Oil Kit Rating and the Grease Resistance Test. The results show that the subject phosphates have superior performance at much lower application levels. Further, the novel phosphates have the potential to pass the Grease Resistance Test at lower Kit Numbers. This allows their application to products requiring better adhesive bonding, better label adhesion, and lessened problems with printing.

% Fluorine on Wt. of Paper		Oil Kit Number	Grease Resistance Test
Compound D 0.045		7	pass Compound E
0.045		5	pass FC-807 0.065
6-7	pass		

EXAMPLE 3

This example describes comparative external size performance of oligomeric twin-R_f tailed compounds,

Compound F $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2S(CH_2CHCONH_2)_{20}\text{-}H$, and

-

Compound G $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2OH)CH_2S(CH_2CHCO_2M^+)_4\text{-}H$

	% Fluorine (Found) on Wt. of Paper	Oil Kit Number Test	Grease Resistance
Compound F	0.048	7	pass
Compound G	0.038	6	pass

The results again show that nonionic or anionic telomers can be designed to function as good external paper sizes.

EXAMPLE 4

This example compares thermal and hydrolytic stabilities of structures that are suitable for purposes of this invention to candidates that are not.

\- +

Compound K of U.S. 4,419,298 $(C_6F_{13}CH_2CH_2S)_2(CH_2CH_2COO)_2(M)_2$

\- +

Compound I $(C_8F_{17}CH_2CH_2SCH_2)_2C(CH_2O_2CCH_2CH_2CO_2NH(C_2H_5)_3)_2$

\- +

Compound J $(C_8F_{17}CH_2CH_2SO_2CH_2)_2C(CH_2O_2CCH_2CH_2CO_2NH(C_2H_5)_3)_2$

Example 3 of U.S. Pat. 4,419,298 -

$(R_fCH_2CH_2S)_2C(CH_3)CH_2CH_2CO_2$-Diethanolammonium salt + Compound L of U. S. Patent 4,419,298 $(R_fCH_2CH_2SO_2)_2C(CH_3)CH_2CH_2CO_2^-M$ triethanolammonium salt

Compound	Hydrolysis 60°C/2 weeks	Thermal Stability 200°C/60 min.	Solubility
A	pass	pass	pass
B	pass	pass	pass
C	pass	pass	pass
H	----	fail	pass
I	fail	pass	pass
J	fail	pass	pass
K	----	fail	pass
L	pass	pass	fail

As shown by Examples I and J, an ester function is not hydrolytically stable.

EXAMPLE 5

This example describes comparative internal size performance evaluations of the subject carboxylic acids, Compounds I and J versus a commercial phosphate size - SCOTCHBAN FC-807 (3M Co.), a bis-perfluoro-alkyl phosphate ester, ammonium salt. The bis-perfluoroalkyl carboxylic acids of the present invention are prepared by dissolving them in water as triethanolamine salts and using a 200 mol % excess of triethanolamine.

Hold-out Tests*

Fluorine on Wt. of paper	Oil Kit Number	Hot, 110°C Corn Oil	Hot, 80°C Water + 0.5% Triton X-165
Compound I*			
0.04	2	15 min.	> 20 min.
0.05	3-4	> 20 min.	"
0.06	4	> 20 min.	"
Compound J			
0.04	2	3	"
0.05	3	> 20	"
0.06	3	> 20 min.	"
FC-807			
0.04	2	3	"
0.05	3	> 20	"
0.06	4	> 20	"

* Compounds I and J are defined in Example 4

EXAMPLE 6

This example describes comparative external size performance of the salts of bis-perfluoroalkyl carboxylic acid (compounds I and J) against the competitive phosphate described in Example 5 and against a prior-art carboxylic-type size as described in U.S. 4,419,298, Example 59. The products are applied to paper by pad application and tested for Oil Kit Rating and the Grease Resistance Test.

The results indicate that the bis-perfluoroalkyl carboxylic acids of the present invention have superior performance at much lower application levels, by the Grease Resistance Test. Further, the novel carboxylates pass the Grease Resistance Test at lower Kit Numbers. This allows their application to products requiring better adhesive bonding and better label adhesion. It further permits the manufacturer to have lessened problems with printing.

	% Fluorine on Wt. of Paper	Oil Kit Number	Grease Resistance Test
Compound I*	0.04	5	pass
	0.05	7-8	"
Compound J	0.04	2	fail
	0.05	3-4	pass
Phosphate	0.07	6	fail
	0.08	7-8	pass
Compound of Example 59 of	0.07	5	fail
U.S.4,419,298	0.08	7	pass

* Compounds I and J are defined in Example 4.

EXAMPLE 7

This example describes comparative Baking Test performance of internally sized paper using the bis-pefluoroalkyl carboxylic acids of the present invention Compounds I and J versus the competitive phosphate described in Example 5. The products are applied as in Example 5 at 0. 1 % Fluorine on Wt. of paper.

The results for the bis-perfluoroalkyl carboxylic acids of the present invention indicate that they have similar heat resistance with regard to oil-hold out, but superior performance with regard to water-holdout.

Hold-out Tests

Time (min)	Oil Kit Number	Hot, 110°C Corn Oil	Hot, 80°C Water + 0.5 % TRITON X-165
Compound I* 30	3	> 20	> 20
Compound J 30	4	> 20	> 20
Phosphate 30	5	> 20	> 15

* Compounds I and J are described in Example 4.

EXAMPLE 8

This example describes comparative internal size performance evaluations of the subject 5,5-bis (pefluoroalkylthiomethyl)-2-hydroxy-2-oxy-1,3,2-dioxaphosphorinane, triethanolammonium salts, Compounds D and E versus a commercial phosphate size SCOTCHBAN FC-807 (3M), a bis-perfluoroalkyl phosphate ester, ammonium salt. The subject phosphoric acids are prepared in water as triethanolamine salts with an excess of triethanolamine.

The results indicate equivalent performance.

Hold-out Tests

Fluorine on Wt. of Paper		Oil Kit Number	Hot, 110°C Corn Oil	Hot, 80°C Water + 0.5 % TRITON X-165
Compund D*	0.05	4	> 20 min.	> 20 min.
Compound E	0.05	4	> 20 min.	> 20 min.
FC-807	0.05	4	> 20 min.	> 20 min.

* Compounds D and E are defined in Example 2.

Claims

1. A method for treating a cellulosic product, paper or non-woven article to impart oil and water repellency thereto, which method comprises

   applying from an aqueous solution or emulsion to said product, paper or non-woven article an effective amount of a fluorochemical compound of formula I

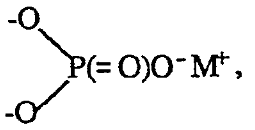
   $$(R_f)_p\text{- G -}(L)_q \quad \text{(I)}$$

   wherein

   R_f is independently a straight or branched chain hydrophobic, oleophobic fluoroaliphatic group of 1 to 20 carbon atoms or perfluoroalkyl of 2 to 12 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms, or an oligo(hexafluoropropene oxide) terminal group,

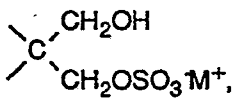
   L is a moiety selected from the group consisting of

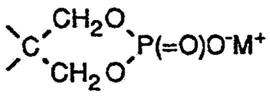
$-COO^-M^+$, $-OSO_3^-M^+$, $-SO_3^-M^+$, $-OPO(O^-M^+)_2$,



$-N^+R_1R_2R_3Q^-$, $-[T_1]_r-[T_2]_t-H$,

$-N^+R_1R_2-G_1-Q_1^-$,





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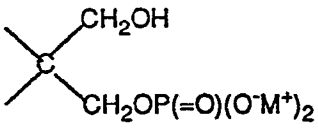
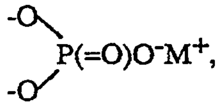


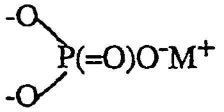
wherein
M is hydrogen, an alkali metal, ammonium or organoammonium ion;
R_1, R_2 and R_3 are independently hydrogen, alkyl of 1 to 4 carbon atoms or said alkyl substituted by hydroxyl;
Q is a halide or an anion derived from an inorganic or organic acid;
Q_1 is an anion of an inorganic or organic acid,
G_1 is a divalent radical of 1 to 6 carbon atoms, or said radical substituted by hydroxy;
T_1 is a monomer unit derived from a hydrophilic vinyl monomer or salt thereof;
T_2 is a monomer unit derived from a hydrophobic vinyl monomer;
r is 1 to 500 with the proviso that the ratio of r to t is > 0,8, t is 0 to 499 and the sum of r plus t is 1 to 500;
p is 2 to 6;
q is 1 to 6; and
G is a (p+q)-valent linking group;
when p plus q is 3, G is alkanetriyl of 4 to 24 carbon atoms, or said alkanetriyl interrupted or terminated by one or more groups selected from the group consisting of -O-, -S-, -N<, -CO-, $-NR_4-$, $-CONR_4-$, -CON<, $-SO_2NR_4-$, $-SO_2N<$, $-SO_2-$, -CH=CH-, $-C(=CH_2)CH_2-$, $-OC_2H_4-$, $-C_6H_4-$, $-C_6H_3<$, $>C_6H_2<$, $-C_6H_3Cl-$, $-C_6Cl_4-$, heteroaromatic radicals, cycloaliphatic radicals, norbornylene and combinations thereof; wherein R_4 is hydrogen or alkyl of 1 to 4 carbon atoms, and n is 1 to 20;

when p plus q is 4 to 12, G is alkanetetrayl, alkanepentayl, alkanehexayl, alkaneheptayl, alkaneoctayl, alkanenonayl, alkanedecayl, alkaneundecayl or alkanedodecayl of 4 to 24 carbon atoms or said alkanepoly-yl interrupted or terminated by one or more groups selected from the group consisting of -O-, -S-, -N<, -CO-, $-NR_4-$, $-CONR_4-$, -CON<, $-SO_2NR_4-$, $-SO_2N<$, $-SO_2-$, -CH=CH-, $-C(=CH_2)CH_2-$, $-OC_2H_4-$, $-C_6H_4-$, $-C_6H_3<$, $>C_6H_2<$, $-C_6H_3Cl-$, $-C_6Cl_4-$, heteroaromatic radicals, cycloaliphatic radicals, norbornylene, and combinations thereof;

with the proviso that when p is 2 and q is 1, L is not $-COO^- M^+$, $-OPO(O^- M^+)_2$ or



and that when p is 4 and q is 1, L is not



.

2. A method according to claim 1 wherein the fluorochemical compounds are of the formulae

$$\overset{+\,-}{[MO_2C]}_m\text{-Y-(CO)}_k\text{-O-}[CH_2C(CH_2X\text{-E-}R_f)_2CH_2O]_n\text{-(OC)}_k\text{-Y-}\overset{-\,+}{[CO_2M]}_m \quad \text{(II)}$$

$$\overset{+\,-}{[MO_2C]}_m\text{-Y-(CO)}_k\text{-O-}[CH_2C(CH_2X\text{-}R_f)_2CH_2O]_n\text{-(OC)}_k\text{-Y-}\overset{-\,+}{[CO_2M]}_m \quad \text{(III)}$$

wherein R_f is a straight or branched chain perfluoroalkyl of 1 to 18 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms, E is branched or straight chain alkylene of 1 to 10 carbon atoms or said alkylene interrupted by one to three groups selected from the group consisting of -NR-, -O-, -S-, $-SO_2-$, -COO-, -OOC-, -CONR-, -NRCO-, $-SO_2NR-$ and $NRSO_2-$ or terminated at the R_f end with -CONR- or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, and for formula I, X is -S--O-, SO_2-, or -NR-, and for formula II, X is -CONR- or $-SO_2NR-$, where R_f is attached to the carbon or sulfur

atom,
k is independently 0 or 1,
when k is 0 and m is 0, Y is hydrogen,
when k is 0 and m is 1, 2 or 3, Y is a straight or branched chain alkanediyl, alkanetriyl or alkanetetrayl of 1 to 10 carbon atoms, a straight or branched chain alkenylene of 2 to 8 carbon atoms, -C(=CH$_2$)CH$_2$-, or benzylene,

when k is 1 and m is 1, 2 or 3, Y is a straight or branched chain alkanediyl, alkanetriyl or alkanetetrayl of 2 to 10 carbon atoms, benzenediyl, benzenetriyl or benzenetetrayl, alkylene of 2 to 8 carbon atoms substituted by one or two halogen atoms or by phenyl, a straight or branched chain alkenylene of 2 to 8 carbon atoms or said alkylene substituted by one or two halogen atoms, -C(=CH$_2$)CH$_2$-, xylylene, benzylene, cyclohexylene, norbornylene, benzenediyl substituted by nitro, pyridin-2,3-diyl, anilino-N,2-diyl or 4-haloanilino-N,2-diyl,
R is independently hydrogen, alkyl or hydroxyalkyl of 1 to 6 carbon atoms;
n is an integer from 1 to 3;
m is independently 0, 1, 2, or 3 with the proviso that m cannot be 0 in both instances;
M is independently hydrogen, an alkali metal, ammonium or organoammonium ion.

3. A method according to claim 1 or 2 wherein said R$_f$ is perfluoroalkyl of 2 to 14 carbon atoms or perfluoroalkyl of 2 to 6 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms, E is alkylene of 2 to 6 carbon atoms, -CONHCH$_2$CH$_2$-, -CH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$-, CH$_2$CH$_2$SO$_2$NCH$_2$CH$_2$- or SO$_2$NCH$_2$CH$_2$-, X is -S- or -SO$_2$-, and m is 1 or 2, M is an organoammonium ion.

4. A method according to one of claim 3 wherein said R$_f$ is a perfluoroalkyl of 6 to 14 carbon atoms.

5. A method according to one of claim 4 wherein said R$_f$ is a perfluoroalkyl of 6 to 12 carbon atoms.

6. A method according to one of claims 1 to 5 wherein said E is a branched or straight chain alkylene of 2 to 6 carbon atoms or said alkylene interrupted by one group selected from the group consisting of -NR-, -O-, -S-, -SO$_2$-, -O$_2$C-, -CONR-, and -SO$_2$NR-.

7. A method according to claim 6 wherein said E is ethylene.

8. A method according to claim 1 or 2 wherein said X is -S-, -SO$_2$-, or -O-.

9. A method according to claim 8 wherein said X is -S-, -SO$_2$-.

10. A method according to claim 1 or 2 wherein said Y is independently hydrogen, a straight or branched chain alkylene of 1 to 4 carbon atoms, -CH=CH-, -C(=CH$_2$)CH$_2$-, phenylene or benzenetriyl.

11. A method according to claim 1 or 2 wherein said R is independently hydrogen, alkyl of 1 to 7 carbon atoms or hydroxyalkyl of 1 to 6 carbon atoms.

12. A method according to claim 11 wherein said R is independently hydrogen, methyl or hydroxyethyl.

13. A method according to claim 11 or 2 wherein said n is 1 or 2 and m is independently 1 to 3.

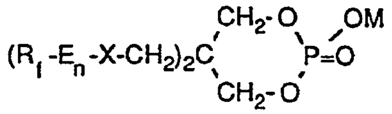
14. A method according to claim 1 or 2 wherein said M is an organoammonium ion

15. A method according to claim 1 wherein said R$_f$ is a perfluoroalkyl of 6 to 14 carbon atoms; E is an alkylene linking of up to 10 carbon atoms; X is -S-; Y is alkylene of 2 to 4 carbon atoms, k is 1, m is 1, and M is an organoammonium ion.

16. A method according to claim 1 wherein said R$_f$ is a perfluoroalkyl of 6 to 12 carbon atoms; E is ethylene, X is -SO$_2$-; Y is alkylene of 2 to 4 carbon atoms, k is 0, m is 1, and M is an organoammonium ion.

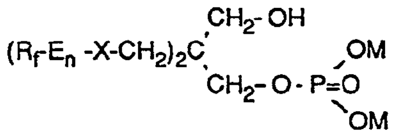
17. A method according to claim 1 wherein said R$_f$ is a perfluoroalkyl of 2 to 14 carbon atoms or perfluoroalkyl of 2 to 6 carbon atoms, substituted by perfluoralkoxy of 2 to 6 carbon atoms, E is alkylene of 2 to 6 carbon atoms, $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $-CH_2CH_2SO_2NCH_2CH_2-$ or $-SO_2NH_2CH_2-$; X is -S- or $-SO_2-$, k is 0 or 1, m is 1 or 2 and M is an organoammonium ion.

18. A method according to claim 1 wherein the fluorochemical compounds are of the formulae



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{matrix}CH_2\text{-}O\\ CH_2\text{-}O\end{matrix}P(=O)OM$$

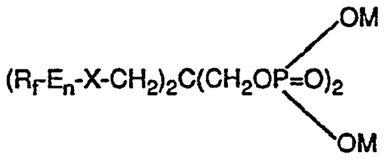
(IV)



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{matrix}CH_2\text{-}OH\\ CH_2\text{-}O\text{-}P(=O)(OM)_2\end{matrix}$$

(V)

Or



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C(CH_2OP(=O)(OM)_2)_2$$

(VI)

wherein R_f is a straight or branched chain perfluoroalkyl of 2 to 12 carbon atoms or perfluoroalkyl of 2 to 6 carbon atoms substituted by perfluoroalkoxy of 2 to 6 carbon atoms,

n = 1 or 0, and when n = 1,

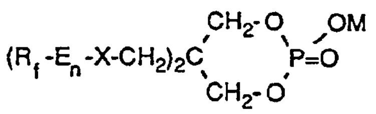
E is a branched or straight chain alkylene of 2 to 10 carbon atoms or said alkylene interrupted by one to three groups selected from the group consisting of -NR-, -O-, -S-, SO_2-, -COO-, -OOC-, -CONR-, -NRCO-, $-SO_2NR-$, and $-NRSO_2-$, or terminated at the R_f end with -CONR- or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, and X is -S-, -O-, $-SO_2-$, or -NR-, and when n = 0,

X is a direct bond, -CONR- or $-SO_2NR-$, where R_f is attached to the carbon or sulfur atom, and where R is independently hydrogen, alkyl of 1 to 6 carbon atoms or hydroxyalkyl of 2 to 6 carbon atoms, and M is independently hydrogen, lower alkyl, an alkyl- or mixed polyalkyl-substituted aromatic group, or represents an ammonium, organoammonium, alkali metal or alkaline earth metal salt of the respective phosphate group.

19. A method according to claim 18 wherein R_f is a perfluoroalkyl of 2 to 12 carbon atoms, E is alkylene of 2 to 6 carbon atoms, $-CONHCH_2CH_2-$, $-CH_2CH_2N(CH_3)CH_2CH_2-$, $CH_2CH_2SO_2NCH_2CH_2\text{-}XCH_2OCH_2CH_2-$, or $SO_2NCH_2CH_2-$, and X is -S- or 0-.

20. A method according to claim 19 wherein the compounds are of the formulae

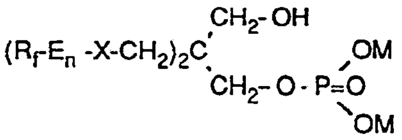
Most preferred are compounds of the formulae



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{matrix}CH_2\text{-}O\\ CH_2\text{-}O\end{matrix}P(=O)OM$$

(IVa)

Or



$$(R_f\text{-}E_n\text{-}X\text{-}CH_2)_2C\begin{matrix}CH_2\text{-}OH\\ CH_2\text{-}O\text{-}P\begin{matrix}OM\\ =O\\ OM\end{matrix}\end{matrix}$$

(Va)

where R_f is perfluoroalkyl of 6 to 12 carbon atoms, E is ethylene, and X is S and M is an organo ammonium ion.

21. A method according to of claim 20 wherein the compound is 5,5-bis(1,1,2,2-perfluorodecylthiomethyl)-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane, triethanolamine salt.

22. A method according to one of claims 1 to 21 wherein the effective amount of a compound of one of the formulae I to VI is applied from a 0.005 to 5 % by weight aqueous solution or emulsion of a compound of one of the formulae I to VI.

23. A method according to one of claims 1 to 21 wherein the effective amount of a compound of one of the formulae I to VI is applied to the cellulosic product, paper or non-woven article substrate to impart oil and water repellency thereto is 0.005 to 5 % by weight of said substrate.

24. A method according to one of claims 1 to 23 wherein the aqueous emulsion or solution additionally contains a cationic polymer retention aid.

25. A method according to one of claims 1 to 24 wherein the aqueous emulsion or solution additionally contains starch or modified starch.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 81 0425

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	DE-B-1260059 (DU PONT DE NEMOURS) * claims 1-2 * ---	1	D21H17/11 D21H17/05
D,X	US-A-4426466 (C A SCHWARTZ) * column 2, line 45; claims 1-19 * ---	1	
D,X	US-A-3953283 (J H WING ET AL) * claims 1-2 * ---	1	
X	EP-A-112297 (CIBA-GEIGY) * claims 1-21 * ---	1	
X	EP-A-73732 (CIBA-GEIGY) * claims 1-15 * ---	1	
D,X	US-A-4239915 (CIBA-GEIGY) * claims 1-11 * ---	1	
X	DE-A-2405042 (HOECHST) * claims 1-2 * ---	1	
X	EP-A-280115 (DAIKIN INDUSTRIES) * claims 1-7 * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,X	EP-A-376882 (CIBA-GEIGY) * claims 1-19 * -----	1-2	D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 SEPTEMBER 1991	FOUQUIER J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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