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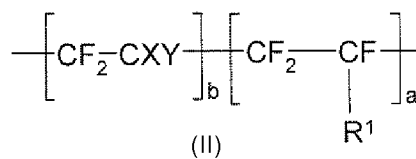
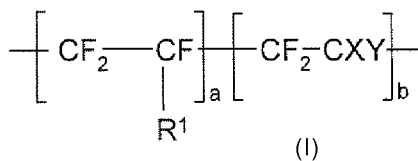
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(54) Title: FLUOROUS TELOMERIC COMPOUNDS AND POLYMERS CONTAINING SAME



(57) Abstract: Claimed are fluororous telomeric compounds of the formula $\text{R}_F - \text{A} - \text{SO}_2 - \text{Z}_2$, where R_F is a perfluoroalkyl radical of 1 to 20 carbon atoms; A is a group of the formulae (I) or (II); R^1 is CF_3 , OR^4 , Cl, Br or I; R^2 is H or alkyl of 1 to 6 carbon atoms; R^3 is alkylene of 1 to 13 carbon atoms; R^4 is perfluoromethyl, perfluoropropyl or perfluoropropoxypropyl; X and Y are H, Cl or F; Z is -OH, -Cl, -OM, $-\text{N}(\text{R}^2)\text{R}^3\text{OH}$, $-\text{N}(\text{R}^2)\text{R}^3\text{OCOCH}=\text{CH}_2$ or $-\text{Z}\text{N}(\text{R}^2)\text{R}^3\text{OCOCH}_3=\text{CH}_2$; M is an alkali metal, ammonium or a mono-, di-, tri- or tetra- C_1 - C_4 -alkylammonium cation; a is from 0 to 10 and b is from 1 to 30. These compounds are copolymerized with further monomers. The copolymers thus obtained are useful for water-, oil- and soil-repellent finishing of fibrous substrates.

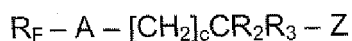
FLUOROUS TELOMERIC COMPOUNDS AND POLYMERS CONTAINING SAME

Fluorochemicals are often used as surfactants or wetting agents and are widely used for the surface treatment of substrates. They find frequent utility for the oil-, water-, and soil-repellent finishing of fibrous substrates such as for example carpets, textiles, leather, nonwovens and paper and of hard substrates such as for example wood, metal or concrete. The imbibition of hydrophilic and hydrophobic liquids is reduced with substrates thus treated, and the removal of existing soils is promoted.

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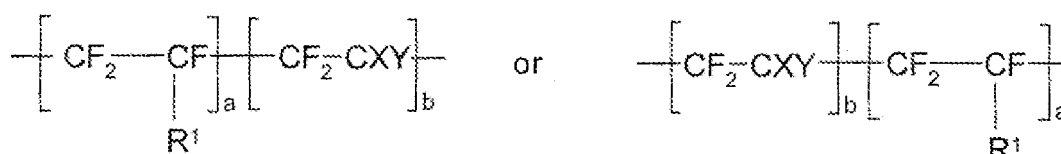
Perfluoroalkyl iodides obtained via telomerization of telogens with fluorinated monomers such as tetrafluoroethene, for example, are an important starting point for the preparation of fluorocompounds.

15 Unpublished German patent application 10 2006 001 218.6 describes fluorous telomeric compounds of the following formula:



in which R_F is a perfluoroalkyl radical of 1 to 20 carbon atoms,

A is a group of the formulae



20

R^1 is CF_3 , OR_4 , Cl, Br or I,

R_2 and R_3 are H, alkyl or aryl

R_4 is perfluoromethyl, perfluoropropyl or perfluoropropyloxypropyl

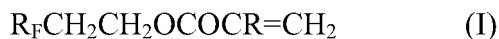
X and Y are H, Cl or F

25 Z is -OH, -OCOCH=CH₂ or -OCOCCH₃=CH₂

a is from 0 to 10, b is from 1 to 30 and c is from 1 to 30.

To be used as a surface-modifying substance, perfluoroalkyl iodides are typically first converted with ethene into a perfluoroalkylethyl iodide. The perfluoroalkylethyl iodide

can then be converted with suitable reagents into the corresponding perfluoroalkylethyl alcohol. From the perfluoroalkylethyl alcohols, then, the corresponding (meth)acrylate monomers of the formula I can be prepared.



5

The preparation of fluoruous acrylates and methacrylates satisfying the formula I from various derivatives of acrylic acid and methacrylic acid respectively is well known and documented.

- 10 Copolymers prepared from these fluoruous acrylates are particularly useful for modifying surfaces to be oil, water and soil repellent, for example for finishing textiles or for coating leather and paper.

The fluoruous monomers of the formula II



are known for similar applications.

The raw materials for these compounds are usually obtained from the corresponding non-fluorinated alkylsulphonyl halides by electrochemical fluorination. The

- 20 corresponding raw materials can also be prepared by reaction of perfluoroalkyl iodides with sulphur dioxide/metal and subsequently with chlorine.

It has been determined for both monomer types (I and II) that the coating of surfaces with longer and ideally straight-chain perfluoroalkyl chains which consist of 8-10

- 25 fluorinated carbon atoms leads to particularly low surface energies.

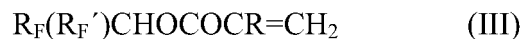
Fluoruous compounds having a linear perfluoroalkyl chain with 8 fluorinated carbon atoms, including the monomers described above, can degrade to form perfluorooctanecarboxylic acid and perfluorooctanesulphonic acid, respectively. These

30 degradation products are considered not further degradable and therefore are persistent. Moreover, these compounds are suspected of accumulating in living organisms.

There have therefore been various proposals in recent years for preparing

environmentally compatible perfluoroalkyl compounds.

WO 02/16306 describes branched fluorous (meth)acrylates having the formula III



- 5 having a straight-chain or branched perfluoroalkyl group R_F of 5 or fewer carbon atoms and a branched perfluoroalkyl chain R_F' of 3 to 5 carbon atoms. These compounds lead specifically to degradation products of low molecular weight and low toxicity.

- 10 It is known that shorter-chain perfluoroalkylsulphonic acid derivatives are more easily eliminated from the body of living organisms. The WO 03/062521 patent describes textile finishes based on perfluorobutanesulphonic acid derivatives conforming to the formula II



- 15 in lieu of perfluorooctanesulphonic acid derivatives having a partially branched perfluoroalkyl radical R_F of 4 fluorinated carbon atoms, $n = 1, 2$ and $R' = H$, alkyl and $R = H, CH_3$.

Compounds having a fluorinated alkyl radical of 4 carbon atoms and conforming to the formula I



are described in EP 1 632 542 A1. It is likely that the degradation products are more easily eliminated from the body of living organisms.

- 25 WO 02/34848 describes the use of polyoxetanes having trifluoromethyl groups or pentafluoroethyl groups as perfluoroalkyl radical. This class of compounds likewise represents environmentally compatible perfluoroalkyl-containing compounds used as fluorosurfactants or for coatings.

- 30 WO 2004/060 964 describes fluorinated polyethers having a molecular weight of greater than 750 g/mol, which are eliminated particularly easily from the body of living organisms. WO 03/100 158 describes the use of such alcohols and acrylates for finishing textiles.

However, it has emerged that the heretofore described proposals for environmentally friendly alternatives to perfluoroalkyl compounds are less effective than them when used as a basis for oil- and water-repellent finishes. This is reflected in the values achieved for water repellency and oil repellency and in coating durability.

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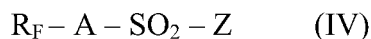
It is an object of the present invention to provide an alternative to polyfluoroalkyl-containing compounds and their derivatives which have no bioaccumulative effect. Its performance profile further includes a high effectivity when they are used for oil- and water repellent coatings. In addition, the compounds have to remain handlable on an industrial scale.

10

It has now been found that, surprisingly, polyfluoroalkyl compounds as hereinbelow defined lead to oil- and water-repellent coatings of high efficiency and durability and are also environmentally compatible.

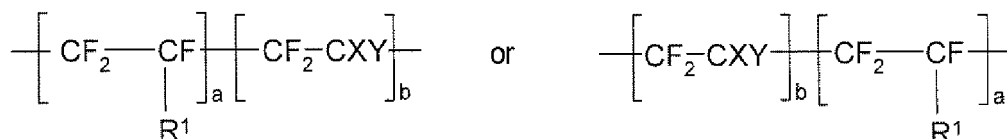
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The present invention provides fluorous telomeric compounds of the formula IV:



where R_F is a perfluoroalkyl radical of 1 to 20 carbon atoms,

A is a group of the formulae



20

R^1 is CF_3 , OR^4 , Cl, Br or I,

R^2 is H or alkyl of 1 to 6 carbon atoms,

R^3 is alkylene of 1 to 13 carbon atoms,

R^4 is perfluoromethyl, perfluoropropyl or perfluoropropoxypropyl,

25

X and Y are H, Cl or F,

Z is $-\text{OH}$, $-\text{Cl}$, OM , $-\text{N}(\text{R}^2)\text{R}^3-\text{OH}$, $-\text{N}(\text{R}^2)\text{R}^3\text{OCOCH}=\text{CH}_2$ or $-\text{N}(\text{R}^2)\text{R}^3-\text{OCOCCH}_3=\text{CH}_2$

M is an alkali metal, ammonium mono-, di-, tri- or tetra- C_1 - C_4 -alkylammonium cation,

30

a is from 0 to 10 and b is from 1 to 30.

Preference is given to fluorous compounds of the formula IV which have a molecular weight of greater than 750 g/mol. Particular preference is given to compounds of the formula IV which have a molecular weight of greater than 1000 g/mol.

5

The polyfluoroalkyl radical R_F can be a polyfluoroalkyl group having a unitary chain length or a mixture of polyfluoroalkyl groups having different chain lengths, for example CF_3 , C_2F_5 , C_3F_7 , C_4F_9 , C_6F_{13} , C_8F_{17} , $C_{10}F_{21}$, $C_{12}F_{25}$, $C_{14}F_{29}$ and $C_{16}F_{31}$ groups. The polyfluoroalkyl radical can be branched or unbranched.

10

Preference is given to compounds in accordance with the invention which have a saturated polyfluoroalkyl radical R_F which has a chain length of 1 to 20 fluorinated carbon atoms and comprises at least one terminal CF_3 group.

15 Particular preference is given to a fully fluorinated carbon chain R_F of 1 to 3 or 4 to 16 fluorinated carbon atoms.

R^1 is a sterically voluminous group which has a crystallization-inhibiting effect on the polyfluoroalkyl chain. Particular preference is given either to a perfluoromethyl group, 20 to a perfluoroalkyl ether group or to a chlorine, bromine or iodine atom. A perfluoromethyl group is most preferable.

R^2 may be hydrogen or an aryl chain of 1 to 6 carbon atoms. Preferably, R^2 is a methyl or ethyl group.

25

R^3 is an alkylene group of 1 to 13 carbon atoms. R^3 is preferably an ethylene group.

One aspect of the invention concerns the production of copolymers of the methacrylate- or acrylate-functionalized telomeric compounds of the formula (IV).

30

The present invention further provides for the use of the specified compounds, or of their copolymers, for applications where the surface energy of a substrate is lowered.

The present invention further provides for the use of the hereindescribed copolymers in the manufacture of compositions used in conferring oil, water and soil repellency on fibrous substrates such as, for example, carpets, textiles, leather, nonwovens and paper and on hard substrates such as, for example, wood, metal or concrete.

5

Preferably, R^4 is a perfluoromethyl group, a perfluoropropyl group or a perfluoropropyloxypropyl group. A perfluoromethyl group is most preferable.

R^{5-8} is any linear or branched alkyl chain of 1 to 20 carbon atoms.

10

Preferably a is from 0 to 10 and more preferably from 0 to 5.

Preferably b is from 1 to 30 and more preferably $a + b > 3$.

15 X and Y may independently be H, Cl or F. Preferably, X and Y are fluorine atoms. Alternatively, X is a fluorine atom and Y is a chlorine atom, or X and Y are hydrogen atoms.

20 The preparation of the polyfluoroalkylsulphonyl chloride of the formula IV ($Z = Cl$) is carried out from the corresponding polyfluoroalkyl iodide in a multistage process.

In the first step of the process, known as telomerization, a fluorous compound (telogen) capable of transferring a free radical chain is reacted with at least one fluorinated monomer (taxogen) via a free radical forming mechanism at 20-250°C to form the
25 telomer of the formula



Useful telogens include fluorous alkyl compounds having a group to be scissioned free-radically, for example fluorous alkyl iodides, bromides, thiols, thioethers and alcohols.
30 Preference is given to perfluoroalkyl iodides having a unitary chain length or to a mixture of perfluoroalkyl iodides having different chain lengths. The perfluoroalkyl radical can be branched or unbranched, for example perfluoromethyl iodide, perfluoroethyl iodide, n-perfluoropropyl iodide, isoperfluoropropyl iodide, n-

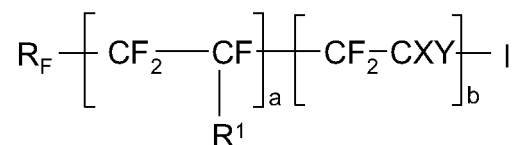
perfluorobutyl iodide, isoperfluorobutyl iodide, tert-perfluorobutyl iodide and isomers of perfluorohexyl iodide, perfluorooctyl iodide, perfluorodecyl iodide and perfluorododecyl iodide and so on.

- 5 Preference is given to perfluoroalkyl iodides in accordance with the invention having a chain length of 1 to 20 carbon atoms and at least one terminal CF_3 group.

- Particular preference is given to perfluoromethyl iodide, perfluoroethyl iodide, perfluoropropyl iodide or perfluoroisopropyl iodide or a technical grade mixture of
 10 various perfluoroalkyl iodides, having chain lengths of 6 to 16 fluorinated carbon atoms or 8 to 16 fluorinated carbon atoms and an average chain length of about 7.5 fluorinated carbon atoms or about 9 fluorinated carbon atoms.

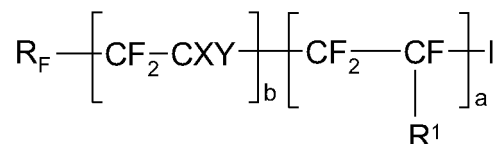
- The addition of the taxogens onto the telogen results in the building up of higher
 15 molecular weights. The telomer thus formed consists of a perfluoroalkyl chain having a terminal iodine group. The way the taxogens are incorporated in the telomer differs according to which of the following three variants is chosen.

- In the first variant, initially only a fluorinated unsaturated monomer $\text{CF}_2=\text{CFR}_1$ is added
 20 onto the telomer. The product then adds under the telomerization conditions the monomers of the formula $\text{CF}_2=\text{CXY}$. The telomer thus obtained has the formula



and exhibits blockwise incorporation of the monomers.

- 25 In the second variant, initially only a fluorinated unsaturated monomer $\text{CF}_2=\text{CXY}$ is added. The product then adds under the telomerization conditions the monomers of the formula $\text{CF}_2=\text{CFR}_1$. The resulting telomer



likewise exhibits blockwise incorporation of the monomers, but with the added monomers in the reverse order.

In the third variant, concurrent addition of a mixture of the two monomers results in
5 random incorporation of the monomers $\text{CF}_2=\text{CFR}_1$ and $\text{CF}_2=\text{CXY}$.

Examples of compounds of the formula $\text{CF}_2=\text{CFR}_1$ are: chlorotrifluoroethene, bromotrifluoroethene, iodotrifluoroethene, perfluoromethyl vinyl ether, perfluoroethyl vinyl ether, perfluoropropyl vinyl ether, perfluoropropoxypropyl vinyl ether and also
10 branched and unbranched perfluoroolefins having a terminal double bond, examples being hexafluoropropene, 1-perfluorobutene, 1-perfluorohexene or perfluorooctene.

Examples of compounds of the formula $\text{CF}_2=\text{CXY}$ are for example tetrafluoroethene, vinylidene fluoride, chlorotrifluoroethene, trifluoroethene, 1,1-dichloro-2,2-
15 difluoroethene and 1-chloro-2,2-difluoroethene.

In the case of iodine-containing compounds, free radicals which initiate the telomerization reactions can be generated by sources capable of forming free radicals. Useful sources for forming free radicals include light or heat. The light source typically
20 has its maximum in the infrared to ultraviolet region. Free radical formation due to heat typically takes place at temperatures between 100°C and 250°C.

Useful sources for forming free radicals further include free radical initiators of the chemical kind, which are also capable of lowering the reaction temperature required for
25 free radical formation to between 0°C and 150°C, examples being organic or inorganic peroxides, azo compounds, organic and inorganic metal compounds and metals and also combinations thereof. Particular preference is given to persulphates, fluorinated and nonfluorinated organic peroxides, azo compounds and metals such as for example Ru, Cu, Ni, Pd and Pt.

30

The telomerization can be carried solventlessly, in solution, in suspension or emulsion. The reaction without a solvent or in emulsion is particularly preferred. In the case of the reaction in emulsion, the telogen is first converted with the aid of surfactants into an

aqueous emulsion. The emulsion can be stabilized by anionic, cationic, nonionic or amphoteric surfactants and combinations thereof. Fluorosurfactants are particularly suitable for example. The reaction typically takes place at elevated temperature through addition of the taxogens and free radical initiators. Additional components can increase
5 the reaction yield, examples being small amounts of aqueous solutions of sulphites, bisulphites or dithionates.

The polyfluoroalkyl iodide obtained via telomerization is next converted into the corresponding polyfluoroalkylsulphonyl chloride with the formula IV ($Z = \text{Cl}$)



For this purpose, the polyfluoroalkyl iodides can be reacted in a reaction as described in DE 2 915 800 in the presence of suspensions of pulverulent metals such as for example iron, cobalt and nickel and also their mixtures in organic solvents, with SO_2 and then
15 with Cl_2 . Useful organic solvents include N,N-dimethylformamide, N,N-dimethylacetamide and N-methylpyrrolidone in pure form or as mixtures with polar solvents, for example nitriles such as acetonitrile, open-chain ethers such as diethyl ether, dimethylglycol or dimethyldiglycol, cyclic ethers such as tetrahydrofuran or 1,4-dioxane, ketones such as acetone or hexamethylphosphoramide. The reaction is carried
20 out at temperatures between 20°C to 80°C . After the reaction, the bulk of the solvent is distilled off and water is added only for elemental chlorine to be subsequently used at a temperature of 0°C to 100°C , which brings about the conversion to the polyfluoroalkylsulphonyl chloride.

25 The distillation residue generated in between can also be hydrolysed with a dilute mineral acid, in which case the polyfluoroalkylsulphinic acid is released. It can be oxidized with hydrogen peroxide, for example, to the corresponding polyfluoroalkylsulphonic acid of the formula IV where $Z = \text{OH}$. The polyfluoroalkylsulphonic acid can also be obtained by primary hydrolysis of the polyfluoroalkylsulphonyl chloride with a
30 base and subsequent acidification.

Correspondingly, the polyfluoroalkylsulphonic acid salts where $Z = \text{OM}$ are obtained by reaction of the polyfluoroalkylsulphonyl chloride with a base such as, for example,

lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, caesium hydroxide or ammonium hydroxide.

The corresponding polyfluoroalkyl sulphonamido alcohol having the formula IV where
5 $Z = N(R^2)R^3OH$ is obtainable from the polyfluoroalkylsulphonyl chloride in one or two reaction steps.

In the case of the one-stage reaction, the polyfluoroalkylsulphonyl chloride of the formula IV ($Z = Cl$), or the polyfluoroalkylsulphonic acid having the formula IV ($Z =$
10 OH), is converted into the polyfluoroalkyl sulphonamido alcohol by reaction with an amino alcohol. This reaction can be carried out at temperatures between 40°C and 80°C with or without solvent. Useful primary amino alcohols include for example 2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 2-amino-1-butanol, 5-aminopentanol, 2-amino-1-pentanol, 6-aminohexanol and useful secondary amino alcohols include for
15 example 2-methylaminoethanol, 3-methylaminopropanol, 4-methylaminobutanol, 2-methylamino-1-butanol, 5-methylaminopentanol, 2-methylamino-1-pentanol, 6-methylaminohexanol, 2-ethylaminoethanol, 3-ethylaminopropanol, 4-ethylaminobutanol, 2-ethylamino-1-butanol, 5-ethylaminopentanol, 2-ethylamino-1-pentanol, 6-ethylaminohexanol, 2-propylaminoethanol, 3-propylaminopropanol, 4-aminobutanol, 2-propylamino-1-butanol, 5-propylaminopentanol, 2-propylamino-1-pentanol, 6-propylaminohexanol, 2-butyaminoethanol, 3-butylaminopropanol, 4-butylaminobutanol, 2-butylamino-1-butanol, 5-butylaminopentanol, 2-butylamino-1-pentanol and 6-butylaminohexanol. Particular preference is given to 2-aminoethanol, 2-methylaminoethanol, 2-ethylaminoethanol and 3-propylaminoethanol.

25

Another possibility is to react the polyfluoroalkylsulphonyl chloride of the formula IV ($Z = Cl$), or the polyfluoroalkylsulphonic acid having the formula IV ($Z = OH$) to form the polyfluoroalkyl sulphonamido alcohol in two steps. First, a primary amine such as for example n-ethylamine, n-propylamine, isopropylamine or n-butylamine is reacted
30 under the same conditions as described above. The polyfluoroalkylsulphonamide thus formed is converted with the aid of a strong base such as for example sodium methoxide into the corresponding amide salt. After purification, the salt is reacted with a halogen-containing alcohol to form the polyfluoroalkyl sulphonamido alcohol. This reaction can

be carried out at temperatures between 80°C and 150°C with or without solvent. After cooling, the product is neutralized and purified by washing, extraction or distillation. Examples of the halogen-containing alcohol are 2-chloroethanol, 3-chloropropanol, 2-chloropropanol, and 4-chlorobutanol.

5

The polyfluoroalkyl sulphonamido alcohols obtained in this way can be reacted with (meth)acrylate esters, acids or acid chlorides to form the corresponding fluoruous (meth)acrylates of the formula IV ($Z = N(R^2)R^3OCOCH = CH_2$ or $N(R^2)R^3OCOCCH_3 = CH_2$).

10

The reaction with the (meth)acrylate acid chlorides is typically carried out in the presence of a base such as triethylamine to bind hydrogen chloride formed. A suitable catalyst, for example a tin catalyst, can be used for the transesterification.

15 The compounds of the formula IV ($Z = N(R^2)R^3OCOCH = CH_2$ or $N(R^2)R^3OCOCCH_3 = CH_2$) can be copolymerized with nonfluorous polymerizable vinyl monomers and/or chlorine-containing polymerizable vinyl monomers and optionally one or more thermally crosslinkable or isocyanate-reactive monomers.

20 The invention also provides copolymers containing, based on the total weight of the copolymer:

a) 20% to 97% by weight and preferably 40% to 90% by weight of a monomer of the formula IV where Z is $N(R^2)R^3OCOCH=CH_2$ or $N(R^2)R^3OCOCCH_3=CH_2$,

b) 0% to 80% by weight and preferably 10% to 50% by weight of one or more

25 nonfluorous polymerizable vinyl monomers and/or

c) 0.5% to 20% by weight and preferably 1% to 10% by weight of one or more thermally crosslinkable or isocyanate-reactive monomers.

The present invention further provides copolymers containing, based on the total weight
30 of the copolymer:

a) 40% to 90% by weight and preferably 45% to 85% by weight of a monomer of the formula IV where Z is $N(R^2)R^3OCOCH=CH_2$ or $N(R^2)R^3OCOCCH_3=CH_2$,

b) 0% to 50% by weight and preferably 0.01% to 30% by weight of one or more

nonfluorous polymerizable vinyl monomers and/or

c) 0.5% to 20% by weight and preferably 1% to 10% by weight of one or more thermally crosslinkable or isocyanate-reactive monomers and

d) 0.5% to 50% by weight and preferably 2% to 30% by weight of a chlorine-
5 containing polymerizable vinyl monomer.

The optional comonomer (b) is not fluorous (does not contain fluorine) and can represent a multiplicity of commercially available acrylates and methacrylates and styrene derivatives.

10

Examples of nonfluorinated comonomers are hydrocarbyl esters and amides of unsaturated carboxylic acids. These include for example the following esters and amides of acrylic acid, methacrylic acid, α -chloroacrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid: vinyl, allyl, methyl, ethyl, propyl, isopropyl, n-
15 butyl, isobutyl, t-butyl, hexyl, 3,3-dimethylbutyl, heptyl, octyl, isooctyl, lauryl, cetyl, stearyl, behenyl, cyclohexyl, bornyl, isobornyl, phenyl, benzyl, adamantyl, tolyl, (2,2-dimethyl-1-methyl)propyl, cyclopentyl, 2-ethylhexyl, 4-ethylcyclohexyl, 2-ethoxyethyl and tetrahydropyranyl.

20 Further nonfluorinated comonomers are allyl esters and vinyl esters such as for example allyl acetate, vinyl acetate, allyl heptanoate and vinyl heptanoate; alkyl vinyl ethers and alkyl allyl ethers such as for example cetyl vinyl ether, dodecyl vinyl ether, octadecyl vinyl ether and ethyl vinyl ether; α,β -unsaturated nitriles such as for example acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, α -cyanoethyl acrylate;
25 aminoalkyl (meth)acrylates such as for example N,N-diethylaminoethyl (meth)acrylate, N-t-butylaminoethyl (meth)acrylate; alkyl (meth)acrylates having an ammonium group such as for example 2-methacryloyloxyethyltrimethylammonium chloride; styrene and its derivative such as for example vinyltoluene, α -methylstyrene, α -cyanomethylstyrene, chloromethylstyrene; olefinic hydrocarbons such as for example
30 ethene, propene, isobutene, butadiene, isoprene; and (meth)acrylates of methoxy polyethylene glycols.

Particularly preferred optional comonomers (b) can be the following esters or amides of

acrylic acid and methacrylic acid: methyl, ethyl, propyl, butyl, isobutyl, 2-ethylhexyl, myristyl, lauryl, octadecyl, methoxy poly(ethylene glycol) and methoxy poly(propylene glycol) as described above.

- 5 The comonomer (c) contains one or more crosslinkable groups. A crosslinkable group is a functional group capable of entering a reaction with the substrate and/or with a further polyfunctional compound added. Such crosslinkable groups can be: carboxylic acid groups, ethylenically unsaturated groups, hydroxyl groups, amino groups, N-alkylolamide groups, isocyanate groups or protected isocyanate groups. Examples of
- 10 comonomers having one or more crosslinkable groups include unsaturated carboxylic acids and anhydrides of acrylic acid, methacrylic acid, α -chloroacrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid, monomers including a hydroxyl group, for example hydroxyethyl (meth)acrylates and hydroxypropyl (meth)acrylates, hydroxybutyl (meth)acrylate, poly(ethylene glycol) mono(meth)acrylate,
- 15 poly(propylene glycol) mono(meth)acrylate, poly(ethylene glycol)-co-poly(propylene glycol) mono(meth)acrylate, polytetrahydrofuran mono(meth)acrylate, N-hydroxymethyl(meth)acrylamide, hydroxybutyl vinyl ether. Further crosslinkable monomers are for example vinyl (meth)acrylate, allyl (meth)acrylate, N-methoxymethylacrylamide, N-isopropoxymethylacrylamide, N-
- 20 butoxymethylacrylamide, N-isobutoxymethylacrylamide, glycidyl (meth)acrylate and α,α -dimethyl-m-isopropenylbenzyl isocyanate. Other examples are monomers which release isocyanates at elevated temperatures or under irradiation with light, examples being phenol-, ketoxime- and pyrazole-protected isocyanate-terminated alkyl (meth)acrylates.

25

The optional comonomer (d) is chlorine containing. Examples of chlorine-containing comonomers are halogenated olefinic hydrocarbons such as for example vinyl chloride, vinylidene chloride, 3-chloro-1-isobutene, 1-chlorobutadiene, 1,1-dichlorobutadiene and 2,5-dimethyl-1,5-hexadiene. Vinylidene chloride and vinyl chloride are particularly

30 preferred optional comonomers (c).

The copolymer described hereby is typically prepared by a free radical polymerization technique, for example by solvent, emulsion, microemulsion or miniemulsion

polymerization techniques. Variants of the emulsion polymerization are particularly preferred. The emulsion polymerization of the monomers takes place in the presence of water, surfactants and an optional organic solvent. The mixture can have been pre-emulsified before the polymerization, by means of a high pressure homogenizer or a
5 similar apparatus. The polymerization is typically carried out at temperatures between 50°C and 150°C in the presence of a free radical initiator.

Various anionic, cationic, nonionic or amphoteric surfactants can be employed, alone or in combination. Examples of nonionic surfactants include poly(ethylene glycol) lauryl
10 ether, poly(ethylene glycol) tridecyl ether, poly(ethylene glycol) cetyl ether, poly(ethylene glycol)-co-poly(propylene glycol) cetyl ether, poly(ethylene glycol) stearyl ether, poly(ethylene glycol) oleyl ether, poly(ethylene glycol) nonylphenol ether, poly(ethylene glycol) octylphenol ether, poly(ethylene glycol) monolaurate, poly(ethylene glycol) monostearate, poly(ethylene glycol) monooleate, sorbitan
15 monolaurate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate, poly(ethylene glycol) sorbitan monolaurate, poly(ethylene glycol) sorbitan monopalmitate, poly(ethylene glycol) sorbitan monostearate, poly(ethylene glycol) sorbitan monooleate, poly(ethylene glycol)-co- poly(propylene glycol), polyglycerol fatty acid esters, polyether-modified
20 silicone oils and perfluoroalkyl-ethylene oxide adducts. The amount of nonionic surfactant used ranges from 0.1 to 100 percent by weight, relative to the weight of the polymer.

Examples of the cationic surfactants in accordance with the invention are ammonium
25 compounds based on saturated and unsaturated fatty acid amines, for example octadecylammonium acetate, dodecyltrimethylammonium chloride; ammonium compounds based on amino-functionalized polyethoxylates and polypropoxylates and their interpolymers such as for example polyoxyethylene laurylmonomethylammonium chloride; ammonium compounds based on arylamines such as for example
30 biphenyltrimethylammonium chloride, imidazoline derivatives such as for example ammonium salts formed from tallow and imidazoline; silicone-based cationic surfactants and fluorine-based cationic surfactants. The amount of cationic surfactant used ranges from 0.1 to 100 percent by weight relative to the weight of the polymer.

Examples of the anionic surfactants in accordance with the invention include fatty alcohol sulphates, for example sodium dodecylsulphate and poly(ethylene glycol) lauryl ether sulphate; alkylsulphonates such as for example sodium laurylsulphonate;
5 alkylbenzenesulphonates, for example nonylphenol ether sulphates, sulphosuccinates, for example sodium hexyl diether sulphosuccinate; fatty alcohol phosphates, for example sodium laurylphosphate and fatty acid salts, such as for example sodium stearic acid salt. The amount of anionic surfactant used ranges from 0.1 to 100 percent by weight, relative to the weight of the polymer.

10

Examples of free radical initiators are organic or inorganic peroxides, azo compounds, organic and inorganic metal compounds and metals and also combinations thereof.

Particular preference is given to azo compounds such as azobisisobutyronitriles (AIBNs), azobisvaleronitrile and azobis(2-cyanovaleric acid), 2,2'-azobis(2-

15

amidinopropane) dihydrochloride; hydroperoxides such as cumene hydroperoxide, t-butyl hydroperoxide and t-amyl hydroperoxide, dialkyl peroxides such as di-t-butyl peroxide and dicumyl peroxide, peroxyesters such as t-butyl perbenzoate and di-t-butyl peroxyphthalate, diacyl peroxides, such as benzoyl peroxide and lauroyl peroxide; inorganic peroxides such as ammonium persulphate and potassium persulphate and also

20

combinations of the specified compounds with organic or inorganic metal compounds and metals.

A chain transfer agent can be used in the polymerization, an example being an alkylthiol.

25

Examples of the organic solvent in the solvent and emulsion polymerization are: ketones such as for example acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohols such as for example ethanol, isopropanol and butanol, polyalcohols such as for example 1,3-butanediol, 1,6-hexanediol, ethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and glycerol; ethers and esters of polyalcohols, such as for
30 example dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, triethylene glycol dimethyl ether and diethylene glycol monobutyl ether acetate; esters such as for example ethyl acetate, propyl acetate, butyl acetate, dibutyl adipate and

dibutyl succinate; hydrocarbons and halogenated hydrocarbons such as for example toluene, xylene, octane, perchloroethylene and 1,3-dichloro-2,2,3,3,3-pentafluoropropane.

- 5 The preferred solids content for the polymer dispersion prepared is between 20 and 40 percent by weight.

- The fluorous copolymers containing a fluorous monomer of the formula IV ($Z = N(R^2)R^3OCOCH = CH_2$ or $N(R^2)R^3OCOCCH_3 = CH_2$) are suitable for coating fibrous
- 10 substrates such as for example carpets, textiles, leather, nonwovens or paper or hard substrates such as for example wood, metal or concrete. They endow these substrates with water-, oil- and soil-repellent properties.

- The invention thus also provides a process for surface treatment of fibrous substrates
- 15 with an effective amount of the fluorous aqueous dispersion.

- The content of the preparation for finishing textiles and other sheetlike structures in accordance with this invention is chosen so that sufficient repellent properties are transferred to the treated substrate. The wet pick-up was determined by weighing the
- 20 finished specimens before and after application.

- The fluorous textile-finishing agents according to the invention can be used together with other additives, including water-repellent materials, such as for example waxes, silicones, zirconium compounds or stearic acid salts, and also other oil-repellent
- 25 materials, surfactants, insecticides, flame retardants, antistatic additives, plasticizers, dye fixatives and crease resist additives in an amount which does not impair fixing on the textile and the stability of the composition.

- The fluorous textile-finishing agents according to the invention can be crosslinked by
- 30 addition of reactive additives such as for example melamine resins, protected isocyanates or epoxides.

The fibrous substrates to be coated with the fluorous polymeric dispersion can be for

example carpets, textiles, leather, nonwovens and paper. These consist inter alia of natural fibres such as for example cotton, linen and silk; of synthesis fibres such as for example polyamides, polyesters, polyurethanes, polyolefins, poly(meth)acrylates, poly(vinyl chlorides), poly(vinyl alcohols); semisynthetic fibres such as for example
5 rayon or acetate; inorganic fibres such as for example glass fibres or ceramic fibres or any desired combination of the specified fibres or any desired combination of woven products composed of these materials.

For coating, the substrate is typically immersed in a dilute dispersion consisting of
10 copolymer and optional additives. Alternatively, the dilute dispersion can be sprayed onto the substrate. The saturated substrate is subsequently pressed by a system of rolls to remove excess dispersion, dried in an oven and crosslinked at a temperature and for a time sufficient to ensure crosslinking on the treated substrate. This crosslinking process is typically carried out at temperatures between 50 and about 190°C. In general, a
15 temperature of about 120°C to 180°C and in particular of about 130°C to 170°C for a period of 20 seconds up to 10 minutes is suitable, preference being given to 5 seconds to 5 minutes.

A further alternative for applying the preparation to a substrate is foam application
20 wherein the preparation is applied to the substrate as a foam which is then dried and crosslinked. For foam application, the preparation is typically added in a concentrated form which has been admixed with an additional foamer. A highly concentrated preparation for foam application typically contains the fluoropolymer in an amount of up to 20% by weight.

25

For the finishing on textiles, these can be examined in specific tests for their water-, isopropanol- and oil-repellent properties before and after washing.

Water repellency is determined by the spray test as per AATCC Standard Test Method
30 22. Distilled water is sprayed onto the textile substrate to be tested and a subsequent visual comparison of the pattern of wetting with reference pictures of an evaluation standard recited in the test method was used to generate a numerical value. The reported numerical values relate to the appearance of the surface after spraying with water and

have the following connotation (Table 1):

Table 1

Water repellency rating	Connotation
100	No clinging of water droplets or wetting of the upper surface
90	Occasional clinging of water droplets or wetting of the upper surface
80	Wetting of the upper surface at water impact points
70	Partial wetting of total upper surface
50	Complete wetting of total upper surface
0	Complete wetting of total upper and lower surfaces

- 5 A second test with a series of water-isopropanol test solutions can be used to determine the isopropanol repellency (IPA) of a substrate. The reported IPA rating is the highest numbered test solution where the fabric is not wetted within 10 seconds and the drops still have the shape of a sphere or a hemisphere. Wetted substrates or substrates which are only repellent to 100% water (0% isopropanol), i.e. the least wetting test solution, are rated 0, whereas substrates which are repellent to 100% isopropanol (0% water) are rated 10. Intermediate ratings can be assigned as well.

- Oil repellency as per AATCC Standard Test Method 118 tests the ability of a substrate to repel oily soiling, higher ratings in the assessment scale denoting better repellency of such soil, in particular of oily liquids. In the test, drops of standardized test liquids, consisting of a selected series of hydrocarbons having different surface tensions, are applied in succession to the surface of the specimen to be tested, by careful pipetting, and the wetting is visually assessed after a defined contact time. The oil repellency value corresponds to the highest numbered test liquid which causes no wetting of the surface. The standard test liquids have the following composition (Table 2):

Table 2

Oil repellency	Composition
Rating 1	Nujol [®]
Rating 2	65 vol% of Nujol/35 vol% of n-hexadecane
Rating 3	n-hexadecane
Rating 4	n-tetradecane
Rating 5	n-dodecane
Rating 6	n-decane
Rating 7	n-octane
Rating 8	n-heptane

Note: Nujol is a mineral oil from Plough Inc. having a Saybolt viscosity of 360/390 at 38°C and a specific weight of 0.880/0.900 at 15°C.

5

Prior art FC polymers are currently giving oil repellency values of 6; however, a rating of 5 is usually already considered excellent.

Examples

- 10 The examples which follow illustrate the subject matter and advantages of the invention, but the materials and amounts cited in the examples shall not be viewed as limiting.

Syntheses

15

Example 1: Synthesis of $C_8F_{17}(CF_2CF(CF_3))_a(CF_2CF_2)_bI$

- 20 An emulsion of 110 g (0.18 mol) of Fluowet I812* (Clariant), 15 g of Fluorolink C (Solvay Solexis), 5 g of ammonia and 90 g of water was prepared by intensive stirring at 60°C and introduced into an autoclave as an initial charge together with 2.5 g of ammonium persulphate. The pressure test was followed by repeated purging with nitrogen. During the heating-up phase to 80°C, hexafluoropropene and tetrafluoroethene were added to the stirred emulsion in a ratio of 3:5 up to an overall pressure of 17 bar. The pressure is kept constant at 17 bar until 82.5 g (0.55 mol) of hexafluoropropene and 90 g (0.90 mol) of tetrafluoroethene have been added. After a drop in pressure, the

autoclave is cooled down to room temperature and the fluorochemical phase is separated off by addition of salt and washed. The low molecular weight constituents are separated off by distillation. The iodine content of 11.2% suggests an average molecular weight of about 1400 g/mol.

5

Elemental analysis: %C=11.0/11.1 (calc. 11.0), %H=0.0/0.0 (calc. 0.0), %N=0.0/0.0(calc.0.0), %S=0.0/0.0 (calc. 0.0).

10

^{19}F NMR (solvent: $\text{CDCl}_3/\text{C}_6\text{F}_6$, versus CFCl_3): -59.8 (2F, $-\text{CF}_2\text{I}$), -71.8 to -77.0 (in each case 3F, $-\text{CF}-\text{CF}_3$), -81.9 (3F, $-\text{CF}_2-\text{CF}_3$), -110.2 to -126.9 (in each case 2F, $-\text{CF}_2-$), -184.6 to -185.5 (in each case 1F, $-\text{CF}(\text{CF}_3)-$).

It is evident from the ^{19}F NMR spectrum that about 2 molecules of hexafluoropropene have been incorporated per perfluoroalkyl iodide used.

15

* The compound designated I812 is a perfluoroalkyl iodide mixture having 6 to 14 fluorinated carbon atoms per molecule having an average chain length of about 9 fluorinated carbon atoms.

20

Fluorolink C is a perfluoro polyether carboxylic acid.

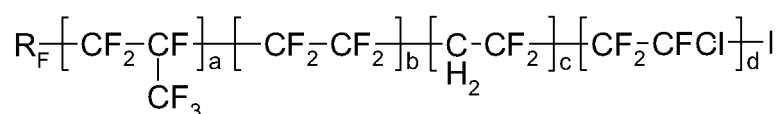
Examples 2 to 10: Synthesis of polyfluoroalkyl iodides

Example 1 was repeated to prepare corresponding polyfluoroalkyl iodides (Examples 2 to 10). The results of the syntheses are shown in Table 3.

25

Table 3

Telomerization reactions to prepare polyfluoroalkyl iodides having the general composition:



Ex. No. Iodide	R _F	R _F [mol]	a [mol]	b [mol]	c [mol]	d [mol]	M _n * [kg/mol]
2	(CF ₃) ₂ CF-	0.25	0.55	2.23	-	-	1.3
3	C ₈ F ₁₇ -	0.25	0.71	-	3.06	-	1.5
4	C ₂ F ₅ -	0.20	0.43	4.04	-	-	2.4
5	C ₈ F ₁₇ -	0.35	0.68	-	-	1.75	1.2
6	I812- **	0.30	-	2.49	-	1.23	1.7
7	C ₈ F ₁₇ -	0.25	-	-	1.98	1.01	1.3
8	(CF ₃) ₂ CF-	0.18	0.20	-	1.83	-	0.9
9	I612- **	0.22	0.87	1.32	-	-	1.5
10	C ₈ F ₁₇ -	0.26	-	-	-	2.07	1.8

* determined from iodine content

** the compounds designated Fluowet I612 and Fluowet I812 are perfluoroalkyl iodide mixtures from Clariant, each having 6 to 14 fluorinated carbon atoms per molecule having an average chain length of about 7.5 fluorinated carbon atoms and 9 fluorinated carbon atoms respectively.

Example 11: Synthesis of C₈F₁₇(CF₂CF(CF₃))_a(CF₂CF₂)_bSO₂Cl

A nitrogen-purged 2 litre four neck flask equipped with stirrer, thermometer, gas inlet tube, dropping funnel with pressure equilization and a mounted gas valve with sealing fluid was charged with a suspension of 14.7 g of nickel powder (0.25 mol) in 800 ml of dimethylformamide, prepared by stirring. At 30 to 35°C, 48.3 g of gaseous SO₂ (0.31 mol) and 292.8 g of the polyfluoroalkyl iodide from Example 1 (0.21 mol) were added concurrently over 3 hours, which was followed by a further 12 hours of stirring at 30°C. Then, 300 ml of dimethylformamide were distilled off at 16 mbar. Following the addition of 500 ml of water to the reaction mixture, a stream of chlorine was introduced with vigorous stirring for a total 32 g of Cl₂ while the internal temperature was maintained between 35 and 40°C by cooling. The organic phase was separated off at 70°C and repeatedly washed with warm water. 602.2 g of product were obtained after drying.

Elemental analysis: %C=11.1/11.0 (calc. 11.0), %H=0.0/0.0 (calc. 0.0), %N=0.0/0.0 (calc. 0.0), %S=2.3/2.4 (calc. 2.3).

Examples 12 to 20: Synthesis of polyfluoroalkylsulphonyl chlorides

- 5 Example 11 was repeated to prepare corresponding polyfluoroalkylsulphonyl chlorides (Examples 12 to 20). The results of the syntheses are reported in Table 4.

Example 21: Synthesis of $C_8F_{17}(CF_2CF(CF_3)_a(CF_2CF_2)_bSO_2N(CH_3)CH_2CH_2OH$

- A nitrogen-purged 1 litre three neck flask equipped with stirrer, thermometer and a
 10 reflux condenser was charged with 300 ml of methyl tert-butyl ether and 92.2 g of N-methylethanol (1.23 mol) with stirring. At 25 to 30°C, 576.9 g of the polyfluoroalkylsulphonyl chloride from Example 11 (0.41 mol) were introduced over 4 hours, which was followed by a further 3 hours of stirring at 30°C. Then, the reaction mixture was washed with 200 ml of dilute hydrochloric acid (10% strength) and
 15 repeatedly with water. The solvent was distilled off to leave 533.6 g of polyfluoroalkyl sulphonamido alcohol having a hydroxyl content of 1.22% of OH.

Elemental analysis: %C=13.2/13.2 (calc. 13.2), %H=0.5/0.6 (calc. 0.5), %N=1.0/1.0 (calc. 1.0), %S=2.3/2.3 (calc. 2.2).

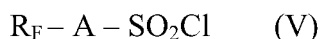
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Examples 22 to 30: Synthesis of polyfluoroalkyl sulphonamido alcohols

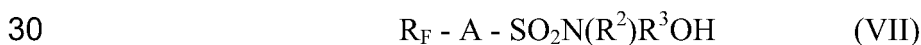
Example 21 was repeated to prepare corresponding polyfluoroalkyl sulphonamido alcohols (Examples 22 to 30). The results of the syntheses are reported in Table 4.

25 **Table 4**

Reactions to prepare polyfluoroalkyl sulphonyl chlorides and polyfluoroalkyl sulphonylamido alcohols of the general composition:



and



Ex. No. Iodide	Ex. No. Sulphonyl Chloride	S content of sulphonyl chloride	Ex. No. Sulphonyl amido alcohol	R ² *	R ²	OH% of sulphonyl amido alcohol
2	12	2.6	22	Me	-C ₂ H ₄ -	1.36
3	13	2.3	23	Et	-C ₂ H ₄ -	1.11
4	14	1.3	24	Me	-CH ₂ H ₄ -	0.79
5	15	2.8	25	Et	-C ₂ H ₄ -	1.36
6	16	2.0	26	Et	-C ₃ H ₆ -	1.01
7	17	2.6	27	Pr	-C ₂ H ₄ -	1.25
8	18	3.8	28	Pr	-C ₂ H ₄ -	1.97
9	19	2.3	29	Et	-C ₄ H ₈ -	1.14
10	20	1.8	30	Me	-C ₂ H ₄ -	0.94

*Me = methyl, Et = ethyl, Pr = n-propyl

Example 31:

Synthesis of C₈F₁₇(CF₂CF(CF₃)_a(CF₂CF₂)_bSO₂N(CH₃)CH₂CH₂OCOCH=CH₂

5

A three neck flask was charged with 91.0 g (0.06 mol) of the alcohol from Example 21, 23.0 g of acrylic acid, 0.3 g of methanesulphonic acid and 0.4 g of p-methoxyphenol and this initial charge was heated to 80°C. The water of reaction was separated during the reaction within 24 hours at the reaction temperature and a pressure of 200 mbar. The organic phase was repeatedly washed with warm water and dried in a rotary evaporator.

10

Elemental analysis: %C=15.0/15.0 (calc. 15.1), %H=0.7/0.6 (calc. 0.7), %N=0.9/1.0 (calc. 0.9), %S=2.1/2.1 (calc. 2.1).

15 Examples 32 to 40: Synthesis of polyfluoroalkyl (meth)acrylates

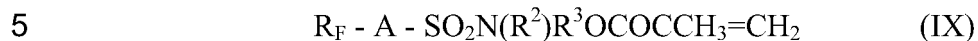
Example 31 was repeated to convert the polyfluoroalkyl amido alcohols into polyfluoroalkyl acrylates (AC) or, with methacrylic acid, into polyfluoroalkyl (meth)acrylates (MA). The compositions are reported in Table 5.

Table 5

Reactions to prepare polyfluoroalkyl (meth)acrylates having the general composition:



or



Ex. No. Sulphonyl amido alcohol	Ex. No. (Meth)acrylate	R ² *	R ²	AC/MA
22	32	Me	-C ₂ H ₄ -	AC
23	33	Et	-C ₂ H ₄ -	AC
24	34	Me	-C ₂ H ₄ -	AC
25	35	Et	-C ₂ H ₄ -	AC
26	36	Et	-C ₃ H ₆ -	AC
27	37	Pr	-C ₂ H ₄ -	MA
28	38	Pr	-C ₂ H ₄ -	MA
29	39	Et	-C ₄ H ₈ -	MA
30	40	Me	-C ₂ H ₄ -	MA

Example 41: Preparation of a dispersion for textile finishing (recipe 1)

10 The dispersion was prepared by intensively stirring the following components in a four neck flask equipped with stirrer, reflux condenser, inert gas supply and internal thermometer:

- 37.5 g of polyfluoroalkyl acrylate (from Example 31)
- 31.0 g of stearyl acrylate (SAC)
- 5.0 g of glycidyl methacrylate (GMA)
- 15 4.5 g of hydroxyethyl methacrylate (HEMA)
- 30.0 g of dipropylene glycol
- 0.4 g of dodecanethiol
- 6.0 g of lauryl alcohol/16 ethylene oxide adduct (nonionic surfactant A)
- 4.5 g of N,N-dimethyldodecylammonium acetate (cationic surfactant A)
- 20 200.0 g of water

The emulsion was heated to 60°C under a constant stream of nitrogen. Then, 0.2 g of

the initiator 2,2'-azo-bis-isobutyronitrile (AIBN) was added. The polymerization time was 10 hours at 60°C.

The resulting dispersion had a solids content of about 34%. For finishing textiles, the
5 dispersion was acidified and diluted to 30 g/l. The dispersion was applied to fibrous substrates on an HVF 59301 laboratory pad-mangle from Mathis AG (Switzerland) followed by drying and heat treatment at 160°C/30 seconds in an LTE laboratory dryer from Mathis AG (Switzerland). The commercially available textile Sahara 530306 from NEL GmbH, Neugersdorf, was used as PES/Co 65/35 substrate to compare the
10 applications. The wet pick-up was about 66% for all examples recited. The washing/drying procedure included 5 wash cycles at 60°C. The corresponding pieces of fabric were made up with ballast fabric to a wash load of one kilogram. The amount of laundry detergent needed was 7 g of "Coral intensive" per wash cycle. The fabric pieces were not dried between the wash cycles. After washing, the laundry was dried in a
15 laundry dryer.

Example 42: Preparation of a dispersion for textile finishing (recipe 2)

To prepare the dispersion, the following components were intensively stirred under an inert gas atmosphere in an autoclave equipped with a stirrer, reflux condenser and
20 internal thermometer:

- 69.5 g of polyfluoroalkyl acrylate (from Example 31)
- 19.0 g of lauryl acrylate (LA)
- 8.5 g of vinyl chloride (VC)
- 2.5 g of N-methoxymethylacrylamide (N-MAM)
- 25 3.5 g of hydroxyethyl methacrylate
- 30.0 g of dipropylene glycol
- 0.5 g of dodecanethiol
- 7.0 g of stearyl/11 ethylene oxide adduct (nonionic surfactant B)
- 4.0 g of lauryltrimethylammonium chloride (cationic surfactant B)
- 30 200.0 g of water

After the emulsion had been heated to 60°C, 0.6 g of the initiator 2,2'-azo-bis-2-amidinopropane dihydrochloride was added. The polymerization time was 6 hours at

60°C. After the reaction, the excess of vinyl chloride was stripped off.

The resulting dispersion had a solids content of about 38%. For finishing of textiles, the dispersion was acidified and diluted to 30 g/l. Application to textile substrates was

5 carried as described in Example 41.

Example 43: Preparation of a dispersion for textile finishing (recipe 3)

To prepare the dispersion, the following components were intensively stirred under an inert gas atmosphere in an autoclave equipped with a stirrer, reflux condenser and

10 internal thermometer:

60.5 g of polyfluoroalkyl acrylate (from Example 31)

12.5 g of 2-ethylhexyl acrylate (2-EHAC)

15.0 g of vinylidene chloride (VDC)

3.5 g of N-methoxymethylacrylamide

15 1.0 g of hydroxyethyl methacrylate

35.0 g of dipropylene glycol

0.7 g of dodecanethiol

6.0 g of stearyl/11 ethylene oxide adduct (nonionic surfactant B)

5.0 g of sodium dodecylsulphate (SDS)

20 200.0 g of water

After the emulsion had been heated to 60°C, 0.5 g of the initiator 2,2'-azo-bis-2-amidinopropane dihydrochloride was added. The polymerization time was 6 hours at 60°C. After the reaction, the excess of vinylidene chloride was stripped off.

25

The resulting dispersion had a solids content of about 36%. The dispersion was acidified and admixed with Cassurit HML (Clariant) and 20% by weight aqueous magnesium chloride solution, so that the concentration per l of liquor was in each case 30 g. Application to textile substrates was carried out as described in Example 41.

30

Examples 44-47: Preparation, application and testing of dispersions for textile finishing similarly to Example 41

Examples 48-51: Preparation, application and testing of dispersions for textile finishing similarly to Example 42

Examples 52-55: Preparation, application and testing of dispersions for textile finishing
5 similarly to Example 43

The formulation of the dispersions and the results of isopropanol repellency (IPA), oil repellency (Oleo) and water repellency (Hydro) for the dispersions of Examples 41 to 55 are reported in Table 6.

10

Example 56: Synthesis of $C_8F_{17}(CF_2CF(CF_3)_a(CF_2CF_2)_bSO_3K$

To a potassium hydroxide solution (45% by weight) were added 150.2 g (0.11 mol) of the polyfluoroalkylsulphonyl chloride of Example 11, which was followed by stirring for 12 hours. After concentrating, the product was dried by azeotropic distillation with
15 toluene.

Examples 57-60: Synthesis of polyfluoroalkylsulphonic acid salts

Example 56 was repeated to convert the polyfluoroalkylsulphonyl chloride of Example 11 into the corresponding polyfluoroalkylsulphonic acid salts by reaction with
20 sodium hydroxide, lithium hydroxide and ammonium hydroxide.

Example 61: Synthesis of $C_8F_{17}(CF_2CF(CF_3)_a(CF_2CF_2)_bSO_3H$

To a potassium hydroxide solution (45% by weight) were added 150.8 g (0.11 mol) of the polyfluoroalkylsulphonyl chloride of Example 11, which was followed by stirring
25 for 12 hours. Then, the hydrolysed product mixture was carefully acidified with sulphuric acid and the organic phase repeatedly washed with sulphuric acid.

Examples 62-70: Synthesis of polyfluoroalkylsulphonic acids

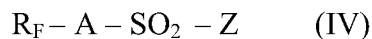
Example 61 was repeated to hydrolyse the polyfluoroalkylsulphonyl chlorides of
30 Examples 12 to 20 to the polyfluoroalkylsulphonic acids.

Table 6: Preparation, application and testing of dispersions for textile finishing

		Examples																	
		Recipe 1									Recipe 2								
		41	44	45	46	47	48	49	50	51	42	43	44	45	46	47	48	49	50
	Polyfluoroacrylate No.	31	34	35	36	38	32	33	39	40	31	31	32	33	39	40	31	32	39
	Polyfluoroacrylate amount	37.5	37.5	37.5	37.5	37.5	69.5	69.5	69.5	69.5	69.5	60.5	60.5	60.5	60.5	60.5	60.5	60.5	60.5
	SAC	31.0	31.0	31.0	31.0	31.0	-	-	-	-	-	-	-	-	-	-	-	-	-
	LA	-	-	-	-	-	19	19	19	19	19	-	-	-	-	-	-	-	-
	2-EHAC	-	-	-	-	-	-	-	-	-	-	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
	VC	-	-	-	-	-	8.5	8.5	8.5	8.5	8.5	-	-	-	-	-	-	-	-
	VDC	-	-	-	-	-	-	-	-	-	-	15	15	15	15	15	15	15	15
	GMA	5.0	5.0	5.0	5.0	5.0	-	-	-	-	-	-	-	-	-	-	-	-	-
	N-MAM	-	-	-	-	-	2.5	2.5	2.5	2.5	2.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
	HEMA	4.5	4.5	4.5	4.5	4.5	3.5	3.5	3.5	3.5	3.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Nonionic surfactant A	6.0	6.0	6.0	6.0	6.0	-	-	-	-	-	-	-	-	-	-	-	-	-
	Nonionic surfactant B	-	-	-	-	-	7.0	7.0	7.0	7.0	7.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	Cationic surfactant A	4.5	4.5	4.5	4.5	4.5	-	-	-	-	-	-	-	-	-	-	-	-	-
	Cationic surfactant B	-	-	-	-	-	4.0	4.0	4.0	4.0	4.0	-	-	-	-	-	-	-	-
	SDS	-	-	-	-	-	-	-	-	-	-	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Dipropylene glycol	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0
	IPA	90	80	60	60	30	50	50	70	30	80	80	40	60	60	60	60	60	90
	Oleo	6	6	4-5	5	4	5-6	5-6	6	3	6	6	5	5-6	37	6-7	37	6-7	6-7
	Hydro	100	100	90	90	80	90-100	90-100	100	80	100	100	90	80-90	80	100	80	100	100
	After 5 washes	90	60	40	50	20	40	40	50	30	60	60	20	60	50	70	50	50	70
		6	5-6	4	4-5	3	4-5	4-5	6	2	5	5	4-5	5	3	6	3	3	6
		100	90-100	80	80	80	90	90	100	80	100	100	90	80	80	90-100	80	80	90-100

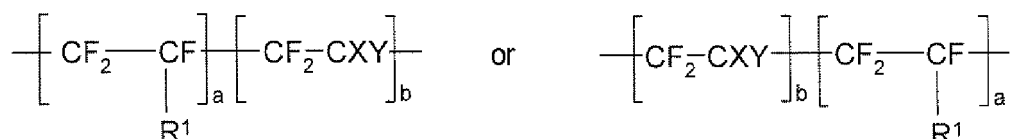
Claims

1. Fluorous telomeric compounds of the formula IV:



5 where R_F is a perfluoroalkyl radical of 1 to 20 carbon atoms,

A is a group of the formulae



R^1 is CF_3 , OR^4 , Cl, Br or I,

R^2 is H or alkyl of 1 to 6 carbon atoms

10 R^3 is alkylene of 1 to 13 carbon atoms

R^4 is perfluoromethyl, perfluoropropyl or perfluoropropyloxypropyl

X and Y are H, Cl or F

Z is -OH, -Cl, -OM, - $\text{N}(\text{R}^2)\text{R}^3\text{OH}$, - $\text{N}(\text{R}^2)\text{R}^3\text{OCOCH}=\text{CH}_2$ or -
- $\text{N}(\text{R}^2)\text{R}^3\text{OCOCCH}_3=\text{CH}_2$

15 M is an alkali metal, ammonium or a mono-, di-, tri- or tetra- C_1 - C_4 -alkylammonium cation

a is from 0 to 10 and b is from 1 to 30.

20 2. Compounds according to Claim 1, characterized in that R_1 is Cl.

3. Compounds according to Claim 1, characterized in that R_1 is CF_3 .

4. Compounds according to Claim 1, characterized in that X and Y are F or X is F
25 and Y is Cl or X and Y are hydrogen.

5. Compounds according to Claim 1, characterized in that a is from 0 to 5.

6. Compounds according to Claim 1, characterized in that R^2 is a methyl, ethyl or
30 propyl group.

7. Compounds according to Claim 1, characterized in that R_F is a polyfluoroalkyl radical of 1 to 3 fluorinated carbon atoms.
- 5 8. Compounds according to Claim 1, characterized in that R_F is a polyfluoroalkyl radical of 4 to 16 fluorinated carbon atoms.
9. Compounds according to Claim 1, characterized in that the molecular weight of the compounds of the formula IV is more than 750 g/mol.
- 10 10. Compounds according to Claim 1, characterized in that $a + b$ is > 3 .
11. Copolymers containing a monomer of the formula IV where Z is -
 $N(R^2)R^3OCOCH=CH_2$ or $-N(R^2)R^3OCOCCH_3=CH_2$, one or more nonfluorous
15 polymerizable vinyl monomers, one or more thermally crosslinkable or isocyanate-reactive monomers and optionally a chlorine-containing polymerizable vinyl monomer.
12. Copolymers containing, based on the total weight of the copolymer:
- 20 a) 20% to 99.5% by weight and preferably 40% to 90% by weight of a monomer of the formula IV according to Claim 1, where Z is $-N(R^2)R^3OCOCH=CH_2$ or -
 $N(R^2)R^3OCOCCH_3=CH_2$,
- b) 0% to 80% by weight and preferably 10% to 50% by weight of one or more nonfluorous polymerizable vinyl monomers and/or
- 25 c) 0.5% to 20% by weight and preferably 1% to 10% by weight of one or more thermally crosslinkable or isocyanate-reactive monomers.
13. Copolymers containing, based on the total weight of the copolymer:
- 30 a) 40% to 99% by weight and preferably 45% to 85% by weight of a monomer of the formula IV according to Claim 1, where Z is $-N(R^2)R^3OCOCH=CH_2$ or -
 $N(R^2)R^3OCOCCH_3=CH_2$,
- b) 0% to 50% by weight and preferably 0.01% to 30% by weight of one or more

nonfluorous polymerizable vinyl monomers and/or

c) 0.5% to 20% by weight and preferably 1% to 10% by weight of one or more thermally crosslinkable or isocyanate-reactive monomers and

d) 0.5% to 50% by weight and preferably 2% to 30% by weight of a chlorine-

5 containing polymerizable vinyl monomer.

14. Use of the copolymers according to Claims 11 to 13 for water-, oil- and soil-repellent finishing of fibrous substrates.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/056179

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C69/653 D06M15/277 C08F20/24 C07C67/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F C07C D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DE 27 54 457 A1 (HOECHST AG) 13 June 1979 (1979-06-13) example 10 -----	1-10
X	US 4 288 646 A (OLAH GEORGE A) 8 September 1981 (1981-09-08) column 3, lines 14-17; examples 1,3 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

31 October 2007

Date of mailing of the international search report

13/11/2007

Name and mailing address of the ISA/

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Baekelmans, Didier

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/056179

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5 518 788 A (INVIE JUDITH M [US]) 21 May 1996 (1996-05-21) claim 2 -----	1-10
X	WO 96/18691 A (MINNESOTA MINING & MFG [US]) 20 June 1996 (1996-06-20) pages 19-20 -----	1-10
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/056179

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2007/056179

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: claim 1-10 (parts), 11-14

- A compound of the formula IV (see claim 1) wherein Z is $N(R_2)R_3OCOCH=CH_2$ or $N(R_2)R_3COCCH_3=CH_2$
 - A copolymer containing the above fluorous telomeric compound
 - The use of the above copolymer for water-, oil- and soil-repellent finishing of fibrous substrates
-

2. claims: 1-10 (parts)

- A compound of the formula IV (see claim 1) wherein Z is OH or OM
-

3. claims: 1-10 (parts)

- A compound of the formula IV (see claim 1) wherein Z is Cl
-

4. claims: 1-10 (parts)

- A compound of the formula IV (see claim 1) wherein Z is $N(R_2)R_3OH$
-

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/056179

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International application No

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