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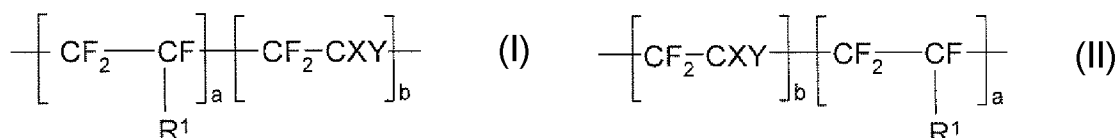
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(54) **Title:** FLUOROUS TELOMERIC COMPOUNDS AND POLYMERS CONTAINING SAME



(57) **Abstract:** Claimed are fluoruous telomeric compounds of the formula $R_F - A - CXY - Z$ (IV), where R_F is a perfluoroalkyl radical of 1 to 20 carbon atoms, A is a group of the formulae (I) or (II), Z is CH_2OR^3 , or $\text{COO}^- 1/q \text{M}^{q+}$ or $\text{CON}(\text{R}^4)\text{R}^5\text{OR}^3$; X and Y are H, Cl or F; R^1 is CF_3 , OR^2 , Cl, Br or I; R^2 is perfluoromethyl, perfluoropropyl or perfluoropropoxypropyl; R^3 is H or $\text{COCR}^6=\text{CH}_2$; R^4 is H or alkyl of 1 to 6 carbon atoms; R^5 is alkylene of 1 to 13 carbon atoms; R^6 is H or CH_3 ; M is H or a metal cation or an ammonium cation or a substituted ammonium cation; q is the valency of M; 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.



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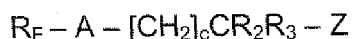
FLUOROUS TELOMERIC COMPOUNDS AND POLYMERS CONTAINING SAME

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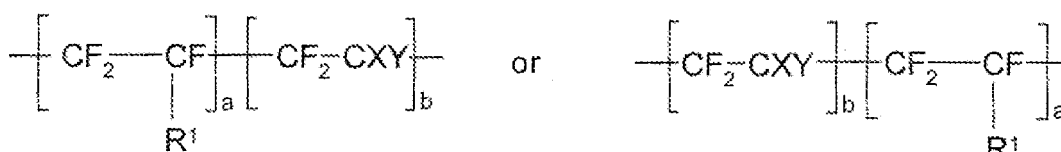
Perfluoroalkyl iodides obtained via telomerization of telogens with fluorinated monomers such as tetrafluoroethene, for example, are an important starting point for the preparation of fluorocompounds.

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 perfluoropropoxypropyl

X and Y are H, Cl or F

25 Z is $-OH$, $-OCOCH=CH_2$ or $-OCOCCH_3=CH_2$

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.



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.

15 The fluoruous monomers of the formula II



are known for similar applications.

20

The fluorinated alkylsulphonic acid fluoride used in their synthesis is obtained via electrochemical fluorination.

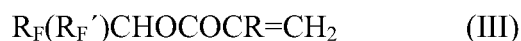
It has been determined for both monomer types (I and II) that the coating of surfaces
25 with longer and ideally straight-chain perfluoroalkyl chains which consist of 8-10 fluorinated carbon atoms leads to particularly low surface energies.

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

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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.

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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

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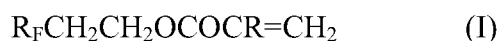


in lieu of perfluorooctanesulphonic acid derivatives having a partially branched perfluoroalkyl radical R_F of 4 fluorinated carbon atoms, $n = 1, 2$ and $R' = H, \text{ alkyl}$ and $R = H, CH_3$.

20

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

25



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.

30

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.

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
5 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
10 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.

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
15 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.

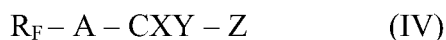
It has now been found that, surprisingly, polyfluoroalkyl compounds as hereinbelow
20 defined lead to oil- and water-repellent coatings of high efficiency and durability and are also environmentally compatible.

The invention accordingly provides fluorous carboxylic acids and/or fluorous alcohols and derivatives thereof having molecular weights of greater than 750 g/mol.
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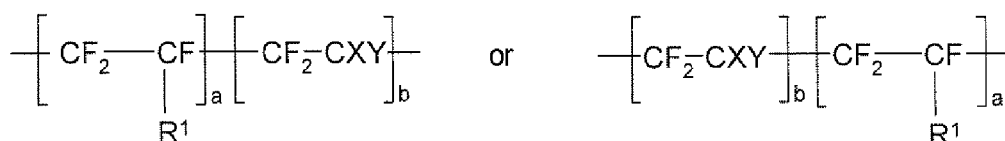
The invention further provides fluorous compounds which, owing to their being composed of a polyfluoroalkyl chain which is partly branched and partly linear, melt at lower temperatures than their molecular weight equivalents consisting of a linear
polyfluoroalkyl chain.

30 The invention further provides fluorous carboxylic acids, carboxylic acid salts and ester derivatives which are prepared from the corresponding polyfluorous alkyl alkyl iodides.

The present invention provides 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



Z is CH_2OR^3 , or $\text{COO}^- 1/q \text{M}^{q+}$ or $\text{CON}(\text{R}^4)\text{R}^5\text{OR}^3$

X and Y are H, Cl or F

- 10 R^1 is CF_3 , OR^2 , Cl, Br or I,
 R^2 is perfluoromethyl, perfluoropropyl or perfluoropropyloxypropyl
 R^3 is H or $\text{COCR}^6=\text{CH}_2$
 R^4 is H or alkyl of 1 to 6 carbon atoms
 R^5 is alkylene of 1 to 13 carbon atoms
 15 R^6 is H or CH_3
 M is H or a metal cation or an ammonium cation or a substituted ammonium cation
 q is the valency of M
 a is from 0 to 10 and b is from 1 to 30.

- 20 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.

- The polyfluoroalkyl radical R_F can be a polyfluoroalkyl group having a unitary chain
 25 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} , $\text{C}_{10}\text{F}_{21}$, $\text{C}_{12}\text{F}_{25}$, $\text{C}_{14}\text{F}_{29}$ and $\text{C}_{16}\text{F}_{31}$ groups. The polyfluoroalkyl radical can be branched or unbranched.

- Preference is given to compounds in accordance with the invention which have a
 30 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.

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

5

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.

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

The functional group Z is either a carboxylic acid, a carboxylic acid salt, a carboxamido alcohol, a carboxamidoalkyl (meth)acrylate, an alcohol, a methacrylate or acrylate.

20

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, to a perfluoroalkyl ether group or to a chlorine, bromine or iodine atom. A perfluoromethyl group is most preferable.

Preferably, R^2 is a perfluoromethyl group, a perfluoropropyl group or a perfluoropropoxypropyl group. A perfluoromethyl group is most preferable.

25

R^3 is either hydrogen or $\text{COCR}^6=\text{CH}_2$.

R^4 is hydrogen or an alkyl chain of 1 to 6 carbon atoms, preferably a methyl or an ethyl group.

30

R^5 is an alkylene chain of 1 to 13 carbon atoms, preferably an ethylene group.

R^6 is either hydrogen or a methyl group.

The compounds of the invention are prepared from the corresponding polyfluoroalkyl iodides in a multistage process.

- 5 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 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. Preference is given to perfluoroalkyl iodides having a unitary chain length or to a
15 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
20 perfluorododecyl iodide and so on.

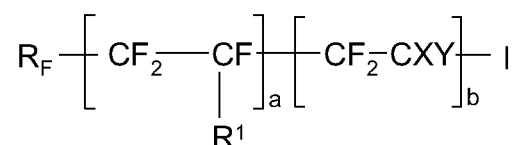
Preference is given to perfluoroalkyl iodides in accordance with the invention having a chain length of 1 to 20 carbon atoms and at least one terminal CF₃ group.

- 25 Particular preference is given to perfluoromethyl iodide, perfluoroethyl iodide, perfluoropropyl iodide or perfluoroisopropyl iodide or a technical grade mixture of 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.

- 30 The addition of the taxogens onto the telogen results in the building up of higher 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.

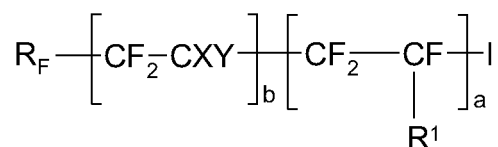
In the first variant, initially only a fluorinated unsaturated monomer $\text{CF}_2=\text{CFR}_1$ is added onto the telomer. The product then adds under the telomerization conditions the
5 monomers of the formula $\text{CF}_2=\text{CXY}$. The telomer thus obtained has the formula



and exhibits blockwise incorporation of the monomers.

10

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



15

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

20 In the third variant, concurrent addition of a mixture of the two monomers results in 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
25 vinyl ether, perfluoropropyl vinyl ether, perfluoropropoxypropyl vinyl ether and also branched and unbranched perfluoroolefins having a terminal double bond, examples being hexafluoropropene, 1-perfluorobutene, 1-perfluorohexene or perfluorooctene.

Examples of compounds of the formula $CF_2=CXY$ are for example tetrafluoroethene, vinylidene fluoride, chlorotrifluoroethene, trifluoroethene, 1,1-dichloro-2,2-difluoroethene and 1-chloro-2,2-difluoroethene.

5 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 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.

10

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 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.

The telomerization can be carried solventlessly, in solution, in suspension or emulsion. 20 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 25 addition of the telogens and free radical initiators. Additional components can increase 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 a 30 polyfluoroalkyl carboxylic acid of the formula IV ($Z = COOH$)



Various preparative methods can be used for the oxidation to polyfluoroalkyl carboxylic acid. One reaction, described in DE 3 043 249 for example, involves polyfluoroalkyl iodides being oxidized with fuming sulphuric acid at temperatures of 100 to 180°C to form polyfluoroalkyl carboxylic acid.

5

The polyfluoroalkyl carboxylic acid salts of formula IV where $Z = \text{COO}^- 1/q \text{M}^{q+}$ are obtained by reaction of the polyfluoroalkyl carboxylic acids with a base such as for example lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, caesium hydroxide, ammonium hydroxide or tetrabutylammonium hydroxide.

10

The polyfluoroalkyl carboxylic acid is used as a starting material for preparing various alcohols according to the formula IV $Z = \text{CH}_2\text{OH}$ and $Z = \text{CON}(\text{R}^4)\text{R}^5\text{OH}$.

15

In the first version, the polyfluoroalkyl carboxylic acid is hydrogenated, as described for example in DE 22 22 682, in the presence of suitable catalysts and hydrogen at temperatures of 150 to 220°C to form 1H,1H-polyfluoroalkyl alcohol ($Z = \text{CH}_2\text{OH}$). Metal and metal oxide catalysts are preferred. Ruthenium catalysts are particularly preferred.

20

In the second version, a polyfluoroalkyl carboxamido alcohol is prepared by reaction of the polyfluoroalkyl carboxylic acid with an amino alcohol. This reaction can be carried out with or without solvent at temperatures between 20°C and 80°C. The amino alcohols used can be primary amino alcohols such as for example 2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 2-amino-1-butanol, 5-aminopentanol, 2-amino-1-pentanol, 6-aminohexanol or secondary amino alcohols such as for 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-butylaminoethanol, 3-butylaminopropanol, 4-butylaminobutanol, 2-butylamino-1-

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butanol, 5-butylaminopentanol, 2-butylamino-1-pentanol and 6-butylaminohexanol. Particular preference is given to 2-aminoethanol, 2-methylaminoethanol, 2-ethylaminoethanol and 3-propylaminoethanol.

- 5 The 1H,1H-polyfluoroalkyl alcohols and polyfluoroalkyl carboxamido alcohols obtained in this way can be reacted with (meth)acrylate esters, acids or acid chlorides to form the corresponding fluoruous (meth)acrylates having the formulae



10

and



- 15 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.

20 These acrylates and methacrylates 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.

25 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 $CH_2OCOCR^6=CH_2$ or $CON(R^4)R^5OOCOCR^6=CH_2$,
- b) 0% to 80% by weight and preferably 10% to 50% by weight of one or more nonfluorous polymerizable vinyl monomers and/or
- 30 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

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 $\text{CH}_2\text{OOCOR}^6=\text{CH}_2$ or $\text{CON}(\text{R}^4)\text{R}^5\text{OOCOR}^6=\text{CH}_2$,
- b) 0% to 50% by weight and preferably 0.01% to 30% by weight of one or more nonfluorous polymerizable vinyl monomers and/or
- 5 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-containing polymerizable vinyl monomer.

10

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

- 15 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-butyl, isobutyl, t-butyl, hexyl, 3,3-dimethylbutyl, heptyl, octyl, isooctyl, lauryl, cetyl,
- 20 stearyl, behenyl, cyclohexyl, bornyl, isobornyl, phenyl, benzyl, adamantyl, tolyl, (2,2-dimethyl-1-methyl)propyl, cyclopentyl, 2-ethylhexyl, 4-ethylcyclohexyl, 2-ethoxyethyl and tetrahydropyranyl.

- Further nonfluorinated comonomers are allyl esters and vinyl esters such as for example
- 25 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; aminoalkyl (meth)acrylates such as for example N,N-diethylaminoethyl (meth)acrylate,
- 30 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

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
5 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.

The comonomer (c) contains one or more crosslinkable groups. A crosslinkable group is
10 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 comonomers having one or more crosslinkable groups include unsaturated carboxylic
15 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, poly(propylene glycol) mono(meth)acrylate, poly(ethylene glycol)-co-poly(propylene
20 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-butoxymethylacrylamide, N-isobutoxymethylacrylamide, glycidyl (meth)acrylate and
25 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.

30 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

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
5 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 similar apparatus. The polymerization is typically carried out at temperatures between
10 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 ether, poly(ethylene glycol) tridecyl ether, poly(ethylene glycol) cetyl ether,
15 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 monolaurate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monostearate,
20 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 silicone oils and perfluoroalkyl-ethylene oxide adducts. The amount of nonionic
25 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 compounds based on saturated and unsaturated fatty acid amines, for example
30 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

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.

5

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

20

25

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

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

30

glycol, tripropylene glycol and glycerol; ethers and esters of polyalcohols, such as for 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
5 dibutyl succinate; hydrocarbons and halogenated hydrocarbons such as for example toluene, xylene, octane, perchloroethylene and 1,3-dichloro-2,2,3,3,3-pentafluoropropane.

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

The fluorous copolymers containing a fluorous monomer of the formula IV, where Z is $\text{CH}_2\text{OCOCR}^6=\text{CH}_2$ or $\text{CON}(\text{R}^4)\text{R}^5\text{OOCOCR}^6=\text{CH}_2$, are suitable for coating fibrous substrates such as for example carpets, textiles, leather, nonwovens or paper or hard
15 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 with an effective amount of the fluorous aqueous dispersion.

20

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 finished specimens before and after application.

25

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 materials, surfactants, insecticides, flame retardants, antistatic additives, plasticizers,
30 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

addition of reactive additives such as for example melamine resins, protected isocyanates or epoxides.

The fibrous substrates to be coated with the fluoruous 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 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 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 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 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.

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 attained by the spray test as per AATCC Standard Test Method 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
 5 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

10 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,
 15 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
 20 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

5

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.

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

Examples

15 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

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.

¹⁹F NMR (solvent CDCl₃/C₆F₆, versus CFCI₃): -59.8 (2F, -CF₂I), -71.8 to -77.0 (in each case 3F, -CF-CF₃), -81.9 (3F, -CF₂-CF₃), -110.2 to -126.9 (in each case 2F, -CF₂-), -184.6 to -185.5 (in each case 1F, -CF(CF₃)).

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

* 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.

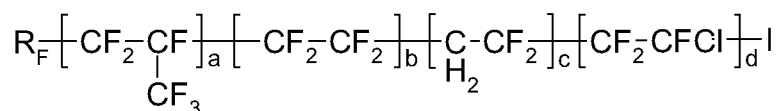
Fluorolink C is a perfluoro polyether carboxylic acid.

Examples 2 to 9: Synthesis of polyfluoroalkyl iodides

Example 1 was repeated to prepare corresponding polyfluoroalkyl iodides (Examples 2 to 9). The results of the syntheses are shown in Table 3.

Table 3

Telomerization reactions to prepare polyfluoroalkyl iodides having the general composition:



30

Ex. No.	R _F	R _F	a	b	c	d	M _n
Iodide		[mol]	[mol]	[mol]	[mol]	[mol]	*
							[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

* 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 10: Synthesis of C₈F₁₇(CF₂CF(CF₃))_a(CF₂CF₂)_bCF₂COOH

10

146.5 g (0.11 mol) of the polyfluoroalkyl iodide from Example 1, 2.1 g of zinc sulphate and 105.5 g of oleum (65% SO₃) were weighed into a shaker autoclave and reacted at 155°C for 8 hours. After the reaction, the reaction mixture was cooled down and admixed with 1,1,2-trichloroethane. After shaking, the lighter phase is separated off and carefully hydrolysed with warm water. Repeated washing with warm water left 110.7 g (0.10 mol) of polyfluoroalkyl carboxylic acid.

15

The acid number was 48.9 mg of KOH/g of product.

Examples 11 to 18: Synthesis of polyfluoroalkyl carboxylic acids

Example 10 was repeated to prepare corresponding polyfluoroalkyl carboxylic acids (Examples 11 to 18). The results of the syntheses are shown in Table 4.

5

Example 19: Synthesis of $C_8F_{17}(CF_2CF(CF_3))_a(CF_2CF_2)_bCF_2CH_2OH$

2.0 g of H 101 B/W ruthenium catalyst (Degussa) and 90.2 g of the polyfluoroalkyl carboxylic acid from Example 10 were introduced as an initial charge under nitrogen.

10 Following a pressure test with 50 bar of nitrogen, 40 bar of hydrogen were injected. The reaction mixture was maintained at 140°C for 20 hours. After decompression, the product was filtered at 70°C, washed with hot water and the volatile constituents were removed to obtain 85 g of polyfluoroalkyl alcohol.

15 The OH number was 46.7 mg of KOH/g of product.

Example 20: Synthesis of $C_8F_{17}(CF_2CF(CF_3))_a(CF_2CF_2)_bCF_2CON(CH_3)CH_2CH_2OH$

A 250 ml four neck flask was charged with 86.4 g of the polyfluoroalkyl carboxylic acid from Example 10 at 60°C. 15.4 g of N-methylaminoethanol were added in the course of 30 minutes with stirring. The reaction mixture was slowly heated to 180°C. Water formed was removed via a Dean-Stark apparatus. The reaction mixture was stirred at that temperature for a further 4 hours for supplementary reaction. The reaction mixture was cooled down to 70°C and mixed with 150 ml of ethanol preheated to 70°C and precipitated in water. Washing and drying left 83.7 g of polyfluoroalkyl amido alcohols.

20

25

The OH number was 48.2 mg of KOH/g of product.

Examples 21 to 24: Synthesis of polyfluoroalkyl alcohols

Example 19 was repeated to prepare corresponding polyfluoroalkyl alcohols (Examples 21 to 24). The results of the syntheses are reported in Table 4.

Examples 25 to 28: Synthesis of polyfluoroalkyl amido alcohols

Example 20 was repeated to prepare corresponding polyfluoroalkyl amido alcohols
5 (Examples 25 to 28). The results of the syntheses are reported in Table 4.

Example 29: Synthesis of $C_8F_{17}(CF_2CF(CF_3)_a(CF_2CF_2)_bCF_2CH_2OCOCH=CH_2$

A three neck flask was charged with 80.1 g of the alcohol from Example 19, 23.5 g of
10 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.
Conversion was verified by 1H NMR measurements.

15

Examples 30 to 38: Synthesis of polyfluoroalkyl (meth)acrylates

Example 29 was repeated to convert the alcohols into polyfluoroalkyl acrylates or, with
methacrylic acid, into polyfluoroalkyl (meth)acrylates. The compositions are reported in
20 Table 4.

Table 4

Reactions to prepare polyfluoroalkyl telomeric compounds of the general composition:

25



Ex. No. Iodide	Ex. No. Carboxylic acid ^a	Acid number of carboxylic acid	Ex. No. alcohol ^b	OH number of alcohol	Ex. No. (meth)-acrylate	R ² ^c	R ³	R ⁶
1	10	48.3	19	46.7	29	-	-	H
1	10	48.3	20	48.2	30	Me	- C ₂ H ₄ -	H
2	11	54.3	21	52.4	31	-	-	H
3	12	42.6	22	44.0	32	-	-	H
4	13	25.6	23	25.3	33	-	-	CH ₃
5	14	57.0	24	58.3	34	-	-	H
6	15	38.9	25	37.5	35	Me	- C ₂ H ₄ -	
7	16	51.7	26	52.4	36	Pr	- C ₂ H ₄ -	H
8	17	86.4	27	83.9	37	Me	- C ₂ H ₄ -	CH ₃
9	18	44.6	28	44.0	38	Et	- C ₂ H ₄ -	H

^a Z = COOH

^b Examples 19, 21-24: Z = CH₂OCOCR⁶=CH₂;

5 Examples 20, 25-28: Z = CON(R⁴)R⁵OCOCR⁶=CH₂

^c Me = methyl-, Et = ethyl-, Pr = n-propyl-

Example 39: 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 29)

31.0 g of stearyl acrylate (SAC)

- 5.0 g of glycidyl methacrylate (GMA)
- 4.5 g of hydroxyethyl methacrylate (HEMA)
- 30.0 g of dipropylene glycol
- 0.4 g of dodecanethiol
- 5 6.0 g of lauryl alcohol/16 ethylene oxide adduct (nonionic surfactant A)
- 4.5 g of N,N-dimethyldodecylammonium acetate (cationic surfactant A)
- 200.0 g of water

The emulsion was heated to 60°C under a constant stream of nitrogen. Then, 0.2 g of
10 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
dispersion was acidified and diluted to 30 g/l. The dispersion was applied to fibrous
15 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
applications. The wet pick-up was about 66% for all examples recited. The
20 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
laundry dryer.

25

Example 40: 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
30 internal thermometer:

- 69.5 g of polyfluoroalkyl acrylate (from Example 29)
- 19.0 g of lauryl acrylate (LA)
- 8.5 g of vinyl chloride (VC)

- 2.5 g of N-methoxymethylacrylamide (N-MAM)
- 3.5 g of hydroxyethyl methacrylate
- 30.0 g of dipropylene glycol
- 0.5 g of dodecanethiol
- 5 7.0 g of stearyl/11 ethylene oxide adduct (nonionic surfactant B)
- 4.0 g of lauryltrimethylammonium chloride (cationic surfactant B)
- 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-
10 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
15 carried as described in Example 39.

Example 41: Preparation of a dispersion for textile finishing (recipe 3)

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

- 60.5 g of polyfluoroalkyl acrylate (from Example 29)
- 12.5 g of 2-ethylhexyl acrylate (2-EHAC)
- 15.0 g of vinylidene chloride (VDC)
- 25 3.5 g of N-methoxymethylacrylamide
- 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)
- 30 5.0 g of sodium dodecylsulphate (SDS)
- 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.

The resulting dispersion had a solids content of about 36%. The dispersion was
5 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 39.

Examples 42-45:

10 Preparation, application and testing of dispersions for textile finishing similarly to
Example 39

Examples 46-49:

15 Preparation, application and testing of dispersions for textile finishing similarly to
Example 40

Examples 50-53:

20 Preparation, application and testing of dispersions for textile finishing similarly to
Example 41

The results of isopropanol repellency (IPA), oil repellency (oleo) and water repellency
(hydro) for the dispersions from Examples 39 to 53 are reported in Table 5.

Example 54: Synthesis of $C_8F_{17}(CF_2CF(CF_3)_a(CF_2CF_2)_bCF_2COOK$

25 76.2 g (0.55 mol) of polyfluoroalkyl carboxylic acid from Example 11 were added to a
dilute potassium hydroxide solution (10% by weight) and stirred at 80°C for 12 hours.
After concentrating by evaporation, the polyfluoroalkyl carboxylic acid potassium salt
was dried by azeotropic distillation with toluene.

30

Examples 55-57: Synthesis of polyfluoroalkyl carboxylic acid salts

Example 54 was repeated to convert the polyfluoroalkyl carboxylic acid from Example 11 into the corresponding polyfluoroalkyl carboxylic acid salts by reaction with sodium
5 hydroxide, lithium hydroxide and ammonia.

Table 5: Preparation, application and testing of dispersions for textile finishing

		Examples														
		Recipe 1					Recipe 2					Recipe 3				
		39	42	43	44	45	46	47	48	49	41	50	51	52	53	
Polyfluoroacrylate No.		29	30	31	34	37	32	33	35	38	29	33	34	36	37	
Polyfluoroacrylate amount		37.5	37.5	37.5	37.5	37.5	69.5	69.5	69.5	69.5	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	-	-	-	-	-	
2-EHAC		-	-	-	-	-	-	-	-	-	12.5	12.5	12.5	12.5	12.5	
VC		-	-	-	-	-	8.5	8.5	8.5	8.5	-	-	-	-	-	
VDC		-	-	-	-	-	-	-	-	-	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	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	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	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	-	-	-	-	-	
SDS		-	-	-	-	-	-	-	-	-	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	35.0	35.0	35.0	35.0	35.0	
Prior to washing	IPA	80	95	45	90	60	80	90	40	80	90	95	60	40	60	
	oleo	6-7	6	4-5	5	5	5-6	6	5	6-7	6	6	4-5	4	4-5	
	hydro	100	100	90	90-100	80	90-100	100	80-90	100	100	100	80-90	90	80-90	
After 5 washes	IPA	60	80	40	90	45	80	90	45	80	70	90	45	40	60	
	oleo	6	5-6	4	5	5	5-6	5	4-5	5-6	6	5-6	4	4	3-4	
	hydro	90-100	100	70-80	90	80	80	90-100	80	100	90-100	100	70-80	80	80	

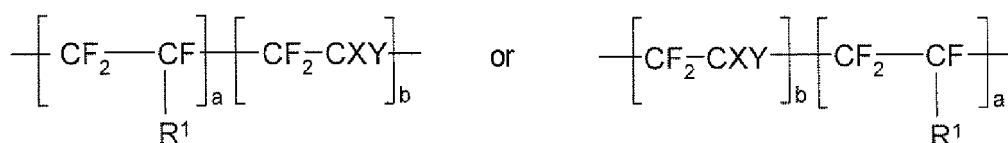
Claims

1. 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



10 Z is CH_2OR^3 or $\text{COO}^- 1/q \text{M}^{q+}$ or $\text{CON}(\text{R}^4)\text{R}^5\text{OR}^3$

X and Y are H, Cl or F

R^1 is CF_3 , OR^2 , Cl, Br or I,

R^2 is perfluoromethyl, perfluoropropyl or perfluoropropyloxypropyl

R^3 is H or $\text{COCR}^6=\text{CH}_2$

15 R^4 is H or alkyl of 1 to 6 carbon atoms

R^5 is alkylene of 1 to 13 carbon atoms

R^6 is H or CH_3

M is H or a metal cation or an ammonium cation or a substituted ammonium cation

q is the valency of M

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

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

25

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
30 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.

5

6. Compounds according to Claim 1, characterized in that R_F is a polyfluoroalkyl radical of 1 to 3 fluorinated carbon atoms.

10 7. Compounds according to Claim 1, characterized in that R_F is a polyfluoroalkyl radical of 4 to 16 fluorinated carbon atoms.

15 8. Compounds according to Claim 1, characterized in that the molecular weight of the compounds of the formula IV is more than 750 g/mol.

9. Compounds according to Claim 1, characterized in that $a + b$ is > 3 .

20

10. Copolymers containing a monomer of the formula IV, where Z is $CH_2OCOCR^6=CH_2$ or $CON(R^4)R^5OCOCR^6=CH_2$, one or more nonfluorous polymerizable vinyl monomers, one or more thermally crosslinkable or isocyanate-reactive monomers and optionally a chlorine-containing polymerizable vinyl monomer.

25

11. Copolymers containing, based on the total weight of the copolymer:

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

30 $CH_2OCOCR^6=CH_2$ or $CON(R^4)R^5OCOCR^6=CH_2$,

b) 0% to 80% by weight and preferably 10% to 50% by weight of one or more nonfluorous polymerizable vinyl monomers and/or

- c) 0.5% to 20% by weight and preferably 1% to 10% by weight of one or more thermally crosslinkable or isocyanate-reactive monomers.
- 5 12. Copolymers containing, based on the total weight of the copolymer:
- 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 $\text{CH}_2\text{OCOCR}^6=\text{CH}_2$ or $\text{CON}(\text{R}^4)\text{R}^5\text{OCOCR}^6=\text{CH}_2$,
- 10 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-containing polymerizable vinyl monomer.
- 15
13. Use of the copolymers according to Claims 10 to 12 for water-, oil- and soil-repellent finishing of fibrous substrates.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/056176

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06M15/277 C08F20/24 C07C67/08 C07C69/653

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)
D06M C08F C07C

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	US 3 498 958 A (RAY-CHAUDHURI DILIP K ET AL) 3 March 1970 (1970-03-03) column 5, lines 14-22; claims 1,9 -----	1-13
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X	EP 0 457 610 A2 (NIPPON OILS & FATS CO LTD [JP]) 21 November 1991 (1991-11-21) page 6, compound 4 ----- -/--	1-13

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

22/11/2007

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/056176

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 3 304 278 A (MURRAY HAUPTSCHHEIN ET AL) 14 February 1967 (1967-02-14) column 3, lines 55-60,70-75 -----	1-13
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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/056176

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/EP2007/056176

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	IIJIMA, HIROSHI ET AL: "NMR Study of the Transformation of Perfluorinated Surfactant Solutions" BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN , 72(2), 171-177 CODEN: BCSJA8; ISSN: 0009-2673, 1999, XP002457239 the whole document -----	1-9
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2007/056176

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 report covers 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 1-13 (parts)

- A compound of the formula IV (see claim 1) wherein Z is $\text{CON}(\text{R}_4)\text{R}_5\text{OCOCR}_6=\text{CH}_2$
- 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: 1-13 (parts)

- A compound of the formula IV (see claim 1) wherein Z is $\text{CH}_2\text{OCOCR}_6=\text{CH}_2$
- A copolymer containing the above fluorous telomeric compound
- The use of the above copolymer for water-,oil- and soil-repellent finishing of fibrous substrates

3. claims: 1-9 (parts)

- A compound of the formula IV (see claim 1) wherein Z is $\text{CON}(\text{R}_4)\text{R}_5\text{OH}$

4. claims: 1-9 (parts)

- A compound of the formula IV (see claim 1) wherein Z is CH_2OH

5. claims: 1-9 (parts)

- A compound of the formula IV (see claim 1) wherein Z is $\text{COO}-1/\text{qMq}+$

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/056176

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