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(54) RECOVERY OF FLUORINATED CARBOXYLIC ACID FROM ADSORBENT PARTICLES

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(57) **ABSTRACT**

A process for the recovery of fluorinated carboxylic acid or derivative thereof from adsorbent particles on which fluorinated carboxylic acid or a salt thereof is adsorbed. The process includes contacting the adsorbent particles with a liquid composition capable of removing at least part of the fluorinated carboxylic acid or salt thereof from the adsorbent particles. The fluorinated carboxylic acid or salt thereof is selected from the group consisting of fluorinated carboxylic acids or salts thereof that correspond to the general formula:

$$[R_fO\text{-}L\text{-}COO^-]_iX^{i+} \quad (I)$$

wherein L represents a linear partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a linear partially or fully fluorinated aliphatic group or a linear partially or fully fluorinated aliphatic group interrupted with one or more oxygen atoms, X^{i-} represents a cation having the valence i and i is 1, 2 or 3.

RECOVERY OF FLUORINATED CARBOXYLIC ACID FROM ADSORBENT PARTICLES

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application claims priority to Great Britain Application No. 0525978.3, filed on Dec. 21, 2005; Great Britain Application No. 0523853.0, filed on Nov. 24, 2005; Great Britain Application No. 0514398.7, filed on Jul. 15, 2005; and Great Britain Application No. 0514387.0 filed on Jul. 15, 2005, all of which are herein incorporated by reference in their entirety.

[0002] The present invention relates to the recovery of fluorinated carboxylic acids and derivatives thereof from adsorbent particles.

[0003] Polymerization of fluoroolefins to manufacture fluoropolymers, i.e. polymers having a fluorinated backbone, is often performed in aqueous media. In one such process referred to as emulsion polymerization, fluorinated carboxylic acids are typically used as surfactants in the aqueous media. Examples of these fluorosurfactants include the perfluorinated alkanecarboxylic acids having 7 to 10 carbon atoms, in particular perfluorooctanoic acid (PFOA). These acids are generally used in the salt form, preferably as ammonium salts. Fluoropolymerization to make "granular fluoropolymer" is also done in aqueous media in a process sometimes referred to as suspension polymerization, though with less fluorosurfactant (or none) than is used in dispersion polymerization. For a discussion of the processes, see "Tetrafluoroethylene Polymers" in the Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, New York, 1989, Vol. 16, p. 580.

[0004] Because of its expense and to avoid undesirable release in the environment, the fluorosurfactant used in the polymerization processes is typically removed from the dispersions and waste streams generated in the manufacturing of the fluoropolymer, including waste waters and exhaust gas. An effective and frequently used method involves adsorbing the fluorosurfactant to adsorbent particles such as activated carbon and anion exchange resins. Such processes have been described in EP 1514848, EP 1093441, EP 1084097 and WO 2005/082785. Following the adsorption to the adsorbent particles, the fluorosurfactant is typically recovered there from using an eluting liquid as disclosed in for example EP 0014431, EP1069078, U.S. Pat. No. 6,642,415, EP 1323677 and U.S. Pat. No. 3,882,153.

[0005] These processes are typically practiced for recovering perfluorooctanoic acid or salts thereof, which is the most widely used surfactant in making fluoropolymers through aqueous emulsion polymerization. Unfortunately, these surfactants are eliminated only slowly from the body of living organisms and they hence show an undesirably high bioaccumulation. Notwithstanding the fact that these surfactants are recovered from the adsorbent particles, these processes themselves are disadvantages because operators of these processes may come into contact with the surfactants or derivatives thereof and hence special measures are typically necessary to avoid such contact or to at least minimize exposure of the operators to these compounds.

[0006] There was therefore a desire to find alternative surfactants that can be used in the making of fluoropolymer in aqueous emulsion polymerization and that can be recovered from adsorbent particles. It was in particular desirable to find alternative surfactants that eliminate faster from the body of living organisms and that thus have lower bioaccumulation than perfluorooctanoic acid or salts thereof.

[0007] In accordance with one aspect of the present invention, there is provided a process comprising recovery of fluorinated carboxylic acid or derivative thereof from adsorbent particles on which fluorinated carboxylic acid or a salt thereof is adsorbed, by contacting said adsorbent particles with a liquid composition capable of removing at least part of said fluorinated carboxylic acid or salt thereof from said adsorbent particles, wherein said fluorinated carboxylic acid or salt thereof is selected from the group consisting of fluorinated carboxylic acids or salts thereof that correspond to the general formula:

$$[R_fO\text{-}L\text{-}COO^-]_iX^{i+} \quad (I)$$

wherein L represents a linear partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a linear partially or fully fluorinated aliphatic group or a linear partially or fully fluorinated aliphatic group interrupted with one or more oxygen atoms, X^{i-} represents a cation having the valence i and i is 1, 2 or 3.

[0008] It has been found that the fluorinated carboxylic acids or salts thereof according to formula (I) are suitable for making fluoropolymers by aqueous emulsion polymerization. These compounds can be removed from dispersions and waste streams by adsorbing them on adsorbent particles. They can furthermore be recovered from these adsorbent particles using a liquid composition capable of removing at least part of said fluorinated carboxylic acid or salt thereof from said adsorbent particles so that the fluorinated carboxylic acid can be re-used (after possible further purification) in the polymerization of fluorinated monomers. The fluorinated carboxylic acids or salts thereof typically have lower bioaccumulation than perfluorooctanoic acids or salts thereof and hence the elution process according to the invention provides advantages for the operators involved with the process.

[0009] By the term 'liquid composition capable of removing at least part of said fluorinated carboxylic acid or salt thereof from said adsorbent particles' is meant a liquid that is capable of dissolving and/or desorbing the fluorinated carboxylic acid and/or its salt or that alternatively converts the fluorinated carboxylic acid or salt into a derivative such as an ester that may be recovered from the mixture of adsorbent particles and the liquid. For sake of convenience, the liquid composition capable of removing at least part of said fluorinated carboxylic acid or salt thereof from said adsorbent particles will hereinafter be referred to as eluting liquid.

[0010] Fluorinated Carboxylic Acid

[0011] For the sake of convenience, the term 'fluorinated carboxylic acid' is hereinafter used to indicate the free acid as well as salts thereof. The fluorinated carboxylic acid used in the process of the invention corresponds to formula (I) above. Generally, the fluorinated carboxylic acid will be a low molecular weight compound, for example a compound having a molecular weight for the anion part of the compound of not more than 1000 g/mol, typically not more than

600 g/mol and in particular embodiments, the anion of the fluorinated carboxylic acid may have a molecular weight of not more than 500 g/mol.

[0012] Particularly preferred fluorinated carboxylic acids are those that when administered to rats show a recovery of at least 45%, for example at least 50% of the administered amount after 96 hours via renal elimination and that have a renal elimination half-life of not more than 35 hours, for example of not more than 30 hours in rats as tested according to the method set forth in the examples. Generally, fluorinated carboxylic acids in which each of the fluorinated aliphatic moieties in the compound have not more than 3 carbon atoms fulfill the aforementioned conditions of renal recovery and half-life. Thus, preferred compounds are those in which any fluorinated alkylene groups have not more than 3 carbon atoms and in which a fluorinated alkyl group of the compound has not more than 3 carbon atoms.

[0013] In the above formula (I), L represents a linking group. In one embodiment, the linking group can be a linear partially or fully fluorinated alkylene. Fully fluorinated alkylene groups include alkylene groups that consist of only carbon and fluorine atoms whereas partially fluorinated alkylene groups may additionally contain hydrogen. Generally, a partially fluorinated alkylene group should not contain more than 2 hydrogen atoms so as to be highly fluorinated and be non-telogenic or at least have minimal telogenic effects. Examples of fully fluorinated alkylene groups include linear perfluorinated alkylenes that have from 1 to 6 carbon atoms, for example linear perfluorinated alkylene groups of 1, 2, 3, 4 or 5 carbon atoms.

[0014] Examples of linear partially fluorinated alkylene groups include those that have from 1 to 6 carbon atoms. In a particular embodiment the linear partially fluorinated alkylene linking group has 1, 2, 3, 4, 5 or 6 carbon atoms and has only 1 or 2 hydrogen atoms. When the partially fluorinated alkylene group has 2 hydrogen atoms, they may be attached to the same carbon atom or they can be attached to different carbon atoms. When they are attached to different carbon atoms, such carbon atoms can be adjacent to each other or not. Also, in a particular embodiment, a carbon atom having 1 or 2 hydrogen atoms may be adjacent the ether oxygen atom to which the linking group is attached or adjacent the carboxylic group to which the linking group is attached at its other end.

[0015] In a further embodiment, the linking group L is an aliphatic hydrocarbon group. Examples of aliphatic hydrocarbon groups include linear, branched or cyclic aliphatic groups. Particular examples of aliphatic groups include linear or branched alkylene groups of 1 to 4 carbon atoms such as for example methylene or ethylene.

[0016] Particular examples of linking groups L may be selected from the following:

[0017] $—(CF_2)_g—$ wherein g is 1, 2, 3, 4, 5 or 6;

[0018] $—CFH—(CF_2)_h—$ wherein h is 0, 1, 2, 3, 4 or 5;

[0019] $—CF_2—CFH—(CF_2)_d—$ wherein d is 0, 1, 2, 3 or 4;

[0020] $—CH_2—(CF_2)_h—$ wherein h is 1, 2, 3 or 4;

[0021] $—(CH_2)_c—$ wherein c is 1, 2, 3 or 4;

[0022] In the above examples, the left side of the formula of the linking group is the site where the linking group is connected to the ether oxygen in formula (I).

[0023] The R_f group in formula (I) represents a linear partially or fully fluorinated aliphatic group or a linear partially or fully fluorinated aliphatic group interrupted with one or more oxygen atoms. In one embodiment, R_f is a linear perfluorinated aliphatic group having 1 to 6 carbon atoms, preferably having 1, 2, 3 or 4 carbon atoms. According to another embodiment R_f is a linear perfluorinated aliphatic group interrupted with one or more oxygen atoms of which the alkylene groups between oxygen atoms have not more than 4 or 6 carbon atoms, for example 3 or less carbon atoms and wherein the terminal alkyl group has not more than 4 or 6 carbon atoms, for example 3 or less carbon atoms. According to a still further embodiment, R_f is a linear partially fluorinated aliphatic group having 1 to 6 carbon atoms and not more than 2 hydrogen atoms or a linear partially fluorinated aliphatic group interrupted with one or more oxygen atoms and which has not more than 2 hydrogen atoms. In the latter embodiment, it will generally be preferred that any perfluorinated alkylene moiety has not more than 4 or 6 carbon atoms and any terminal perfluorinated alkyl group, likewise preferably should not have more than 6 carbon atoms, for example not more than 4 carbon atoms. A particular example of a partially fluorinated aliphatic group R_f is $CF_3CFH—$.

[0024] In a particular embodiment, R_f may correspond to the following formula:

$$R_f^1—[OR_f^2]_p—[OR_f^3]_q— \quad (II)$$

[0025] wherein R_f^1 is a perfluorinated linear aliphatic group of 1 to 6 carbon atoms (for example 3 or less), R_f^2 and R_f^3 each independently represents a linear perfluorinated alkylene of 1, 2, 3 or 4 carbon atoms and p and q each independently represent a value of 0 to 4 and wherein the sum of p and q is at least 1.

[0026] In another embodiment, R_f may correspond to the following formula:

$$R^7_f—(O)_t—CFH—CF_2— \quad (III)$$

[0027] wherein t is 0 or 1 and R^7_f represents a linear partially or fully fluorinated aliphatic group optionally interrupted with one or more oxygen atoms. Typically R^7_f does not contain perfluorinated aliphatic moieties of more than 4 or 6 carbon atoms. For example, in one embodiment, R^7_f is a perfluorinated linear aliphatic group of 1 to 6 carbon atoms. In another embodiment, R^7_f is a group corresponding to above formula (II).

[0028] In yet a further embodiment, R_f may correspond to the following formula:

$$R_f^1—(OCF_2)_a— \quad (IV)$$

[0029] wherein a is an integer of 1 to 6 and R_f^8 is a linear partially fluorinated aliphatic group or a linear fully fluorinated aliphatic group having 1, 2, 3 or 4 carbon atoms. When R_f^8 is a partially fluorinated aliphatic group, the number of carbon atoms preferably is between 1 and 6 and the number of hydrogen atoms in the partially fluorinated aliphatic groups is preferably 1 or 2.

[0030] In a still further embodiment, R_f may correspond to the following formula:

$$R_f^9—O—(CF_2)_b— \quad (V)$$

[0031] wherein b is an integer of 1 to 6, preferably 1, 2, 3 or 4 and R_f^9 is a linear partially fluorinated aliphatic group or a linear fully fluorinated aliphatic group having 1, 2, 3 or 4 carbon atoms. When R_f^9 is a partially fluorinated aliphatic group, the number of carbon atoms preferably is between 1 and 6 and the number of hydrogen atoms in the partially fluorinated groups is preferably 1 or 2.

[0032] In a particular embodiment of the present invention, the fluorinated carboxylic acid corresponds to the following formula:

$$[R_f^a—(O)_t—CHF—(CF_2)_n—COO^-]_iX^{i+} \quad (VI)$$

[0033] wherein R_f^a represents a linear partially or fully fluorinated aliphatic group optionally interrupted with one or more oxygen atoms, t is 0 or 1 and n is 0 or 1, X^{i+} represents a cation having a valence i and i is 1, 2 or 3, with the proviso that when t is 0, the R_f^a contains at least one ether oxygen atom.

[0034] In a particular aspect of this embodiment, the R_f^a is selected from the group consisting of linear perfluorinated aliphatic groups of 1 to 6 carbon atoms, preferably having 1 to 4 carbon atoms, perfluorinated groups of the formula $R_f^1—[OR_f^2]_p—[OR_f^3]_q—$ wherein R_f^1 is a linear perfluorinated aliphatic group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, R_f^2 and R_f^3 each independently represents a linear perfluorinated alkylene of 1, 2, 3 or 4 carbon atoms and p and q each independently represent a value of 0 to 4 and wherein the sum of p and q is at least 1 and perfluorinated groups of the formula $R_f^4—[OR_f^5]_k—[OR_f^6]_m—O—CF_2—$ wherein R_f^4 is a linear perfluorinated aliphatic group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, R_f^5 and R_f^6 each independently represents a linear perfluorinated alkylene of 1, 2, 3 or 4 carbon atoms and k and m each independently represent a value of 0 to 4.

[0035] Fluorinated carboxylic acid of formula (VI) can be derived from fluorinated olefins of the general formula:

$$R^a_f—(O)_t—CF=CF_2 \quad (VIa)$$

[0036] wherein R^a_f and t are as defined above. Compounds according to formula (VIa) are well known in the art and include fluorinated olefins such as perfluorinated alkyl vinyl compounds, vinyl ethers in particular perfluorovinyl ethers and allyl ethers, in particular perfluorinated allyl ethers.

[0037] Fluorinated carboxylic acids according to formula (VI) wherein n is 0 can be prepared by reacting a fluorinated olefin of formula (VIa) with a base. The reaction is generally carried out in aqueous media. An organic solvent may be added to improve the solubility of the fluorinated olefin. Examples of organic solvents include glyme, tetrahydrofuran (THF) and acetonitrile. Additionally or alternatively a phase transfer catalyst may be used. As a base, use can be made of for example ammonia, alkali and earth alkali hydroxides. Without intending to be bound by any theory, it is believed, that the reaction proceeds according to the following sequence when ammonia is used as a base:

$$R_f—(O)_t—CF=CF_2+NH_3+H_2O \rightarrow R_f—(O)_t—CHF—COONH_4+NH_4F$$

[0038] The reaction is generally carried out between 0 and 200° C., for example between 20-150° C. and at a pressure between about 1 bar up to about 20 bar. For further purification, the obtained salts can be distilled via the free acid or by first converting the acid into an ester derivative and then distilling the ester derivative followed by hydolysis of the ester to obtain the purified acid or salt thereof.

[0039] Fluorinated carboxylic acids of formula (VI) wherein n is 0 can also be prepared by reacting a fluorinated olefin of formula (VIa) with a hydrocarbon alcohol in an alkaline medium and then decomposing the resulting ether in acidic conditions thereby forming the corresponding carboxylic acid. Suitable hydrocarbon alcohols include aliphatic alcohols such as lower alkanols having 1 to 4 carbon atoms. Specific examples include methanol, ethanol and butanol including t-butanol. The reaction of the fluorinated olefin with the alcohol in an alkaline medium may be carried out as described in "Furin et al., Bull Korean Chem. Soc. 20, 220 (1999)". The reaction product of this reaction is an ether derivative of the fluorinated olefin. This resulting ether can be decomposed under acidic conditions as described in "D. C. England, J. Org. Chem. 49, 4007 (1984)" to yield the corresponding carboxylic acid or salt thereof.

[0040] To prepare fluorinated carboxylic acids of formula (VI) wherein n is 1, a free radical reaction of the fluorinated olefin of formula (VIa) with methanol may be carried out followed by an oxidation of the resulting reaction product. The free radical reaction is typically carried out using a free radical initiator as is typically used in a free radical polymerization reaction. Examples of suitable free radical initiators include persulfates such as for example ammonium persulfate. Detailed conditions of the free radical reaction of the fluorinated carboxylic acid with an alcohol can be found in "S. V. Sokolov et al., Zh. Vses. Khim Obsh 24, 656 (1979)". The resulting alcohol derivative of the fluorinated olefin can be chemically oxidized with an oxidizing agent to the corresponding carboxylic acid. Examples of oxidizing agents include for example potassium permanganate, chromium (VI) oxide, RuO_4 or OsO_4 optionally in the presence of NaOCl, nitric acid/iron catalyst, dinitrogen tetroxide. Typically the oxidation is carried out in acidic or basic conditions at a temperature between 10 and 100° C. In addition to chemical oxidation, electrochemical oxidation may be used as well.

[0041] In another embodiment, the fluorinated carboxylic acid corresponds to the following formula:

$$R_f^b—(O)_t—CFH—CF_2—O—R\text{-}G \quad (VII)$$

[0042] wherein R_f^b represents a linear partially or fully fluorinated aliphatic group optionally interrupted with one or more oxygen atoms, R is an aliphatic hydrocarbon group, G represents a carboxylic acid or salt thereof, t is 0 or 1. Particular examples for R include a methylene group or an ethylene group.

[0043] In a particular aspect of this embodiment, the R_f^b is selected from the group consisting of linear perfluorinated aliphatic groups of 1 to 6 carbon atoms, preferably having 1 to 4 carbon atoms, perfluorinated groups of the formula $R_f^1—[OR_f^2]_p—[OR_f^3]_q—$ wherein R_f^1 is a linear perfluorinated aliphatic group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, R_f^2 and R_f^3 each independently represents a linear perfluorinated alkylene of 1, 2, 3 or 4 carbon atoms and p and q each independently represent a value of 0 to 4 and wherein the sum of p and q is at least 1 and perfluori-

nated groups of the formula R_f^4—$[OR_f^5]_k$—$[OR_f^6]_m$—O—CF_2— wherein R_f^4 is a linear perfluorinated aliphatic group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, R_f^5 and R_f^6 each independently represents a linear perfluorinated alkylene of 1, 2, 3 or 4 carbon atoms and k and m each independently represent a value of 0 to 4.

[0044] Fluorinated carboxylic acids according to formula (VII) may be prepared through the preparation of an intermediate of formula (VIIa):

$$R_f^b—(O)_t—CFH—CF_2—O—R\text{-}Z$$

[0045] wherein R_f^b, t and R have the same meaning as defined above. Z represents a carboxylic acid ester or a carboxylamide.

[0046] The intermediate compound according to formula (VIIa) can be prepared by reacting a fluorinated olefin of the general formula (VIa) with an organic compound of the formula

$$HO—R\text{-}Z \quad (VIIb)$$

[0047] wherein Z and R are as defined above. Compounds according to formula (VIIb) are well known in the art and/or are commercially available. The reaction of compound (VIa) with compound (VIIb) is typically carried out in the presence of a base although it is also possible to carry out the reaction under acidic or neutral conditions. Suitable bases include carbonates such as potassium carbonate, sodium carbonate and lithium carbonate, hydroxides, alkoholates etc. The amount of base used may vary widely. For example a catalytic amount may be used. Generally the amount of base used will be about at least 1 or 2% by weight based on the amount of reactant of formula (VIIb). In a particular embodiment, the amount of base can be upto 2 times the molar amount of the reactant of formula (VIIb). The reaction is typically carried out in an aprotic solvent such as for example, tetrahydrofuran, acetonitrile, glyme, diglyme etc. Further suitable aprotic solvents are disclosed in DE 3828063. The reaction is typically carried out a temperature between 0 and 200° C., for example between 10 and 150° C. The reaction is generally carried out at an ambient pressure (1 bar) or up to 20 bar. Following the reaction, the resulting compound may be isolated and purified by distillation.

[0048] The fluorinated carboxylic acids of formula (VII) can be readily prepared by hydrolyzing the intermediate compound of formula (VIIa) above. In formula (VIIa) above, Z represents a carboxylic acid ester or a carboxylamide. Typically a carboxylic acid ester is used. In one embodiment, the ester can be an aliphatic ester, e.g. an alkyl ester in which the number of carbon atoms in the alkyl group are from 1 to 4. Hydrolysis of the intermediate compound may be carried out under acidic or basic conditions and is generally carried out in an alcoholic acidic or basic solution of the intermediate compound. Alternatively the intermediate compound may be hydrolysed in an acidic or basic solution of other water miscible organic solvents such as ketones, ethers etc. Typically, a basic alcoholic solution is used such as for example a methanol or ethanol solution containing an alkali metal hydroxide as the base. Typically the hydrolysis is carried out at room temperature but it is also possible to use elevated temperatures of for example up to the boiling point of the solution.

[0049] Alternatively, the fluorinated surfactant may be prepared by reacting the fluorinated olefin of formula (VIa) above with a hydroxy substituted carboxylic acid or salt thereof.

[0050] Thus, in accordance with this embodiment the fluorinated olefin of formula (VIa) is reacted with a compound of the formula:

$$HO—R\text{-}G \quad (VIc)$$

[0051] wherein G is a carboxylic acid group or salt thereof and R is as defined above. The reaction of a fluorinated olefin of formula (VIa) with a hydroxy compound or formula (VIIc) can be carried out under the same conditions described above for the reaction with compounds of formula (VIIb).

[0052] In a still further embodiment, the fluorinated carboxylic acid corresponds to one of the following formulas:

$$R_f^c—(OCF_2)_u—O—(CF_2)_v\text{-}AC \quad (VIII)$$

[0053] wherein u is an integer of 1 to 6, v is an integer of 1 to 6, R_f^c represents a linear perfluorinated aliphatic group of 1, 2, 3 or 4 carbon atoms and AC represents a carboxylic acid group or salt thereof, and

$$R_f^c—O—(CF_2)_y—O\text{-}L^1\text{-}AC \quad (IX)$$

[0054] wherein y has a value of 1, 2, 3, 4, 5 or 6, L^1 represents a linear perfluorinated alkylene of 1, 2, 3, 4, 5 or 6 carbon atoms or a linear partially fluorinated alkylene having 1 to 6 carbon atoms and 1 or 2 hydrogen atoms, R_f^c is as defined in above formula (VIII) and AC represents a carboxylic acid group or salt thereof. A particular example for L^1 includes a group of the formula —CFH—. Particular compounds according to formula (IX) include those wherein R_f^c represents CF_3CFH—. Such groups can be obtained from decarboxylation of —$CF(CF_3)COOX$ groups (X is a cation) in the presence of a protic substance as described in JOC 34, 1841 (1969).

[0055] Fluorinated carboxylic acids of formula (VIII) are commercially available from Anles Ltd., St. Petersburg, Russia. These compounds may be prepared for example as described by Ershov and Popova in Fluorine Notes 4(11), 2002. Also, these fluorinated carboxylic acids typically form as byproducts in the manufacturing of hexafluoropropylene oxide by direct oxidation of hexafluoropropylene.

[0056] Fluorinated carboxylic acids according to formula (IX) can be derived from reactants that are also used in the manufacturing of fluorinated vinyl ethers as described in U.S. Pat. No. 6,255,536.

[0057] In another embodiment acid fluorides of formula (X) are reacted with a metal fluoride like KF or CsF:

$$R_f^g—COF \quad (X)$$

[0058] wherein R_f^g is a partially or perfluorinated linear aliphatic chain optionally interrupted with one or more oxygen atoms. This reaction results in an alkoxylate that can be further reacted with a carboxylic acid derivative of formula (XI)

$$Y—(CH_2)_n\text{-}Q \quad (XI)$$

[0059] wherein Y represents a leaving group like iodide, bromide, chloride, mesylate, tosylate and the like, n is an integer from 1 to 3, and Q represents a carboxyl acid group or a lower alkyl ester. The reaction results in fluorinated carboxylic acid derivatives of formula (XII)

$$R_f^g—CF_2—O—(CH_2)_nQ \quad (XII)$$

[0060] with R_f^g n, and Q having the same meaning as above. The corresponding salts can be obtained by saponification.

[0061] In yet a further embodiment the fluorinated carboxylic acids correspond to formula (XIII)

$$CF_3—CF_2—O—R_f^h—COOX \quad (XIII)$$

[0062] with R_f^h representing a linear partially or fully fluorinated linear carbon chain of 1 to 8 carbon atoms optionally interrupted with one or more oxygen atoms, for example a perfluorinated linear aliphatic group of 1 to 6 carbon atoms, for example 1, 2, 3 or 4 carbon atoms and X is a monovalent cation. Compounds of this formula can be made by conversion of diacid difluorides of formula (XIV) in the presence of e.g. antimony pentafluoride.

$$FOC—CF(CF_3)—O—R_f^h—COF \quad (XIV)$$

[0063] This conversion may be carried out at elevated temperature according to the method described in U.S. Pat. No. 3,555,100 resulting preferably in the decarbonylation of the secondary COF group. The resulting mono acid fluoride can be converted to the corresponding salt using well known methods.

[0064] Fluorinated carboxylic acids having a —O—CF_2—COOX group can be obtained from the corresponding vinyl ethers —O—CF═CF_2. Reaction of the vinyl ether with oxygen according to U.S. Pat. No. 4,987,254 results in acid fluorides carrying a —O—CF_2COF group which can be readily converted to the corresponding acid or salt.

[0065] Specific examples of compounds according to formula (I) include the following:

$$R_f—O—CHF—COOH$$

[0066] C_3F_7—O—CHF—COOH

[0067] CF_3—O—CF_2CF_2—CF_2—O—CHF—COOH

[0068] $CF_3CF_2CF_2$—O—CF_2CF_2—CF_2—O—CHF—COOH

[0069] CF_3—O—CF_2—CF_2—O—CHF—COOH

[0070] CF_3—O—CF_2—O—CF_2—CF_2—O—CHF—COOH

[0071] CF_3—(O—CF_2)$_2$—O—CF_2—CF_2—O—CHF—COOH

[0072] CF_3—(O—CF_2)$_3$—O—CF_2—CF_2—O—CHF—COOH

$$R_f—O—CHF—CF_2—COOH$$

[0073] CF_3—O—CHF—CF_2—COOH

[0074] CF_3—O—CF_2—CF_2—O—CHF—CF_2—COOH

[0075] CF_3—CF_2—O—CHF—CF_2—COOH

[0076] CF_3—O—CF_2—F_2—CF_2—O—CHF—CF_2—COOH

[0077] CF_3—O—CF_2—O—CF_2—CF_2—O—CHF—CF_2—COOH

[0078] CF_3—(O—CF_2)$_2$—O—CF_2—CF_2—O—CHF—CF_2—COOH

[0079] CF_3—(O—CF_2)$_3$—O—CF_2—CF_2—O—CHF—CF_2—COOH

$$R_f—O—CF_2—CHFCOOH$$

[0080] CF_3—O—CF_2—CHF—COOH

[0081] C_3F_7—O—CF_2—CHF—COOH

[0082] CF_3—O—CF_2—CF_2—CF_2—O—CF_2—CHF—COOH

[0083] CF_3—O—CF_2—O—CF_2—CF_2—O—CF_2—CHF—COOH

[0084] CF_3—(O—CF_2)$_2$—O—CF_2—CF_2—O—CF_2—CHF—COOH

[0085] CF_3—(O—CF_2)$_3$—O—CF_2—CF_2—O—CF_2—CHF—COOH

$$R_f—O—CF_2—CHF—CF_2COOH$$

[0086] CF_3—O—CF_2—CHF—CF_2—COOH

[0087] C_2F_5—O—CF_2—CHF—CF_2—COOH

[0088] C_3F_7—O—CF_2—CHF—CF_2—COOH

[0089] CF_3—O—CF_2—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH

[0090] CF_3—O—CF_2—O—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH

[0091] CF_3—(O—CF_2)$_2$—O—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH

[0092] CF_3—(O—CF_2)$_3$—O—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH

$$R_f—(O)_m—CHF—CF_2—O—(CH_2)_n—COOH$$
n=1,2 or 3; m=0 or 1

[0093] CF_3—O—CHF—CF_2—O—CH_2—COOH

[0094] CF_3—O—CF_2—CF_2—CF_2—O—CHF—CF_2—O—CH_2—COOH

[0095] C_3F_7—O—CHF—CF_2—O—CH_2—COOH

[0096] C_3F_7—O—CHF—CF_2—O—CH_2—CH_2—COOH

[0097] C_3F_7—O—CF_2—CF_2—O—CHF—CF_2—OCH_2COOH

[0098] C_3F_7—O—CF_2—CF_2—CF_2—O—CHF—CF_2—OCH_2COOH

[0099] C_3F_7—O—CF_2—CHF—CF_2—OCH_2COOH

[0100] CF_3—CHF—CF_2—O—CH_2COOH

[0101] C_3F_7—CF_2—CHF—CF_2—OCH_2—COOH

[0102] CF_3—O—CF_2—CF_2—O—CH_2—COOH

[0103] CF_3—O—CF_2—CF_2—CF_2—O—CF_2—CF_2—O—CH_2—COOH

[0104] C_3F_7—O—CF_2—CF_2—O—CH_2—COOH

[0105] C_3F_7—O—CF_2—CF_2—O—CH_2—CH_2—COOH

[0106] C_3F_7—O—CF_2—CF_2—O—CF_2—CF_2—OCH_2COOH

[0107] C_3F_7—O—CF_2—CF_2—CF_2—O—CF_2-CF_2—OCH_2COOH

[0108] C_3F_7—O—CF_2—CF_2—CF_2—OCH_2COOH

[0109] C_4F_9—O—CH_2—COOH

[0110] C_4F_9—O—CH_2—CH_2—COOH

[0111] C_3F_7—O—CH_2COOH

[0112] C_6F_{13}—OCH_2—COOH

R_f—O—CF_2—CF_2—COOH

[0113] CF_3—O—CF_2—CF_2—COOH

[0114] C_2F_5—O—CF_2—CF_2—COOH

[0115] C_3F_7—O—CF_2—CF_2—COOH

[0116] C_4F_9—O—CF_2—CF_2—COOH

R_f—$(O—CF_2)_u$—O—CF_2—COOH with u being as defined above

[0117] CF_3—$(O—CF_2)_3$—O—CF_2—COOH

[0118] CF_3—$(O—CF_2)_2$—O—CF_2—COOH

[0119] CF_3—$(O—CF_2)_1$—O—CF_2—COOH

R_f—$(O—CF_2—CF_2)_k$—O—CF_2—COOH with k being 1, 2 or 3

[0120] CF_3—$(O—CF_2—CF_2)_1$—O—CF_2—COOH

[0121] C_2F_5—$(O—CF_2—CF_2)_1$—O—CF_2—COOH

[0122] C_3F_7—$(O—CF_2—CF_2)_1$—O—CF_2—COOH

[0123] C_4F_9—$(O—CF_2—CF_2)_1$—O—CF_2—COOH

[0124] C_2F_5—$(O—CF_2—CF_2)_2$—O—CF_2—COOH

[0125] CF_3—$(O—CF_2—CF_2)_2$—O—CF_2—COOH

[0126] C_3F_7—$(O—CF_2—CF_2)_2$—O—CF_2—COOH

[0127] C_4F_9—$(O—CF_2—CF_2)_2$—O—CF_2—COOH

R_f—O—CF_2—COOH

[0128] C_3F_7—O—CF_2—COOH

[0129] CF_3—O—CF_2—CF_2—CF_2—O—CF_2—COOH

CF_3—CHF—O—$(CF_2)_o$—COOH with o being an integer of 1, 2, 3, 4, 5 or 6

[0130] CF_3CFH—O—$(CF_2)_3$—COOH

[0131] CF_3CFH—O—$(CF_2)_5$—COOH

CF_3—CF_2—O—$(CF_2)_o$—COOH with o being as above

[0132] CF_3—CF_2—O—$(CF_2)_3COOH$

[0133] CF_3—CF_2—O—$(CF_2)_5COOH$

[0134] In the above generic formulas, R_f has the meaning as defined above in respect of generic formula (I). It is understood that while the above list of compounds only lists the acids, the corresponding salts, in particular the NH_4^+, potassium, sodium or lithium salts can equally be used.

[0135] Adsorbent Particles

[0136] By the term 'absorbent particles' in connection with the present invention is meant particles that are capable of physically adsorbing the fluorinated carboxylic acid or salt thereof by whatever mechanism of physical adsorption including but not limited to ionic interactions causing physical adsorption. Accordingly, the term 'adsorbent particles' include ion exchange resins, which typically bind fluorinated carboxylic acids, which have ionic groups, as a result of an ion exchange process although the adsorption to the exchange resin may also occur by a physical adsorption process other than the ion exchange process.

[0137] Suitable adsorbent particles further include activated carbon, silica gel, clays and zeolites. Conveniently used are activated carbon particles. The shape of the adsorbent particles is not particularly critical. For example, the adsorbent particles may have a plate shape, can be spherical, cylindrical or they can be rods. Also, adsorbent particles having a variety of different shapes may be used as a mixture. The size of the adsorbent particles is typically between 0.05 mm and 20 mm, generally between 0.1 and 10 mm. A practical range is between 0.5 and 5 mm. The adsorbent particles typically adsorb the fluorinated carboxylic acid on their surface and it will thus generally be preferred to optimize the specific surface area of the particles, i.e. the amount of surface per unit of weight. Typically, the specific surface area of the adsorbent particles will be between 10 and 5000 m^2/g, generally between 100 and 3000 m^2/g with a practical range being from 300 to 2000 m^2/g.

[0138] Additionally, anion exchange resin particles can be used as adsorbent particles. Examples of anion exchange resin that can be used to adsorb a fluorinated carboxylic acid include strong, medium strong as well as weak basic anion exchange resins. The terms strong, medium strong and weak basic anion exchange resin are defined in "Encyclopedia of Polymer Science and Engineering", John Wiley & Sons, 1985, Volume 8, page 347 and "Kirk-Othmer", John Wiley & Sons, 3rd edition, Volume 13, page 687. Strong basic anion exchange resin typically contain quaternary ammonium groups, medium strong resins usually have tertiary amine groups and weak basic resins usually have secondary amines as the anion exchange functions. Examples of anion exchange resins that are commercially available for use in this invention include AMBERLITE® IRA-402, AMBERJET® 4200, AMBERLITE® IRA-67 and AMBERLITE® IRA-92 all available from Rohm & Haas, PUROLITE® A845 (Purolite GmbH) and LEWATIT® MP-500 (Bayer AG).

[0139] Eluting Liquid

[0140] The fluorinated carboxylic acids that are adsorbed on an adsorbent particle may be recovered therefrom by eluting the loaded adsorbent particles with an eluting liquid capable of desorbing and/or dissolving the fluorinated carboxylic acid or a derivative thereof. The nature and composition of the eluting liquid typically depends on the nature of the adsorbent particles to which the fluorinated carboxylic acid is adsorbed and typically includes an organic solvent. Also, the recovery or elution of the adsorbent particles may be practiced over a wide range of temperature. For example, in one embodiment, the recovery is practiced at ambient temperature, i.e. between 10 and 35° C. In another embodiment, the recovery may be carried out at elevated tempera-

ture of for example 40° C. or more up to in certain embodiments the boiling point of the eluting liquid.

[0141] In one embodiment, the fluorinated carboxylic acid may be recovered from strongly, medium strong or weak basic anion exchange resin particles. The terms strong, medium strong and weak basic anion exchange resin are defined in "Encyclopedia of Polymer Science and Engineering", John Wiley & Sons, 1985, volume 8, page 347 and "Kirk-Othmer", John Wiley & Sons, 3rd edition, Volume 13, page 687. Strong basic anion exchange resins typically contain quaternary ammonium groups, medium strong resins usually have tertiary amine groups and weak basic resins usually have secondary amines as the anion exchange functions.

[0142] Suitable eluting liquids for eluting the fluorinated carboxylic acids from basic anion exchange resin particles include a mixture of a mineral acid and a water miscible organic solvent. Suitable mineral acids are all those the anions of which confer a salt form upon the anion exchanger (anion form) which is appropriate to the further adsorption of fluorinated emulsifying acids. Under the conditions of elution their oxidation strength should generally be so low that the anion exchanger will not be damaged oxidatively. Mineral acids that can be used include, for example ortho-, meta-, and diphosphoric acid, nitric acid and preferably hydrochloric acid and sulfuric acid.

[0143] Suitable organic solvents include polar organic solvents such as alcohols, aliphatic or aromatic ethers, nitrites, amides, sulfoxides, ketones and carboxylic acid esters. Preferred solvents include those that are substantially miscible with water, i.e. miscible to at least 40% by volume when mixing equal volumes, or solvents that are completely miscible with water. Solvents of this type are especially aliphatic alcohols having from 1 to 4 carbon atoms, preferably methanol and ethanol, as well as mono- and dimethyl ethers and mono- and diethyl ethers of ethylene glycol or of the corresponding monoethers of polyglycols having a chain length up to that of decaethylene glycol. It is likewise possible to use mixtures of the aforesaid solvents.

[0144] A typical eluting liquid may be prepared from the mineral acid and the organic solvent to be used the acid concentration of which, calculated on the total mixture, is adjusted in the range of from 0.5 to 10 N, preferably 0.5 to 2 N. In said mixture the proportion of mineral acid (including the water portion) to solvent ranges from 1:0.25 to 1:20, preferably 1:3 to 1:10 parts by volume.

[0145] For a quantitative elution of the adsorbed fluorinated carboxylic acids 50 to 500 and preferably 100 to 225 parts by volume, calculated on 100 parts of anion exchanger matrix, of the mixture of mineral acid and organic solvent is typically used.

[0146] When the elution is terminated the eluate generally separates into two layers of which the lower layer having the higher specific gravity contains approximately the entire amount of fluorinated carboxylic acid. The lower layer may be neutralized with dilute, usually 2 N sodium hydroxide solution and the fluorinated carboxylic acid is typically precipitated in compact form and easy to separate by adding the neutralized phase while stirring to dilute hydrochloric acid.

[0147] In another embodiment, the eluting mixture for the elution of fluorinated carboxylic acid adsorbed to an anion exchange resin comprises a) water, b) a compound of the formula M-X in which M is an alkali metal or alkyl ammonium ion, and X is hydroxyl, fluoride or chloride, and c) at least one organic solvent capable of dissolving the other components a) and b) and thus provides a sufficient quantity of anions X for the elution of the fluorinated carboxylic acid from the anion exchanger resin.

[0148] In a particular aspect of this embodiment, the eluting liquid has the following composition:

[0149] a) from 15 to 40% of water,

[0150] b) from 1 to 10 of the compound M-A, and

[0151] c) from 60 to 70% of the solvent.

[0152] In another aspect, the eluting mixture has the following composition:

[0153] a) from 18 to 35% of water,

[0154] b) from 2 to 8% of M-A, and

[0155] c) from 60 to 70% of solvent.

[0156] Useful solvents include those mentioned above. Suitable cations M include lithium, sodium, potassium, tetramethylammonium and tetraethylammonium, and the preferred anion A is hydroxyl.

[0157] In yet a further embodiment, the fluorinated carboxylic acid may be recovered from a strongly basic anion exchange resin using an eluting liquid comprising an ammonium salt and a water miscible organic solvent. The ammonium salt is typically one that corresponds to the general formula:

$(NH_4)_nA$

[0158] wherein A represents an anion other than OH^- and n equals the valence of A. Examples of anions A include inorganic as well as organic anions. Particular examples of inorganic anions include halogen or halogen containing inorganic anions such as for example F^-, Cl^-, Br^-, I^-, ClO_4^-, phosphates, sulfates, sulfonates, carbonates including HCO_3^- and CO_3^{2-}. Examples of organic anions include in particular carboxylic anions such as for example $HCOO^-$ and CH_3COO^-.

[0159] The amount of ammonium salt in the eluting liquid will generally depend on the nature of the anion exchange resin and the amount of fluorinated carboxylic acid adsorbed on the anion exchange resin and/or the percentage of recovery that is desired. A suitable amount of ammonium salt is generally at least 0.1% by weight. According to a particular embodiment, the amount of ammonium salt is between 0.1 and 5% by weight based on the total weight of the composition used for eluting the exchange resin.

[0160] The eluting composition further includes a water-miscible solvent. By 'water miscible solvent' is generally meant an organic solvent that has solubility in water of at least 5% by weight, for example at least 10% by weight or at least 20% by weight. Suitable water-miscible solvents are typically polar solvents including for example alcohols, ketones, ethers and mixtures thereof Particular examples of solvents include lower alkanols having between 1 and 6 carbon atoms such as for example methanol, ethanol and propanol; glycols, mono- and dialkyl ethers or monoglycol and diglycol wherein the alkyl groups have between 1 and

4 carbon atoms; ketones such as acetone and methyl ethyl ketone. The amount of water miscible organic may vary widely but should generally be enough to dissolve the ammonium salt. The amount of water-miscible organic solvent is generally at least 50% by weight of the total weight of the eluting composition. Exemplary ranges are 50 to 99.9% by weight, or between 60 and 90% by weight or between 90 and 98% by weight.

[0161] The eluting liquid comprising the ammonium salt and a water-miscible solvent may contain further components that may aid in the recovery of the fluorinated carboxylic acid from the anion exchange resin. In one particular embodiment, the eluting composition further comprises water. Water may for example be used in the eluting composition in an amount of up to 45% by weight, for example in an amount of 0.1 to 40% by weight or in amount between 1 and 15% by weight or in an amount between 4 and 10% by weight.

[0162] A further component that may be present in the eluting liquid is a base. Suitable bases that may be used are alkali metal hydroxides such as for example sodium hydroxide and potassium hydroxide. Other bases that may be used include earth alkali metal hydroxides, aluminium hydroxide or alcoholates such as for example sodium methylate. When present, the amount of base included in the composition is generally up to about 5% by weight. An exemplary range is from 0.1 to 5% or from 0.5 to 2% by weight.

[0163] Further eluting liquids include those disclosed in U.S. Pat. No. 6,642,415 and EP 1,323,677. The latter discloses eluting liquids comprising an alkaline mixture of water and an organic solvent. An aqueous ammonia solution as disclosed in U.S. Pat. No. 3,882,153 may also be used.

[0164] According to a further embodiment, the fluorinated carboxylic acid may be recovered by mixing the adsorbent particles (e.g. ion exchange resin or activated carbon) with an alcohol and optionally an acid. The mixture is then generally heated to cause esterification of the fluorinated carboxylic acid with the alcohol so as to form an ester derivative of the fluorinated carboxylic acid. The so obtained mixture may then be distilled to form a distillate comprising the ester derivative followed by separation of the ester derivative from the distillate. Generally, the eluting liquid will also comprise water.

[0165] Suitable alcohols that may be used include in particular lower aliphatic alcohols having 1 to 5 carbon atoms such as methanol, ethanol and propanol. However aromatic alcohols may be used as well. Additionally, the alcohol may be added under the form of a precursor of the alcohol. Such a precursor should however form an alcohol under the conditions used to cause the esterification. Suitable precursors of the alcohol may include compounds such as ketals that readily form a corresponding alcohol under the acidic conditions existing in the eluting liquid or mixture thereof with the adsorbent particles. The acid used with the eluting fluid is preferably an inorganic acid but the use of organic acids is not excluded. Also, the acid is preferably a strong acid such as for example sulphuric acid, hydrochloric acid, phosphoric acid or nitric acid. The amount and nature of the acid used is typically such that a pH of less than 4, preferably not more than 3 and more preferably not more than 2 is attained in the mixture of eluting liquid and adsorbent particles.

[0166] Depending on the amount of water present in the distillate the ester derivative may separate out as a separate phase, typically the lower phase, from the distillate. Thus the ester derivative can be easily separated from the distillate and the remainder of the distillate can be re-introduced into the mixture being distilled. Such a circulating regeneration process thus allows a convenient regeneration of the adsorbent particles with a minimal amount of eluting fluid being needed. The received ester can be further purified by distilllation and is then converted to the fluorinated acid salt by saponification typically with ammonia. The eluated purified fluorinated carboxylic acid salt will typically have a purity sufficient to allow use of the compound in emulsion polymerization of fluorinated monomers. The adsorbent particles can be regenerated several times before their efficiency drops below an uneconomical level at which point the adsorbent particles need to be disposed of.

[0167] Following their recovery, the fluorinated carboxylic acids can be purified to the desired high purity enabling re-use of the fluorinated carboxylic acid in an aqueous emulsion polymerization. A suitable purification method is disclosed in U.S. Pat. No. 5,312,935. Herein the liberated and dewatered carboxylic acids are treated with oxidants like dichromates, peroxodisulfates or permanganates at a temperature of about 60° C. to the boiling point of the mixture. The pure product is then isolated by crystallization e.g. at low temperature or preferably by distillation if desired under reduced pressure. Alternatively, the method of WO 2004/031141 may be used.

EXAMPLES

[0168] Test Method:

[0169] Content of Fluorinated Carboxylic Acid

[0170] The amount of fluorinated carboxylic acid in aqueous solution was determined by conversion of the fluorinated emulsifier into the methyl ester followed by an analysis with gas chromatography (head space) using methyl ester of perfluorodecanoic acid as an internal standard. The detection limit was about 10 ppm.

[0171] Particle Size

[0172] The latex particle size determination was conducted by means of dynamic light scattering with a Malvern Zetazizer 1000 HAS in accordance to ISO/DIS 13321. Prior to the measurements, the polymer latexes as yielded from the polymerizations were diluted with 0.001 mol/L KCl-solution, the measurement temperature was 25° C. in all cases. The reported average is the Z-average particle diameter.

[0173] SSG: Standard specific gravity was measured according ASTM 4894-04

[0174] Solid Content: Determination of solid content was done by subjecting the latex sample to a temperature up to 250° C. for 30 min.

[0175] Polymerization of Fluorinated Monomers (Fluoroolefin) Using a Fluorinated Carboxylic Acid

[0176] The polymerization experiments were performed in a 40 l kettle equipped with an impeller agitator and a baffle. The kettle was charged with 30 l of deionized water and set to 35° C.; the kettle was evacuated repeatedly to

remove oxygen; Agitation speed was set to 165 rpm. The oxygen free kettle was charged with 70 mmol fluorinated emulsifier (unless specified differently) as listed in table 3 and the following materials were added: 0.5 ml of a solution containing 40 mg of copper sulphate penta hydrate and 1 mg of conc. sulphuric acid; 15 g of a 25 w-% of aqueous ammonia solution and 5.6 g of $CF_3CF_2CF_2$—O—$CF(CF_3)$—CF_2—O—CF═CF_2 (PPVE-2). Finally the reactor was pressurized with tetrafluoroethylene (TFE) to 0.2 MPa and 47 g of hexafluoropropylene (HFP) were added. The kettle was then set to 1.5 MPa using TFE and 100 ml of an aqueous initiator solution containing 140 mg of sodium disulfite followed by 100 ml of a solution containing 340 mg of ammonium peroxodisulfate was pumped into the reactor. The beginning of the polymerization is indicated by a pressure drop. During polymerization the pressure was maintained at 1.5 MPa by feeding TFE continuously. After 3.2 kg of TFE had been added, the monomer valve was closed and the pressure was released. The characteristics of the obtained polymer latices are summarized in table 3.

[0177] 1000 ml of this polymer dispersion were coagulated by adding 20 ml hydrochloric acid under agitation. The coagulated material was agglomerated with gasoline and washed repeatedly. The agglomerated polymer was dried overnight at 200° C. in a vacuum oven; test data are given in table 3.

TABLE 1

Emulsifiers used:	
$C_7F_{15}COONH_4$	Comparative example C-1
CF_3—O—$(CF_2)_3$—O—CF(CF_3)—$COONH_4$	Comparative example C-2
C_3F_7—O—CF(CF_3)—CF_2—O—CF_2—$COONH_4$	Comparative example C-3
CF_3—O—$(CF_2)_3$—O—CF_2—$COONH_4$	Compound 1
CF_3—OCF_2—O—CF_2—$COONH_4$	Compound 2
CF_3—OCF_2—OCF_2—OCF_2—$COONH_4$	Compound 3
CF_3—$(OCF_2)_3$—OCF_2—$COONH_4$	Compound 4
C_3F_7—O—CF_2—$COONH_4$	Compound 5
CF_3—O—CF_2—CF_2—$COONH_4$	Compound 6
C_2F_5—O—CF_2—CF_2—$COONH_4$	Compound 7
C_3F_7—O—CF_2—CF_2—$COONH_4$	Compound 8
C_4F_9—O—CF_2—CF_2—$COONH_4$	Compound 9
C_2F_5—O—CF_2—CF_2—O—CF_2—$COONH_4$	Compound 10
CF_3—O—CF_2—CF_2—CF_2—O—CHF—CF_2—$COONH_4$	Compound 11
CF_3—O—CF_2—CF_2—CF_2—O—CHF—$COONH_4$	Compound 12
C_3F_7—O—CFH—CF_2COONH_4	Compound 13
CF_3—CFH—O—$(CF_2)_5$—$COONH_4$	Compound 14
CF_3—CFH—O—$(CF_2)_3$—$COONH_4$	Compound 15
C_3F_7—O—CFH—CF_2—O—CH_2—$COONH_4$	Compound 16
C_3F_7—O—CFH—$COONH_4$	Compound 17

Preparation of compound 1:
$CF_3OCF_2CF_2CF_2OCF_2COONH_4$

[0178] Oxidation of perfluorinated vinyl ethers with oxygen in the presence of SbF_5 was carried out as described in U.S. Pat. No. 4,987,254. The initially formed acid fluorides were esterified with methanol and purified by distillation. The distilled esters were converted to the corresponding ammonium salts by saponification with aqueous ammonia. A dry flask equipped with a magnetic stirrer bar, thermometer, dry ice reflux condenser, dropping funnel, and gas inlet tube was charged with 5 g of graphite. The flask was flushed with nitrogen and 332 g of $CF_3OCF_2CF_2CF_2OCF$═CF_2 were added at room temperature. 2.6 g of SbF_5 was added via the dropping funnel and oxygen was charged to the flask at ambient pressure. An exothermic reaction indicated the oxidation. Total reaction time was 14 h. After the first hour 2.6 g and after 7 hours 3.5 g of SbF_5 were added. Esterification was achieved by slow addition of 50 g of methanol to the reaction mixture. The resulting ester was isolated from the batch by flash distillation after addition of 300 g water and 50 g methanol. The distillate formed two phases. The lower phase was separated and the upper phase retuned to the flask. 310 g of lower phase were collected. GC analysis showed a content of 52% of $CF_3OCF_2CF_2CF_2OCF_2COOCH_3$. Purification via fractionated distillation resulted in 144 g pure ester with a boiling point of 51° C. at 52 mbar. $CF_3OCF_2CF_2COOCH_3$ was isolated as by product. Saponification of the ester with aqueous ammonia at 60-80° C. and removal of methanol by distillation resulted in an aqueous solution of $CF_3OCF_2CF_2CF_2OCF_2COONH_4$. All structures were confirmed by F-NMR spectra.

Preparation of compound 5:
$CF_3CF_2CF_2OCF_2COONH_4$

[0179] Using the procedures described in U.S. Pat. No. 4,987,254, $CF_3CF_2CF_2OCF$═CF_2 was converted to $CF_3CF_2CF_2OCF_2COOCH_3$ (bp 102-104° C.). Saponification with aqueous ammonia and removal of methanol by distillation resulted in an aqueous solution of $CF_3CF_2CF_2OCF_2COONH_4$. Structures were confirmed by F-NMR spectra.

Preparation of compound 17:
$CF_3CF_2CF_2OCHFCOONH_4$

[0180] A 2 liter glass flask equipped with a mechanical stirrer, thermometer and reflux condenser (−80° C.) is used. Heating of the flask is provided by an electric heating mantle. The conversion is carried out as a one pot reaction. 275 g perfluoropropyl vinyl ether (PPVE), 280 g KOH, 602 g water, 151 g t-butanol, and 10 g methyl trioctyl ammonium chloride are placed in the flask. The three phase mixture is subjected to vigorous stirring. After initial heating a moderate exothermic reaction occours. Mixing is continued for nine hours. During this time the internal temperature adjusts to 27-33° C. Mixing is stopped when the exothermic reaction ceases. The reaction mixture forms two layers. The low temperature reflux condenser is replaced by a standard reflux condenser. Sulfuric acid (392 g) is slowly added without external cooling. The batch is heated to reflux. Unreacted PPVE is vented. At about 80° C. internal temperature gas begins to evolve. Heating is continued until the gas evolution has ceased. At this time the internal temperature reaches 101° C. The batch is cooled to RT and the reflux condenser is replaced by a distillation device. No column is used. 110 g methanol is added to the batch and distillation is started.

[0181] The condensed vapors form two layers. The lower layer is separated and the upper layer is returned to the flask. Distillation is stopped when no more lower phase is formed. In total, 234 g of lower phase are collected. Fractionation of the lower phase yields 167 g of $C_3F_7OCHFCOOCH_3$ with a

boiling point of 120-122° C. at ambient pressure. Calculated yield: 59% based on total PPVE used; 70% based on converted PPVE. The ester is converted to the ammonium salt by reaction with aqueous ammonia. Methanol is removed by fractionated distillation. The resulting aqueous solution is used as an emulsifier in the polymerization of fluorinated olefins.

Preparation of compound 12:
$CF_3OCF_2CF_2CF_2OCHFCOONH_4$

[0182] A glass flask equipped with a reflux condenser, thermometer, and magnetic stirrer was used. Perfluoromethoxy propyl vinyl ether (498 g), t-butanol (149 g), water (1007 g), potassium hydroxide (280 g), and methyl trioctyl ammonium chloride (10 g) were added to the flask. The resulting two phase mixture was heated to reflux for 16 hours under vigorous stirring. The mixture was cooled to room temperature and sulphuric acid (588 g) was added. The two phase mixture was heated again under vigorous stirring. At about 70° C. gas began to evolve. Heating was continued until the gas evolution ceased. The reflux condenser was replaced by a distillation device which allowed the separation of a lower phase while returning the upper phase to the flask. Methanol (150 g) was added and the mixture was heated for distillation. Distillation was carried out at ambient pressure without any intent for rectification. The condensed vapors separated into two phases. The lower phase was collected and the upper phase was returned to the flask. Distillation was continued until no more lower phase separated from the condensate. The combined crude ester (493 g) was purified by fractionated distillation, resulting in 401 g $CF_3O(CF_2)_3OCHFCOOCH_3$ with a boiling point of 51 to 52° C./ 22 mbar. This corresponds to a yield of 78%, based on vinyl ether used.

[0183] The ester was converted to the ammonium salt by heating with aqueous ammonia and removal of methanol by fractionated distillation.

[0184] Alternatively, the previous reaction was repeated but 36 g of an aqueous solution containing 11 g of $CF_3O(CF_2)_3OCHFCOONH_4$ was used as phase transfer catalyst instead of methyl trioctyl ammonium chloride. The mixture was slowly heated to 70° C. internal temperature. Total reaction time was 26 hours. Work up was carried out as described above. 438 g of distilled $CF_3O(CF_2)_3OCHFCOOCH_3$ was received. This corresponds to a yield of 83% (calculation includes the amount of phase transfer catalyst). The conversion to the ammonium salt was carried out as above.

Preparation of compound 13:
$C_3F_7OCHFCF_2COONH_4$

a. Preparation of $CF_3CF_2CF_2OCHFCF_2CH_2OH$

[0185] In a 2 liter glass flask equipped with a stirrer, thermometer, reflux condenser, and dropping funnel were placed 1008 g methanol, 266 g perfluoropropyl vinyl ether, and 9.2 g of Rongalit® (sodium hydroxymethyl sulfinate). The reaction mixture was heated to reflux, resulting in an internal temperature of 29° C. 7.1 g t-butyl hydroperoxide (70% in water) is added in aliquots during a 9 h time frame. The internal temperature reached 52° C. at the end. The reaction mixture showed a single liquid phase and some solids. The liquid was analyzed by GC and indicated a content of 223 g of $C_3F_7OCHFCF_2CH_2OH$ which corresponded to a yield of 75%.

[0186] Distillation of the reaction mixture resulted in 171 g of product (bp 54° C./23 mbar) corresponding to an isolated yield of 57%.

b. Preparation of $C_3F_7OCHFCF_2COONH_4$

[0187] A 2 liter glass flask equipped with a thermometer, reflux condenser, dropping funnel and stirrer was used. 674 g water, 136 g KMnO4, and 38 g NaOH are placed in the flask. 169 g $C_3F_7OCHFCF_2CH_2OH$ were added to the well stirred mixture via the dropping funnel. The temperature is held below 50° C. Residual permanganate was destroyed by addition of a small amount of methanol. The resulting slurry was filtered to remove the MnO_2. After washing the filter cake with water, the combined filtrate was transferred to a distillation apparatus and acidified with 65 g of sulfuric acid. 100 g methanol was added and a flash distillation was started. The distillate formed two layers. The lower layer was separated and the upper layer returned to the distillation pot. In total 182 g lower layer were collected. Fractionation of the crude ester resulted in 137 g of $C_3F_7OCHFCF_2COOCH_3$ with a boiling point of 55-56° C./52 mbar. This corresponds to a yield of 77%.

[0188] The ester was converted to the ammonium salt by saponification with aqueous ammonia and subsequent removal of methanol by distillation.

Preparation of compound 11:
$CF_3O(CF_2)_3OCHFCF_2COONH_4$

a. Preparation of $CF_3O(CF_2)_3OCHFCF_2CH_2OH$

[0189] Using equipment similar to the described above, 255 g of perfluoromethoxypropyl vinyl ether and 730 g methanol were converted with Rongalit and t-butylhydroperoxide as radical source. Reaction temperature started at 47° C. and reached 64° C. at the end. Work up by distillation yielded 166 g of pure $CF_3O(CF_2)_3OCHFCF_2CH_2OH$ with a boiling point of 60-61° C./20 mbar. This corresponds to a yield of 59%.

b. Preparation of $CF_3O(CF_2)_3OCHFCF_2COONH_4$

[0190] A 2 liter glass flask equipped with a thermometer, reflux condenser, dropping funnel and stirrer was used. 159 g of $CF_3O(CF_2)_3OCHFCF_2CH_2OH$, 520 g water, and 100 g sulfuric acid were added to the flask. 190 g KMnO4 were added manually to the liquid over a period of 2 hours while stirring. The reaction temperature increased to 95° C. over time. After a post reaction time of two hours, an aqueous solution of sodium bisulfite was added until a clear solution was formed. 100 g of methanol and in total 400 g of 50% aqueous sulphuric acid were added. Flash distillation of the reaction mixture resulted in a two phase distillate. Fractionation of the lower phase (120 g) gave 85.5 g of $CF_3O(CF_2)_3OCHFCF_2COOCH_3$ (bp 34-35° C./6 mbar; yield 50%).

[0191] The ester was converted to the ammonium salt by saponification with aqueous ammonia and subsequent removal of methanol by distillation.

Preparation of Compound 6

[0192] CH_3—O—CF_2—CF_2—$COOCH_3$ was fluorinated as described in WO 01/46116; the acid fluoride CF_3—O—CF_2—CF_2—COF was then converted into the methylester. The distilled ester was converted into the ammonia-salt as described above.

Preparation of compound 14: CF_3—CFH—O—$(CF_2)_5COONH_4$

[0193] A sample of diacid fluoride, FCOCF(CF_3)—O—$(CF_2)_5$COF (500 g, 1.1 mol) prepared from the hexafluoropropylene oxide (HFPO) coupling of perfluoroadipoyl fluoride as described in U.S. Pub. No. 2004/0116742 and was added over 2 hours to a stirred slurry of sodium carbonate (500 g, 4.7 mol) in 500 g of diglyme at 85° C. to make the disalt. The reaction liberated CO_2 gas. Distilled water (25 g, 1.4 mol) was added at 85° C. The mixture was heated up to 168° C. with CO_2 off-gassing and held for 30 minutes. Reaction was cooled down and sulphuric acid (350 g, 3.6 mol) in 1100 g of water was added to make the reaction mixture acidic. Bottom phase was washed with 400 g of 50% sulfuric acid and vacuum distilled to give CF_3—CFH—O—$(CF_2)_5$COOH 426 g, 1.0 mol for a 95% yield having a boiling point of 132-135° C./15 mm. This was followed by the addition of 46 g NaOH in 63 g of water. Dried salts in vacuum oven at 112° C./15 mm Hg to give 386 g of slight yellow sticky solids. To the salt was added sulphuric acid and the lower fluorochemical phase was vacuum distilled. The previous process was repeated two more times to yield a colorless acid. The surfactant CF_3—CFH—O—$(CF_2)_5COONH_4$ having a melting point of 159-165° C. was made quantitatively from the reaction of 200 g of acid reacted with excess ammonium hydroxide and dried.

Preparation of Compound 15: CF_3—CFH—O$(CF_2)_3COONH_4$

[0194] A sample of diacid fluoride, FCOCF(CF_3)—O—$(CF_2)_3$COF (503 g, 1.4 mol) prepared from the HFPO coupling of perfluorosuccinyl fluoride as described in U.S. Pub. No. 2004/0116742 and was added over 2 hours to a stirred slurry of sodium carbonate (387 g, 3.7 mol) in 650 g of diglyme at 78° C. to make the disalt. The reaction liberated CO_2 gas. Distilled water (35 g, 1.9 mol) was added at 85° C. The mixture was heated up to 165° C. with CO_2 off-gassing and held for 30 minutes. Reaction was cooled down and sulphuric acid (250 g, 2.6 mol) in 1250 g of water was added to make the reaction mixture acidic. To the bottom phase was added 60 g NaOH in 60 g of water. Dried the salt in vacuum oven at 112° C./15 mm and recovered 450 g. To the salt was added 300 g of 50% sulphuric acid and the lower fluorochemical phase was washed once with 200 g of 50% sulphuric acid. Vacuum distillation gave CF_3—CFH—O—$(CF_2)_3COOH$ (400 g, 1.3 mol) for a 95% yield having a boiling point of 111° C./15 mm Hg. The acid was treated with caustic followed by sulphuric acid and vacuum distilled. This was repeated a second time to yield a colorless acid. The surfactant CF_3—CFH—O—$(CF_2)_3COONH_4$ having a melting point of 64-68° C. was made quantitatively from the reaction of 208 g of acid reacted with excess ammonium hydroxide and dried.

Preparation of compound C-3

[0195] Conversion of $CF_3CF_2CF_2OCF(CF_3)CF_2OCF{=}CF_2$ to $CF_3CF_2CF_2OCF(CF_3)CF_2OCF_2COOCH_3$ (bp 91-92° C. at 133 mbar) was carried described in U.S. Pat. No. 4,987,254. The ester was reacted with aqueous ammonia and methanol was removed by distillation resulting in $CF_3CF_2CF_2OCF(CF_3)CF_2OCF_2COONH_4$. All structures were confirmed by F-NMR spectra. Due to an isomer content in the vinyl ether, an isomer with the structure $CF_3CF_2CF_2OCF_2CF(CF_3)OCF_2COOX$ (X=CH_3, NH_4) was found.

Preparation of compound 16: C_3F_7—O—C_2HF_3—O—CH_2—$COONH_4$

[0196] A mixture of 320 ml Tetrahydrofurane, 40 g Hydroxy acetic methylester and 188 g PPVE is cooled to 0° C., 27 g KOH-powder are added in small portions—during the addition of KOH, the reaction mixture heats up to 60° C. After the addition of KOH, the whole reaction mixture is agitated for 6 h at 25° C. The precipitated salt is separated by filtration, dissolved in 300 ml water and then treated with 57 g H_2SO_4 (conc). The resulting mixture separates in two layers; the lower phase is C_3F_7—O—C_2HF_3—O—CH_2—COOH, 86 g (56%). The distilled acid (bp. 125° C., 20 mbar) is neutralized with 25% aqueous ammonia solution to provide a 30% solution in water.

[0197] Compounds 2, 3, 4 were prepared from the corresponding carboxylic acids (purchased from Anles Ltd. St. Petersburg, Russia) by neutralizing with aqueous ammonia.

[0198] Compounds 7, 8, 10 were prepared from the corresponding carboxylic acid fluorides (~COF) [purchased from Exfluor, Round Rock, Tex., USA]. The acid fluorides were converted by addition of methanol to the methylester. The distillated methylester were saponified with aqueous ammonia at 60-80° C. and methanol is removed by distillation.

[0199] Compound C-2 was prepared as described in U.S. Pat. No. 6,703,520 (column 7).

[0200] Determination of Bio-Accumulation

[0201] The perfluorinated and partially fluorinated carboxylates were evaluated for urinary clearance using a pharmacokinetic study in rats. The goal was to measure the total amount of parent compound eliminated via urinary output and estimate the rate of elimination. The study was approved by the IACUC (Institutional Animal Care and Use Committees) and was performed in 3M Company's AAALAC (Association for Assessment and Accreditation of Laboratory Animal Care)—accredited facility.

[0202] The study utilized male Sprague Dawley rats, 6 to 8 weeks of age, and approximately 200 to 250 g body weight at study onset. The test compounds of table 2 were administered at a dose of 73 micro Moles per kg body weight in rats (N=3 animals per tested compound). All test compounds were prepared in sterile deionized water and given to rats via oral gavage. After test compounds administration, the rats were housed individually in metabolism cages for urine collection: 0 to 6 hours, 6 to 24 hours, 24 to 48 hours and 72 to 96 hours. Animals were observed throughout the study for clinical signs of toxicity. Gross necropsy was performed at the termination of each study (96 hours post-dose) with sera and liver samples being retained from each animal.

[0203] The concentration of the parent compound or metabolites thereof were quantitatively measured via fluorine NMR on each urine sample for each animal at each time point based on internally added standards.

[0204] The bioaccumulation data obtained in accordance with the above test are reported in table 2 below.

TABLE 2

	T½ (h)	% Recovery (96 h)	Compound-related Effects
C-1	~550	6	Hepatomegaly
C-2	29	40	Hepatomegaly
C-3	95	5	Hepatomegaly
Compound 1	10	73	—
Compound 2	12	96	—
Compound 3	12	100	—
Compound 4	15	50	—
Compound 5	11	97	—
Compound 6	11	100	—
Compound 7	10	100	—
Compound 8	12	82	—
Compound 9	31	42	Hepatomegaly
Compound 10	10	99	—
Compound 11	12	84	—
Compound 12	11	95	
Compound 13	11	94	—
Compound 14	24	32	Hepatomegaly
Compound 15	8	95	—
Compound 16	13*	65*	—

*No parent compound observed in the urine. T½ and % recovery are based on elimination of the major metabolite —C_3F_7—O—CHFCOO$^-$. $T_{1/2}$ is the renal half-life and is the time required for the amount of a particular substance in a biological system to be reduced to one half of its value by biological processes when the rate of removal is approximately exponential. In these examples the value of $T_{1/2}$ is calculated by exponential least squares curve fitting ($y = Ae^{Bx}$ and $T_{1/2} = 0.693/B$) where y represents the concentration of analyte in urine and x represents time in hours.

[0205]

[0206] Recovery of Fluorinated Ether Carboxylic Acids from Adsorbents

[0207] 300 ml of Amberlite IRA 402 OH a strong basic anion exchanger from Rohm & Haas was charged with $CF_3O(CF_2)_3OCF_2COONH_4$ until break-through. The resin was transferred into a column and washed with 3 1 of deionized water.

[0208] 700 ml of a mixture of 60:20:20 wt-% of methanol:water: sulphuric acid (conc.) (herein called regeneration solution) was circulated for 6 hours through the column with a flow rate of about 1.4 l/h. The regeneration solution was pumped from the top of a feeding tank through the column and back into the feeding tank (flow direction through the column from top to bottom). The elution was done at room temperature. During the recovery step phase separation occurred in the tank due to the formation of the corresponding ester ($CF_3O(CF_2)_3OCF_2COOCH_3$). The lower phase, essentially consisting of the ester was separated.

[0209] The resin was then washed with 1.5 l of methanol/water (90:10 wt-%) and 800 ml of deionized water (both with a flow rate of 300 ml/h). The washing solutions and the upper phase of the tank were allowed to stand for a period of 16 hours to achieve additional phase separation. The lower phase was separated and added to the ester phase.

[0210] The upper phase, mainly containing methanol, water, sulphuric acid and residual ester, was distillated under atmospheric pressure. The purified methanol contained residual amount of ester and was used for the next regeneration process. The overall recovery efficiency calculated on ester was about 88%. The regenerated ion-exchange resin could be re-used several times.

[0211] Recycling of Fluorinated Ether Carboxylic Acids

[0212] 70 g of $CF_3O(CF_2)_3OCF_2COOCH_3$, 50 g methanol, 30 g water and 7 g of sulphuric acid were flash

TABLE 3

	C-1	C-2	C-3	1	2 (140 mmol)	3	4	5	6
Polymerization time (min)	101	77	87	74	109	69	82	73	84
Average Particle Size (nm)	111	118	113	110	129	115	109	122	122
SSG (g/cm^3)	2.166	2.165	2.149	2.169	2.157	2.165	2.163	2.169	2.175
Solid content (w-%)	9.9	10.0	10.3	10.3	9.7	10.1	10.2	10.0	7.1

	7 (140 mmol)	8	9	10	11	12	13	14 (140 mmol)	15
Polymerization time (min)	73	79	72	72	82	82	83	75	78
Average Particle Size (nm)	129	115	113	102	126	108	128	127	105
SSG (g/cm^3)	2.159	2.167	2.165	2.166	2.168	2.167	2.164	2.151	2.154
Solid content (w-%)	10.1	10.0	10.2	10.1	10.2	10.3	10.2	8.1	10.

distillated at atmospheric pressure. The distillate formed two phases and the upper phase was returned to the flask. The lower phase, mainly consisting of the ester ($CF_3O(CF_2)_3OCF_2COOCH_3$) was separated and purified in a further step via fractionated distillation. 53 g of pure ester were collected at a boiling point of about 50° C. at 50 mbar. The ester was saponified with aqueous ammonia at 60-80° C. and methanol was removed by distillation. The resulting aqueous solution of $CF_3O(CF_2)_3OCF_2COONH_4$ was used as an emulsifier for tetrafluoroethylene polymerization to show "polymerization grade" of the product after the recycling process. No deviation between virgin and recycled material was observed during polymerization process.

What is claimed is:

1. A process comprising recovery of fluorinated carboxylic acid or derivative thereof from adsorbent particles on which fluorinated carboxylic acid or a salt thereof is adsorbed, by contacting said adsorbent particles with a liquid composition capable of removing at least part of said fluorinated carboxylic acid or salt thereof from said adsorbent particles, wherein said fluorinated carboxylic acid or salt thereof is selected from the group consisting of fluorinated carboxylic acids or salts thereof that correspond to the general formula:

$$[R_f\text{—O-L-COO}^-]_iX^{i+}$$

wherein L represents a linear partially or fully fluorinated alkylene group or an aliphatic hydrocarbon group, R_f represents a linear partially or fully fluorinated aliphatic group or a linear partially or fully fluorinated aliphatic group interrupted with one or more oxygen atoms, X^{i+} represents a cation having the valence i and i is 1, 2 or 3.

2. A process according to claim 1 wherein said liquid composition is capable of dissolving said fluorinated carboxylic acid or a salt thereof.

3. A process according to claim 1 wherein said liquid composition is capable of converting said fluorinated carboxylic acid or salt thereof into a corresponding ester and wherein said ester is removed by distillation from a mixture of adsorbent particles and said liquid composition.

4. A process according to claim 1 wherein said adsorbent particles are selected from the group consisting of anion exchange resin, active carbon, alumina, celites, clay and zeolites.

5. A process according to claim 3 wherein said liquid composition comprises an alcohol.

6. A process according to claim 5 wherein liquid composition further comprises an acid.

7. A process according to claim 2 wherein said liquid composition comprises an alkaline solution.

8. A process according to claim 7 wherein the liquid composition comprises an organic solvent and a base selected from the group consisting of ammonia, alkali hydroxides and mixtures thereof.

9. A process according to claim 1 wherein said adsorbent particles comprise an anion exchange resin and wherein said liquid composition comprises an ammonium salt dissolved in an organic solvent.

10. A process according to claim 1 wherein the anion of said fluorinated carboxylic acids or salts thereof have a molecular weight of not more than 1000 g/mol.

11. A process according to claim 1 wherein the anion of said fluorinated carboxylic acids or salts thereof have a molecular weight of not more than 500 g/mol.

12. A process according to claim 1 wherein the fluorinated carboxylic acid or salt thereof when administered to rat shows a renal recovery rate of at least 50% of the administered amount, 96 hours after administration and wherein the renal half-life ($T_{1/2}$) is not more than 30 hours.

13. A process according to claim 1 wherein the fluorinated carboxylic acid or salts are selected from fluorinated carboxylic acid or salts of which any fluorinated aliphatic portion has not more than 3 carbon atoms.

14. A process according to claim 1 wherein L in said formula is selected from the group consisting of linear perfluorinated alkylene groups having 1 to 6 carbon atoms, linear partially fluorinated alkylene groups having 1 to 6 carbon atoms having not more than 2 hydrogen atoms and aliphatic hydrocarbon groups having 1 to 6 carbon atoms.

15. A process according to claim 1 wherein R_f is selected from the group consisting of linear perfluorinated aliphatic groups having 1 to 6 carbon atoms; linear perfluorinated aliphatic groups interrupted with one or more oxygen atoms of which alkylene groups between oxygen atoms have not more than 6 carbon atoms and wherein the terminal alkyl group has not more than 6 carbon atoms; linear partially fluorinated aliphatic groups having 1 to 6 carbon atoms and not more than 2 hydrogen atoms and linear partially fluorinated aliphatic groups interrupted with one or more oxygen atoms and which have not more than 2 hydrogen atoms.

16. A process according to claim 1 wherein L is selected from the group consisting of

$—(CF_2)_g—$ wherein g is 1, 2, 3, 4, 5 or 6; $—CFH—(CF_2)_h—$ wherein h is 0, 1, 2, 3, 4 or 5;

$—CF_2—CFH—(CF_2)_d—$ wherein d is 0, 1, 2, 3 or 4; $—CH_2—(CF_2)_h—$ wherein h is 1, 2, 3 or 4;

and $—(CH_2)_c—$ wherein c is 1, 2, 3 or 4.

17. A process according to claim 1 wherein R_f corresponds to the following formula:

$$R_f^1—[OR_f^2]_p—[OR_f^3]_q— \quad \text{(II)}$$

wherein R_f^1 is a perfluorinated linear aliphatic group of 1 to 6 carbon atoms, R_f^2 and R_f^3 each independently represents a linear perfluorinated alkylene of 1, 2, 3 or 4 carbon atoms and p and q each independently represent a value of 0 to 4 and wherein the sum of p and q is at least 1.

18. A process according to claim 1 wherein R_f corresponds to the following formula:

$$R^7_f—(O)_t—CFH—CF_2— \quad \text{(III)}$$

wherein t is 0 or 1 and R^7_f represents a linear partially or fully fluorinated aliphatic group optionally interrupted with one or more oxygen atoms.

19. A process according to claim 1 wherein R_f corresponds to the formula:

$$R_f^8—(OCF_2)_a— \quad \text{(IV)}$$

wherein a is an integer of 1 to 6 and R_f^8 is a linear partially fluorinated aliphatic group or a linear fully fluorinated aliphatic group having 1, 2, 3 or 4 carbon atoms.

20. A process according to claim 1 wherein R_f corresponds to the formula:

$$R_f^9—O—(CF_2)_b— \quad \text{(V)}$$

wherein b is an integer of 1 to 6, preferably 1, 2, 3 or 4 and R_f^9 is a linear partially fluorinated aliphatic group or a linear fully fluorinated aliphatic group having 1, 2, 3 or 4 carbon atoms.

21. A process according to claim 1 wherein the fluorinated carboxylic acid corresponds to the following formula:

$$[R_f^a—(O)_t—CHF—(CF_2)_n—COO^-]_iX^{i+} \quad (VI)$$

wherein R_f^a represents a linear partially or fully fluorinated aliphatic group optionally interrupted with one or more oxygen atoms, t is 0 or 1 and n is 0 or 1, X^{i+} represents a cation having a valence i and i is 1, 2 or 3, with the proviso that when t is 0, the R_f^a contains at least one ether oxygen atom.

22. A process according to claim 1 wherein the fluorinated carboxylic acid corresponds to the following formula:

$$R_f^b—(O)_t—CFH—CF_2—O—R\text{-}G \quad (VII)$$

wherein R_f^b represents a linear partially or fully fluorinated aliphatic group optionally interrupted with one or more oxygen atoms, R is an aliphatic hydrocarbon group, G represents a carboxylic acid or salt thereof, t is 0 or 1.

23. A process according to claim 1 wherein the fluorinated carboxylic acid corresponds to one of the following formulas:

$$R_f^c—(OCF_2)_u—O—(CF_2)_v\text{-}AC \quad (VIII)$$

wherein u is an integer of 1 to 6, v is an integer of 1 to 6, R_f^c represents a linear perfluorinated aliphatic group of 1, 2, 3 or 4 carbon atoms and AC represents a carboxylic acid group or salt thereof, and

$$R_f^c—O—(CF_2)_y—O\text{-}L^1\text{-}AC \quad (IX)$$

wherein y has a value of 1, 2, 3, 4, 5 or 6, L^1 represents a linear perfluorinated alkylene of 1, 2, 3, 4, 5 or 6 carbon atoms or a partially fluorinated alkylene having 1 to 6 carbon atoms and 1 or 2 hydrogen atoms, R_f^c is as defined in above formula (VIII) and AC represents a carboxylic acid group or salt thereof.

24. A process according to claim 1 wherein the fluorinated carboxylic acid or salt thereof is selected from the group consisting of

$C_3F_7—O—CHF—COOH$

$CF_3—O—CF_2CF_2—CF_2—O—CHF—COOH$

$CF_3CF_2CF_2—O—CF_2CF_2—CF_2—O—CHF—COOH$

$CF_3—O—CF_2—CF_2—O—CHF—COOH$

$CF_3—O—CF_2—O—CF_2—CF_2—O—CHF—COOH$

$CF_3—(O—CF_2)_2—O—CF_2—CF_2—O—CHF—COOH$

$CF_3—(O—CF_2)_3—O—CF_2—CF_2—O—CHF—COOH$

$CF_3—O—CHF—CF_2—COOH$

$CF_3—O—CF_2—CF_2—O—CHF—CF_2—COOH$

$CF_3—CF_2—O—CHF—CF_2—COOH$

$CF_3—O—CF_2—CF_2—CF_2—O—CHF—CF_2—COOH$

$CF_3—O—CF_2—O—CF_2—CF_2—O—CHF—CF_2—COOH$

$CF_3—(O—CF_2)_2—O—CF_2—CF_2—O—CHF—CF_2—COOH$

$CF_3—(O—CF_2)_3—O—CF_2—CF_2—O—CF_2—CF_2—O—CHF—CF_2—COOH$

$CF_3—O—CF_2—CHF—COOH$

$C_3F_7—O—CF_2—CHF—COOH$

$CF_3—O—CF_2—CF_2—CF_2—O—CF_2—CHF—COOH$

$CF_3—O—CF_2—O—CF_2—CF_2—O—CF_2—CHF—COOH$

$CF_3—(O—CF_2)_2—O—CF_2—CF_2—O—CF_2—CHF—COOH$

$CF_3—(O—CF_2)_3—O—CF_2—CF_2—O—CF_2—CHF—COOH$

$CF_3—O—CF_2—CHF—CF_2—COOH$

$C_2F_5—O—CF_2—CHF—CF_2—COOH$

$C_3F_7—O—CF_2—CHF—CF_2—COOH$

$CF_3—O—CF_2—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH$

$CF_3—O—CF_2—O—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH$

$CF_3—(O—CF_2)_2—O—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH$

$CF_3—(O—CF_2)_3—O—CF_2—CF_2—O—CF_2—CHF—CF_2—COOH$

$CF_3—O—CHF—CF_2—O—CH_2—COOH$

$CF_3—O—CF_2—CF_2—CF_2—O—CHF—CF_2—O—CH_2—COOH$

$C_3F_7—O—CHF—CF_2—O—CH_2—COOH$

$C_3F_7—O—CHF—CF_2—O—CH_2—CH_2—COOH$

$C_3F_7—O—CF_2—CF_2—O—CHF—CF_2—OCH_2COOH$

$C_3F_7—O—CF_2—CF_2—CF_2—O—CHF—CF_2—OCH_2COOH$

$C_3F_7—O—CF_2—CHF—CF_2—OCH_2COOH$

$CF_3—CHF—CF_2—O—CH_2COOH$

$C_3F_7—CF_2—CHF—CF_2—OCH_2—COOH$

$CF_3—O—CF_2—CF_2—O—CH_2—COOH$

$CF_3—O—CF_2—CF_2—CF_2—O—CF_2—CF_2—O—CH_2—COOH$

$C_3F_7—O—CF_2—CF_2—O—CH_2—COOH$

$C_3F_7—O—CF_2—CF_2—O—CH_2—CH_2—COOH$

$C_3F_7—O—CF_2—CF_2—O—CF_2—CF_2—OCH_2COOH$

$C_3F_7—O—CF_2—CF_2—CF_2—O—CF_2—CF_2—OCH_2COOH$

$C_3F_7—O—CF_2—CF_2—CF_2—OCH_2COOH$

$C_4F_9—O—CH_2—COOH$

$C_4F_9—O—CH_2—CH_2—COOH$

$C_3F_7—O—CH_2COOH$

$C_6F_{13}—OCH_2—COOH$

$CF_3—O—CF_2—CF_2—COOH$

C_2F_5—O—CF_2—CF_2—COOH

C_3F_7—O—CF_2—CF_2—COOH

C_4F_9—O—CF_2—CF_2—COOH

CF_3—$(O—CF_2)_3$—O—CF_2—COOH

CF_3—$(O—CF_2)_2$—O—CF_2—COOH

CF_3—$(O—CF_2)_1$—O—CF_2—COOH

CF_3—$(O—CF_2—CF_2)_1$—O—CF_2—COOH

C_2F_5—$(O—CF_2—CF_2)_1$—O—CF_2—COOH

C_2F_5—$(O—CF_2—CF_2)_2$—O—CF_2—COOH

CF_3—$(O—CF_2—CF_2)_2$—O—CF_2—COOH

C_3F_7—O—CF_2—COOH

CF_3—O—CF_2—CF_2—CF_2—O—CF_2—COOH

CF_3CFH—O—$(CF_2)_3$—COOH

CF_3CFH—O—$(CF_2)_5$—COOH

CF_3—CF_2—O—$(CF_2)_3$COOH

CF_3—CF_2—O—$(CF_2)_5$COOH

and salts of any of these fluorinated carboxylic acids.

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