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[54] **PROCESS FOR PREPARING PERHALOETHERS FROM PERHALOOLEFINS AND NEW PERHALOETHERS SO OBTAINED**

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[58] **Field of Search** 568/677, 685, 568/683, 689; 570/172, 135, 142; 560/300

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[57] **ABSTRACT**

A process for preparing perhaloethers from perhaloolefins by reacting at least one fluorooxy compound R_x—OF, wherein R_x is a perhaloalkyl radical, with a perfluoroolefin in a liquid phase, optionally containing an organic solvent inert to the perfluoroolefin, while maintaining the temperature of the liquid phase in the range of −30° to −120° C. The process includes continuously feeding to the liquid phase a stream of an inert gas and a gaseous stream of the fluorooxy compound.

14 Claims, No Drawings

PROCESS FOR PREPARING PERHALOETHERS FROM PERHALOOLEFINS AND NEW PERHALOETHERS SO OBTAINED

This application is a continuation of application Ser. No. 08/283,614, filed Aug. 1, 1994 (abandoned), which in turn is a continuation of application Ser. No. 08/038,188 filed Mar. 29,1993 (abandoned) which in turn is a continuation of application Ser. No. 07/722,408 filed Jun. 20, 1991 (abandoned), which in turn is a continuation of application Ser. No. 07/540,639 filed Jun. 19, 1990 (abandoned).

DESCRIPTION OF THE INVENTION

The present invention relates to a process for preparing perhaloether compounds starting from perhaloolefins.

In particular, the present invention relates to a process for preparing perhalomonoethers and perhalopolyethers having defined structure and molecular weight, by reacting at least a perhaloolefin with at least a fluoroxy compound. The invention relates al so to new perhaloethers obtained by the and said process.

The obtained compounds are used in particular in the fields of the electric insulating liquids, of the lubricants and of the heat transmission means.

Processes for preparing fluorinated polyethers by fluorination of substrates or of hydrogenated polymers and rupture of the polymeric chain are known in the art (U.S. Pat. No. 4,523,039). This type of process involves long operative times, of the order of a few days, to obtain a complete fluorination.

On the other hand it is known (U.S. Pat. No. 3,962,348) to obtain perfluoropolyether from fluoroolefins and hydrogenated polyols and subsequent electrofluorination. Also in this case the process requires very long reaction times and, in addition, the use of HF involves several technological, safety problems etc.

There are known processes for preparing mixtures of perfluoropolyethers of undefined molecular weights and determinable as average molecular weight of the terms contained in the mixtures, on the basis of the ethereal units present in the chains, by photo-oxidation or polymerization of perfluoroolefins. In this case too the processes in question are complicate and at any rate alien to the one which is the object of the present invention.

Lastly, it is known how to prepare perfluoromonoethers by addition reaction of CF_3OF on olefins, carried out for example by using stoichiometric amounts of the reactants at low temperatures and in the presence of ultraviolet light (U.S. Pat. Nos. 4,077,857 and 4,149,016), or in the gas phase at high temperatures (from 20° to 175° C.) (Int. J. Chem. Kinet. 1984, 1612, 103–115). There are obtained, following modalities different from the ones forming the object of the present invention, exclusively monoethereal addition products other than the ones being the object of the present invention.

It is known too (J. Org. Chem. 1985, 50, 3698–3701) that the use of complex oxidative mixtures consisting of perfluoroacylipofluorites in combination with mono- and bis-fluoroxy compounds, produced in situ in an aqueous medium, and utilized as liquids under pressure as starters for the polymerization of perfluorinated monomers, leads to the obtaining solid polymeric materials having a very high molecular weight.

The Applicant has now surprisingly found a simple and economic method for preparing perhaloethers endowed with

defined structure and molecular weight, which is not affected by the drawbacks illustrated in connection with the above-discussed prior art.

It was found, in fact, that by reacting a perhalomonoolefin with a fluoroxy compound, better defined hereinafter, in certain temperature and dilution conditions in an inert gas,it is possible to obtain perhaloether compounds exhibiting a strictly delimited structure and molecular weight.

A portion of said perhaloether compounds is per se new and represents a further surprising feature of the intrinsic novelty of the process Object of the present invention.

Thus, it is an object of the present invention to provide a simple and economic process for preparing perhaloethers (mono- and poly-ethers) with ether end groups, having a structure and molecular weight selectively restricted falling within the defined limits of a low oligomerization.

Another object is to provide the abovesaid perhaloethers in the form of a mixture useful in the above cited fields.

Lastly, still another object is to provide "per se" new perhaloethers or mixtures thereof.

These and still further objects, which will be better apparent to those skilled in the art from the following description, are achieved, according to the present invention, by means of a process for preparing perhaloethers, which is characterized in that at least a perhalomonoolefin is reacted with at least a fluoroxy compound R_x—OF, wherein R_x represents a straight or branched perhaloalkyl radical containing from 1 to 10 carbon atoms, at a temperature not higher than 20° C., in the presence of a gas which is inert to the reaction conditions.

In the present specification, fluoroxy compound R_x—OF will be also referred to as "starter".

Furthermore, the term "perhalomonoolefin" defines monoolefins, in which all the hydrogen atoms have been substituted by atoms of chlorine and fluorine, or of fluorine.

As regards fluoroxy compound R_x—OF, the halogen component can be Cl, F, Br, I, preferably it is selected from F and Cl or F.

Accordingly, it is possible to use all the perhalomonoolefins compatible with the above-described process.

For illustrative purposes, and in consideration of the applicative purposes of the obtained products, there are usually utilized one or more perfluorinated and/or fluorochlorinated perhalomonolefins and/or mixtures thereof selected from perfluoromonoolefins, fluorochloromonoolefins, perfluoroalkylvinylethers and mixtures thereof, defined as follows:

1) one or more perfluoromonoolefins;
2) a fluorochloromonoolefin in combination with a perfluoroalkylvinylether and/or another perfluoromonoolefin;
3) one or more perfluoroalkylvinylethers;
4) a perfluoromonoolefin in combination with a perfluoroalkylvinylether.

Preferably, fluoroxy compound R_x—OF contains from 1 to 3 carbon atoms furthermore, the halogen component is selected from chlorine and fluorine, even better, it consists of fluorine.

As regards the perhalomonoolefins, they preferably contain from 2 to 6 carbon atoms, the halogen component of which being selected, as mentioned hereinbefore, from a mixture of F and Cl, or F.

It resulted to be advantageous to use, among the perfluoromonoolefins, perfluoropropene and tetrafluoroeth-

ylene and, among the fluorochloromonoolefins, chlorotrifluoroethylene and 1,2-dichloro-difluoroethylene. Last, as regards the perfluoroalkylvinylethers, they are corresponding to the following formula:

$$CF_2=CF—O—R_F$$

wherein R_F represents a straight or branched perfluoroalkyl radical containing from 1 to 10 and preferably from 1 to 3 carbon atoms, such as perfluoromethylvinylether, perfluoroethylvinylether or perfluoropropylvinylether.

According to a preferred embodiment, the process of the present invention is carried out in a liquid phase, which consists of an inert organic medium and/or of one or more perhalomonoolefins, with a gaseous stream consisting of the starter or of the starter mixture, an inert gas stream and, optionally, a gaseous or liquid stream consisting of the perhalomonolefinic reactant or of mixtures thereof, the last-mentioned stream being always present, if the liquid phase does not contain perhalomonoolefins prior to the reaction starting.

Preferably, the inert gas is fed to the liquid phase in admixture with the gaseous stream consisting of the starter or of its mixtures, in determined quantitative ratios, and it is preferably selected from nitrogen, helium, argon, CF_4 and C_2F_6 and mixtures thereof.

The inert organic solvent medium, when used, consists of a straight or cyclic fluorocarbon or chlorofluorocarbon. $CFCl_3$; CF_2Cl_2; c.C_4F_8; $CF_3—CF_2C_1$; $CF_2Cl_1—CFCl_2$ and $CF_2Cl_1—CF_2Cl_1$ have proved to be suitable solvents.

Preferably, the liquid phase is composed of one or more perhalomonoolefins.

The starter $R_x—OF$ or its mixtures can be utilized in association with minor amounts of starter fluorine ranging from 1 to 30% by mols, preferably from 5 to 20% by mols with respect to $R_x—OF$.

Analogous results are obtainable also by operating in a fully gaseous phase.

The ether products, in which A=B=F in formulas II–IV, as defined hereinafter, can be selectively obtained also by using only elemental fluorine diluted with the inert gas, in the same conditions as already described.

As mentioned before, the reaction temperature shall be lower than 20° C., and exactly: the minimum temperature at which the liquid phase is maintained during the reaction shall be such that the component or components of said phase remain in the liquid state. The reaction temperature can range, on the whole, from −120° C. to +20° C., approximately, and usually it is maintained approximately from −100° C. to −30° C. The total pressure is generally maintained around the ambient values (about 1 atmosphere).

The gaseous volume ratio of the starter or starters to the inert gas can vary over a wide range, for example from 0.01 to 5.

The concentration of the perhalomonoolefin or of its mixtures in the liquid phase usually ranges from 0.01 to 10 moles/liter of total liquid phase, higher values being allowable up to the molar concentration of the perhalomonoolefin and mixtures thereof in the pure state.

The feeding of the starter or of its mixtures in the gas phase is adjusted in such a way as to keep its flowrate rate ranging from 0.01 to 5 moles per hour per one liter of liquid phase and usually it ranges from 0.05 to 2 moles per hour per liter of liquid phase.

When tetrafluoroethylene is utilized as a perhalomonoolefin, this is preferably fed in the gaseous state by bubbling it into the liquid phase of the solvent and/or of another liquid perhaloolefin.

At the end of the adjusted reaction time, which is usually comprised between approximately 2 and 20 hours, the perhaloether products, which are obtained, in mixture, are separated by distillation from the unreacted perhaloolefin monomer or monomers and from the solvent, if any. In such manner, mixtures of perhaloether products are obtained, which have the appearance of colorless transparent liquids.

A further separation of the components or of narrower cuts of mixtures,starting from the mixtures of the obtained perhaloether products,can be carried out by fractionated distillation, gas-chromatographic techniques, etc., thereby obtaining products or product cuts having a narrow range, for example, of the boiling points or an analogous boiling point (isomeric mixtures, etc.).

The reaction can be conducted in a completely continuous manner, by continuously withdrawing a liquid phase portion from the reactor, subjecting said portion to distillation and recycling the solvent, if any, and the unreacted monomer or monomers and separating the reaction product.

As mentioned before, the reaction product consists of a mixture of monoperhaloethers or of perhalopolyethers and optionally of minor amounts of perhaloalkanes, depending on the type of the starting perhalomonoolefin or of mixtures thereof and depending on the utilized starter or starters. Said mixtures, in most of cases, can be used directly without further separation treatments, etc.

Hereinafter are described in particular a few embodiments of the process object of the present invention and the obtained products or mixtures thereof, a few of said products being new "per se" and are intended for being included in the scope of the present invention.

I) When a perfluoromonoolefin having at least three carbon atoms and, as a starter, a fluoroxy compound $R_x—OF$ either alone or associated with elemental fluorine are used, the obtained products have the following formula:

$$A\left(\begin{array}{c} CF—CF_2 \\ | \\ R_f \end{array}\right)_l B \qquad (I)$$

wherein

A is like or different from B and consists of R_xO; R_yO; R_y;F;

R_f represents a straight or branched perfluoroalkyl radical containing from 1 to 10 carbon atoms and preferably from 1 to 3 carbon atoms;

R_y represents a straight or branched perhaloalkyl radical containing at least 1 carbon atom less than R_x, and 1 is 1 or 2;

R_f preferably represents CF_3 and R_y=CF_3 or $—CF_2—CF_3$.

The products having formula I, in which 1=2 and A and B are not R_y or F simultaneously, are new "per se".

In particular, when the starting perhalomonoolefin is perfluoropropene alone and the starter consists of a fluoroxy compound as defined above either alone or in admixture with fluorine, the following products are obtained, in which M represents the monomeric unit derived from perfluoropropene:

$$F—(M)_1—F \qquad (A)$$

$$R_xO—(M)_1—F \qquad (B)$$

$$R_xO—(M)_1—OR_x \qquad (C)$$

$$R_y—(M)_1—F \qquad (D)$$

$$R_y—(M)_1—OR_x \qquad (E)$$

$$R_yO—(M)_1—F \qquad (F)$$

$R_xO-(M)_l-OR_y$ (G)

$R_y-(M)_l-R_y$ (H)

wherein R_x and R_y are the same as defined above. The products B, C, E, F and G for 1=2 are new "per se".

In the case under examination, the starting perfluoromonoolefin is perfluoropropene and the monomeric unit M represents, therefore, a diradical

$$\left(\begin{array}{l}-CF-CF_2- \\ \quad | \\ \quad CF_3\end{array}\right) \quad \text{or} \quad \left(\begin{array}{l}-CF_2-CF- \\ \quad\quad\ | \\ \quad\quad CF_3\end{array}\right)$$

wherefore to products A–H, for example to product (B) for 1=1, two specific isomeric products correspond, which have respectively the formulas:

$$R_xO-\left(\begin{array}{l}CF_2-CF \\ \quad\quad | \\ \quad\quad CF_3\end{array}\right)-F \qquad (B_1)$$

and

$$R_xO-\left(\begin{array}{l}CF-CF_2 \\ | \\ CF_3\end{array}\right)-F \qquad (B_2)$$

and furthermore for 1=2, all the combinations between the isomeric monomeric units are possible, wherefore, for example, always in the case of the product of formula (B), four specific products having the following formulas can be present:

$$R_xO-\left(\begin{array}{l}CF-CF_2-CF_2-CF \\ | \quad\quad\quad\quad | \\ CF_3 \quad\quad\quad CF_3\end{array}\right)-F \qquad (B_3)$$

$$R_xO-\left(\begin{array}{l}CF-CF_2-CF-CF_2 \\ | \quad\quad | \\ CF_3 \quad\quad CF_3\end{array}\right)-F \qquad (B_4)$$

$$R_xO-\left(\begin{array}{l}CF_2-CF-CF-CF_2 \\ \quad\quad | \quad | \\ \quad\quad CF_3 \ CF_3\end{array}\right)-F \qquad (B_5)$$

$$R_xO-\left(\begin{array}{l}CF_2-CF-CF_2-CF \\ \quad\quad | \quad\quad | \\ \quad\quad CF_3 \quad\quad CF_3\end{array}\right)-F \qquad (B_6)$$

When the abovesaid reaction is carried out with elemental F_2 only, the perfluoroalkane products (A), known "per se", where 1=1 and 2, are selectively obtained.

The obtained perhaloether mixtures can contain, generally in little amounts, also products different from the ones indicated, for example due to the re-arrangement of the monomeric unit or units, under such reaction conditions as to promote local exothermicities.

For example, when it is operated with perfluoropropene alone or in combination, monomeric units of the type

$$(-CF_2-CF_2-CF_2-) \quad \text{and} \quad \left(\begin{array}{l}\quad CF_3 \\ \quad | \\ -C- \\ \quad | \\ \quad CF_3\end{array}\right)$$

can be present.

Therefore, when perfluoropropene is reacted, as above mentioned, with CF_3OF and with elemental F_2, the mixture A–H of the obtained products is composed in particular of:

$CF_3-CF(CF_3)-CF_3$	(1)	1 = 1
$CF_3-CF_2-CF_2-CF_3$	(2)	1 = 1
$CF_3-CF_2-CF(CF_3)-CF_3$	(3)	1 = 1
$CF_3-CF_2-CF_2-CF_2-CF_3$	(4)	1 = 1
$CF_3O-CF(CF_3)-CF_3$	(5)	1 = 1
$CF_3O-CF_2-CF_2-CF_3$	(6)	1 = 1
$CF_3-CF(CF_3)-CF(CF_3)-CF_3$	(7)	1 = 1
$CF_3-CF(CF_3)-CF_2-CF_2-CF_3$	(8)	1 = 1
$CF_3(CF_2)_4CF_3$	(9)	1 = 2
$CF_3-CF(CF_3)-(CF_2)_3CF_3$	(10)	1 = 2
$CF_3-(CF_2)_2-C(CF_3)_3$	(11)	1 = 2
$CF_3O-(CF_2)_3-CF(CF_3)_2$	(12)	1 = 2
$CF_3O-CF_2-CF(CF_3)-CF(CF_3)-CF_3$	(13)	1 = 2
$CF_3O-CF(CF_3)-CF_2-CF(CF_3)-CF_3$	(14)	1 = 2
$CF_3O-CF_2CF(CF_3)-(CF_2)_2-CF_3$	(15)	1 = 2
$CF_3O-CF(CF_3)-(CF_2)_3CF_3$	(16)	1 = 2
$CF_3O-(CF_2)_6-CF_3$	(17)	1 = 2
$CF_3O-CF_2-CF(CF_3)-CF(CF_3)-CF_2-OCF_3$	(18)	1 = 2
$CF_3O-CF_2-CF(CF_3)-CF_2-CF(CF_3)-OCF_3$	(19)	1 = 2
$CF_3O-CF(CF_3)-CF_2)_2-CF(CF_3)-OCF_3$	(20)	1 = 2
$CF_3O-CF(CF_3)-(CF_2)_4-OCF_3$	(21)	1 = 2

Products (11), (12) and (21) are characterized by a re-arrangement of the monomeric unit and the products from (12) to (21), belonging to series A–H, are "per se" new.

Furthermore, the dimeric products (1=2) can represent up to 90% and above of the obtained products, of which the mono- and bis-ether products can represent even more than 60%.

When the abovesaid reaction is conducted at rather high temperatures, for example at about –30° C., with a high CF_3OF/inert gas volume ratio, for example $\geqq 5$ ether products, prevailingly consisting of products (12), (13), (17), (18), (20) and (21), are present in the mixture.

Conversely, when the abovesaid volume ratio is of about 0.25, the ether products present in the mixture prevailingly consist of products (13)–(16) and (18)–(20).

When perfluoropropene is reacted with C_2F_5OF or with a mixture of C_2F_5OF and elemental fluorine, the mixture of the obtained products is almost exclusively composed of:

$CF_3-CF(CF_3)-CF(CF_3)-CF_3$	(7)	1 = 2
$CF_3-CF(CF_3)-CF_2-CF_2-CF_3$	(8)	1 = 2
$CF_3-(CF_2)_4-CF_3$	(9)	1 = 2
$CF_3-CF(CF_3)-(CF_2)_3-CF_3$	(10)	1 = 2
$C_2F_5-O-CF(CF_3)_2$	(1A)	1 = 1
$C_2F_5O-CF_2-CF_2-CF_3$	(2A)	1 = 1
$CF_3O-CF_2-CF(CF_3)-(CF_2)_2-CF_3$	(3A)	1 = 2
$CF_3O-CF(CF_3)-(CF_2)_3-CF_3$	(4A)	1 = 2
$C_2F_5O-(CF_2)_3-CF(CF_3)_2$	(5A)	1 = 2
$C_2F_5O-CF(CF_3)-CF_2-CF(CF_3)_2$	(6A)	1 = 2
$C_2F_5O-CF_2CF(CF_3)-CF(CF_3)_2$	(7A)	1 = 2
$C_2F_5O-CF_2CF(CF_3)-(CF_2)_2-CF_3$	(8A)	1 = 2
$C_2F_5O-CF(CF_3)-(CF_2)_3-CF_3$	(9A)	1 = 2
$C_2F_5O-CF_2CF(CF_3)-CF(CF_3)CF_2CF_3$	(10A)	1 = 2
$C_2F_5O-CF_2-CF(CF_3)-CF_2-CF(CF_3)_2$	(11A)	1 = 2
$C_2F_5O-CF(CF_3)-(CF_2)_2-CF(CF_3)_2$	(12A)	1 = 2
$C_2F_5O-CF(CF_3)-CF_2-CF(CF_3)-CF_2-CF_3$	(13A)	1 = 2
$C_2F_5O-CF_2CF(CF_3)-CF_2-CF(CF_3)-OC_2F_5$	(14A)	1 = 2
$C_2F_5O-CF_2-CF(CF_3)-CF(CF_3)-CF_2-OC_2F_5$	(15A)	1 = 2
$C_2F_5O-CF(CF_3)-CF_2)_2-CF(CF_3)-OC_2F_5$	(16A)	1 = 2

The products from (3A) to (16A) are new "per se".

Product (5A) derives from a re-arrangement of the monomeric unit.

(II) When a perfluoroalkylvinylether having formula:

$R_f-O-CF=CF_2$

wherein R_f is the same as defined hereinbefore, is used as a starting monoolefin, the resulting products have the general formula:

$$A(CF-CF_2)_mB \quad (II)$$
$$\quad\quad |$$
$$\quad\quad OR_f$$

wherein R_f represents a perfluoroalkyl radical containing from 1 to 10 and preferably from 1 to 3 carbon atoms, as defined before, and m=1 or 2.

The products having formula II where m=2 are "per se" new.

When a perfluoroalkylvinylether alone is used as a starting perfluoromonoolefin and a fluoroxy compound either alone or in admixture with elemental fluorine is used as a starter, the following products, wherein letter N represents the monomeric unit, are obtained:

$$F-(N)_m-F \quad (A')$$

$$R_xO-(N)_m-F \quad (B')$$

$$R_xO-(N)_m-OR_x \quad (C')$$

$$R_y-(N)_m-F \quad (D')$$

$$R_y-(N)_m-OR_x \quad (E')$$

$$R_yO-(N)_m-F \quad (F')$$

$$R_xO-(N)_{m-OR_y} \quad (G')$$

$$R_y-(N)_m-R_y \quad (H')$$

wherein R_x, R_y are the same as defined hereinbefore.

In the indicated formulae of products A'–H', (N) represents a diradical

$$-CF_2-CF- \quad \text{and} \quad -CF-CF_2-$$
$$\quad\quad |\quad\quad\quad\quad\quad |$$
$$\quad\quad O-R_f\quad\quad\quad OR_f$$

so that, analogously with what discussed above in relation to the reaction with perfluoropropene, two specific products correspond to each formula A'–H' where m=1, and four specific products correspond to each formula A'–H' where m=2.

When it is operated with perfluoroalkylvinylethers alone or in combination, monomeric units, caused by a re-arrangement, of the type

$$\left(\begin{array}{c} CF_3 \\ | \\ -C- \\ | \\ ORF \end{array}\right) \quad \text{and} \quad \left(\begin{array}{c} -CF- \\ | \\ CF_2-ORF \end{array}\right)$$

wherein R_f is the same as defined before, can be present.

When the abovesaid reaction is carried out with elemental fluorine, only the ether products of formula (A'), where m=1 and 2, are obtained.

When perfluoromethylvinylether $CF_3O-CF=CF_2$ is reacted with CF_3OF either alone or in admixture with elemental F_2, the mixture of the obtained products is almost exclusively composed of:

$CF_3-CF(OCF_3)-CF(OCF_3)-CF_3$	(1a)	m = 2
$CF_3-CF(OCF_3)-CF_2-CF_2-OCF_3$	(2a)	m = 2
$CF_3O-(CF_2)_4-OCF_3$	(3a)	m = 2
$CF_3O-CF(OCF_3)-CF_3$	(4a)	m = 1
$CF_3O-CF_2-CF_2-OCF_3$	(5a)	m = 1
$CF_3O-CF(OCF_3)-CF_2-CF(OCF_3)-CF_3$	(6a)	m = 2
$CF_3O-CF(OCF_3)-(CF_2)_3-OCF_3$	(7a)	m = 2
$CF_3O-CF_2-CF(OCF_3)-CF(OCF_3)-CF_3$	(8a)	m = 2
$CF_3O-CF_2-CF(OCF_3)-(CF_2)_2-OCF_3$	(9a)	m = 2
$CF_3O-CF(OCF_3)-CF_2-CF(OCF_3)-CF_2-OCF_3$	(10a)	m = 2
$CF_3O-CF(OCF_3)-(CF_2)_2-CF(OCF_3)-OCF_3$	(11a)	m = 2
$CF_3O-CF_2-CF(OCF_3)-CF(OCF_3)-CF_2-OCF_3$	(12a)	m = 2

These products,with the exception of (5a), are new "per se".

When perfluoromethylvinylether is reacted with C_2F_5OF alone or in admixture with elemental fluorine, the mixture of the obtained products is composed of:

$CF_3-CF(OCF_3)-CF_3$	(5)	m = 1
$CF_3-CF_2-CF_2-O-CF_3$	(6)	m = 1
$C_2F_5O-CF(OCF_3)-CF_3$	(3c)	m = 1
$C_2F_5O-(CF_2)_2OCF_3$	(4c)	m = 1
$CF_3-CF(OCF_3)-CF(OCF_3)-CF_3$	(1a)	m = 2
$CF_3-CF(OCF_3)-(CF_2)_2-OCF_3$	(2a)	m = 2
$CF_3O(CF_2)_4-OCF_3$	(3a)	m = 2
$C_2F_5O-CF_2-CF(OCF_3)CF_3$	(5c)	m = 2
$C_2F_5O-CF(OCF_3)-CF_2-CF_3$	(6c)	m = 2
$CF_3-CF(OCF_3)-(CF_2)_3-OCF_3$	(7c)	m = 2
$CF_3-CF(OCF_3)-CF_2-CF(OCF_3)-CF_3$	(8c)	m = 2
$CF_3-CF_2-CF(OCF_3)-CF(OCF_3)-CF_3$	(9c)	m = 2
$CF_3-CF_2-CF(OCF_3)-CF_2-CF_2-O-CF_3$	(10c)	m = 2
$C_2F_5O-CF(OCF_3)-(CF_2)_{3-OCF3}$	(11c)	m = 2
$C_2F_5O-CF(OCF_3)-CF_2-CF(OCF_3)-CF_3$	(12c)	m = 2
$C_2F_5O-CF_2-CF(OCF_3)-CF(OCF_3)-CF_3$	(13c)	m = 2
$C_2F_5O-CF_2-CF(OCF_3)-(CF_2)_2-OCF_3$	(14c)	m = 2
$C_2F_5O-CF(OCF_3)-CF_2-CF(OCF_3)-CF_2-O-C_2F_5$	(15c)	m = 2
$C_2F_5O-CF(OCF_3)-(CF_2)_2-CF(OCF_3)-O-C_2F_5$	(16c)	m = 2
$C_2F_5O-CF_2-CF(OCF_3)-CF(OCF_3)-CF_2-O-C_2F_5$	(17c)	m = 2
$C_2F_5-C(CF_3)(OCF_3)-CF(CF_3)-OCF_3$	(18c)	m = 2
$CF_3CF(OCF_3)-CF(OC_2F_5)-CF_2-OCF_3$	(19c)	m = 2

The products, with the exception of (5), (6), (14c), are new "per se". Products (18c) and (19c) are characterized by a re-arrangement in the monomeric unit.

When perfluoropropylvinylether is reacted with C_2F_5OF alone or in admixture with elemental fluorine, in the product mixture the following new products are present:

$$C_3F_7-O-CF(CF_3)-O-C_2F_5 \quad (1d)$$

$$C_3F_7-O-CF_2-CF_2-O-C_2F_5 \quad (2d)$$

$$C_3F_7-O-CF(CF_3)-CF(CF_3)-O-C_3F_7 \quad (3d)$$

$$C_3F_7-O-CF(CF_3)-CF_2-CF_2-O-C_3F_7 \quad (4d)$$

$$C_3F_7-O-(CF_2)_4-O-C_3F_7 \quad (5d)$$

$$C_2F_5OCF_2CF(OC_3F_7)(CF_2)_2OC_3F_7 \quad (6d)$$

$$C_2F_5OCF(OC_3F_7)(CF_2)_3OC_3F_7 \quad (7d)$$

When perfluoroethylvinylether $C_2F_5-O-CF=CF_2$ is reacted with CF_3OF, the resulting mixture prevailingly contains the following new products:

$$CF_3-CF(OC_2F_5)-CF(OC_2F_5)-CF_3 \quad (1b)$$

$$CF_3-CF(OC_2F_5)-(CF_2)_2-OC_2F_5 \quad (2b)$$

$$C_2F_5O-(CF_2)_4-OC_2F_5 \quad (3b)$$

besides (14c), (15c), (16c) and (17c).

The new products (1a), (2a) and (3a); (1b), (2b) and (3b; (1c), (2c) and (3c); (3d), (4d) and (5d), have been furthermore selectively obtained by reacting the respective perfluoroalkylvinylethers with elemental fluorine.

III) When a mixture of a perfluoroalkylvinylether and a perfluoroolefin is utilized as starting monoolefins, the products of formula:

(III)

are obtained, wherein

A, B and R_f are the same as defined hereinbefore,

m is 0, 1, 2; 1=0, 1, 2 such that m+1=2,

x represents a fluorine atom or a radical R_f, with R_f being the same as defined before. Preferably, x=F or CF_3.

The products with m=1=1 are new "per se".

Analogously with what has been considered before, the monomeric units are enchained with one another according to any possible combinations.

When the abovesaid mixture consists of R_fO—$CF{=}CF_2$ and perfluoropropene, the following new products are obtained, in which M represents the perfluoropropene monomeric unit and N the one of R_fO—$CF{=}CF_2$:

F(M)(N)F (A")

R_xO(M)(N)F (B")

R_xO(M)(N)OR_x (C")

R_y(M)(N)F (D")

R_y(M)(N)OR_x (E")

R_yO(M)(N)F (F")

R_xO(M)(N)OR_y (G")

R_y(M)(N)R_y (H")

besides the products A–H and A'–H'.

When CF_3—O—$CF{=}CF_2$ is reacted with perfluoropropene by using CF_3OF either alone or in combination with elemental fluorine, the resulting mixture contains, besides the new compounds (1a), (2a), (3a), (13), (15), (16), (19), the new compounds:

CF_3O—CF_2—CF_2—$CF(CF_3)_2$ (1e)

CF_3O—$(CF_2)_4CF_3$ (2e)

CF_3O—$CF(CF_3)$—$(CF_2)_2$—CF_3 (3e)

CF_3O—$CF(CF_3)$—$CF(CF_3)$—CF_3 (4e)

CF_3O—CF_2—$CF(OCF_3)$—CF_2—CF_2—CF_3 (4e)

CF_3O—$CF(OCF_3)$—CF_2—$CF(CF_3)_2$ (6e)

CF_3O—CF_2—$CF(OCF_3)$—CF_2—$CF(CF_3)$—OCF_3 (7e)

CF_3O—CF_2—$CF(OCF_3)$—$CF(CF_3)$—CF_2—OCF_3 (8e)

When CF_3O—$CF{=}CF_2$ is reacted with tetrafluoroethylene by using CF3OF either alone or in combination with elemental fluorine, the resulting mixture contains the new compounds (1a), (2a), (3a), (7a), (9a) and

CF_3O—$CF(CF_3)$—CF_2—CF_3 (1f)

CF_3O—$(CF_2)_3$—CF_3 (2f)

CF_3O—CF_2—$CF(OCF_3)$—CF_2—CF_3 (3f)

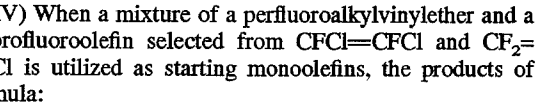
CF_3O—$CF(OCF_3)$—$(CF_2)_3CF_3$ (4f)

$CF_3O(CF_2)_4OCF_3$ (5f)

$CF_3O(CF_2)_2$—$CF(CF_3)OCF_3$ (6f)

The new products (1f), (2f), (1e), (2e), (3e), (4e) are selectively obtained also by reacting the above-said mixtures with elemental fluorine.

(IV) When a mixture of a perfluoroalkylvinylether and a chlorofluoroolefin selected from CFCl=CFCl and CF_2=CFCl is utilized as starting monoolefins, the products of formula:



(IV)

are obtained, wherein

A, B and R_f are the same as defined before and m=0, 1, 2;

n=0, 1, 2 so that m+n=2; represents an atom of F or Cl.

The products with m=n=1 are new "per se".

Analogously with what has been discussed before, the monomeric units are enchained with each other according to any possible combinations.

When the abovesaid mixture is composed of $R_fOCF{=}CF_2$ and CFCl=CFCl, the following new products are obtained, in which N represents the monomeric unit of R_f—O—$CF{=}CF_2$ and L the one of CFCl=CFCl:

F(N)(L)F (A''')

R_xO(N)(L)F (B''')

R_xO(N)(L)OR_x (C''')

R_y(N)(L)F (D''')

R_y(N)(L)OR_x (E''')

R_yO(N)(L)F (F''')

R_xO(N)(L)OR_y (G''')

R_y(N)(L)R_y (H''')

besides products A'–H'.

When CF_3O—$CF{=}CF_2$ is reacted with CFCl=CFCl using CF_3OF alone or in combination with fluorine, the mixture of obtained products contains the following new products (1a), (2a), (3a) and

CF_3—$CF(OCF_3)$—CFCl—CF_2Cl (1g)

CF_3O—$(CF_2)_2$—CFCl—CF_2Cl (2g)

CF_3O—CF_2—$CF(OCF_3)$—CFCl—CF_2Cl (3g)

CF_3O—CF_2—$CF(OCF_3)$—CFCl—CFCl—OCF_3 (4g)

CF_3O—CF(OCF3)—CF_2—$(CFCl)_2$—OCF_3 (5g)

When in the abovesaid reaction CF_2=CFCl is used as a chlorofluoroolefin, the mixture of obtained products contains the following new products (1a), (2a), (3a) and

CF_3O—$CF(CF_3)$—CFCl—CF_3 (1h)

CF_3O—$(CF_2)_2$—CFCl—CF_3 (2h)

CF_3O—$(CF_2)_2$—CF_2—CF_2Cl (3h)

CF_3O—$CF(CF_3)$—CF_2—CF_2Cl (4h)

CF_3O—$CF(CF_3)$—CFCl—CF_2—OCF_3 (5h)

$CF_3O(CF_2)_2$—CFCl—CF_2—OCF_3 (6h)

Products (1g), (2g), (1h)–(4n) were also obtained selectively by reacting the abovesaid mixtures of olefins with elemental fluorine.

The process forming the object of the present invention permits to achieve several advantages, which can be briefly indicated as the possibility of obtaining perhaloethers having defined structure and molecular weight, by means of a simple and flexible process, operating on the concerned parameters,such as the choice of the perhalomonoolefin and of the fluoroxy starter compound, in a single reaction step.

The art has not offered so far such a possibility.

The perhalogenated products which contain fluorine and chlorine, prepared by means of the process of the present invention,have an important applicative field as electric insulating materials, lubricants and heat transmission media.

The perfluorinated ethers of the invention are compounds, which are well known for their exceptional thermal stability, thermooxidative stability and stability to chemical agents as well as for their uninflammability properties and are utilizable in very different sectors and under extremely severe operative conditions.

The perfluoropolyethers known in the art generally consist of mixtures of products, from which it is difficult to obtain the individual compounds. Reference should be made in this connection to British Patent No. 1,226,566. The perfluoropolyethers of the present invention are generally obtainable as isomeric mixtures of compounds having their boiling points in a very narrow temperature range.

The perfluoropolyethers of the invention are particularly useful as fluids for the testing in electronics, for example for the leak testing, thermal shock testing, hot spot location, dew point determination and the like.

The polyethers containing bromine and/or iodine atoms are utilized as intermediates for the preparation of functionalized derivatives.

EXAMPLES

The following examples are given for merely illustrative purposes and are not to be regarded as limitative of any possible embodiment of the process.

Example 1

218 g of C_3F_6 were condensed in a glass reactor having a volume of 500 ml, equipped with a stirrer, thermometer, gas feeding pipes reaching the reactor bottom, and with cooler with a liquid at –78° C. connected to the atmosphere. Subsequently, while maintaining an outer cooling such as to keep the inner temperature at –40° C., a flow of 2.0 Nl/h of CF_3OF and 1 Nl/h of N_2 was fed during 14 hours by bubbling into the liquid phase.

260 g of a rough reaction product were obtained, from which, after having distilled off the unreacted C_3F_6 and the volatile by-products, 52 g of a limpid and colorless liquid were obtained, which, analyzed by means of gas mass in electronic impact with 1% SP-1100 column and FT-NMR spectrometry for ^{19}F, resulted to be composed of products 1 to 21, the content of dimeric 12 to 21) (1=2) monoether (12–17) and bisether (18–21) products, thereof determined by gas--chromatography, amounted to about 55% by weight of the mixture the bisether dimers/monoether dimers weight ratio being of 1 to 2.

The dimeric monoether products (12–17) have boiling point in the temperature range of –91°±2° C. at atmospheric pressure.

The dimeric bisether products have boiling point in the temperature range of –121°±2° C.

Ether products (12), (17) and (21) were present in traces.

Example 2

Example 1 was repeated according to the same modalities, using 2.8 Nl/h of CF_3OF diluted with 0.5 Nl/h of N_2 bubbled into 186 g of C_3F_6 maintained at –40° C.

The products obtained,after removal of C_3F_6, were the same as in example 1. The ether terms (12), (13), (17), (18) and (21) represented about 90% of the dimeric ether products obtained. The ether terms (12), (17) and (21) were characterized by a re-arrangement of the monomeric unit.

Example 3

By operating according to the modalities described in example 1, a flow of 1 Nl/h of C_2F_5OF and 0.2 Nl/h of F_2 diluted with 5 Nl/h of N_2 was bubbled for 11.5 hours into 233 g of C_3F_6 kept in liquid phase at –48° C.

There were obtained 214 g of a rough reaction mixture which, after C_3F_6 removal, was analyzed by means of gas-chromatography, gas-mass and ^{19}F NMR; it resulted to be composed of products 1A to 16A. Products 3A to 16A represented about 20% of the mixture. The dimeric monoether products (3A–13A) were in a weight ratio of about 1:1 with respect to the dimeric bisether products (14A–16A).

Example 4

Into a steel AISI 316 tubular reactor having an inside diameter of ⅛ inch and a length of 1 m, equipped with a circulating-liquid cooling jacket, maintained at –10° C. and downstream connected with a trap maintained at –80° C., a flow of 2 Nl/h of gaseous C_3F_6 diluted with 10 Nl/h of N_2 and a flow of 1 Nl/h of CF_3OF diluted with 10 Nl/h of N_2 were simultaneously and separately fed during 2 hours by means of a two-way inlet connection.

The resulting reaction products leaving the reactor and condensed in the trap, after removal of C_3F_6, of the perfluoroalkane dimers and of the monomeric monoethers (1=1), were analyzed by means of the above-cited techniques; they resulted to be composed of dimeric monoethers and diethers (12)–(21), the weight ratio being 5:1.

Example 5

By operating according to the procedure described in example 1, 1 Nl/h of CF_3OF diluted with 3 Nl/h of N_2 was bubbled into 230 g of C_3F_6 in the liquid state at –60° C. and was reacted for 19 hours.

After removal of C_3F_6 and of the other products which had formed (1–11), the dimeric monoethers and diethers (1=2) were in a ratio of about 1:1.

Example 6

By operating according to the procedure described in example 1, a flow of 1 Nl/h of CF_3OF diluted with 5 Nl/h of N_2 was bubbled for 6 hours into 200 g of $CF_3O—CF=CF_2$ kept in the liquid state at –60° C.

190 g of a rough reaction mixture were obtained, from which, by means of distillation, 45 g of ether products consisting of (1a)–(12a) were recovered.

Example 7

Example 6 was repeated,by bubbling for 12 hours a flow of 1 Nl/h of F diluted with 50 Nl/h of N_2, into 186 g of $CF_3O—OF=CF_2$ maintained at –97° C.

185 g of, a rough reaction mixture were obtained, from which, after removal of the unreacted $CF_3O—CF=CF_2$and of the volatile by.-products, 81 g of dimeric bis ether products (1a), (2a) and (3a), which boil at about 60° C.±2° C., were obtained.

Example 8

By operating according to the modalities of example 1, after bubbling a flow of 1.5 Nl/h of C_2F_5OF diluted with 7.5 Nl/h of N_2 into 200 g of $CF_3O—CF=CF_2$ in the liquid state at −50° C. during 6 hours 200 g of a rough reaction mixture were obtained, from which, by distillation, 58 g of ether products were recovered; these products, subjected to the analyses, resulted to be composed of products (1a), (2a), (3a), (5), (6) and from (3c) to (19c) in the following weight ratio: tetraethers/triethers/diethers=1/3/6.5.

Products (18c) and (19c) were present in little amounts.

Example 9

By operating according to the modalities described in example 1, after bubbling of 0.75 Nl/h of C_2F_5OF and of 0.75 Nl/h of F_2 diluted with 60 Nl/h of N_2 into 112 g of $C_3F_7—O—CF=CF_2$ in the liquid state at −50° C., during 5 hours, 127.5 g of a rough reaction mixture were obtained, which was composed for 65% of products (1d)–(7d) and in which the products (3d)–(5d) represented 20%.

Example 10

Example 9 was repeated by bubbling a flow of 1 Nl/h of F_2 diluted with 70 Nl/h of N_2 during 6 hours into 178 g of $C_3F_7—O—CF=CF_2$ in the liquid state at −75° C.: 177 g of a rough reaction product were obtained, from which, by distillation, 65 g of his-ether products (1d), (2d) and (3d), which boil at about 120° C.±2° C., were separated.

Example 11

By operating according to the modalities described in example 1, after bubbling a flow of 1 Nl/h of CF_3OF diluted with 3 Nl/h of N_2, during 6 hours, into 200 g of $C_2F_5—O—CF=CF_2$ in the liquid state at −60° C., after removal of the unreacted monomer and of the volatile by-products, a mixture was obtained containing bisether products (1b)–(3b) and (14c)–(17c).

Example 12

By operating according to the modalities described in example 1, after bubbling, during 3 hours, a flow of 1 Nl/h of F_2 diluted with 50 Nl/h of N_2 into 225 g of liquid $C_2F_5O—CF=CF_2$ maintained at −75° C., 180 g of a rough reaction product were obtained, which consisted by 66% of dimeric diethers (1), (2b) and (3b), which boil at about 98° C.±2° C.

Example 13

By operating according to the modalities described in example 1,after bubbling, during 6 hours, a flow of 2 Nl/h of CF_3OF diluted with 5 Nl/h of N_2 into a liquid phase maintained at −60° C. and composed of 115 g of $CF_3O—CF=CF_2$ and of 105 g of C_3F_6, after removal of the unreacted monomers and of the volatile by-products, a mixture was obtained containing products (1a)–(3a), (13), (15), (16), (19) and (1e)–(8e).

Example 14

Example 13 was repeated by bubbling, for 6 hours, a flow of 1.5 Nl/h of F_2 diluted with 50 Nl/h of N_2 into 116.2 g of $CF_3O—CF=CF_2$ and 105 g of C_3F_6 at −100° C.; after removal of the unreacted monomers and of the volatile by-products, 74 g of products consisting of (1a)–(3a) (63.5%), (7)–(9) (11.4%) and (1e)–(4e) (24.7%) were obtained.

Example 15

By operating according to the modalities described in example 1, after bubbling, during 5 hour, a flow of 1 Nl/h of CF_3OF diluted with 3 Nl/h of N_2 and, simultaneously but separately, a flow of 3 Nl/h of gaseous C_2F_4 into 106 g of liquid $CF_3O—CF=CF_2$ maintained at −75° C., after removal of the unreacted monomers and of the volatile by-products, a mixture containing products (1a)–(13a), (7a), (9a) and (1f)–(6f) was obtained.

Example 16

Example 15 was repeated by bubbling, during 5 hours, a flow of 1 Nl/h of F_2 diluted with 50 Nl/h of N_2into the same liquid phase at −100° C. with the same flow of C_2F_4; after the separation, 31.5 g of dimeric products consisting by 52% of (1f) and (2f) and by 48% of (1a)–(3a) were obtained.

Example 17

By operating according to the modalities described in example 1 and after bubbling for 5 hours 1.5 Nl/h of CF_3OF diluted with 2 Nl/h of N_2 into liquid 55 g of $CF_3O—CF=CF_2$ and 42 g of CFCl=CFCl maintained at −65° C., after removal of the unreacted monomers and of the volatile by-products, a mixture was obtained, which contained products (1a)–(3a) and (1g)–(5g).

Example 18

Example 17 was repeated by bubbling, during 5 hours, a flow of 1.5 Nl/h of F_2 diluted with 80 Nl/h of N_2 into the same liquid phase at −100° C., there were obtained by distillation 43.4 g of dimeric products consisting by 28% of products (1a)–(3a), by 26% of products (3g) and by 46% of products (1g) and (2g).

Example 19

By operating according to the modalities described in example 1 and after bubbling, during 5 hours, 1.2 Nl/h of CF_3OF diluted with 3 Nl/h of N_2 into liquid 80 g of $CF_3O—CF=CF_2$ and

57 g of $CF_2=CFCl$ maintained at −70° C., after removal of the unreacted monomers, a mixture was obtained containing products (1 h)–(6 h) besides (1a)–(3a).

Example 20

Example 19 was repeated by bubbling, during 5 hours a flow of 1.2 Nl/h of F_2 diluted with 60 Nl/h of N_2 into the same liquid phase maintained at −100° C. there were obtained, after separation, products (1a)–(3a) and (1 h)–(4 h), the latter products representing 41% of the obtained mixture.

Example 21

By operating according to the modalities described in example 1 and after bubbling, during 14 hours, 0.5 Nl/h of CF_3OF diluted with 2 Nl/h of N_2 into a liquid phase consisting of 50 g of $CF_2Cl—CF_2Cl$ and of 54.7 g of C_3F_6, there were obtained, after removal of the volatile by-products, 8.5 g of a product consisting of (5)–(10), (13)–(16) and (18)–(20).

Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations willl be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and varations that will fall eithin the spirit and scope of the appended claims. The above references are hereby incorporated by reference.

What is claimed is:

1. A process for preparing perhaloether compounds with ether end groups having the general formula:

(III)

wherein:

A and B, which may be equal to or different from each other, are R_xO or F, provided that A and B are not simultaneously F, and

R_x is a straight or branched perhaloalkyl radical containing from 1 to 10 carbon atoms;

R_f is a straight or branched perhaloalkyl radical containing from 1 to 10 carbon atoms;

X represents a fluorine atom or a radical R_f;

m is 0 or an integer from 1 to 2;

l is 0 or an integer from 1 to 2 and m+l=2;

said process comprising: reacting at least one fluorooxy compound R_x—OF, wherein R_x is a straight or branched perhaloalkyl radical containing from 1 to 10 carbon atoms, with a perfluoroolefin in a liquid phase, said liquid phase containing the whole amount of perfluoroolefin to be reacted and optionally containing an organic solvent inert to said perfluoroolefin, the temperature of said liquid phase being maintained in the range of from −120° to −30° C., by continuously feeding to the liquid phase a stream of an inert gas and a gaseous stream of said at least one fluorooxy compound, said perfluoroolefin being selected from the group consisting of

a) one perfluoromonoolefin selected from the group consisting of CF_2=CF_2; and R—CF=CF_2 wherein R is a perfluoroalkyl group containing 1 to 4 carbon atoms,

b) one perfluoroalkylvinylether of the formula CF_2=CF—O—R_f, wherein R_f represents a straight or branched perfluoroalkyl group containing from 1 to 10 carbon atoms,

and

c) one perfluoromonoolefin and one perfluoroalkylvinylether as defined above.

2. The process according to claim **1**, wherein the perhaloalkyl radical R_f contains from 1 to 2 carbon atoms.

3. The process according to claim **2**, wherein X is selected from the group consisting of F and CF_3.

4. The process, according to claim **1** wherein the at least one fluoroxy compound R_x—OF contains 1 to 3 carbon atoms, and the halogen component of the at least one fluoro compound is selected from the group consisting of chlorine, fluorine, bromine, iodine and a mixture of chlorine and fluorine.

5. The process, according to claim **4**, wherein the halogen component of the fluoroxy compound is selected from fluorine or a mixture of chlorine and fluorine.

6. The process according to claim **1** wherein the perfluoromonoolefin is selected from the group consisting of perfluoropropene and tetrafluoroethylene.

7. The process, according to claim **1** wherein the inert gas is fed in admixture with the fluoroxy compound in the gaseous stream.

8. The process according to claim **1** wherein the inert gas is selected from the group consisting of nitrogen, helium, argon, CF_4, C_2F_6 mixtures thereof.

9. The process, according to claim **1**, wherein the organic solvent is composed of at least a straight or cyclic fluorocarbon or chlorofluorocarbon.

10. The process, according to claim **9**, wherein the organic solvent is selected from the group consisting of $CFCl_3$; CF_2Cl_2; cyclic C_4F_8; CF_3CF_2Cl; CF_2Cl—$CFCl_2$; CF_2Cl—CF_2Cl.

11. The process, according to claim **1**, wherein the temperature ranges from −100° C. to −30° C.

12. The process according to claim **1** wherein the volume ratio of the at least one fluoroxy compound, in the gaseous stream, to the inert gas ranges from 0.01 to 5.

13. The process according to claim **1**, wherein the at least one fluoroxy compound is fed to the liquid phase at a flowrate ranging from 0.01 to 5 moles per hour per liter of liquid phase.

14. The process according to claim **13**, wherein the at least one fluoroxy compound is fed to the liquid phase at a flowrate ranging from 0.05 to 2 moles per hour per liter of liquid phase.

* * * * *