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(54) Title: PROCESS FOR THE PREPARATION OF PEROXIDIC PERFLUOROPOLYETHERS

(57) Abstract

A process is disclosed for preparing peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms, characterized in that one or more perfluoroolefins, except tetrafluoroethylene used alone, are reacted with oxygen in the liquid phase at a temperature not exceeding 50°C and in the presence of one or more compounds having one or more F-X bonds, in which X is selected from the group consisting of F, O and Cl.

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PROCESS FOR THE PREPARATION OF PEROXIDIC PERFLUOROPOLYETHERS

The present invention relates to a process for the preparation of peroxidic perfluoropolyalkylenoxy compounds, more commonly referred to as peroxidic perfluoropolyethers.

In particular, the present invention relates to a process for preparing peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms. These compounds are prepared, according to the art, by reacting perfluoroolefins with oxygen under irradiation with ultraviolet light.

This technique exhibits the drawback of being delicate and complex, as it requires the use of ultraviolet radiation generators and of reactors of suitable construction in order to permit the radiation to penetrate and to spread inside the reacting phase. Furthermore, since these reactions are usually conducted at very low temperatures, even lower than -50°C, it is necessary to have available efficient means of eliminating the heat associated with the generation of the ultraviolet radiation. Moreover, the reaction yield and the product structure are strongly affected by the amount and distribution of the radiation inside the reaction medium, which considerably limits the desired production flexibility provided by a given reactor.

US-A-4 460 514 relates to the preparation of non-peroxidic oligomers of (CF_2O) having a $-CF_2-COF$ end group. These oligomers are useful for the preparation of s-triazines with perfluoroxymethylene substituent groups. In example IIa, perfluoro-3-methylbutene-1, $CF_2=CF-CF(CF_3)_2$, is reacted, in the gas phase, with oxygen in the presence of CF_3OF without the use of ultraviolet radiation, which affords, at the end of the reaction, the unreacted olefin, $(CF_3)_2CF-CFO$ and a small amount of non-peroxidic oligomers

of (CF_2O) having a CF_2-COF end group.

It has now, surprisingly, been found that the preparation of peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms may be effected without the use of ultraviolet radiation if the perfluoroolefins are reacted, in the liquid phase, with oxygen in the presence of particular reagents.

It is, thus, an object of the present invention to provide a process which affords peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms without using ultraviolet radiation or using UV-irradiation only as complementary measure.

Another object is to provide a process which is simple, can be carried out in apparatus commonly used in the field of chemical processes and can be controlled simply by regulating the amount of reagents introduced in the course of the reaction.

A further object is to provide a very flexible process which permits to obtain, by varying the operative modalities, a wide range of products with different structural characteristics.

Still another object is to provide a process which results in peroxidic perfluoropolyethers having a very low ratio of -COF end groups to non-functional end groups.

These and still further objects are achieved by the process according to the present invention for preparing peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms.

This process is characterized in that one or more perfluoroolefins (except tetrafluoroethylene used alone)

are reacted with oxygen in the liquid phase at a temperature not exceeding 50°C and in the presence of one or more compounds having one or more F-X bonds, in which X is selected from the group consisting of F, O and Cl.

In particular, when X is oxygen, said compound is an oxygen fluoride or an organic compound containing one or more fluoroxy groups. More usually, it is a perhalogenated alkyl or alkylene compound (the halogen atoms of which being F atoms or F and Cl atoms), containing one or more fluoroxy groups and, optionally, one or more heteroatoms, in particular oxygen atoms.

Said compound usually contains one or two fluoroxy groups. Preferably it is a perfluorinated compound; when it is a perhalogenated compound containing F and Cl atoms, the number of Cl atoms present in the molecule generally ranges from 1 to 10. The heteroatoms, if present, preferably are ether oxygen atoms. The number of said heteroatoms in the molecule generally ranges from 1 to 100 and, more usually, from 1 to 10.

When X is F, the compound is F_2.
When X is Cl, the compound is a chlorine fluoride.

In the following, the compounds having one or more F-X bonds will be referred to as initiators, the use of this term being, however, not binding for the characterization of the reaction mechanism.

It cannot be excluded that a significant amount of reaction initiators may actually be formed in the reaction medium, due to the action exerted by the substances containing one or more F-X bonds on the components of the reaction medium and the products of the reaction, i.e. O_2, fluoroolefins, peroxide bonds and carbonyl bonds.

Examples of preferred initiators are:

1) F_2;

2) R^5-OF, wherein R^5 is a C_{1-10}-, preferably C_{1-3}-perhaloalkyl radical containing only fluorine atoms or containing fluorine atoms and from 1 to 5 chlorine atoms. Preferably, R^5 is a perfluoroalkyl radical;

3) $$R^6\text{-}O\text{-}(R^7O)_n(\underset{\underset{\displaystyle D}{|}}{CF})_t\text{-}CF_2OF$$

wherein:
D represents F or CF_3;
t is zero or 1;
R^6 is a C_{1-3}-perfluoroalkyl radical or a C_{1-3}-perhaloalkyl radical containing fluorine atoms and (one or more, preferably one) chlorine atom(s); preferably R^6 is a perfluoroalkyl radical;
R^7 represents one or more perfluoroalkylene radicals, the same or different from one another, selected from $-CF_2-$, $-CF_2-CF_2-$ and $-CF_2-\underset{\underset{\displaystyle CF_3}{|}}{CF}-$

and n ranges from 0 to 50, preferably from 0 to 3; (frequently n ranges from 1 to 10 and, more commonly, from 1 to 3); when different units (R^7O) are present, these units are statistically distributed along the chain;

4) $$R^8\text{-}\overset{\displaystyle OF}{\underset{\displaystyle OF}{C}}\text{-}R^9$$

wherein R^8 is F or a C_{1-9}-, preferably

C_{1-3}-perhaloalkyl radical containing F atoms or F atoms and from one to three Cl atoms; preferably R^8 is F or a perfluoroalkyl radical; R^9 is F, R^8 or a perfluoroalkylmonoether or perfluoroalkylpolyether group $R^6O-(R^7O)_n-CF_2-$, in which R^6, R^7 and n are as defined above;

5) $FO-(R^7O)_s-F$
wherein R^7 is as defined above and s ranges from 1 to 100, preferably 1 to 10, provided that, when R^7 represents $-CF_2-$, s has a value higher than 1;

6) $FO-(CF_2)_v-OF$, wherein v ranges from 3 to 5.

Usually, the starting perfluoroolefins are selected from:

(a) one or more perfluoromonoolefins, provided that C_2F_4 is always employed in admixture with at least one other perfluoroolefin;

(b) a perfluorodiolefin;

(c) a perfluorodiolefin in combination with one or more monoolefins;

(d) one or more perfluoromonoolefins in combination with one or more perfluorovinylethers.

Usually, the starting perfluoromonoolefin or perfluoromonoolefins contain from 2 to 5, preferably from 2 to 4 carbon atoms. Preferred perfluoromonoolefins are hexafluoropropene, as such or in admixture with tetrafluoroethylene.

The preferred starting perfluorodiolefin is perfluorobutadiene.

Generally, the starting perfluorovinylethers have the general formula:

$$CF_2 = CF - O - R^2$$

wherein:
R^2 is $(R^3O)_mR^4$ or R^4;
R^3 is selected from the group consisting of $-CF_2-$, $-CF_2-CF_2-$ and $-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-$;
R^4 is a perfluoroalkyl group selected from linear groups containing from 1 to 10 carbon atoms, branched groups containing from 3 to 10 carbon atoms and cyclic groups containing from 3 to 6 carbon atoms; and
m ranges from 1 to 6, particularly from 1 to 3.

Preferably R_2 is R_4. R_4 is, preferably, selected from CF_3, C_2F_5, n- and i-C_3F_7 and n-, i- and tert-C_4F_9.

Usually, into a liquid phase comprising a solvent and/or one or more perfluoroolefins, there are introduced a gaseous stream of oxygen, a gaseous or liquid stream of initiator or initiators and, optionally, a gaseous or liquid stream of one or more perfluoroolefins, the last-mentioned stream always being present if the liquid phase does not contain perfluoroolefins prior to the start of the reaction.

Instead of feeding the initiator or initiators in the form of a gaseous or liquid stream into the liquid phase, it is possible to introduce said initiator(s) into the liquid phase before the commencement of the reaction. This procedure can be employed, for example, when the initiator(s) is (are) liquid at rooom temperature.

Preferably, also an inert gas is introduced into the

liquid phase. Said inert gas usually is fed in admixture with the initiator(s) if said compound(s) is (are) added to the liquid phase in the form of a gaseous stream. The inert gas can also be employed, in part or as a whole, in combination with the oxygen. In other words, instead of oxygen, it is possible to use mixtures of oxygen and inert gases, in particular air.

The streams of oxygen, gaseous initiator(s) and inert gas can be introduced into the liquid phase in the form of mixtures of two or more components.

The minimum temperature at which the liquid phase is maintained during the reaction is such that the component or components of said phase are in the liquid state. Generally, the reaction temperature ranges from -120 to +50°C, more usually from -100 to +25°C and particularly from -100 to +20°C. The most preferred reaction temperatures range from -100 to 0°C.

The solvent, when used, preferably is selected from linear and cyclic fluorocarbons, chlorofluorocarbons, perfluoroamines, perfluorinated ethers and mixtures thereof.

Examples of suitable fluorocarbons or chlorofluorocarbons are $CFCl_3$, CF_2Cl_2, cyclo-C_4F_8, cyclo-C_6F_{12}, chloropentafluoroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2-dichlorotetrafluoroethane and 1,1,1-trifluorotrichloroethane.

Examples of suitable perfluoroamines are those sold under the designation Fluorinert$^{(R)}$ (produced by 3M).

Examples of suitable perfluorinated ethers are the perfluoropolyethers having perfluoroalkyl end groups and a

boiling point lower than 250°C such as Galden(R), produced by Montefluos.

The inert gas, when employed, preferably is selected from nitrogen, argon, helium, CF_4, C_2F_6 and mixtures thereof.

Into the liquid phase oxygen is continuously introduced at a partial oxygen pressure in the reactor generally ranging from 0.01 to 10 atmospheres and, more usually, from 0.05 to 1 atmosphere.

The total pressure of the reaction medium generally ranges from about 1 to 10 atmospheres/abs. More usually, the reaction is carried out at about atmospheric pressure.

The concentration of the perfluoroolefin or perfluoroolefins in the liquid phase generally ranges from 0.01 to 10 moles/liter and more, i.e., up to the molar concentrations of the perfluoroolefin or perfluoroolefins in the pure (undiluted) state.

When the initiator or initiators are continuously fed into the liquid phase in the gaseous or liquid state, the flow rate thereof generally ranges from 0.001 to 5 moles per hour per liter of liquid phase and, more usually, from 0.01 to 2 moles per hour per liter of liquid phase.

If the initiator or initiators are introduced into the liquid phase prior to the start of the reaction, the molar ratio:

$$\frac{\text{initiator(s)}}{\text{total of introduced perfluoroolefin(s)}}$$

generally ranges from 0.01 to 0.1.

At the end of the reaction, for example after 0.1 to 20 hours, the reagent feed is discontinued. The solvent, if any, and the unreacted monomer(s) are removed, preferably by distillation, and the peroxidic perfluoropolyether is obtained as residue in the form of an oily liquid or a semi-solid material.

The reaction can also be conducted in a fully continuous manner, by continuously withdrawing a liquid phase portion from the reactor, subjecting it to distillation, recycling the solvent, if any, and the unreacted monomer(s) and recovering the reaction product.

The resulting peroxidic perfluoropolyethers comprise perfluoroalkylenoxy units having at least two carbon atoms. This means that they never consist only of units (CF_2O) but that, besides such units, there are always present the usual perfluoroalkylenoxy units having 2, 3 and more carbon atoms such as (CF_2-CF_2O), (CF-CF_2O), etc.,

$$\begin{array}{l} \\ | \\ CF_3 \end{array}$$

which units may be obtained by reacting perfluoroolefins with oxygen under the action of ultraviolet radiation according to the state of the art, as will be discussed below.

The molar concentration of perfluoroalkylenoxy units having at least two carbon atoms in the obtained perfluoropolyethers generally ranges from 50 to 99.9% and, more usually, from 70 to 99%. The process of the present invention usually affords peroxidic perfluoropolyethers having a very low ratio, generally lower than 25% of -COF end groups to non-functional end groups.

The number average molecular weight of the products obtained generally ranges from a few hundred to several hundred-thousands, for example 300000. More usually, it

ranges from 500 to 100000.

The amount of peroxidic oxygen in the products obtained generally ranges from 0.1 to 9 grams per 100 grams of product.

As is known, the obtained peroxidic perfluoropolyethers may be used as radical polymerization initiators and as crosslinking agents for polymers, in particular, for fluorinated polymers. By means of known methods, they can be converted into inert perfluoropolyethers (i.e., free of peroxide groups and reactive end groups) which are widely used as inert fluids for various applications; for example, for testing in the electronic sector, welding in the vapour phase and in the liquid phase, protection of building materials, lubrication, etc.

The peroxidic perfluoropolyethers obtained are also precursors of functional perfluoropolyethers which are useful, for example, as surfactants and intermediates for polymers.

After elimination of the peroxidic groups, the perfluoropolyethers obtained may be subjected to a cleavage process, for example, by means of heating in the presence of catalytic amounts of $AlBr_3$ or AlF_3, as described in US-A-4 755 330. In this manner, products having a considerably lower average molecular weight than that of the starting materials may be obtained.

Molecules free of peroxidic oxygen may, of course, be present in the mixtures of polymer molecules obtained through the process of the present invention.

When a mixture of tetrafluoroethylene and hexafluoropropene is used as starting material, the following products may be obtained:

$$A\text{-}O\text{-}(CF_2O)_{a1}\ (CF_2\text{-}CF_2O)_{d1}\ (CF_2\text{-}CFO)_{b1}\ (CFO)_{c1}\ (O)_{e1}\ \text{-}\ B \qquad (I)$$

(with CF_3 on the $(CF_2\text{-}CFO)_{b1}$ unit and CF_3 on the $(CFO)_{c1}$ unit)

wherein:

A and B are end groups, which will be defined below,

a1 = 0-5000

b1 = 0-1000

c1 = 0-100

d1 = 0-5000

e1 = 1-1000

b1+c1+d1 = 1-5000 and, more usually, 4-2000

$\frac{a1}{b1+c1+d1}$ = 0.001-1 and, more usually, 0.01-0.45

$\frac{e1}{a1+b1+c1+d1}$ = 0.01-0.9

When perfluoropropene alone is used as starting perfluoroolefin, products having the following formula may be obtained:

$$A\text{-}O\text{-}(CF_2O)_{a5}(CF_2\text{-}CFO)_{b5}(CFO)_{c5}(O)_{e5}\text{-}B \qquad (V)$$

(CF_3 on the $(CF_2\text{-}CFO)_{b5}$ unit and CF_3 on the $(CFO)_{c5}$ unit)

wherein:

a5 = 0-100 and, more usually, 0-50

b5 = 1-1000 and, more usually, 1-500

c5 = 0-100 and, more usually, 0-50

e5 = 1-1000 and, more usually, 1-300

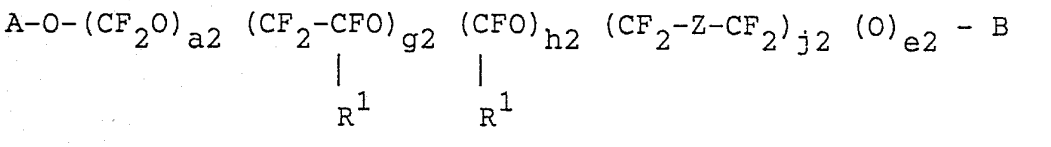
a5+b5+c5 = 2-1000 and, more usually, 2-500

a5+c5/b5 = 0.001-100 and, more usually, 0.01-50

a5/b5+c5 = 0.001-1 and, more usually, 0.01-0.45

e5/a5+b5+c5 = 0.01-0.5.

When perfluorobutadiene alone is used as starting perfluoroolefin, products having the following formula may be obtained:



(II)

wherein:

R^1 is $-CF-CF_2$ (with O bridging) and/or $-CF=CF_2$ and/or $-CF_2-COF$ and/or $-COF$;

Z is $-CF=CF-$ and/or $-CF-CF-$ (with O bridging)

a2 = 0-100

g2 = 1-1000

h2 = 0-100

j2 = 0-1000

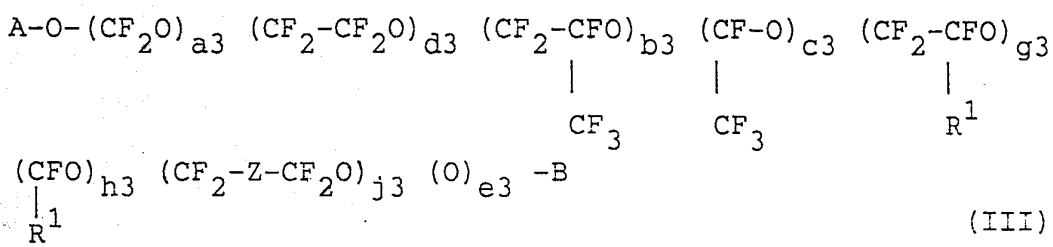
e2 = 1-1000

g2+h2+j2 = 1-1000 and, more usually, 2-500

a2+g2+h2+j2 = 2-1000 and, more usually, 2-500

$$\frac{e2}{a2+g2+h2+j2} = 0.01-0.5$$

When perfluorobutadiene and tetrafluoroethylene and/or perfluoropropene are used as starting perfluoroolefins, products having the following formula may be obtained:



(III)

wherein R^1 and Z are as defined above

a3 = 0-1000

b3 = 0-1000

c3 = 0-100

d3 = 0-1000

g3 = 1-1000

h3 = 0-100

j3 = 0-1000

e3 = 1-1000

a3+b3+c3+d3 = 1-1999 and, more usually, 2-1000

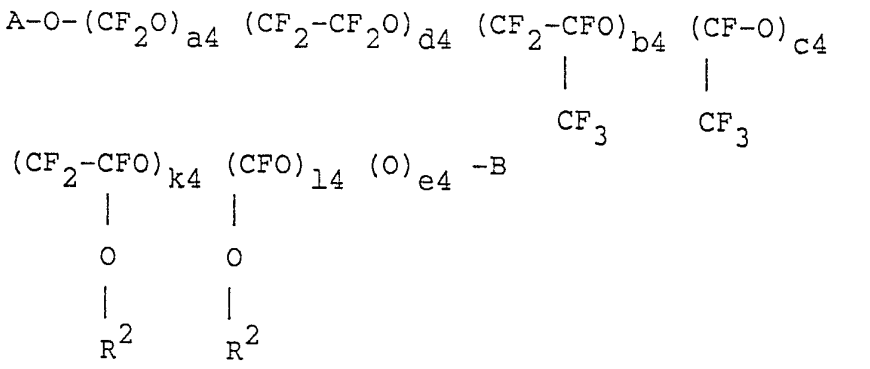
g3+h3+j3 = 1-1000 and, more usually, 1-500

a3+b3+c3+d3+g3+h3+j3 = 2-2000 and, more usually, 3-1000

$$\frac{g3+h3+j3}{a3+b3+c3+d3} = 0.01\text{-}100 \text{ and, more usually, } 0.1\text{-}100$$

$$\frac{e3}{a3+b3+c3+d3+g3+h3+j3} = 0.01\text{-}0.5$$

When one or more perfluorovinylethers of formula $CF_2=CF-OR^2$ and tetrafluoroethylene and/or hexafluoropropene are employed, products having the following formula may be obtained:



(IV)

wherein:

R^2 is as defined above

a4 = 0-1000

b4 = 0-1000

c4 = 0-100
d4 = 0-1000
k4 = 0-1000
l4 = 0-1000
e4 = 1-1000
a4+b4+c4+d4 = 1-1999 and, more usually, 1-1000
k4+l4 = 1-1999 and, more usually, 1-1000
a4+b4+c4+d4+k4+l4 = 2-2000 and, more usually, 2-1000

$$\frac{k4+l4}{a4+b4+c4+d4} = 0.01\text{-}100$$

$$\frac{e4}{a4-b4-c4-d4-k4-l4} = 0.01\text{-}0.5$$

In the products of formulae (I), (II), (III), (IV) and (V) the values of the indexes refer to the individual molecules which are present in the mixtures of polymer molecules. In these mixtures, said indexes take average values which can be integers or intermediate values between zero and one or between an integer and the successive integer. The ratios between the indexes apply both to the individual molecules and to the mixtures of polymer molecules.

In formulae (I), (II), (III), (IV) and (V), the units (O) are oxygen atoms of peroxidic nature and the perfluoroalkylenoxy units and the (O) units are statistically distributed within the chain.

The term "oxygen atom of peroxidic nature" denotes an oxygen atom bound to an oxygen of any of the perfluoroalkylenoxy units, thereby forming a peroxide group -O-O-.

The end groups A and B, the same or different from each other, reperesent the following radicals:
WCF_2-, WCF_2-CF_2-, $CF_3-CFW-CF_2-$, CF_3-CF_2-CFW-, -CFO, $-CF_2CFO$

and -CF-CFO,
|
CF_3

wherein W represents a fragment derived from the initiator(s) and/or the solvent molecule. Generally, W is F, Cl or a perfluoroalkyl or perfluoroalkoxy group optionally containing one or more heteroatoms. When the initiator contains two O-F bonds, a fragment thereof can bind to two growing polymer molecules, thereby becoming incorporated in the molecular chain of the perfluoropolyether product.

Consequently, the nature of the end groups varies from product to product, depending on the nature of the initiator(s) (solvent), on the nature of the monomer or monomers and on the process conditions.

Various parameters permit to influence the molecular weight and the structural composition of the products obtained. For instance, by increasing the concentration of the monomer or monomers in the liquid phase, an increase in the molecular weight may be obtained. Especially when the monomer is perfluoropropene or the monomer mixture contains perfluoropropene and/or when the temperature is increased, the molecular weight decreases.

By reducing the ratio initiator(s)/perfluoroolefin(s), the product molecular weight can, usually, be increased.

The process according to the present invention can be conducted in the presence of ultraviolet radiation in conventional manner.

On the basis of the results described in example IIa of the previously mentioned US-A-4 460 514, it could not be expected that, by reacting perfluoroolefins with oxygen in

the liquid phase in the presence of, for example, CF_3OF, it would be possible to obtain, with high yields and with a generally very reduced formation of by-products, peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms and having a very low ratio of -COF end groups to non-functional end groups.

The main advantages of the present invention are:

- Use is made of a chemical initiator instead of delicate and complex photochemical technologies;
- The process is very flexible, allowing a wide range of products with different structural characteristics to be obtained by changing the process parameters (conditions).

The following examples merely serve to illustrate the invention and do not limit its scope in any way.

Example 1

A total of 200 g of perfluoropropylene was condensed in a 500 ml glass reactor equipped with stirrer, thermometer, cooler with a liquid at -78°C connected to the atmosphere and gas feeding pipes reaching the reactor bottom. Subsequently, while maintaining external cooling so as to keep the internal temperature at -48°C, an anhydrous oxygen stream of 2 Nl/h and a stream of 2.7 Nl/h of CF_3OF and 0.14 Nl/h of F_2, diluted with 5 Nl/h of nitrogen, were separately bubbled into the liquid phase over 2.5 hours.

At the end of the reaction the unreacted perfluoropropylene and the reaction products having a boiling point of lower than 30°C were distilled and removed from the reactor in an anhydrous nitrogen stream.

A total of 80 g of crude reaction product having the

appearance of a colourless, transparent and viscous oil was obtained. The crude product, examined by means of infrared spectroscopy, exhibited a band in the region of 5.25 μm due to the presence of end groups -COF.

The crude product obtained, subjected to iodometric analysis, exhibited a content of active oxygen (i.e., of peroxidic oxygen) of 0.53 percent by weight.

The ^{19}F-N.M.R. analysis revealed that the products was a perfluoropolyether containing peroxidic groups (-O-O-) and having the general formula:

$$A\text{-}O\text{-}(CF_2\text{-}CFO)_b(CFO)_c(O)_e\text{-}B$$
$$\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad CF_3 \quad X$$

wherein:

X = F or CF_3

A and B represent end groups -COF, $-CF_3$, $-CF_2CF_3$, $-CF_2CF_2CF_3$ and $-CF(CF_3)_2$ in a molar ratio: $COF/CF_3 + CF_2CF_3 + CF_2CF_2CF_3 + CF(CF_3)_2 = 1:4.5$ and a ratio: c/b = 0.027:1. The number average molecular weight was 2400.

Examples 2 to 6

By employing the apparatus and the procedure of example 1, a series of tests was carried out, varying the intiator, the temperature, the flow rate of the initiator and of the inert gas (N_2).

In example 2, CF_3OF, diluted with nitrogen and, separately, oxygen were employed.

In example 3, CF_3OF in admixture with oxygen and an inert diluent (N_2) was introduced.

In example 6, CF_3OF in admixture with F_2, diluted with nitrogen and, separately, oxygen were fed.

Operative conditions and main data relating to the products obtained are reported in table 1.

The products obtained, examined by means of ^{19}F-N.M.R. spectroscopy, proved to contain the same structural units and the same end groups as the product of example 1, but in different ratios.

Example 7

A stream of 0.5 Nl/h of $n\text{-}C_3F_7OCF(CF_3)CF_2OF$, diluted with 5 Nl/h of nitrogen, was introduced into a 500 ml reactor, maintained at a temperature of -67°C and containing 150 g of stirred C_3F_6 while, simultaneously, feeding 5 Nl/h of O_2 for 2 hours. At the end of the reaction, after removal of the volatile products and of the unreacted C_3F_6, 12 g of an oily product were obtained. The ^{19}F-N.M.R. analysis revealed that the product was composed of peroxidic polyether chains of general formula:

$$A\text{-}O(CF_2O)_a(CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_b(CFO)_c(O)_e\text{-}B$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CF_3$$

wherein A and B represent CF_3, $CF_2CF_2CF_3$ and $CF(CF_3)_2$, the ratio $(a+c)/b = 0.05$. The number average molecular weight was 3600 and the active oxygen content equaled 0.65 percent by weight.

TABLE 1

EXAMPLE NO.	2	3	4	5	6
Reactions Conditions					
Temperature (°C)	-72	-74	-71	-35	-48
Oxygen (Nl/h)	2	2	2	2	2
Elemental F_2 (Nl/h)	-	-	0.5	0.5	0.05
CF_3OF (Nl/h)	1	1	-	-	0.95
Nitrogen (Nl/h)	3	3	10	10	3
Perfluoropropylene (g)	204	210	185	186	200
Time (hours)	4	4	3.5	0.4	6
Peroxidic polyether products obtained (g)	45	38	77	4.3	31.7
Characteristics of the products obtained					
Number average molecular weight	3200	4000	2600	2100	3000
Active oxygen content $\left(\frac{\text{g of active oxygen}}{\text{100 g of product}}\right)$	0.4	0.39	0.51	0.76	1.23
Average structure: $AO-(C_3F_6O)_b(CFO)_c(O)_e-B$ with X = F or CF_3					
c/b	0.003	0.003	0.002	0.043	0.02
$\frac{\text{End groups } C_nF_{2n+1}}{\text{End groups } -COF}$ (molar ratio)	13.2	10.2	30.8	6.5	6.2

Example 8

Using the apparatus of example 1, maintained at -71°C, 150 ml of perfluoropropylene were condensed. Then a stream of 1.5 Nl/h of tetrafluoroethylene, a stream of 0.5 Nl/h of

elemental F_2, diluted with 2 Nl/h of nitrogen and, separately, a stream of 3 Nl/h of oxygen were bubbled through over a period of three hours.

At the end of the reaction 41.5 g of crude reaction product were recovered in the form of a colourless, transparent and viscous oil.

The crude product, subjected to iodometric analysis, exhibited an active oxygen content of 2.43 percent by weight and the ^{19}F-N.M.R. spectrum corresponded to that of a peroxidic perfluoropolyether of general formula:

$$A\text{-}O(CF_2O)_a(CF_2CF_2O)_d(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_b(\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_c(O)_e\text{-}B$$

wherein A and B represent CF_3, CF_2CF_3, $CF_2CF_2CF_3$, $CF(CF_3)_2$ and COF in a molar ratio:

$COF/CF_3 + CF_2CF_3 + CF_2CF_2CF_3 + CF(CF_3)_2 = 0.076$

$b/d = 1.02$

$d/a = 35$

$b/a+c = 7.47$

$a+c/a+d+b+c = 0.06$.

The product had a number average molecular weight of 2700.

Example 9

Using the apparatus of example 1, maintained at -71°C, 150 ml of dichlorodifluoromethane were condensed and, subsequently, there were introduced, by separately bubbling into the liquid solvent, a stream of 2.5 Nl/h of tetrafluoroethylene, a stream of 1.67 Nl/h of perfluorobutadiene and, separately, 7 Nl/h of oxygen, 0.47 Nl/h of trifluoromethyl hypofluorite and 1 Nl/h of nitrogen.

After 2 hours the introduction of reactants was discontinued and the solvent and the reaction products having a boiling point of lower than 30°C were distilled in an anhydrous nitrogen stream. A total of 34 g of product was obtained. According to ^{19}F-N.M.R. analysis, the product consisted of a perfluoropolyether containing peroxide groups (O-O) of general formula:

$$A\text{-}O(CF_2O)_a(CF_2CF_2O)_d(CF_2\underset{\underset{R}{|}}{CFO})_b(\underset{\underset{R}{|}}{CFO})_c(CF_2\text{-}Z\text{-}CF_2O)_h(O)_e\text{-}B$$

wherein R = $-CF\underset{O}{<}CF_2$, -COF, $-CF=CF_2$ and $-CF_2$-COF;

Z = $-CF\underset{O}{<}CF-$, -CF = CF-;

A and B represent end groups -COF, $-CF_3$ and $-CF_2CF_3$ in a molar ratio $COF/CF_3+CF_2CF_3$ of 0.4;
b/a equals 14.
(b+c+h)/(a+d) = 0.2, the ratio d/a being equal to 14.

The number average molecular weight was 2500.

The IR-FT (Fourier Transform) spectrum confirmed the presence of groups
$-CF\underset{O}{<}CF_2$ (1537 cm^{-1}) and $-CF\underset{O}{<}CF-$ (1504 cm^{-1})
the former groups prevailing, and the presence of groups $-CF=CF_2$ (1785 cm^{-1}) and -CF=CF- (1719 cm^{-1}), the latter groups being predominant.

Example 10

Using the apparatus of example 1, maintained at -71°C, 150 ml of difluorodichloromethane were condensed and, subsequently, a stream of 3.5 Nl/h of perfluorobutadiene

and a mixture of 11 Nl/h of oxygen, 0.7 Nl/h of trifluoromethyl hypofluorite and 2 Nl/h of nitrogen were introduced by bubbling through the liquid solvent.

After 2 hours the introduction of the reactants was stopped and the solvent and the reaction products having a boiling point of lower than 30°C were distilled in an anhydrous nitrogen stream. A total of 35 g of product was obtained. According to the ^{19}F-N.M.R. analysis the product consisted of perfluoropolyethers containing peroxide groups (-O-O-) of general formula:

$$A\text{-}O\text{-}(CF_2O)_a(CF_2CFO)_b(CFO)_c(CF_2\text{-}Z\text{-}CF_2)_h(O)_e\text{-}B$$
$$\qquad\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad\quad R\qquad\quad R$$

wherein

Z = $-CF\underset{O}{\diagdown\diagup}CF-$ and $-CF=CF-$;

R = $-CF\underset{O}{\diagdown\diagup}CF_2$, $-COF$ and $-CF=CF_2$;

and A and B represent end groups CF_3, COF and CF_2COF.

The IR-FT spectrum confirmed the presence of groups $-CF\underset{O}{\diagdown\diagup}CF_2$, $-CF\underset{O}{\diagdown\diagup}CF-$, $-CF=CF_2$ and $-CF=CF-$.

Example 11

A total of 1.5 g of a mixture of products of average formula $n\text{-}C_3F_7O(CF_2\text{-}CFO)_{1.3}CF(CF_3)CF_2OF$,

$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad CF_3$$

dissolved in 20 ml of $CFCl_3$, was gradually introduced into a 500 ml reactor, maintained at a temperature of -70°C and containing 150 g of stirred C_3F_6, with simultaneous feeding

of 5 Nl/h of O_2, over a period of 2 hours. At the end of the reaction, after removal of the volatile products and of unreacted C_3F_6, 10.5 g of an oily product were obtained. The ^{19}F-N.M.R. analysis revealed that it was composed of peroxidic polyether chains of general formula:

$$A\text{-}O\text{-}(CF_2O)_a(CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_b(CF\underset{\displaystyle CF_3}{\underset{|}{}}O)_c(O)_e\text{-}B$$

wherein A and B represent end groups $-CF_3$, $-CF_2CF_2CF_3$ and $-CF(CF_3)_2$, and (a+c)/b is 0.03. The number average molecular weight was 4200 and the active oxygen content was 0.6%.

Example 12

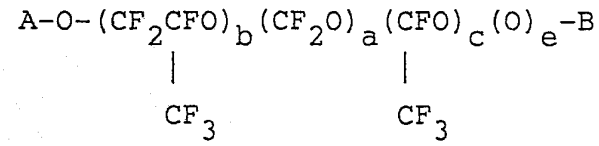
A total of 400 g of C_3F_6 was introduced, at a temperature of -60°C, into a cylindrical 300 ml glass reactor (optical path 0.5 cm), equipped with coaxial inner quartz sheath, two plunge pipes for feeding the gases, a sheath with thermocouple for measuring the internal temperature and a reflux cooler maintained at a temperature of -80°C.

Through the plunge pipes, 20 Nl/h of O_2 and 0.15 Nl/h of F_2 were separately bubbled into the reactor. By means of a refrigerating bath surrounding the reactor, the temperature of the reacting liquid phase was maintained at 60°C throughout the entire course of the reaction.

Into the quartz sheath there was introduced an ultraviolet ray lamp, type HANAU TQ 150 (wavelength 200 to 600 nm), which was switched on simultaneously with the beginning of the gas feed and irradiation and feeding of the two reacting gases were continued for 2 hours.

The lamp was then switched off, the gases were discharged

and the unreacted C_3F_6 was recovered from the reactor by evaporation at room temperature. Thus an oily polymeric residue (83.2 g) was obtained. The iodometric analysis of said residue indicated an active oxygen content of 0.28%. According to ^{19}F-N.M.R. analysis the product consisted of peroxidic polyether chains having the general formula:

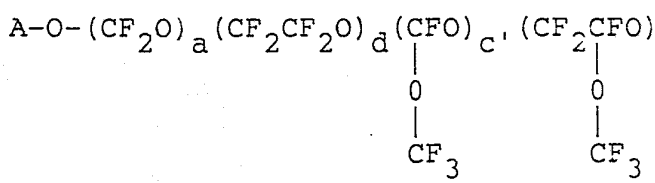


wherein A and B represent end groups $-CF_3$ and $-COF$ and (a+c)/b is equal to 0.1. The product had a number average molecular weight of 5300.

Example 13

Using the apparatus of example 1, maintained at -71°C, 150 ml of CF_2Cl_2 were condensed and then a stream of 2.5 Nl/h of C_2F_4 and a stream of 2.76 Nl/h of $CF_3OCF=CF_2$ were separately fed by bubbling into the liquid solvent.

After 5 minutes a stream consisting of 7 Nl/h of O_2, 0.35 Nl/h of CF_3OF and 1 Nl/h of N_2 was introduced without interrupting the monomer flow. After 2 hours the feeding of the reagents was stopped and the solvent and the reaction products having a boiling point lower than 30°C were distilled in an anhydrous nitrogen stream. A total of 37 g of an oily product was obtained. According to ^{19}F-N.M.R. analysis the product consisted of peroxidic polyether chains having the general formula:



wherein A and B represent end groups $-CF_3$, $-CF_2CF_3$, $-CF(OCF_3)CF_3$, d/a equals 0.83, c'+b'/a+d equals 0.17 and c'/b' is 3.

The number average molecular weight of the product was 2300.

The iodometric analysis of the product indicated an active oxygen content of 1.26 percent by weight.

Example 14

Using the apparatus of example 1, maintained at -71°C, 88 g of C_3F_6 and 93 g of $CF_3OCF=CF_2$ were condensed and, subsequently, a stream of 3 Nl/h of O_2, 0.5 Nl/h of F_2 and 10 Nl/h of nitrogen was fed by bubbling into the liquid phase. After 3.5 hours the feeding of the reagents was stopped and the unreacted olefins and the reaction products having a boiling point lower than 30°C were distilled in an anhydrous nitrogen stream. A total of 41 g of an oily product was obtained.

According to ^{19}F-N.M.R. analysis the product was composed of polyperoxidic polyether chains of general formula:

$$A\text{-}O\text{-}(CF_2O)_a(CF_2\underset{\underset{CF_3}{|}}{CFO})_b(\underset{\underset{CF_3}{|}}{CFO})_c(CF_2\underset{\underset{O}{|}\\ \underset{CF_3}{|}}{CFO})_{b'}(\underset{\underset{O}{|}\\ \underset{CF_3}{|}}{CFO})_{c'}(O)_e\text{-}B$$

wherein A and B represent end groups CF_3, $CF(OCF_3)CF_3$, a+c/b = 1, b'+c'/a+b+c = 1.62 and b' /c' = 8.75.

The number average molecular weight of the product was 5000.

The iodometric analysis of the product indicated an active oxygen content of 1.23 percent by weight.

Example 15

As initiator, a perfluoropolyether product of formula
$A\text{-}O\text{-}(CF_2CF_2O)_m(CF_2O)_n\text{-}B$
as described in example 3 of EP-A-308 905, wherein A and B are groups CF_2OF (with a functionality of 1.65) and CF_3 was prepared. This product had a number average molecular weight of 2950.

A total of 1.1 g of said initiator was diluted with 20 g of $CFCl_3$ and introduced into a reactor maintained at a temperature of -67°C and containing 150 ml of stirred perfluoropropylene. Over a period of 2 hours 5 Nl/h or oxygen were introduced. At the end of the reaction, after removal of the volatile products and the unreacted perfluoropropylene by means of distillation, 2.5 g of a product were obtained which product, according to ^{19}F-N.M.R. analysis was composed of peroxidic perfluoropolyethers of general formula:

$$A\text{-}O(CF_2O)_a(CF_2CF_2O)_d(CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FO)_b(CF\underset{\displaystyle CF_3}{\underset{|}{}}O)_c(O)_e\text{-}B$$

wherein A and B are end groups CF_3, CF_2CF_3, $CF_2CF_2CF_3$ and $CF(CF_3)_2$, b/d is 0.63 and d/a+c is 0.69.

The number average molecular weight of the product was 7200.

The iodometric analysis revealed an active oxygen content of 0.3 percent by weight.

Claims:

1. A process for the preparation of peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms, characterized in that one or more perfluoroolefins, except tetrafluoroethylene used alone, are reacted with oxygen in the liquid phase at a temperature not exceeding 50°C and in the presence of one or more compounds having one or more F-X bonds, in which X is selected from the group consisting of F, O and Cl.

2. The process according to claim 1, characterized in that the compunds having one or more F-O bonds are oxygen fluorides or organic compounds containing one or more fluoroxy groups.

3. The process according to claim 2, characterized in that the compounds having one or more F-O bonds are perhalogenated alkyl or alkylene compounds, the halogen atoms of which are F atoms or F and Cl atoms, containing one or more fluoroxy groups and, optionally, one or more heteroatoms.

4. The process according to claim 3, characterized in that the heteroatom or heteroatoms are ether oxygen atoms.

5. The process according to claim 3 or 4, characterized in that the perhalogenated alkyl or alkylene compound containing one or more fluoroxy groups and, optionally, one or more heteroatoms is a perfluorinated compound.

6. The process according to claim 3 or 4, characterized in that the perhalogenated alkyl of alkylene compound containing one or more fluoroxy groups and,

optionally, one or more heteroatoms is a compound, the halogen atoms of which consist of F and Cl, in which the number of Cl atoms ranges from 1 to 10.

7. The process according to claim 4, characterized in that the number of ether oxygen atoms ranges from 1 to 100.

8. The process according to claim 7, characterized in that the number of ether oxygen atoms ranges from 1 to 10.

9. The process according to claim 1, characterized in that, when X is F, the compound having one or more F-X bonds if F_2.

10. The process according to claim 1, characterized in that, when X is Cl, the compound having one or more F-X bonds is a chlorine fluoride.

11. The process according to claim 1, characterized in that the compound or compounds having one or more F-X bonds are selected from the group consisting of:

1) F_2;

2) R^5-OF, wherein R^5 is a C_{1-10}-perhaloalkyl radical containing fluorine atoms or fluorine atoms and from 1 to 5 chlorine atoms;

3) $R^6\text{-O-}(R^7O)_n\underset{\substack{|\\ D}}{(CF)}_t\text{-}CF_2OF$

wherein:
D represents F or CF_3;
t is zero or 1;

R^6 is a C_{1-3}-perfluoroalkyl radical or a C_{1-3}-perhaloalkyl radical containing fluorine atoms and one or more chlorine atoms;
R^7 represents one or more perfluoroalkylene radicals, the same or different from one another, selected from

$-CF_2-$, $-CF_2-CF_2-$ and $-CF_2-CF(CF_3)-$

and n ranges from 0 to 50;

4) $R^8-C(OF)(OF)-R^9$

wherein R^8 is F or a C_{1-9}-perhaloalkyl radical containing F atoms or F atoms and from one to three Cl atoms; R^9 is F, R^8 or a perfluoroalkylmonoether o- perfluoroalkylpolyether group $R^6O-(R^7O)_n-CF_2-$, in which R^6, R^7 and n are as defined above;

5) $FO-(R^7O)_s-F$
wherein R^7 is as defined above and s ranges from 1 to 100, provided that, when R^7 represents $-CF_2-$, s has a value higher than 1;

6) $FO-(CF_2)_v-OF$, wherein v ranges from 3 to 5.

12. The process according to claim 1, characterized in that the perfluoroolefins are selected from the group consisting of:

(a) one or more perfluoromonoolefins, except C_2F_4,

when used alone

(b) a perfluorodiolefin

(c) a perfluorodiolefin in combination with one or more perfluoromonoolefins

(d) one or more perfluoromonoolefins in combination with one or more perfluorovinylethers.

13. The process according to claim 12, characterized in that the perfluoromonoolefins are selected from the group consisting of hexafluoropropene and of hexafluoropropene in admixture with tetrafluoroethylene.

14. The process according to claim 12, characterized in that the perfluorodiolefin is perfluorobutadiene.

15. The process according to claim 12, characterized in that the perfluorovinylethers have the general formula

$$CF_2 = CF - O - R^2$$

wherein:
R^2 is $(R^3O)_m R^4$ or R^4;
R^3 is selected from the group consisting of $-CF_2-$, $-CF_2-CF_2-$ and $-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-$;

R^4 is a perfluoroalkyl group selected from linear groups containing from 1 to 10 carbon atoms, branched groups containing from 3 to 10 carbon atoms and cyclic groups containing from 3 to 6 carbon atoms, and m ranges from 1 to 6.

16. The process according to claim 15, characterized in that in the group $(R^3O)_mR^4$ m ranges from 1 to 3.

17. The process according to claim 15, characterized in that R_4 is selected from the CF_3-, C_2F_5-, n-C_3F_7-, i-C_3F_7-, n-C_4F_9-, i-C_4F_9- and tert-C_4F_9-radicals.

18. The process according to claim 1, characterized in that into a liquid phase comprising a solvent and/or one or more perfluoroolefins there are introduced a gaseous stream of oxygen, a gaseous or liquid stream of one or more compounds having one or more F-X bonds and, optionally, a gaseous or liquid stream of one or more perfluoroolefins, the last-mentioned stream being always present if the liquid phase does not contain perfluorcolefins prior to the start of the reaction.

19. The process according to claim 1, characterized in that into a liquid phase comprising a solvent and/or one or more perfluoroolefins and containing one or more compounds having one or more F-X bonds, there are fed a stream of gaseous oxygen and, optionally, a gaseous or liquid stream of one or more perfluoroolefins, the latter stream being always present if the liquid phase does not contain perfluoroolefins prior to the start of the reaction.

20. The process according to any one of claims 18 and 19, characterized in that also an inert gas is fed into the liquid phase.

21. The process according to any one of claims 1, 11, 18 and 19, characterized in that the temperature ranges from -120 to +50°C.

22. The process according to claim 21, characterized in that the temperature ranges from -100 to +20°C.

23. The process according to claim 22, characterized in that the temperature ranges from -100 to 0°C.

24. The process according to any one of claims 18 and 19, characterized in that the solvent is selected from the group consisting of linear and cyclic fluorocarbons, chlorofluorocarbons, perfluoroamines, perfluorinated ethers and mixtures thereof.

25. The process according to any one of claims 1, 11, 18 and 19, characterized in that the oxygen partial pressure in the reactor ranges from 0.01 to 10 atmospheres.

26. The process according to claim 25, characterized in that the oxygen partial pressure in the reactor ranges from 0.05 to 1 atmosphere.

27. The process according to any one of claims 1, 11, 18 and 19, characterized in that the total pressure at which the reaction is conducted ranges from about 1 to about 10 atmospheres absolute.

28. The process according to claim 18, characterized in that, when a gaseous or liquid stream of one or more compounds having one or more F-X bonds is fed into the liquid phase, the flow rate of said compound(s) ranges from 0.001 to 5 moles per hour per liter of liquid phase.

29. The process according to claim 28, characterized in that the flow rate of the compound(s) having one or more F-X bonds ranges from 0.01 to 2 moles per hour per liter of liquid phase.

30. The process according to claim 19, characterized in that, when the liquid phase already contains compound(s) having one or more F-X bonds prior to the start of the reaction, the molar ratio:

compound(s) having one or more F-X bonds
total of introduced perfluoroolefin(s)

ranges from 0.01 to 0.1

31. The process according to claim 20, characterized in that the inert gas is selected from the group consisting of nitrogen, argon, helium, CF_4, C_2F_6 and mixtures thereof.

32. The process according to any one of claims 1, 11, 18 or 19, characterized in that the reaction is conducted in the presence of ultraviolet radiation.

33. Peroxidic perfluoropolyethers comprising perfluoroalkylenoxy units having at least two carbon atoms, obtainable by the process of any one of claims 1, 11, 18 and 19.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 90/00638

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 08 G 65/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]	
Classification System	Classification Symbols
IPC[5]	C 08 G, C 07 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	EP, A, 0259980 (3M) 16 March 1988 see page 11, line 31 - page 13, line 56; examples; claims	1
A	EP, A, 0244839 (AUSIMONT) 11 November 1987 see page 3, line 21 - page 4, line 7; examples 1A,2A,3A	1
A	US, A, 4460514 (K.B. BAUCOM) 17 July 1984 see example 2 (cited in the application)	1

* Special categories of cited documents: [10]

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

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

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

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

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

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11th July 1990	30. 07. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	F.W. HECK

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9000638 SA 36030

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/07/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0259980	16-03-88	US-A- 4743300	10-05-88
		AU-A- 7735587	03-03-88
		JP-A- 63083134	13-04-88
		US-A- 4820588	11-04-89
EP-A- 0244839	11-11-87	AU-B- 596176	26-04-90
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		US-A- 4853097	01-08-89
		ZA-A- 8703178	28-10-87
US-A- 4460514	17-07-84	US-A- 4374715	22-02-83