Perfluoropolyethers. Synthesis and application

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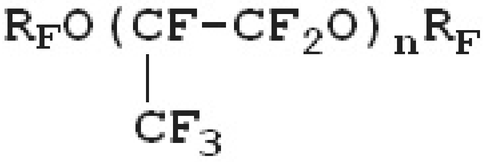
Perfluoropolyethers, generally produced through the oxidation of hexafluoropropylene, are f fluorinated oligomers with alternating fluorocarbon and oxygen links. The general formula perfluoroethers is as follows:



$$R_FO(\underset{\displaystyle CF_3}{CF}-CF_2O)_nR_F$$

Those oligomers are known for wide range of their boiling temperatures: from 50-70 °C to 2 320 °C at 1 mm Hg, while their freezing temperatures are about -60 °C or even low Perfluoropolyethers possess also a number of very unique properties [1]: high heat resistan chemical stability in very aggressive media, incombustibility, non-toxicity, excellent dielec characteristics, viscosity nearly unchanged in wide temperature range, excellent lubricat properties, radioimmunity, etc. The mentioned set of properties makes perfluoropolyeth applicable in various fields of modern industry for liquid dielectrics, heat-carriers, greases a lubricants. Some properties of specific perfluoropolyether fractions are shown in table 1.

Table 1. *Some properties of perfluoropolyethers*

Boiling range, °C/1 mm Hg	Steam tension, torr	Viscosity, cSt	Molecular weight	Solidification temperature
80-130	10^{-3}	5-15	1200	< -80
130-180	10^{-5}	50-90	1500	~ -70
180-240	10^{-7} - 10^{-8}	100-150	2500	~ -50
>240	10^{-10}	400-700	5000	~ -40
>320	10^{-14}	1000-1800	10 000	~ -30

The methods for the manufacture the most popular perfluoropolyethers are all based hexafluoropropylene (**CF_3-CF=CF_2**) that is an industrially available fluoromonomer used for r material in the manufacture of many fluoroplastics. The current state of perfluoropolyet technology development was preceded by worldwide research undertaken by a number Russian, USA and Italian companies, the world leaders in this field, in [2-5] in 1970 - 1980 They have studied the possibility for perfluoropolyether manufacture starting with all kind fluoromonomers and using various routs: gas-phase and liquid-phase processes at vari temperatures, pressures, etc. The research and development of perfluoropolyether technolog was complicated by the necessity of certain safety conditions observance because oxidatior fluoroolefines by oxygen results in potentially explosive peroxides. Basing both on published d and our own results a process for perfluoropolyethers manufacture is now being developed RSC "Applied chemistry" using hexafluoropropylene for initial raw material. The process is to conducted in liquid at low temperature (below -30^{o}C) and under UV-irradiation or under the act of elemental fluorine.

The boiling point of hexafluoropropylene (**CF_3-CF=CF_2**) is -29.1^{o}C. The density of lic hexafluoropropylene at different temperatures is shown in table 2.

Table 2. *Density of hexafluoropropylene at various temperatures*

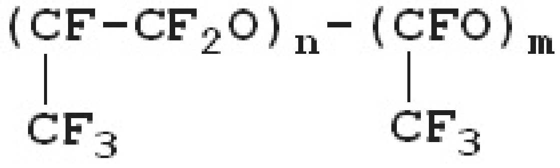
Temperature, ^{o}C	***Density, g/cm^3***	***Temperature, ^{o}C***	***Density, g/cm^3***
-40	1,565	+20	1,332
-20	1,498	+40	1,321
0	1,419	+60	1,105

Manufacture of perfluoropolyethers

The process for target "neutral" perfluoropolyethers preparation involves the steps as follows

- low-temperature liquid-phase oxidation of hexafluoropropylene initiated either by irradiation or by fluorine resulting in perfluoropolyether peroxide with fluoroanhydı terminal groups (-COF);
- stabilization of perfluoropolyether peroxide in order to eliminate peroxide groups terminal groups (-COF) through the treatment of perfluoropolyether peroxide with elemer fluorine or CoF_3, etc.;
- vacuum-fractional distillation of stabilized perfluoropolyether resulting in target fractions;
- finish sorption cleaning of perfluoropolyether.

The analysis has shown that photochemically produced perfluoropolyethers have "irregular" structure:



$$(\underset{\displaystyle CF_3}{\underset{|}{CF}}-CF_2O)_n-(\underset{\displaystyle CF_3}{\underset{|}{CF}}O)_m$$

and that the low-temperature properties of such perfluoropolyethers exceed those regular-structured perfluoropolyethers.

Study on hexafluoropropylene oxidation in liquid phase

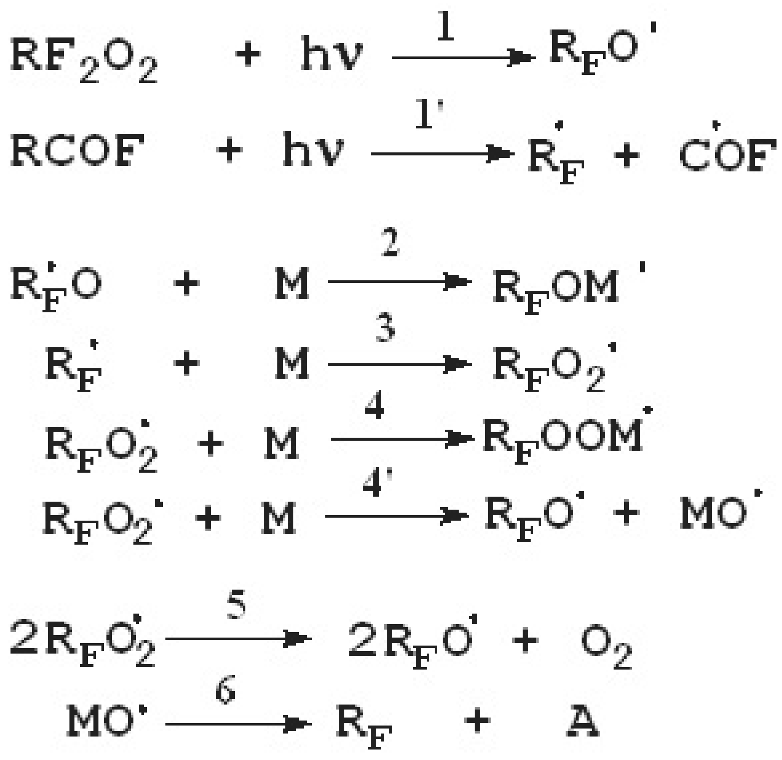
Oxidation of hexafluoropropylene was conducted either in quartz or in a metal (stainl steel) reactor at various temperatures (-20 ÷ -40°C). The metal reactor (steel X18H10T) w a cylinder capped with a screw cap provided with a quartz window, and equipped wit pocket for thermocouple, Gopher valve, and thermostating jacket. High-pressure mercu quartz lamp DRT-400 (220 V, AC) was used for the irradiation source. Hexafluoropropyl from a cylinder passed a column filled with silica gel and molecular sieves (to rem humidity and other impurities) and then condensed in a reactor. The reactor was coolec the predetermined temperature and oxygen was fed into it under UV-irradiation. completion of the process we evacuated all gaseous reaction products, opened the reac and poured the reaction mass into a special tank for further stabilization and the tar products isolation through vacuum distillation. Photooxidation is a complicated chain react with the participation of three types of radicals:

perfluoroalkyl (**R_F**),

perfluoroalkoxy (**$R_FO^{\cdot}$**),

perfluoroperoxide (**$R_FOO^{\cdot}$**)

The most important elemental reactions (5) are as follows:



initiation

chain development reactions

radical reactions

chain interruption reactions

Here:

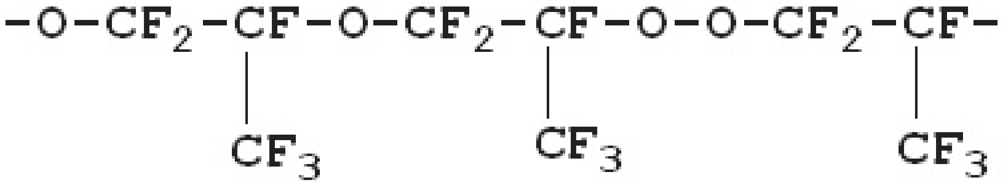
M = **C_3F_6**, R_F = **CF_3**, **M**,

A = **CF_2O**, **CF_3COF**

Oxidation reactions start under the action of UV emission with wavelength less than 3 nm; low-pressure or medium-pressure mercury lamps are applicable for this purpose (e DRT-400). Hexafluoropropylene, other fluoroolefines and their mixtures with oxygen, wh free of impurities and oxidation products, do not absorb UV with wavelength more than 2 nm. That is why the reaction has got a short induction period during which fluoroolefi that are present in negligible amounts convert to some UV-absorbing substances, such CF_3COF or peroxides, and their further photolysis results in peroxide **O-O** bonds rupt (reaction 1) and/or in acylfluoride **C-C** bonds rupture (reaction **1'**) followed by the format of free radicals that initiate chain reactions between olefins and oxygen (reactions 2 -

One cannot also rule out another mechanism of the reaction active centre originat through the formation of donor-acceptor oxygen-hexafluoropropylene complexes w absorption spectra shifted to longer wavelengths. Photolysis of such complexes may res in active species able to initiate oxidation reactions. It is well known that even at temperature perfluoroalkoxy radicals tend to undergo degradation by C-C bonds, a consequently the radical decomposition (reactions 5, 6) contributes much to the ch development reactions.

According to the available test results and published data reactions of peroxyradicals is most important among all chain interruption processes [6]. Some fluorine-contair peroxyradicals thus formed may undergo recombination (reaction 5) resulting in t perfluoroalkoxyradicals that readily continue the chain. Basing on our mass-spectrosc results and in conformity with available published data [7] we made the conclusions ab the structure of hexafluoropropylene oxidation products: it contains a linear skeleton t consists of perfluoroalkyls C_3F_6, connected through oxygen atoms or through oxygen-bric bonds:



$$-O-CF_2-\underset{CF_3}{\underset{|}{CF}}-O-CF_2-\underset{CF_3}{\underset{|}{CF}}-O-O-CF_2-\underset{CF_3}{\underset{|}{CF}}-$$

The molecules contain two types of terminal groups: alkoxy- (R_FO) and fluoroanhydrid COF) groups.

The product molecular weight depends on the hexafluoropropylene oxidation paramete at -30 — 40°C it is about 3000 - 4000. Polyether peroxides are the mane products hexafluoropropylene low-temperature liquid-phase photochemical oxidation. The produ composition depends on the process conditions, low-molecular gaseous fluorosubstan (COF_2, CF_3COF, hexafluoropropylene oxide) are also formed though in small amounts. process parameters dependence of the reaction products yields is shown.

Temperature dependence of the rate of hexafluoropropylene oxidation

Effective activation energies for fluorosubstances formation within temperature range — +25°C at oxygen pressure 7 bar are shown below in table 4.

Table 4. *Effective activation energies for fluorosubstances formation*

Substance	**$E_{effective}$(kcal/mole)**	
-45°C — -5°C	-5°C —+25°C	
Polyether peroxide	4,43	0
Hexafluoropropylene oxide	3,05	12,6
CF_3COF	5,26	2,13
COF_2	1,52	3,75

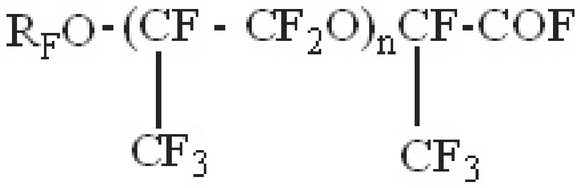
At low temperature (-35 — -5^{o}C) only ~5% of hexafluoropropylene convert to l molecular compounds: COF_2, CF_3OF, hexafluoropropylene oxide; while >95% of orig hexafluoropropylene turns into oligomer with average molecular weight ~40 Perfluoropolyether peroxide remains the main reaction product up to -15^{o}C, the yield of l molecular products (COF_2, CF_3OF etc.) grows considerably as the temperature exce -15^{o}C.

Oxygen pressure dependence of the rate of hexafluoropropylene oxidation

Our studies on the pressure dependence at -35^{o}C and -15^{o}C within the pressure rang 13 bar have shown that the rate of polyetherpolyperoxide formation grows directly w oxygen pressure between 0 and 2 bar, and does not depend on oxygen pressure abov bar. It was also shown that as the process temperature increases the average molecu weight of perfluoropolyperoxide decreases (at +25^{o}C, MW= 1000), and the yield hexafluoropropylene oxide grows with temperature.

As UV-irradiation intensity grows the oligomer molecular weight goes down to const value. The induction period of hexafluoropropylene fluorooxidation by oxygen is negligible. the reaction products (perfluoropolyether peroxides) are accumulated initiation accelera at the expense of their photolysis. It is well known that the main disadvantages fluoroolefine photochemical oxidation are as follows:
- low process productivity;
- sophisticated hardware implementation;
- low performance of UV sources, etc.

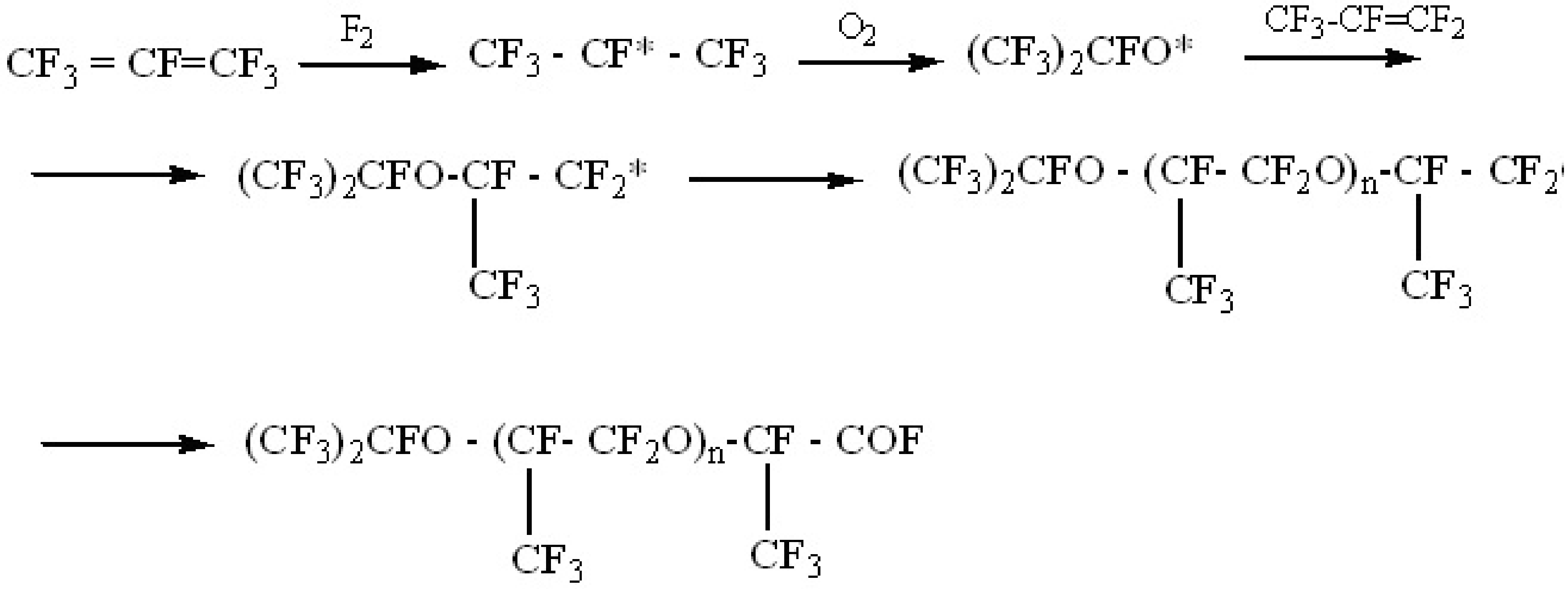
With allowance maid for the above it seems more promising to apply the method fluoroolefine/oxygen radical co-polymerization using some chemicals that undergo l temperature homolytical dissociation e.g., elemental fluorine [6]. According to NMR F^{19} structure of thus produced HFP-based perfluoropolyethers is as follows:



$$R_FO-(\underset{\displaystyle CF_3}{CF}-CF_2O)_n\underset{\displaystyle CF_3}{CF}-COF$$

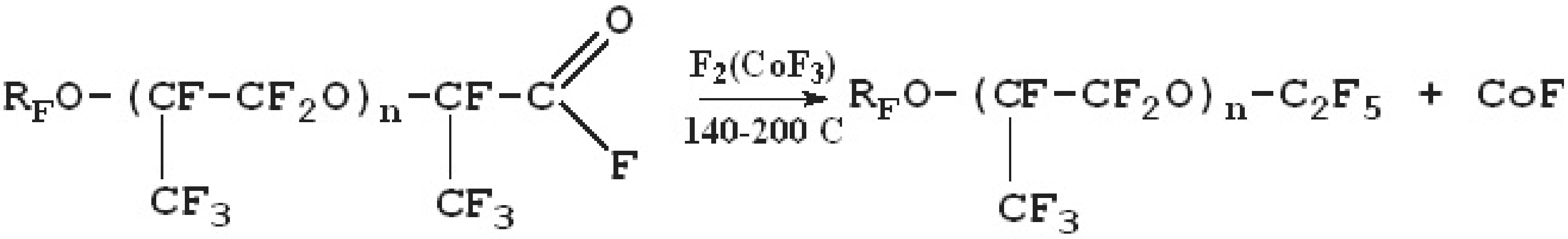
here: R_F=**CF_3,$(CF_3)_2CF$-**

It is typical for chemical fluorine-initiated processes that their products in fact do involve neither fluoroformiate nor difluoromethylene oxide groups those being, howev mandatory in photochemical oxidation products. It is anticipated that chemical fluori initiated hexafluoropropylene/oxygen co-polymerization occurs according to as follows:



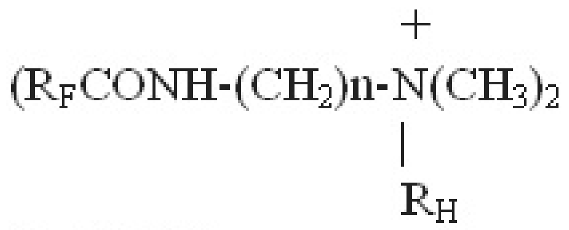
In the case of chemical fluorine-initiated hexafluoropropylene/oxygen co-polymerization production of difluorophosgene (COF_2) is rather small (0.01-0.2 mole/mole perfluoropolyether) that is ten times less than in photochemical process. A peculiarity of process chemical initiation is the absence of inhibition effects due to the reaction by-produ (COF_2, CO, CO_2, CF_3OF etc.).

Unlike it, in the case of photochemical hexafluoropropylene/oxygen oxidation by-produ completely inhibit co-polymerization process if their concentration in gas phase exceeds 3 by volume. However, chemical initiation of hexafluoropropylene/oxygen co-polymerizat requires strict compliance with the process parameters. Fluorine slippage can result in s ignition and monomer combustion in oxygen medium. In this specific case the choice of method for perfluoropolyether manufacture was dictated both by the safety considerati and by hardware implementation possibilities for the process of hexafluoropropylene/oxy co-polymerization. Fluoroanhydride group from perfluorooligoethers produced hexafluoropropylene/oxygen co-polymerization is eliminated on exposure to elemer fluorine, CoF_3 or other fluorinating agent:



The reaction results in neutral perfluoropolyethers.

Starting from fluoroanhydrides of perfluoropolyether acids a range of efficient fluorina surfactants was prepared: cationogenic, anionogenic, non-ionogenic [7]



$(R_FCONH\text{-}(CH_2)n\text{-}\underset{\displaystyle R_H}{\overset{+}{N}}(CH_3)_2$

R_FCOOMe,

$R_FCOO(C_2H_4o)_nH$,

Those surfactants have found many applications as components of fire-fighting foams products fire extinguishing), oil additives, lubricants, diesel fuels, addition agents decreas friction and improving performance of various machines, mechanisms and other techn devices.

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