

Commercial fluorine containing compounds

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The engineering studies in the field of commercial fluorine containing compounds are given following: ozone-friendly hydrofluorocarbons (chladones), fluoroolefines, compounds containing functional groups, heat-resistant liquids, oils, lubricants, fluorine surfactants etc..

1. Ozone-friendly compounds.

Chlorofluorocarbons and bromofluorocarbons (chladones and halons) as compounds possess a number of unique properties such as chemical inertness, non-toxicity, fire and explosion safety. They were widely used in engineering as aerosol propellants, refrigerants, foaming agents for plastic foams, solvents, highly efficient extinguishers etc. But a destructive impact of some chlorine- and bromine-containing compounds on the ozone layer discovered in the 1980s drew attention to a large group of commercial chladones containing chlorine and bromine in their composition because of their potential danger. Up-to-date evaluations of relative role of antropogenic and natural factors in ozone layer depletion have shown that the relative contribution of the antropogenic factors is 75% over Western Europe, 60% over Eastern coast of the USA, 50% over Japan, Baikal and the Far East.

The Vienna Convention for the protection of the ozone layer signed in 1985y was the first international document envisaging measures for the protection of the ozone layer. The countries that signed the Convention, undertook obligations on collaboration in the field of control and prevention of the activity potentially dangerous to the stratosphere ozone layer. In September 1987y the Montreal Protocol (MP) was passed on the substances depleting the ozone layer, with Annex listing ozone depleting substances (ODS) subject to the control by all the countries party to the MP. It contained chlorofluorocarbons (CFC), bromofluorocarbons (halons) and hydrochlorofluorocarbons (HCFC). The Protocol laid the obligations on the Parties to limit consumption, production and import/export of ODS.

The Soviet Union was one of the first-rate producers of ODS: in 1987 its share in production of ODS (~200thous.tons/year) was around 15% of the world production, at the same time the Soviet Union was one of the main exporters of ODS supplying not only all republics of the former USSR but also a number of countries of Europe and Asia. Almost all industrial branches consumed chladones in Russian Federation [1,2,3]. The structure of consumption in 1990y was the following: 27% for production, repair and service of domestic and commercial industrial refrigerating equipment, 11% for production of goods in aerosol packages, 11% for production of foam materials, 14% for the use of chladones as solvents, 2% for fire extinguishing, 1 % for other purposes.

The Russian Federation, being the assignee of the USSR, ratified the Montreal Protocol and has accepted all the obligation on the Protocol to terminate production and consumption of ODS.

RSC "Applied Chemistry" together with a number of institutes of the country has fulfilled a large work volume to transfer the industry to the new class of chemical compounds instead of

prohibited ODS. As a result of the fulfilled investigations the following nomenclature of the chladones was proposed: hydrofluorocarbons 134a(CF₃CFH₂), 152a(CF₂HCH₃), 125(CF₃C 32(CH₂F₂) etc. The main difference of ozone-friendly substances from ODS was in the absence of their molecules of chlorine and bromine atoms which may participate in "chlorine" and "bromine" cycles of the ozone depletion. Beside the zero value of ODP (ozone depleting potential) and acceptable value of GWP (global warming potential) the main criteria in the choice of alternatives of ODS was the proximity of physical and chemical and operational properties to analogues characteristics of ODS to be replaced. The basic nomenclature of ozone-friendly compounds, accepted for development and implementation in commercial production in the EU Federation is given in Table 1.

Table 1. MAIN CHARACTERISTICS OF HYDROFLUOROCARBONS (OZONE-FRIENDLY CHLADONES)

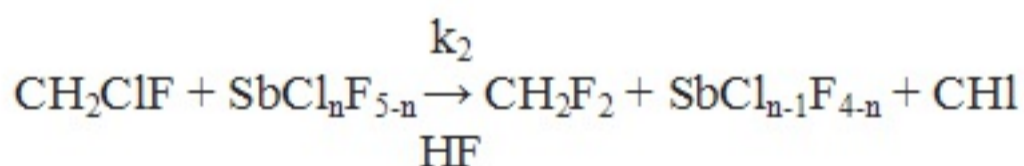
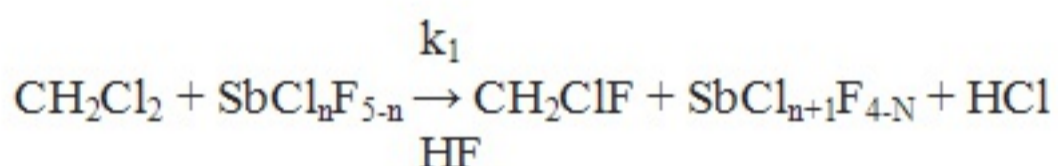
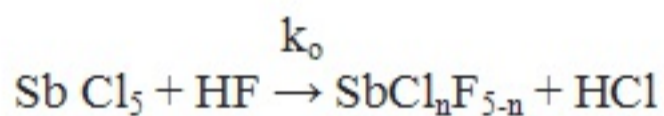
Chladone	Formula	BP, 0,1 MPa	MP	ODP	GWP	MPC mg/m ³
		°C				
23	CHF ₃	-82,2	-155,15	0	14800	3000
32	CH ₂ F ₂	-51,7	-136	0	880	3000
125	C ₂ F ₅ H	-48,5	-103	0	3800	1000
134	CHF ₂ CHF ₂	-22,5	-89,0	0	1200	-
134a	CH ₂ FCF ₃	-26,5	-101	0	1600	3000
143a	CF ₃ CH ₃	-47,6	-111,3	0	5400	3000
152a	CH ₃ CHF ₂	-24,55	-117,0	0	190	3000
227ea	CF ₃ CFHCF ₃	-18,3	-131,2	0	3800	-
236fa	CF ₃ CH ₂ CF ₃	-0,7	-93,6	0	9400	-
C336	C ₄ F ₆ H ₂ - cyclo	63	-	0	-	-
C438	C ₅ F ₈ H ₂ -cyclo	79	-	0	-	-
43-						

10mee	CF ₃ CHFCHFCF ₂ CF ₃	47	-80	0	1700	-
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The development of technologies for ozone-friendly fluorohydrocarbons in dependence on structure and taken into account the existing production capacities of CFC 11, 12, 113 and replaced was realized at the plants of Russian Federation (RF) by main two production methods: liquid phase fluorination with anhydrous hydrogen fluoride of chloroorganic compounds (HFC 32, 143a and etc.) and gas phase catalytic fluorination of chloroorganic compounds with anhydrous hydrogen fluoride (chlorofluorones 134a, 125 and etc.)

The main materials for manufacture of ozone friendly chlorofluorones (trichloroethylene, perchloroethylene, vinylidene chloride, vinyl chloride and chloromethanes) are produced at enterprises of RF: JSC "Caustic", Volgograd, JSC "Khimprom", Volgograd, JSC "Caustic", Sterlita JSC "Usolyekhimprom", Usolye Sibirskoe and etc. Special features of the liquid phase catalytic hydrofluorination are seen on the example of difluoromethane (chlorofluorone 32) synthesis [4] synthesis process proceeds according to scheme 1

Scheme 1



The kinetics of methylene chloride fluorination is described by the following equations [5]:

$$-r_{\text{CH}_2\text{Cl}_2} = 2.2 \cdot 10^5 / \{ \exp(-5.8 \cdot 10^7 / RT) \cdot C_{\text{CH}_2\text{Cl}_2} \cdot C_k \},$$

$$r_{\text{CH}_2\text{F}_2} = 8.3 \cdot 10^5 / \{ \exp(-6.2 \cdot 10^7 / RT) \cdot C_{\text{CH}_2\text{ClF}} \cdot C_k \},$$

where $C_{\text{CH}_2\text{Cl}_2}$, $C_{\text{CH}_2\text{ClF}}$, C_k are the concentrations of dichloromethane, chlorofluoromethane and catalyst accordingly.

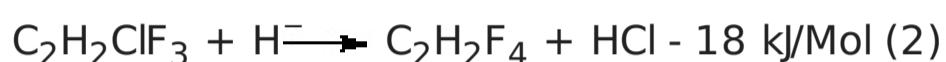
The kinetics data have been used as a basis for calculation of a reactor for synthesis of CFC-32 with an annual production capacity of 1000 tons and for development of a flow chart of the synthesis of CFC-32 which is typical for liquid-phase synthesis of ozone-friendly substances. The synthesis is carried out at a temperature of 95-105 °C at pressure of 1.5-2.0 MPa. The synthesis of CFC-32 from vinyl chloride and hydrogen fluoride proceeds according to the similar scheme at a temperature of 90°C and pressure of 0.6-0.8 MPa in the presence of the catalyst (tetrachloride [6], as well as the synthesis of CFC 245fa from pentachloropropane and hydrogen fluoride in the presence of SbCl₅ at a temperature of 100-120°C and pressure of 1.6-1.8 MPa.

But the liquid-phase hydrofluorination method has a number of the limitations:

- it is quite difficult to replace the chlorine atom for the fluorine atom in $-CH_2Cl$ and $=CHCl$ groups
-in hydrofluorination the catalyst $SbCl_nF_{5-n}$ may act as a chlorinating agent to form ozone depleting chloroalkanes.

Therefore in order to obtain hydrofluorocarbons with a substantial fluorine content in the molecule (CF₃CFH₂, CF₃CF₂H) the method of gas phase catalytic hydrofluorination is used. The peculiar features of the gas phase catalytic hydrofluorination are well seen from the example of synthesis of 1,1,1,2-tetrafluoroethane (CFC 134a) from trichloroethylene and hydrogen fluoride. The synthesis process runs in two stages (scheme 2).

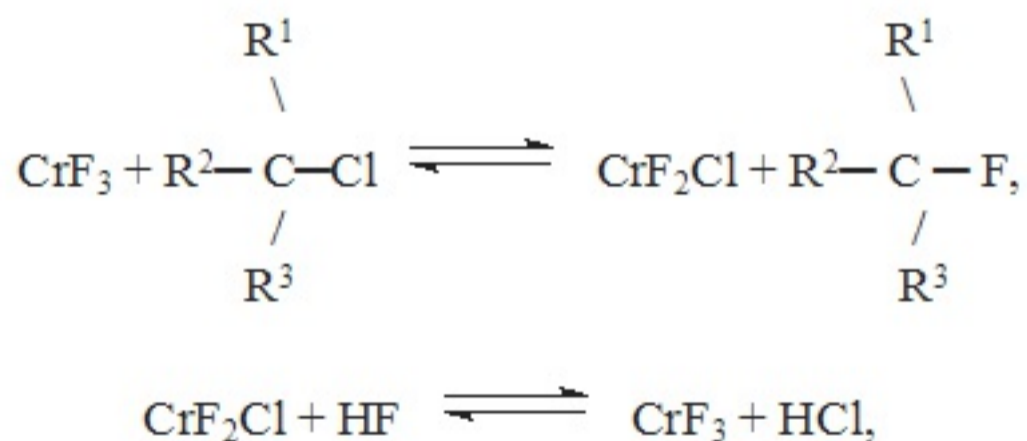
Scheme 2



As it follows from the experimental data and thermodynamical calculation of stage (1) the content of CFC 133a in organic part of the synthesis products may reach 90-98%.

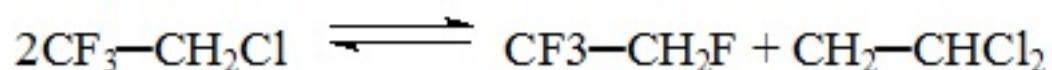
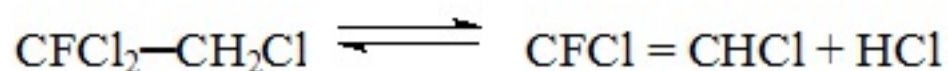
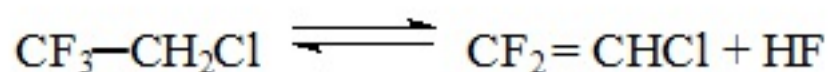
Stage (2) is reversible. In dependence on the conditions the content of CFC134a in organic part of the synthesis products may attain 10-40% (of organic part of the synthesis products). The chromium fluoride catalyst used in the process was made by impregnation of magnesium fluoride powder with a solution of chromium chloride with subsequent mixing, molybdenum drying and treatment with hydrogen fluoride to transfer CrCl₃ to fluoride CrF₃ [9,10]. Investigation of the mechanism of the catalyst action in this process has shown that the catalyst acts as a carrier of fluorine and chlorine atoms [11,12]. It may be considered that the process of hydrofluorination of fluoroethanes proceeds according to scheme 3.

Scheme 3



where chromium fluoride replaces chlorine by fluorine in fluoroethanes by changing its composition to CrF₂Cl and after that hydrogen fluoride replaces chlorine by fluorine in active part of the catalyst to form hydrogen chloride and CrF₃. Besides main hydrofluorination processes, reactions of dehydrofluorination, dehydrochlorination and disproportionation are carried out in the presence of this catalyst (scheme 5).

Scheme 4



The obtained unsaturated fluorine-containing compounds(especially $\text{CF}_2=\text{CHCl}$ forming azeotrope with 1,1,1,2-tetrafluoroethane) subsequently make difficult isolation of end product the reaction mixture. The mechanism of the reaction of trichloroethylene hydrofluorination has studied and laid as a basis for a kinetic model of the synthesis of 1,1,1,2-tetrafluoroethane with the use of route method for complex reactions [13].

A typical flow chart for the synthesis of ozone-friendly substances was developed by a meth gas-phase catalytic hydrofluorination. In the Russian Federation have been created and continue to be created industrial facilities for production of ozone-friendly substances on the basis of conducted investigations.

Table 2. Production of ozone-friendly CFCs at the plants in RF

Ozone-friendly and transition substances	Producer	Existing capacities	
		Consumption area	ton/year
HFC-134a	JSC Halogen	Refrigerants, aerosol propellants, solvents, foaming agents	Production under planning
HFC-23	Redkino Plant Pilot RSC AC	Refrigerants, extinguishers	200
HFC-32	JSC Halogen	Refrigerants	Production under planning
HFC-152a	JSC "Caustic"	Refrigerants, aerosol propellants	4000
HFC-143a	KCCW	Refrigerants	100
HFC-125	JSC Halogen	Refrigerants, extinguishers	1000
HFC-227a	RSC AC	Refrigerants, aerosol propellants, solvents,	30
	KCCW	extinguishers	100

FC-218	KCCW	Refrigerants, aerosol	120
	AECC	propellants, solvents, gases for	100
	JSC Halogen	extinguishers, electronics	40
FC-C318	KCCW	Refrigerants	100
	JSC Halogen		40
Transition chladones			
HCFC-141b,142b	JSC "Altaichimprom"	Solvents, foaming agents	3000
HCFC-142b	KCCW	Foaming agents	2000
HCFC-22	JSC "Khimprom"	Refrigerants, aerosol propellants, semiproducts for fluoroplasts	12000
	KCCW		20000
	JSC Halogen		12000
HCFC-21	JSC Halogen	Refrigerants, aerosol propellants	100

KCCW- Kirovo-Chepetsk Chemical Works, OJSC,
 AECC - Angarsk Electrolysis Chemical Complex,
 RSC AC - FSUE RSC "Applied Chemistry" Saint Petersburg

A new class of ozone-friendly substances, fluorine-containing ethers, given in Table 3, is of int for a detailed investigation.

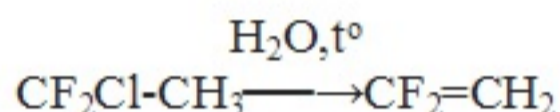
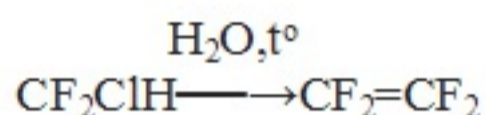
Table 3. PROMISING OZONE-FRIENDLY SUBSTITUTES ODP=0; GWP<300; (F/H+F)>65%

Substances	Formula	MM	BP	MP	ODP	GWP	Toxicity: ppm (vol./vol.)	MPC mg/m ³
			°C					
HFE- 7000	C ₃ F ₇ OCH ₃	200	34	-122,5	0	400	-	-
HFE- 7100	C ₄ F ₉ OCH ₃	250	61	-138	0	320	750	-

HFE-7500	C ₇ F ₁₆ OC ₂ H ₅	433	128	-100	0	210	-	-
R131l	CF ₂ I	196	-2,0	-128	0	-	-	-

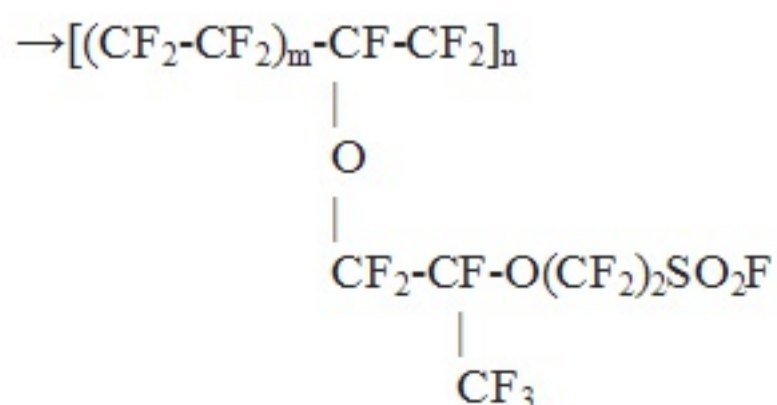
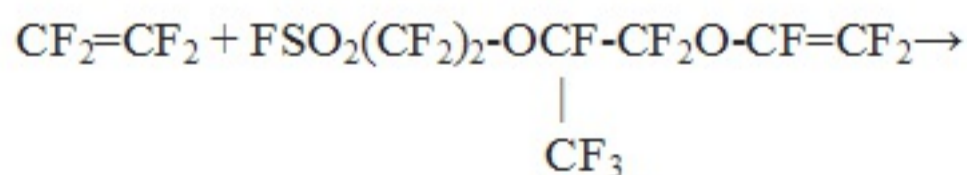
2. Fluorine-containing olefines

In recent years FSUE RSC "Applied Chemistry" has carried out widespread investigation and improvement of commercial technologies for production of fluoroolefines such as tetrafluoroethylene, vinylidene fluoride and etc. The technology for production of commercial fluoroolefines was developed by pyrolysis of starting fluorochlorohydrocarbons in the presence of water vapor:



The conversion of the starting compounds and selectivity of the fluoroolefines in these processes considerably exceed the appropriate indices for "dry" pyrolysis process. Thus, in the pyrolysis of difluorochloromethane at 750-850°C the tetrafluoroethylene selectivity made 90-95% and difluorochloromethane conversion of 80%, while in the pyrolysis of 1,1-difluoro-1-chloroethane at 800-840°C the process selectivity towards 1,1-difluoroethylene was 98-99% at the almost complete conversion of starting 1,1-difluoro-1-chloroethane.

The new technology for tetrafluoroethylene production was implemented at Kirovo-Chepetsk chemical plant. The technology for fluoromonomers production for ion exchange membranes has been developed and improved. The perfluorinated membranes of Nafion type (DuPont, USA) are the most effective membranes at present for fuel cells. Investigations on creation of proton-conducting membranes for fuel cells and other applications derived from co-polymers of tetrafluoroethylene and perfluoro(-3,6-dioxo-4-methyl-7-octene)-sulfonyl fluoride are also under development by FSUE "Applied chemistry". The overall scheme of the synthesis of this copolymer is given below:



On the basis of this copolymer are obtained by extrusion films, that are used for creating the exchange membranes. RSC "Applied Chemistry" conducts investigations on creation of effective fluorine-containing membranes due to the use in the copolymers of new fluoromonomers such as perfluoroalkylvinyl ethers and etc..

3. Fluorine-containing inert dielectric liquids, oils, lubricants

3.1. The experts of RSC Applied Chemistry have developed a series of fluorine-containing dielectric liquids obtained by a standard scheme by the method of electrochemical fluorination [

Fluorine-containing liquids derived from perfluorinated tertiary amines have a wide range of application due to their unique properties:

- a low solidification point (-100°C and lower),
- a low dielectric constant (~1.8 and lower),
- a wide range of boiling temperature (45-250°C),
- electric strength (40-50 kV/mm) etc.

Some properties of the perfluorinated dielectric liquids are given in Table 4.

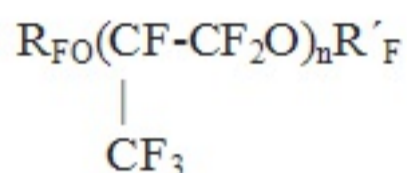
Table 4. Perfluorinated dielectric heat-transfer agents

Technical name	BP, °C	MP, °C	D(20°C), kg/m ³	Specific volumetric resistance, hm-m (20°C)	Electric strength, Hz, kV/m
PFDT-3-perfluoropentane	30	-125	1660	-	-
PFDT-50 perfluorodiethylmethylamine (MD-46)	46	-163	1670	1,5-10 ¹³	30
PFDT-70 perfluorotriethylamine (MD-3f)	70	-145	1750	5-10 ¹³	30
PFDT-100 perfluorodibutyl ether (DEF)	100	-70	1730	4-10 ¹³	46
PFDT-130 perfluorotripropyl amine	130	-70	1730	3-10 ¹⁴	44
Fozhalin (a mixture of perfluoroamines)	180	-50	1890	4, -10 ¹⁴	44

PFDT-180 perfluorotriamylamine	195- 205	~-50	~1900	-	40-50
PFDT-249 perfluorotrihexylamine	235- 245	~-50	~1950	-	-

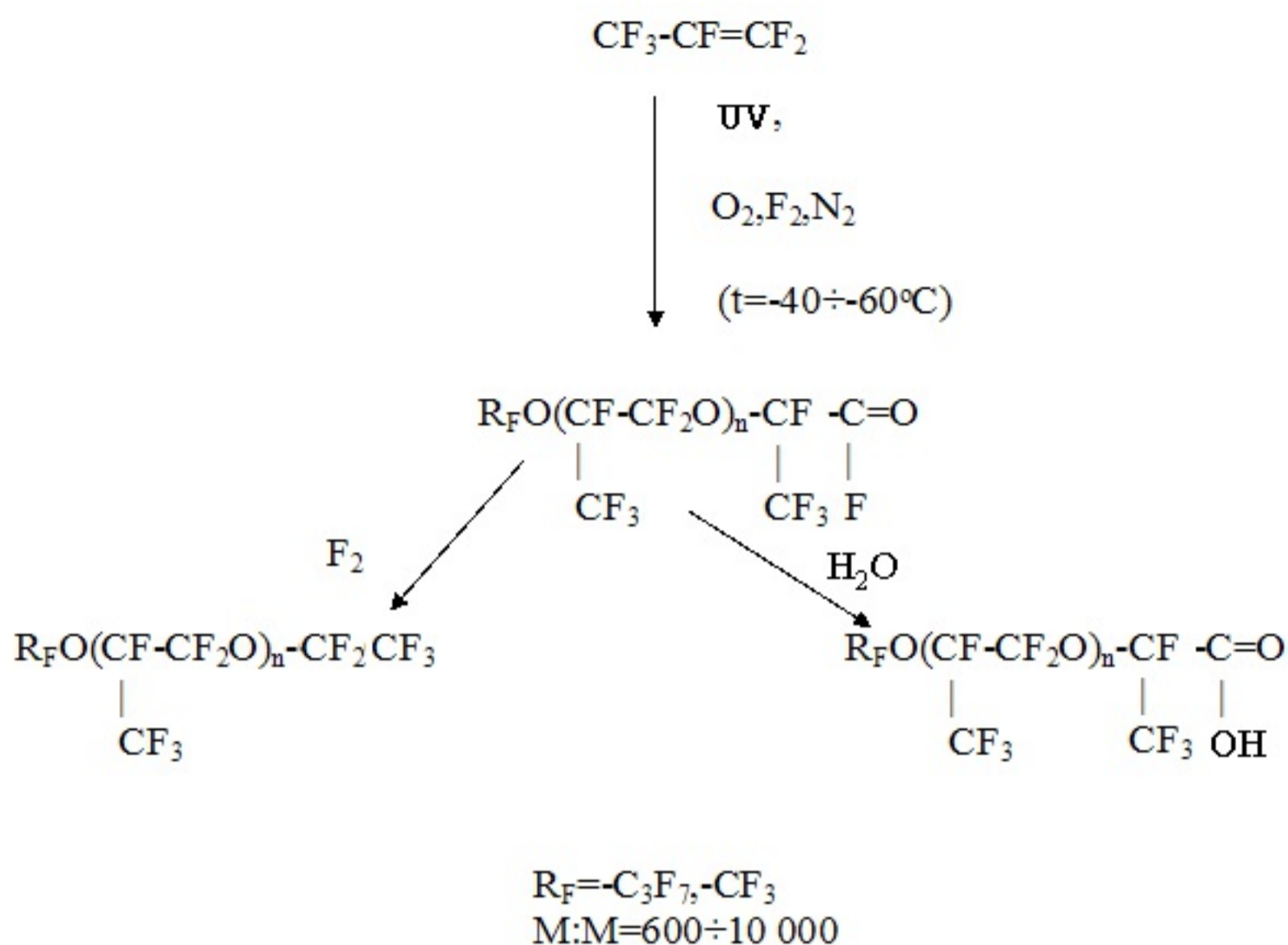
Together with the fluorine-containing compounds, given in Table 4, the method of electrochemical fluorination is widely used in the developments of RSC "Applied Chemistry" for the synthesis of perfluoromonocarboxylic acids C2-C9 on the basis of various raw materials as well as perfluorosulpho acids or their derivatives, for example perfluoroethylsulpho fluoride, perfluoro(ethylcyclohexyl sulphofluoride) and etc.

3.2. In RSC "Applied Chemistry" has been developed and implemented the technology of manufacture of oligomers of hexafluoropropylene oxide, unique in their properties, perfluoropolyethers of general formula



The technology of manufacture of these compounds consists in the oxidation of hexafluoropropylene (CF₃-CF=CF₂) with oxygen at low temperatures (-30°C and below) initiated by UV, fluorine and etc. [3,15].

Scheme Synthesis of perfluoropolypropylene oxides



The stabilized oligomers obtained according to this method possess a wide range of the boiling temperature (from 50°C to 320°C) at 1 mm Hg in combination with the low freezing point (- and below). Simultaneously the perfluoropolyethers possess the combination of unique properties: they are highly thermostable (up to +450°C), chemically stable in highly aggressive media, nontoxic, they possess high dielectric characteristics, good lubricating qualities, radiation stable and their viscosimetric properties are little changed in the wide temperature range and other combination of the properties listed above makes it possible to use them in different contemporary technology. Some properties of perfluoropolyethers are given in Table 5.

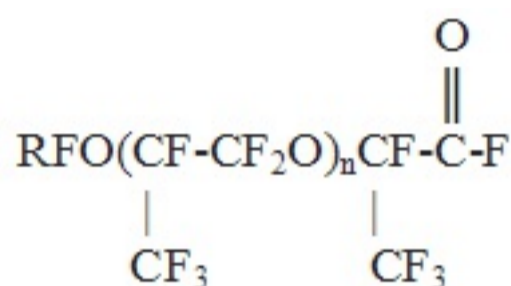
Table 5. Some properties of perfluoropolyethers

Boiling interval of oligomers perfluoropolyethers °C/1mm Hg	Vapor pressure	Viscosity, cst	MM	Solidification point
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

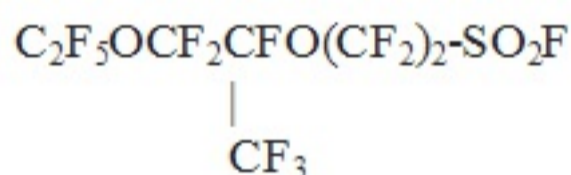
>320	10^{-14} >	1000- 1800	~10 000	~-30
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4. Surfactants

It is known that the fluorine-containing surfactants occupy key place among the k surfactants. Thus, the value of surface tension of derivatives of perfluoroena perfluoropelargonic acids are on the level of 15-16 dyn/cm. The low surface tension and chemical and thermal resistance of fluorine-containing surfactants of different structure deterr their wide application in the contemporary technology. In the RSC "Applied Chemistry" on the of perfluoroenanthic ($C_6F_{13}COOH$), perfluoropelargonic ($C_8F_{17}COOH$) acids and also on the ba perfluoropropylene oxides of the formula

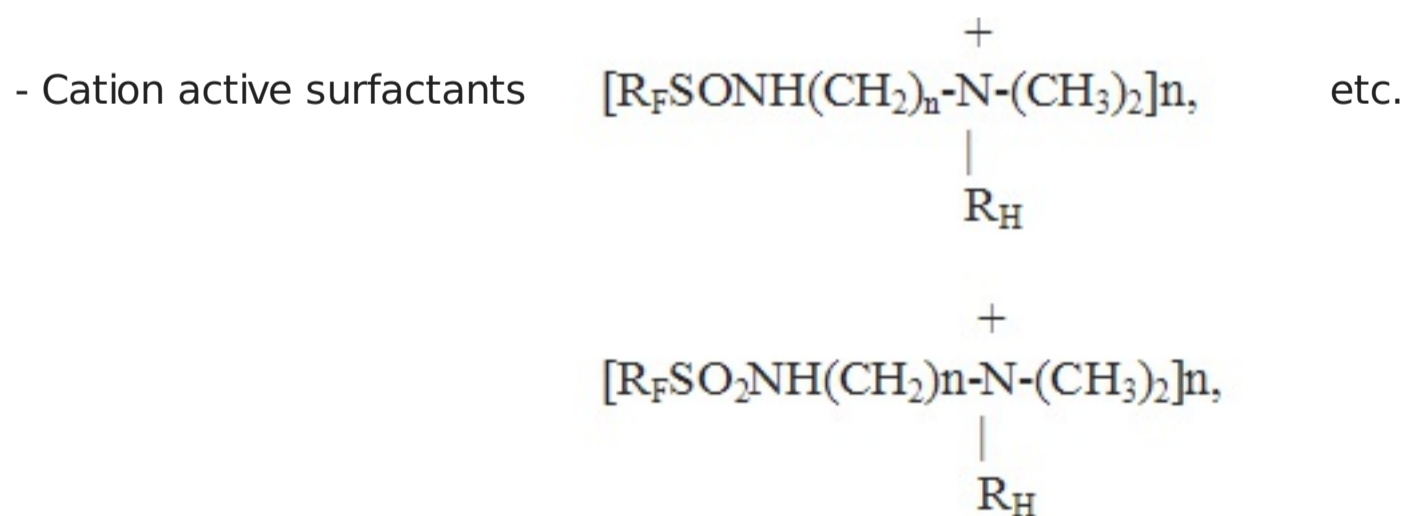


and sulpho-derivatives of the composition



the series of fluorine-containing surfactants of different structure has been developed:

- Anion active surfactants (R_FCOOMe , R_FSO_3Me etc.),

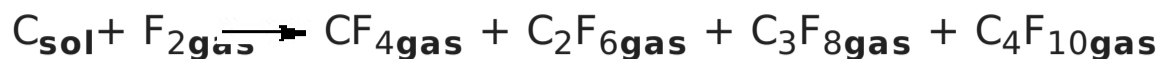


- Non-ionogenic surfactants [$R_FCONH(CH_2CH_2O)_nH$]

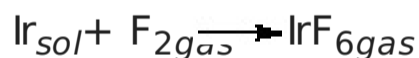
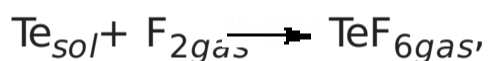
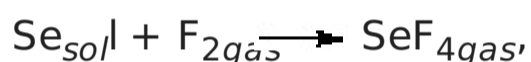
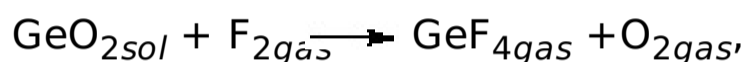
Fluorine-containing surfactants have found wide application as bases for foaming agents extinguishers for the extinguishing of burning petroleum products and polar liquids, additives fo diesel fuel for the purpose to reduce friction and increase the performances of machines mechanisms, in microelectronics in the manufacture of semiconductor materials for cutting grinding silicon plates, in the cleaning of articles, in galvanotechnics, etc.

5. Synthesis of fluorocompounds with the use of elemental fluorine

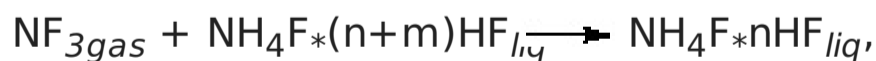
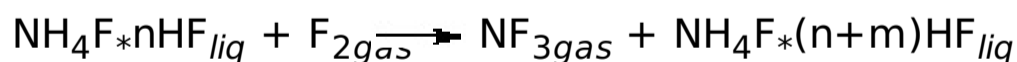
Elemental fluorine has found wide application as the fluorinating agent in the synthesis of different fluorocompounds [16, 17, 18]. The industrial method of the synthesis of lower perfluoroalkanes has been developed:



The interaction of fluorine and graphite runs at a temperature of 550-650°C in two stages. In the first stage a layer of solid carbon polyfluoride (CF_x)_n is formed on the surface of graphite particles at a temperature of 550-600°C in the regime close to the adiabatic. In the second stage in the absence of fluorine is conducted the thermal decomposition of (CF_x)_n at a temperature of 650°C to form perfluoroalkanes. In order to provide thermal stabilization of the reaction zone reactors with dynamic (intermixed, moving) beds are used such as fluidized bed, ascending dust flow and free falling graphite bed. As a result the mixture of gaseous reaction products from the interaction of graphite and fluorine is obtained with the following composition: 40-45 wt% CF₄, 25 wt.% C₂F₆, 15-20% C₃F₈, 10wt% C₄F₁₀. A number of low-tonnage technologies have been realized at the Experimental plant of RSC "Applied Chemistry" on the fluorination of solid elemental fluorine to obtain corresponding fluorides such as hexafluorides of selenium, tellurium, iridium, tetrafluorides of selenium and germanium:



The production processes of these compounds were performed in multiple-heart reactors with a productive capacity up to hundreds of kilograms per year. The reactors were equipped with scanning thermocouples that made it possible to observe the temperature distribution in the reactor, the heat removal was accomplished by free convection. The technology of the synthesis of nitrogen trifluoride by fluorination of NH₄F·nHF melt with fluorine gas has been developed:



where n << m

The fluorination is carried out in the gradient-free reactor with a high-speed mixer in a circulation loop, that makes it possible to remove heat effectively on the basis of forced convection and to support the isothermal conditions of the carrying process as well as to ensure maximum contact of the surface of gaseous fluorine with the melt. With this method of conducting the process the productivity of the fluorination reactor reached 30 g NF₃ · l⁻¹ · h⁻¹ at the fluorine conversion up to 95%. The concentration of nitrogen trifluoride in the synthesis gas attained 90%, nitrogen was the main admixture. The yield of difluoroamine, tetrafluorohydrazine and difluorodiazines did not exceed 2-3%.

The technology of producing a number of inorganic fluorine-containing compounds which are used as oxidizers etc. has been developed with the use of elemental fluorine. The list of these compounds is represented in Table 6.

Table 6. Inorganic fluorine-containing oxidizers

Formula	Molecular weight	T _{decomp} , °C	Density, g/cm ³
ClF ₂ OBF ₄	176,6	473	2,05
(ClF ₂ O) ₂ NiF ₆	351,7	373	2,63
KClF ₄	150,6		2,5
NF ₄ BF ₄	176,8	513	2,27
NO ₂ BrF ₄	202		2,8
(XeF ₅) ₂ MnF ₆	621,5	493	3,65
XeF ₅ BF ₄	313		

6. Fluorine-containing compounds for medicine

In spite of high aggressiveness of initial fluorinating reagents, many fluorinated and perfluorinated compounds due to their unique physical and chemical properties are in particular of great interest for medicine and biology and are widely used all over the world as diagnostic and therapeutic preparations. Such compounds as perfluorodecalin, perfluorotributylamine, perfluorooctylbromide possess a unique ability to dissolve oxygen up to 45-50% by volume and taking into account chemical inertness they are used as a gas-transport agents for various purposes: for creating artificial blood substitute, in ophthalmology for treatment of the retinal detachment, in roentgenography etc.

Some fluorocarbons used in this direction in medicine are represented in Table 7.

Table 7. Fluorocarbons for medicine

	Compound	Chemical formula	MM	BP, °C	D ₄ ²⁰	v, cst
1	Perfluorodecalin	C ₁₀ F ₁₈	462	142	1,938	
2	Perfluoropolyether MF-130	$\text{CF}_3\text{O}-(\text{CF}_2\text{CF}_2\text{O})_n\text{C}_2\text{F}_5$ $\quad \quad \quad $ $\quad \quad \quad \text{CF}_3$	3200	>130 1 mm Hg	1,88	150- 200

3	Perfluorotributyl amine	$N(C_4F_9)_3$	671	179	1,886	3,51
4	Octafluoropropane (R-218)	$CF_3-CF_2-CF_3$	188	-36,8		
5	Perfluoropolyether P-216	$C_2F_5-[(CF-CF_2O)_2-]_2$ CF_3	902	216	1,836	6,15
6	Perfluorooctyl bromide	$C_8F_{17}Br$	499	142	1,93	
7	Perfluorooctane	C_8F_{18}	438	105		

Implementation of these compounds into medical practice is conducted together with medical institutions such as Military Medical Academy (Saint-Petersburg) and others.

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