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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Industrial Fluorine Compounds

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Abstract—-Technological research in the area of the industrial fluorine-containing compounds: ozone safe fluorocarbons (freons), fluoro-olefins, compounds with the functional groups, thermoresistant liquids, oils, lubricants, fluorine surfactants and other.

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OZONE SAFE COMPOUNDS

Chlorofluorocarbons and bromofluorocarbons (freons and halons) as the compounds, which possess a number of unique properties: chemical inertness, nontoxicity, explosive-fire safety, were widely used in the technology as the aerosol propellants, the refrigerants, the frothing agents for plastics, solvents, highly effective fire extinguishers and others. However, discovered in 1980th a destructive action of some chlorine- and bromine-containing compounds on the ozone layer attracted attention to the large group of industrial freons, which contain in their composition chlorine and bromine, as to the potentially dangerous compounds. The contemporary evaluations of the relative role of the anthropogenic and natural factors of the destruction of ozone layer showed that above Western Europe the relative contribution of anthropogenic factors is ~75%, above the East coast of the USA, 60%, above Japan, Baikal and the Far East, 50%. The Viennese convention about the protection of ozone layer, accepted in 1985 was the first international document, which foresees measures for the protection of ozone layer. The states signed convention, accepted obligations regarding collaboration in the area of control and averting activity potentially threatening ozone layer of stratosphere. In September 1987 was accepted Montreal Protocol (MP) on the substances, which destroy ozone layer. In the application to MP was published a list of ozone destroying substances (ODS), that be subject to regulation by all country-parties of MP. To the list were included the chlorofluorocarbons, bromofluorocarbons (halons) and some chlorohydrocarbons. The Montreal Protocol obligated the parties regarding the limitation of consumption, production and import/export of ODS.

The Soviet Union was one of the most important in the world producers of ODS: in 1987 it held ~15% of world volume of ODS productions (~200 thousand ton per year), simultaneously the Soviet Union was one of the largest exporter of ODS, supplying not only all republics of the former USSR, but also many countries of Europe and Asia. Producers of ODS were six large chemical plants in the Russian Federation. The users of freon in the Russian Federation were practically all branches of industry [1−3]. Structure of the application of freon in 1990 appeared as follows: production, repair and service of everyday and commercial industrial refrigeratoring equipment were 27%; the production of aerosols in containers, 45%; the production of foam producing agents, 11%; the use of freon as the solvents, 14%; the production of the means of fire extinguishing, 2%; other, 1%.

The Russian Federation, being the lawful successor of the USSR, which ratified in 1988 the Montreal Protocol on the substances, which destroy ozone layer, completely accepted the obligations on this protocol to cancel production and consumption of ODS.

Russian Scientific Center "Applied Chemistry" together with the number of the institutes in the country is executed large volume of the works on the transfer of industry to produce the new class of the chemical compounds instead of forbidden ODS. As a result of the conducted investigations is proposed the nomenclature of new freons: hydrofluorihydrocarbons 134a (CF_3CFH_2), 152a (CF_2HCH_3), 125 (CF_3CF_2H), 32 (CH_2F_2) and other.

A basic difference in the ozone safe compounds from ODS is absence in their molecules of the atoms of chlorine and bromine, which can participate in “chlorine” and “bromine” cycles of the ozone decomposition. Besides the zero value of the ozone destroying (ODS) and the permissible value of the potential (ODP) and the value of the potential of the global warming of climate (GWP), the main guide for selection of substitutes ODS is the proximity of physicochemical and performance properties to the analogous characteristics of replaced ODS. The basic nomenclature of ozone safe compounds, accepted for the development and the introduction in the industrial production in the Russian Federation, is represented in Table 1.

At the development of the technologies of ozone safe fluorocarbons, depending on their structure and taking into account the existing production capacities of replaced freons 11, 12, 113 at the plants of the country are used in essence two methods of their manufacturing: liquid-phase fluorination by waterless hydrogen fluoride of organochlorine compounds (Freons 152a, 32, 143a and other) and the gas-phase catalytic fluorination of chlororganic compounds by waterless hydrogen fluoride (Freons of 134a, 125 and other).

The basic raw materials for the production of ozone safe Freons including trichloroethylene, perchlorethylene, vinylidene chloride, vinyl chloride and chloromethanes are produced in the enterprises of Russia: Joint Stock Company “Caustic” (Volgograd), Joint Stock Company “Khimprom” (Volgograd), Joint Stock Company “Caustic” (Sterlitamak), Joint Stock Company “Usolekhimprom” (Usole Siberian) and other.

The special features of liquid-phase catalytic hydrofluorination are well seen on the example of the synthesis of difluoromethane (Freon 32) [4]. The process of synthesis proceeds according to Scheme 1.

Scheme 1.

$$SbCl_5 + HF \xrightarrow{k_0} SbCl_nF_{5-n} + HCl$$

$$CH_2Cl_2 + SbCl_nF_{5-n} \xrightarrow[HF]{k_1} CH_2ClF + SbCl_{n+1}F_{4-n} + HCl$$

$$CH_2ClF + SbCl_nF_{5-n} \xrightarrow[HF]{k_2} CH_2F_2 + SbCl_{n+1}F_{4-n} + HCl$$

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

$$-{}^{r}CH_2Cl_2 = 2.2 \times 10^5/\{\exp(-5.8 \times 10^7/RT)C_{CH_2Cl_2}C_k\},$$

$${}^{r}CH_2F_2 = 8.3 \times 10^5/\{\exp(-6.2 \times 10/RT)C_{CH_2ClF}C_k\},$$

Table 1. Principal characteristics of hydrofluorocarbon (ozone safe Freons)

Freon	Formula	bp, °C at 0.1 MPa	fp, °C	ODP	GWP	Maximum concentration limit, mg m^{-3}
23	CHF_3	−82.2	−155.15	0	14800	3000
32	CH_2F_2	−51.7	−136	0	880	3000
125	C_2F_5H	−48.5	−103	0	3800	1000
134	CHF_2CHF_2	−22.5	−89.0	0	1200	–
134a	CH_2FCF_3	−26.5	−101	0	1600	3000
143a	CF_3CH_3	−47.6	−111.3	0	5400	3000
152a	CH_3CHF_2	−24.55	−117.0	0	190	3000
227ea	CF_3CFHCF_3	−18.3	−131.2	0	3800	–
236fa	$CF_3CH_2CF_3$	−0.7	−93.6	0	9400	–
C336	$C_4F_6H_2$-cyclo	63	–	0	–	–
C438	C5F8H2-cyclo	79	–	0	–	–
43-10mee	$CF_3CHFCHFCF_2CF_3$	47	−80	0	1700	–

where $C_{CH_2Cl_2}$, C_{CH_2ClF}, C_k are the concentrations of dichloromethane, chlorofluoromethane and catalyst, respectively.

On the basis of the kinetic data is perfomed calculation of the reactor for the synthesis of Freon 32 1000 ton per year, and the flow chart of the synthesis of Freon 32, which is standard for the liquid-phase synthesis of ozone safe Freons, is developed. Synthesis is carried out at a temperature of 95–105°C and pressure 1.5–2.0 MPa. According to analogous scheme is carried out the synthesis of Freon 152a from vinyl chloride and hydrogen fluoride at the temperature of 90°C and pressure 0.6–0.8 MPa in the presence of catalyst tin tetrachloride [6], and also the synthesis of Freon 245fa from pentachloropropane and hydrogen fluoride in the presence of $SbCl_5$ at a temperature of 100–120°C and pressure 1.6–1.8 MPa [7].

However, the liquid-phase method of hydrofluorination has certain limitations:

– the replacement of chlorine atom by the atom of fluorine in the groups, CH_2C1 and $=CHCl$ proceeds difficultly,

– at the hydrofluorination the catalyst $SbCl_nF_{5-n}$ can behave as a chlorinating agent with the formation of ozone decomposing chlorofluoroalkanes.

Therefore for obtaining the hydrofluohydrocarbons with the high content of fluorine in the molecule (CF_3CFH_2, CF_3CF_2H) is used the method of gas-phase catalytic hydrofluorination.

Features of gas-phase catalytic hydrofluorination are well seen from the example of the synthesis of 1,1,1,2-tetrafluoroethane (Freon of 134a) from trichloroethylene and hydrogen fluoride. The process of synthesis proceeds into two stages (Scheme 2).

Scheme 2.

$$C_2HCl_3 + 3HF \rightarrow C_2H_2ClF_3 + 2HCl + 93\ \text{kJ mol}^{-1} \quad (1)$$

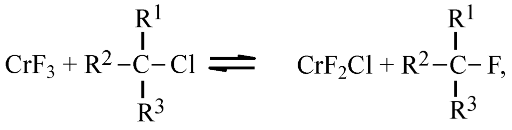
$$C_2H_2ClF_3 + HF \rightarrow C_2H_2F_4 + HCl^{-} - 18\ \text{kJ mol}^{-1} \quad (2)$$

As follows from the experimental data and the thermodynamic calculation of stage (1), the content of Freon of 133a in the organic part of the products of synthesis can reach 90–98%.

The stage (2) is reversible. Depending on the conditions, the content of Freon of 134a in the organic part of the products of synthesis can be 10–40 vol % (of the organic part of the products of synthesis). For conducting the process is used a chromomagnesium fluoride catalyst [8], prepared by impregnation of the powder of magnesium fluoride with the solution of chromium chloride followed by stirring, molding, drying and working up by hydrogen fluoride for the transfer of $CrCl_3$ into the fluoride CrF_3 [9, 10].

A study of the mechanism of the action of catalyst in this process showed that the catalyst bears a function of the carrier of fluorine and chlorine atoms [11, 12]. The process of the hydrofluorination of fluorinechloroethanes can be considered proceeding according to Scheme 3.

Scheme 3.



$$CrF_3 + R^2-\overset{R^1}{\underset{R^3}{C}}-Cl \rightleftharpoons CrF_2Cl + R^2-\overset{R^1}{\underset{R^3}{C}}-F,$$

$$CrF_2Cl + HF \rightleftharpoons CrF_3 + HCl$$

where chromium fluoride replaces chlorine by fluorine in the fluorinechloroethanes, changing its own composition to CrF_2Cl, and then hydrogen fluoride replaces chlorine by fluorine in the active part of the catalyst with the formation of hydrogen chloride and CrF_3.

Besides the basic processes of hydrofluorination, in the presence of this catalyst occur also the reactions of dehydrofluorination, dehydrochlorination and disproportionation (Scheme 4).

Scheme 4.

$$CF_3-CH_2Cl \leftrightarrows CF_2=CHCl + HF$$

$$CFCl_2-CH_2Cl \leftrightarrows CFCl=CHCl + HCl$$

$$2CF_3-CH_2Cl \leftrightarrows CF_3-CH_2F + CH_2-CHCl_2$$

The formed unsaturated fluorine-containing compounds (in particular, $CF_2=CHCl$ that forms azeotrope with 1,1,1,2-tetrafluoroethane) complicate further isolation of the targeted compound from the reaction mixture.

The mechanism of the reaction of hydrofluorination of tetrachloroethylene has been studied , and on this basis using a method of pathways of complicated reaction was developed kinetic model of the process of synthesis of 1,1,1,2-tetrafluoroethane.

The standard flow chart of the synthesis of ozone safe freons by the method of gas-phase catalytic hydrofluorination is developed.

On the basis of the investigations conducted in the Russian Federation are created and continue to be created the industrial productions of ozone safe Freons (Table 2).

It is interesting for more detailed study a new class of ozone safe compounds, the fluorine-containing ethers presented in Table 3.

FLUORINE-CONTAINING OLEFINS

(1) In recent years in the Center “Applied Chemistry” have been carried out wide investigations on the perfection of the industrial technologies of fluoroolefins: tetrafluoroethylene, vinylidene fluoride and other. The technology of manufacturing of industrial fluoroolefins by the pyrolysis of initial fluorochlorohydrocarbons in the presence of water vapor is developed:

$$CF_2ClH \xrightarrow{H_2O,\, t} CF_2{=}CF_2$$

$$CF_2ClCH_3 \xrightarrow{H_2O,\, t} CF_2{=}CH_2$$

In these processes the conversion of initial compounds and the selectivity of fluoroolefins considerably exceed the appropriate indices of the “dry” pyrolysis. Thus, at the pyrolysis of difluorochloromethane at 750–850°C the selectivity on tetrafluorine ethylene is 90–95% at the conversion of difluorochloromethane ~80%, and at the

Table 2. Production of ozone safe Freons at the plants of Russian Federation

Ozone safe and transition substances	Producer	Productive capacity	
		Consumption area	t/year
GFU-134a	Galogen	Refrigerating agents, aerosol propellents, solvents, frothers	Designing stage
GFU-23	Center “Applied Chemistry”	Refrigerating agents, fire extinguisher	200
GFU -32	Galogen	Refrigerating agents	Designing stage
GFU -152a	Kaustik	Refrigerating agents, aerosol propellents	4000
GFU -143A	Kirovo-Chepetsk chemical plant	Refrigerating agents	100
GFU-125	Galogen	Refrigerating agents, fire extinguisher	1000
GFU-227a	Center “Applied Chemistry”, Kirovo-Chepetsk chemical plant	Refrigerating agents, aerosol propellents, solvents, fire extinguisher	30 100
FU-218	Kirovo-Chepetsk chemical plant, AEKhk, Galogen	Refrigerating agents, aerosol propellents, fire extinguisher, gases for electronics	120 100 40
FU C318	Kirovo-Chepetsk chemical plant, Galogen	Refrigeraring agents	100 40
Transition freons			
GKhFU -141b,142b	AltaiKhimProm	Solvents, frothers	3000
GKhFU-142b	Kirovo-Chepetsk chemical plant	Frothers	2000
GKhFU-22	VOKKO, Kirovo-Chepetsk chemical plant, Galogen	Refrigerating agents, aerosol propellents, semiproducts for fluoroplastics production	12000 20000 12000
GKhFU-21	Galogen	Refrigerating agents, aerosol propellents	100

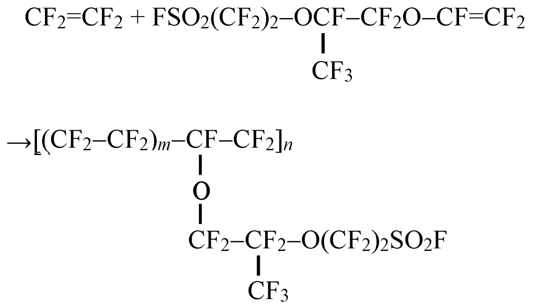
Table 3. Promissing ozone safe alternative compounds: ODP = 0, GWP < 300, (F/H + F) > 65%

Freon	Formula	Molecular weight	bp, °C	Solidification point, °C	ODP	GWP	Toxicity: (vol/vol)	Maximum concentration limit, mg m^{-3}
HFE-7000	$C_3F_7OCH_3$	200	34	–122,5	0	400	–	–
HFE-7100	$C_4F_9OCH_3$	250	61	–138	0	320	750	–
HFE-7500	$C_7F_{16}OC_2H_5$	433	128	–100	0	210	–	–
R13I1	CF_2I	196	–2,0	–128	0	–	–	–

pyrolysis of 1,1-difluoro-1- chloroethane at 800–840°C the selectivity of process on the 1,1- difluorine ethylene equals to 98–99% at the practically complete conversion of initial 1,1-difluoro-1-chloroethane. The new technology of obtaining tetrafluoroethylene is launched in the Kirovo-Chepetsk chemical plant.

(2) The technology of obtaining fluoromonomers for the ion-exchange membranes has been developed and is improved. At present the most effective membranes for the fuel cells are the perfluorinated membranes of the type of Nation (du Pont, USA).

In the Center “Applied Chemistry”also are developed the studies on the creation of promising membranes for the fuel cells and analogous designation on the basis of the copolymers of tetrafluoroethylene and perfluoro(3,6-dioxa-4-methyl-7-octene) sulfonylfluoride. The overall scheme of the synthesis of this copolymer is represented below:



$$CF_2{=}CF_2 + FSO_2(CF_2)_2{-}O\underset{\substack{|\\CF_3}}{CF}{-}CF_2O{-}CF{=}CF_2$$

$$\rightarrow[(CF_2{-}CF_2)_m{-}\underset{\substack{|\\O\\|\\CF_2-\underset{\substack{|\\CF_3}}{CF_2}-O(CF_2)_2SO_2F}}{CF}{-}CF_2]_n$$

The films, which are used for creating the ion-exchange membranes, are obtained by extrusion on the basis of this copolymer.

In Russian Scientific Center “Applied Chemistry” are conducted studies on the development of works on the creation of the highly effective fluorine-containing membranes by means of the use of the copolymers from new fluorinemonomers such as perfluoroalkylvinyl ethers and similar compounds.

FLUORINE-CONTAINING INERT DIELECTRIC LIQUIDS, OILS AND LUBRICANT

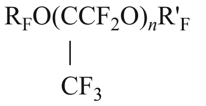
(1) In the Russian Scientific Center “Applied Chemistry” is developed a series of the fluorine-containing liquid dielectrics, obtained according to standard scheme by the method of electrochemical fluorination.

The fluorine-containing liquids based on the perfluorinated tertiary amines have the wide spectrum of application due to their unique properties: low solidification point (–100°C and below), low dielectric constant (~1.8 and below), a wide interval of the boiling point (45–250°C), high dielectric premeability (40–50 kV/mm) and others.

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

Together with the application for the synthesis of fluorine-containing compounds listed in Table 4, the method of electrochemical fluorination is widely used in the developments Russian Scientific Center “Applied Chemistry” for the synthesis of perfluorinemonocarboxylic acids C_2–C_9 on the basis of different forms of source material, and also petrorsulfo acids or of their derivatives, for example, of perfluoroethylsulfofluoride, perfluoro(ethylcyclohexylsulfofluoride) and other.

(2) In the Center “Applied Chemistry” is developed and implemented a technology of manufacturing a perfluoropolyether, unique by their properties oligomers of hexafluoropropylene oxide, of general formula



$$R_FO(\underset{\substack{|\\CF_3}}{C}CF_2O)_nR'_F$$

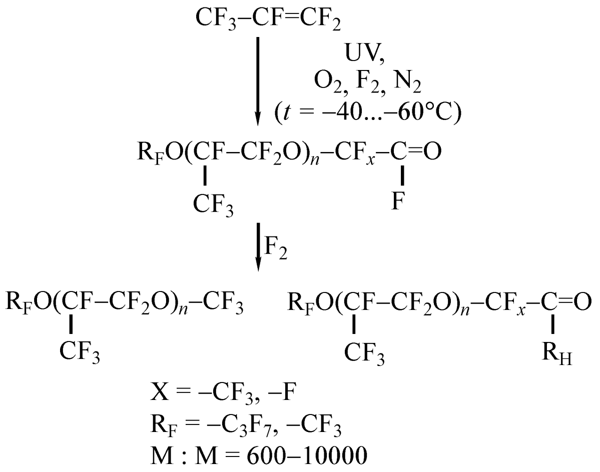
The technology for manufacturing these compopunds consists in oxidation of hexafluoropropylene (CF_3–$CF{=}CF_2$) by oxygen at low temperature (–30° and

Table 4. Perfluorinated dielectric heat-transfer agents.

Name	bp, °C	fp, °C	*D* (20°C), kg/m^3	Specific bulk resistance, Om m (20°C)	Electrical hardness 50 Hz, kV/mm
PFDT-3-perfluoropentane	30	–125	1660	–	–
PFDT-50 perfluorodiethylmethyl amine (MD-46)	46	–163	1670	1.5×10^{13}	30
PFDT-70 perfluoroethyl amine (MD-3f)	70	–145	1750	5×10^{13}	30
PFDT-100 perfluorodibutyl ether, (DEF)	100	–70	1730	4×10^{13}	46
PFDT-130 perdluorotripropyl amine	130	–70	1730	3×10^{14}	44
Fozhalin (mixture of the perfluoroamines)	180	–50	1890	4×10^{14}	44
PFDT-180 perfluorotriamylamine	195–205	~–50	~1900	–	40–50
PFDT-249 perfluorotrihexylamine70	235–245	~–50	~1950	–	–

below) at initiation with UV, by fluorine and by other methods [3, 15].

Scheme 5. Syntgesis of perfluoropopypropylenixides



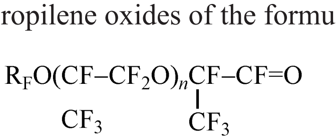
Stabilized oligomers produced by this method, possess have boiling points in a wide range (from 50°C to 320°C at 1 mm Hg), in combination with the low freezing point (-60°C and below). Simultaneously perfluoropolyether possess the combination of unique properties: they are highly thermostable (to +450°C), chemically inert in the highly aggressive media, not combustible, nontoxic, possess the high dielectric characteristics, the little changed viscosimetric properties in the wide temperature range, good lubricating properties, radiation stability and others.

The combination of these properties makes it possible to use them in different areas of contemporary technology. Some properties of perfluoropolyethers are given in Table 5.

SURFACTANTS

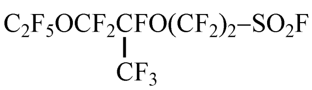
It is known that the fluorine-containing surfactants occupy key place among the known surfactants. Thus, the surface tension of the derivatives of perfluoroenanthic and perfluoropelargonic acids is on the level of 15–16 dyn/cm. The low surface tension, and also the chemical and thermal resistance of fluorine-containing sutfactants of different structure determine their wide application in the contemporary technology.

In the Center "Applied Chemistry" on the basis of perfluoroenanthic ($C_6F_{13}COOH$) and perfluoropelargonic ($C_8F_{17}COOH$) acids, and also on the basis of poly-perfluoropolypropilene oxides of the formula



$$R_FO(\underset{CF_3}{CF}–CF_2O)_n\underset{CF_3}{CF}–CF=O$$

and sulfo derivatives of the composition of



$$C_2F_5OCF_2\underset{CF_3}{C}FO(CF_2)_2–SO_2F$$

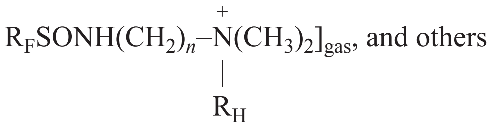
Table 5. Some properties of perfluoropolyethers

Boiling range of oligomers, °C/1 mm Hg	Steam tension	Viscosity	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	~10000	~-30

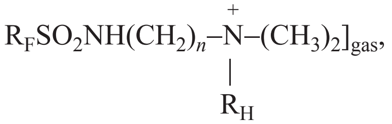
is developed a series of fluorine-containing surfactants different structure:

anion active
(R_FCOOMe, R_FSO_3Me, and others)

cation active



$$R_{F}SONH(CH_{2})_{n}\text{–}\underset{\displaystyle\overset{|}{R_{H}}}{\overset{+}{N}}(CH_{3})_{2}]_{gas}, \text{ and others}$$



$$R_{F}SO_{2}NH(CH_{2})_{n}\text{–}\underset{\displaystyle\overset{|}{R_{H}}}{\overset{+}{N}}\text{–}(CH_{3})_{2}]_{gas},$$

non-ionogenic
$R_FCONH(CH_2\,CH_2\,O)_n$–H].

Fluoro-surfactants found wide application as bases for the frothers: fire extinguishers for the extinguishing of the burning petroleum products and polar liquids, additives for oil and diesel fuel for the decrease in friction and increase in the operational performances of machines and mechanisms, in microelectronics at the production of semiconductor materials at the cutting and grinding of silicic plates, in the processes the cleaning articles, in the galvanotechnics, etc.

SYNTHESIS OF FLUORINE COMPOUNDS WITH THE USE OF ELEMENTAL FLUORINE

Elemental fluorine found wide application as the fluorinating agent in the synthesis of different fluorine compound [16–18].

The industrial method of the synthesis of lowest perfluoroalkanes is developed:

$$C_{sol} + F_{2\,gas} \rightarrow CF_{4gas} + C_2F_{6gas} + C_3F_{8gas} + C_4F_{10gas}$$

Interaction of fluorine and graphite proceeds at the temperature 550–650°C in two steps. In the first step at the temperature 550–600°C in the regime close to the adiabatic on the surface of the graphite particle is formed a layer of solid poly-carbon fluoride $(CF_x)_n$. In the second step in the absence of fluorine proceeds thermal decomposition of $(CF_x)_n$ at the temperature 600–650°C with the formation of perfluoroalkanes.

For providing thermostabilization of the zone of reaction are used the reactors with the dynamic (stirred or mobile) layers, the fluidized bed, which ascends by te gas-dust flow or a freely falling layer of graphite.

A mixture of the gaseous reaction products of fluorine and graphite with the following composition is obtained: CF_4 40–45 wt %, C_2F_6 20–25 wt %, C_3F_8 15–20 wt %, C_4F_{10} 10 wt %.

At the experimental plant of the Russian Scientific Center "Applied Chemistry" was realized a number of low-tonnage technologies on the fluorination of solids by elemental fluorine with obtaining of the corresponding fluorides: selenium, tellurium and iridium hexafluorides, selenium and germanium tetrafluorides:

$$GeO_{2sol} + F_{2gas} \rightarrow GeF_{4gas} + O_{2gas},$$

$$Se_{sol} + F_{2gas} \rightarrow SeF_{6gas},$$

$$Se_{sol} + F_{2gas} \rightarrow SeF_{4gas},$$

$$Te_{sol} + F_{2gas} \rightarrow TeF_{6gas},$$

$$Ir_{sol} + F2 \rightarrow IrF_{6gas}$$

The processes of producing these compounds were achieved in the shelf-type reactors, whose productivity was hundreds kilograms per year. The reactors were equipped with the scanning thermocouples, which made

Table 6. Inorganic fluorine-containing oxidizers

Formula	Molecular weight	$T_{decomp.}$ °C	Density, g/cm^3
ClF_2OBF_4	176.6	473	2.05
$(ClF_2O)_2NiF_6$	351.7	373	2.63
$KClF_4$	150.6		2.5
NF_4BF_4	176.8	513	2.27
NO_2BrF_4	202		2.8
$(XeF_5)_2MnF_6$	621.5	493	3.65
XeF_5BF_4	313		

it possible to observe the temperature distribution in the reactor, in this case the heat removal was accomplished on the basis of free convection.

A technology is developed for the synthesis of nitrogen trifluoride by the fluorination of melted $NH_4F{\cdot}n HF$ by gaseous fluorine:

$$NH_4F{\cdot}nHF_{2\ gas} + F_{2\ gas} \rightarrow NF_{3\ gas} + NH_4F{\cdot}(n+m)HF_{liq}$$

$$NF_{3\ gas} + NH_4F{\cdot}(n+m)HF_{liq} \rightarrow NH_4F{\cdot}nHF_{liq},\ \text{where } n < m.$$

Fluorination is conducted in the gradient-free reactor with the high-speed mixer in the circulation loop, which makes it possible to remove heat effectively on the basis of forced convection and to maintain isothermal regime of the process, and also to provide the maximum contact area of gaseous fluorine with the melt. At this method of the process performing, the productivity of the reactor of fluorination reached 30 g of NF_3 l^{-1} h^{-1} at the conversion of fluorine up to 95%. Nitrogen trifluoride concentration in the gas of synthesis reached 90%, nitrogen was basic admixture. The yield of difluoroamine, tetrafluorinehydrazine and difluorodiazines did not exceed 2–3%.

With the use of elemental fluorine is developed the technology of producing a number of the inorganic fluorine-containing compounds, which are used as the oxidizers, etc

A list of these compounds is given in Table 6.

FLUORINE-CONTAINING COMPOUNDS FOR MEDICINE

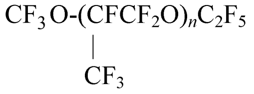
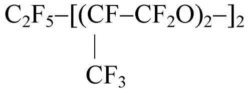
In spite of the high aggressiveness of the initial fluorinating reagents, many flourinated compounds, polyfluorinated and perfluorinated in particular are of great interest for medicine and biology owing to their unique physicochemical properties, and are used widely in the world as diagnostic, and therapeutic preparations.

Such compounds as perfluorodecaline, perfluorotributylamine, perfluorooctyl bromide possess unique ability to dissolve oxygen to about 45–50%. Taking into account chemical inertness they are used as the gas transport means for different purposes: for creating the artificial blood substitute, in ophthalomology at the treatment of the scaling of retina, in roentgenography and in other areas.

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

Introduction of these compounds into medical practice is carried out in collaboration with medical establishments, St. Petersburg Military Medical Academy and other.

Table 7. Fluorohydrocarbons for medicine

Compound	Formula	Molecular weight	bp, °C	D_4^{20}	0_{dip}/cm	Viscosity
Perfluorodeclin	$C_{10}F_{18}$	462	142	1.938	19.8	
Perfluoropolyether MF-130	 $CF_3O\text{-}(\underset{CF_3}{\underset{\vert}{C}}FCF_2O)_nC_2F_5$	3200	>130 1 mm Hg	1.88	20	150–200
Perfluorotributyl amine	$N(C_4F_9)_3$	671	179	1.886	17.1	3.51
Octafluoropropane (R-218)	$CF_3–CF_2–CF_3$	188	–36.8			
Perfluoropolyether P-216	 $C_2F_5–[(\underset{CF_3}{\underset{\vert}{C}}F–CF_2O)_2–]_2$	902	216	1.836	17.8	6.15
Perfluorooctyl bromide	$C_8F_{17}Br$	499	142	1.93	~19	
Perfluorooctane	C_8F_{18}	438	105			

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