

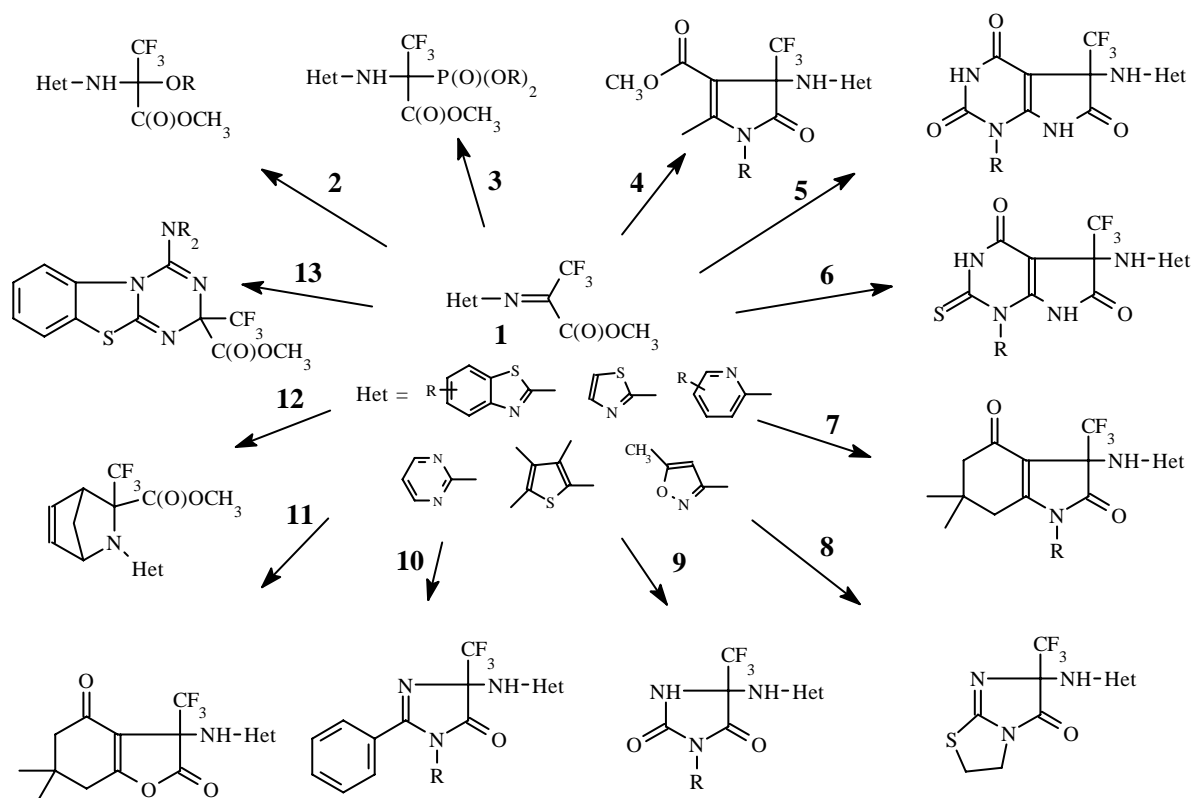
N-HETERYLIMINES METHYL TRIFLUOROPYRUVATE

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The synthesis of unknown early N-heterylimines of methyl trifluoropyruvate (MTFP) **1**, namely, 2-thiazolyl-, 2-benzothiazolyl-, 2-pyridyl-, 2-pirimidyl-, 2-isoxazolyl-, and 2-thenoylimines of MTFP was provided in one-pot synthesis by consecutive addition to solution or suspension of correspondent heterylamine in benzene methyl trifluoropyruvate, pyridine and thionylchloride. Imines **1** were isolated from benzene solution and purified by recrystallization or vacuum distillation.

Imines **1** were studied in reactions with nucleophyles (alcohols **2** and dialkylphosphites **3**), 1,3-binucleophyles (methyl 3-aminocrotonate **4**, 6-aminouracyls **5**, 6-aminothiouracyls **6**, 3-aminocyclohexenones **7**, 2-aminothiazoline **8**, ureas **9**, benzamidines **10**, dimedone **11**) and cycloaddition (cyclopentadiene **12** and cyanoamines **13**).



Structures of compounds synthesized were proved by mass- and NMR-data.

The research was supported financially by Branch of General and Technical Chemistry of Russian Academy of Sciences (program N 10 "Biomolecular and medicinal chemistry").

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MULTICOMPONENT FLUOROPOLYMERS*

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Известна гениальная простота полимера – политетрафторэтилена. Запрограммированное природой вещество, состоящее всего из двух элементов – F и C, и созданный человеком полимерный продукт сделали переворот как в привычных представлениях о реакционной способности тетрагалоидзамещенных олефинов, так и во многих областях деятельности человека.

Однако ПТФЭ не стал идеальным материалом. Известные его недостатки преодолены созданием многочисленного класса термопластичных фторполимеров, которые в большинстве своем являются сополимерами ТФЭ и других фторсодержащих мономеров. Но и двух компонентов оказалось мало.

Одним из популярных и интересных направлений исследований в настоящее время является многокомпонентная сополимеризация. Удачным воплощением этого приема можно назвать фторполимеры Dyneon THV, Lumiflon, Dai-el, которые являются примером целенаправленного синтеза материалов с заданными свойствами.

Нами исследованы терполимеры основных фторсодержащих мономеров: тетрафторэтилена (ТФЭ), гексафторпропилена (ГФП), перфторметилвинилового эфира (МВЭ) и перфтордиокса-4-метил-7-октенсульфонилфторида (ПФДМОС), а также этилена (Э).

Задача состояла в изучении возможности получения термо- и хемостойких материалов, прозрачных в видимой области спектра, полимеров с повышенной эластичностью, а также введения в различные макромолекулы ионообменных групп. Установлено, что в системах ТФЭ-ГФП-(I) и ТФЭ-ГФП-МВЭ (II) могут быть получены прозрачные материалы в определенных областях исходных соотношений мономеров. При этом оба терполимера имеют высокие коэффициенты светопропускания – до 90–95% в видимой (400–700 нм) и ближней инфракрасной (700–2250 нм) областях спектра. Для пленок из (I) наблюдается несколько меньшее по сравнению с (II) снижение пропускания в синей части спектра. Оптические характеристики практически не зависят от толщины образца при изменении последней от 450 микрон до 5 мм, а при увеличении до 10 мм коэффициент светопропускания сохраняется до значения 80–85%. Терполимеры сохраняют прозрачность после прогрева при 200°C, в т.ч. в виде триплекса. Для (I) не наблюдалось зависимости оптических характеристик от температурного режима получения образца.

При терполимеризации ТФЭ с Э и ПФДМОС (III) были получены образцы материалов, сочетающие достаточно высокие механические характеристики, радиационную стойкость со способностью к ионному обмену.

* The authors did not submit an English version.

PROMISING FLUORINE-CONTAINING COMPOUNDS USED IN PROCESSES FLUOROPOLYMER PREPARATION*

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Как известно, основными исходными мономерами для получения широко используемых фторсодержащих полимерных материалов являются фторзамещенные олефины, а также фторсодержащие простые эфиры, фторкетоны, ряд циклосодержащих соединений. Но кроме этой, достаточно обширной группы фторорганических веществ большой интерес для использования в процессах получения фторполимеров (ФП) представляют фторсодержащие пероксиды, фторсодержащие ПАВ и инертные соединения, пригодные в качестве полимеризационных сред. К ним предъявляются два общих требования: максимальная чистота и минимальная возможность участия в побочных нежелательных реакциях при получении ФП.

Изучен ряд перфтордиацилпероксидов (ФДАП) общей формулы $[R_f\text{COO-}]_2$, где R_f – перфтор-, хлорфтор- или полиоксаперфторалкильный радикал, используемых в качестве инициаторов. Разработаны методы синтеза ФДАП различной структуры, определены кинетические параметры термического разложения указанных пероксидов в различных средах. Проведено сравнение характеристик известных и новых ФДАП. Особое внимание уделено гидролитической устойчивости, а также доступности и простоте получения исходного сырья. В качестве перспективных инициаторов признаны хлорфтордиацилпероксиды.

С использованием имеющейся информации и результатов собственных исследований проведен анализ фторсодержащих ПАВ, наиболее применяющихся в процессах получения ФП, в т. ч. традиционных перфторкислот, ПАВ на основе олигомеров окисей гексафторпропилена и тетрафторэтилена, а также соединений, содержащих различные функциональные группы. Высказаны соображения по оптимальным структурам ПАВ для процессов эмульсионной полимеризации фторолефинов.

Фторсодержащие соединения (хладоны) успешно конкурируют с водой в качестве полимеризационной среды, т.к. первоначальное преимущество воды в ее доступности и цене нивелируется необходимостью очистки сточных вод, достаточно энергоемким процессом сушки и часто требуемой стадией дополнительной высокотемпературной обработки полимерного продукта. Однако существует проблема замены озонопасных фторсодержащих соединений. С целью поиска новых растворителей для использования в качестве полимеризационных сред исследованы процессы получения ФП в среде различных озонобезопасных соединений, в т. ч.:

- ✓ PF-5052 – перфтор-N-метилморфолин с $T_{\text{кип}} = 50^\circ\text{C}$;
- ✓ FC-75 – смесь перфторированных алифатических и циклических соединений с $T_{\text{кип}} = 102^\circ\text{C}$.

Сравнительный анализ параметров процесса сополимеризации в этих средах ТФЭ с ГФП или с ПФПВЭ и свойств полученных образцов сополимеров подтвердил возможность их использования в качестве полимеризационных сред.

* The authors did not submit an English version.

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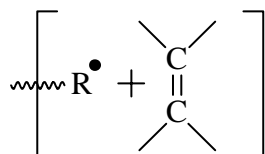
MECHANISM IDENTIFICATION FOR VINYLIDENE FLUORIDE (VDF) / HEXAFLUOROPROPENE (HFP) COPOLYMERIZATION BY NMR ¹⁹F DATA

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The results of calculations probability of adding VDF to the growing chain of copolymer with HFP final unit by using Markovian model of copolymerization gave the values exceeding 1 that breaks the stochastic nature of the process.

We suggested that the Markovian model did not consider a possible existence of transition state complexes bonding the active site with double bond of non-symmetric comonomers in the process of chain growth:



We can formally picture this kind of monomer coordination to the active site in the above scheme where dyad combinations of HFP units are impossible. For the reduction of the number of independent parameters it is necessary to enlarge this model by the states describing the chain growth. The enlargement procedure is based on the single origin of growth states, i.e. we integrate active sites with CH₂• and CF₂• end groups of VDF added to the copolymer chain and CF₂• and CF• groups of HFP added to the chain.

Mole parts [HFP] and [VDF] were determined through NMR¹⁹F spectra analyses for copolymers obtain by both emulsion and solution methods.

The analysis of enlarged statistic model of VDF/HFP copolymerization with the coordination of monomer to the active radical center of the growing chain allows to calculate values of transition probabilities of addition HFP (q_1) and VDF (q_2):

$$q_1 = \frac{[\text{HFP}]}{1 - [\text{HFP}]} = \frac{[\text{HFP}]}{[\text{VDF}]}, \quad q_0 = 1 - q_1 = 1 - \frac{[\text{HFP}]}{[\text{VDF}]} = \frac{[\text{VDF}] - [\text{HFP}]}{[\text{VDF}]}$$

Unlike above classical Markovian model of copolymerization the data are at least not at variance with the stochastic nature of the process. They neither upset normalization conditions of transition probabilities.

Further analysis of enlarged model allowing for monomer-to-radical center coordination makes it possible calculating the parts of VDF unit sequences limited with HFP units:

$$[\text{HFP} - \text{HFP}] = 0; [\text{HFP} - \text{VDF} - \text{HFP}] = q_1; [\text{HFP} - (\text{VDF})_2 - \text{HFP}] = q_0 \cdot q_1;$$

$$[\text{HFP} - (\text{VDF})_3 - \text{HFP}] = q_0^2 \cdot q_1; [\text{HFP} - (\text{VDF})_4 - \text{HFP}] = q_0^3 \cdot q_1 \text{ and so on.}$$

It shows that the varying composition of the copolymer is non-linear with the proportions of the parts of above sequences.

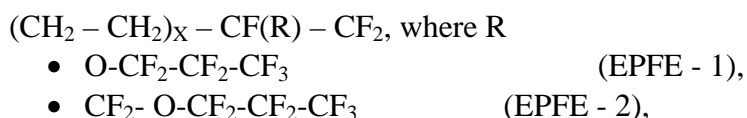
As in -108 ppm region of NMR¹⁹F copolymer spectrum a specific signal C*F₂CH₂ was found attributed to the triade (HFP-VDF-HFP), this makes it possible to experimentally prove the suggested model. It is based on a large number of spectra analyses. The experimental data are evidenced to correlate quite well with the model description.

PECULIARITY OF SUPRAMOLECULAR ORGANIZATION OF PERFLUOROPROPYL-VINYL ETHER/ETHYLENE COPOLYMER

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Filmforming fluoroelastomers are an intensively studied subject of material science due to their high corrosion resistance at even high temperatures. Fluoroelastomer film formation out of solutions is the most convenient way in practice. It should be taken into account that supramolecular assembly of filmforming materials as well as their properties closely correlate with the solution structure. Thus the necessity of studying solution structure is evident as the first step to filmforming materials. From the practical viewpoint it should be allowed for that polymer supramolecular assembly in thin and ultrathin supported films can markedly differ from polymer in bulk Ethylene/perfluorinated ethers (EPFE) copolymers of the below general formula were the subject of the present study:



These polymers made at the Synthetic Rubber Institute are shown to be more stable in polar and nucleophilic media than those based on vinylidene fluoride. Dissolution behavior of EPFE copolymers has been studied by dynamic light scattering. Mechanisms that govern copolymer solubility with time have been also discussed.

Macromolecule associates have been shown present in solution at even lower concentrations. Possible mechanisms of associate formation have been investigated and ways of destruction thereof suggested.

This stage of the study resulted in the choice of solvent that enables EPFE thin films possessing a set of favorable strength properties. The partial molar excess enthalpy of mixing $\Delta H_1^{E\infty}$ is the resultant of all the intermolecular interactions in arising infinite thin solutions.

Thus, the determination of thermal effects of mixing makes it possible to gain valuable information on either peculiarities of molecular interaction in solutions or those of polymer architecture. IGC method was used to calculate $\Delta H_1^{E\infty}$ values within a wide temperature range as functions of polymer chain microstructure, chemical nature and molecular volume of the sorbate, as well as of polymer film thickness.

The analysis of data array has shown that supramolecular structure of polymer films features the presence of methylene – unit clusters despite the alternating microstructure of the copolymer chain. This conclusion has been proved by independent data of atomic force and scanning electron microscopies..

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THE NEWS IN SYNTHESIS OF PERFLUOROBUTADIENE AND ITS UTILIZATION FOR PREPARATION OF BRANCHED PERFLUOROPOLYETHERS

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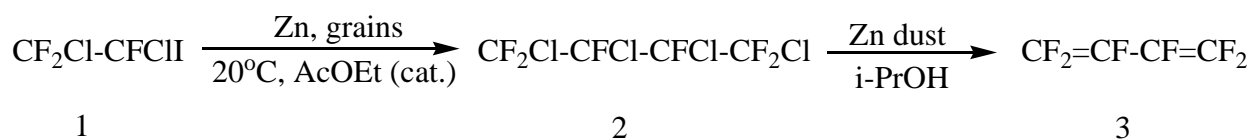
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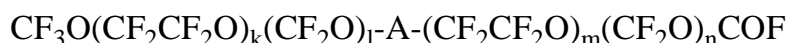
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Perfluorobutadiene (3) is usually prepared by dechlorination of 1,2,3,4-tetrachlorohexafluorobutane (2). The latter is formed by coupling of two 1,2-dichloro-1,2,2-trifluoro-1-iodoethane (1) molecules in different conditions. The yield of compound (2) is low as a rule because of by-products formation, and a complicated procedure for purification of the target product is required.

The technologically convenient procedure for preparing of perfluorobutadiene (3) has been developed by condensation of iodide (1) to tetrachlorobutane (2) with granulated Zn at 20°C without a solvent in the presence of catalytic amount of AcOEt followed by conversion of (2) to diene (3) without preliminary purification (yield 90%)^[1,2].



Hexafluorobutadiene is successfully used as a cross-linking reagent in the synthesis of thermally and chemically stable and frost-resistant polymers based on perfluoroalkylene oxides (4) containing peroxide groups^[3,4]:



4

where A – are peroxide links statistically distributed along the chain:

CF₂CF₂OOCF₂CF₂O-, CF₂CF₂OOCF₂O-, -CF₂OOCF₂O-

active oxygen quantity is from 0.6 to 1.8 mass per cent.

Possibility of the use of perfluoroalkylene oxides with peroxide groups for the creating of the polymer materials possessing a wide range of useful properties and areas for its application is discussed.

¹ Karimova N.M. *et al.* Pat. RF № 2248844 (2005).

² Karimova N.M. *et al.* *Izv. Akad. Nauk, RAS, Ser. Khim.* 2004(10), 2236-2238.

³ Glazkov A.A. *et al.* *Zh. Org. Khim.* 1994, **30**, 1193-1196 (in Russian)

⁴ Krukovsky S. P. *et al.* *J. Fluorine Chem.*, 1999, **96**, 31-33

NEW FLUORINATED ORGANOSILICON COMPOUNDS FOR PROTECTION OF ARTWORKS AGAINST ADVERSE ENVIRONMENTAL IMPACT

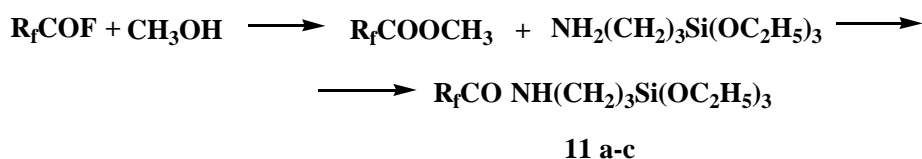
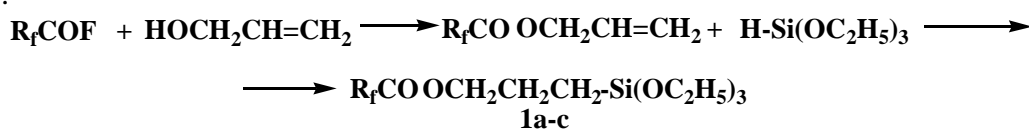
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Methods for the preparation of perfluoroacyl derivatives of alkyltriethoxysilanes were developed in order to use these compounds for the protection of building materials from environmental impact. The synthesis was performed in accordance with the following reaction scheme¹:



Compounds **1a-1c** and **11a-11c** were tested as water-repellent and oleophobic agents for limestone, marble, concrete, brick, plaster, and wood. The contact angles were 130-138^o and 110-115^o for water and decalin, respectively, depending on the structure of the organofluorine substituent at the silicon atom. The water absorption and frost and salt resistance of limestone and plaster samples treated with these compounds were determined in accordance with standard procedures.

It was found that, as compared with commercial organosilicon compounds, the fluorinated organosilicon compounds synthesized imparted better hydrophobic and oleophobic properties to the protected surfaces.

These new fluorinated organosilicon compounds were used for architecture and historic conservation in Moscow and Vladimir (Russia). Although they do not exhibit fungicidal activity, these compounds controlled the growth of microorganisms (fungi, algae, and molds) on the protected surfaces of building materials.

This study was supported by the JSC Moscow Committee on Science and Technologies.

¹ Krukovsky S.P. *et al.* RF Patent №2149151 (2000); Krukovsky S.P. *et al.*, RF Patent №2151151 (2000); Yarosh A.A. *et al.* *Mendeleev Communications*, in press.

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NEW FLUORINATED DIAMINES BASED ON 2,4,6- TRINITROTOLUENE(TNT) AND LOW K POLYIMIDES THEREFROM

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Various aromatic fluorinated diamines were prepared on the basis of TNT- major explosive component of ammunition liable to liquidation [1]. The introduction of fluorinated fragments was achieved through nucleophilic substitution of nitro groups in TNT or its derivatives under the action of the corresponding fluorinated nucleophiles [2]. Subsequent reduction of the dinitrocompounds thus formed has led to the formation of aromatic diamines containing hexafluoroisopropylidene groups as well as perfluoroalkoxy and perfluoroaroxy substituents.

Interaction of the diamines obtained with aromatic tetracarboxylic acids dianhydrides under conditions of high temperature solution polycyclocondensation resulted in organo-soluble low K (2,7-3,0) polyimides. Heat treatment of polyimides films resulted in materials demonstrating K equal to 2,4-2,5.

Tartakovskiy V.A. *et al.* *Conversion*. 1994, **11**, 7-11.

Rusanov A.L. *et al.* «Recent progress in polycondensation». (T. Matsumoto, Ed). Research Signpost, Trivandrum, India, 2002, pp. 117-151.

ACTIVATED ARYLFLUORIDES IN CHEMICAL TRANSFORMATIONS OF END GROUPS OF OLIGOARYLENEETHERKETONES

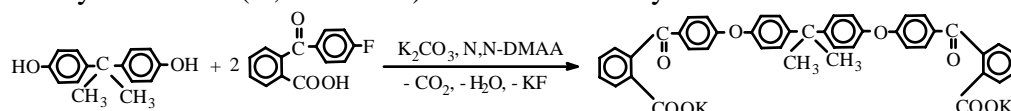
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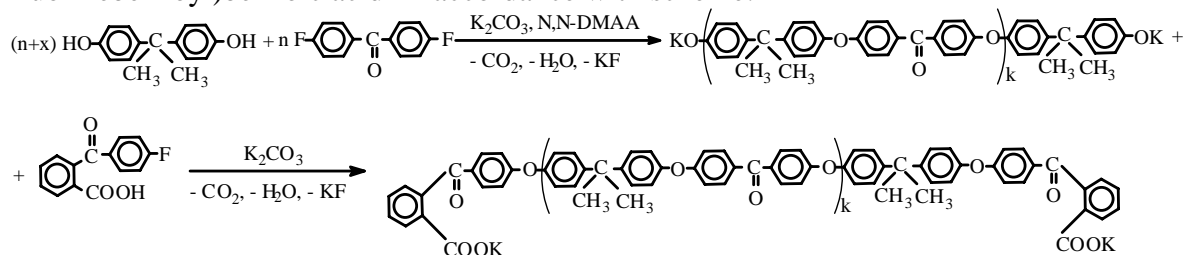
Use of fluorinecontaining monomers of various structure in synthesis of novel condensation polymers retains actuality and extends essentially possibility to influence on structure, and accordingly, on polymers properties. Main aim of this investigation was synthesis of oligomeric products having end reactive groups. These products will apply in future as "intermediates" for preparation of regular blockpolymers. Formation blocks in regular blockpolymers will be result of interaction of block's "intermediates" containing end groups.

For establishment of possibility of replacement of phenolate groups on carboxylate ones in oligoaryleneetherketones model reaction of 2-(4-fluorinebenzoyl)benzoic acid with bisphenol A in N,N-dimethylacetamide (N,N-DMAA) was carried out by the follow scheme:



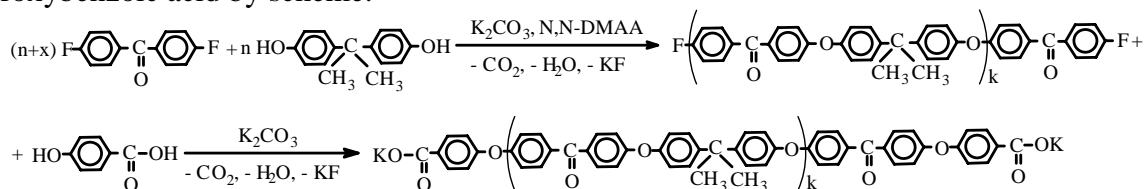
Final product represents glassy transparent substance. Its structure was confirmed by infrared spectroscopy and elemental analysis data.

Synthesis of oligomeric product (k=10), containing end carboxylate groups, based on "intermediates" of block having end phenolate groups was realized out by using in reaction of 2-(4-fluorinebenzoyl)benzoic acid in accordance with scheme:



x = 9,5 % mol.

Another variant of synthesis of oligomeric product (k=10), containing end carboxylate groups, was carried out based on "intermediates" of block having end fluorine groups and 4-hydroxybenzoic acid by scheme:



x = 9,5 % mol.

The research was supported financially by Russian Foundation for Basic Research (Project № 04-03-32104).

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LASER DECOMPOSITION OF PTFE AS A CONVENIENT METHOD OF SMALL-BATCH MANUFACTURE OF TFE

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Tetrafluoroethylene (TFE) presents a handy initial product for certain types of synthesis. Its aptitude to spontaneous polymerization and explosion are a hamper to safe transporting and storage. Since 1950s it has been recommended for laboratory practices to obtain TFE through thermal depolymerization of PTFE. This simple in its essence method brings about a number of problems in practice.

First, to heat up the reactor and polymer till 500-600 °C requires 0.5-1 hour. Comparable time losses are also needed for cooling.

Second, to reach an acceptable decomposition rate, certain parts of the reactor should be heated to a considerably higher temperature (by 150-300 °C). The presence of hot surfaces results in the formation of a significant amount of secondary reaction products (tens of percent).

Named problems are so serious that in spite of the lack of recycling methods of PTFE wastes, its thermal decomposition has not been realized yet at the industrial scale.

We have proposed and employed a new method of laser decomposition of PTFE. A sintered block of PTFE is exposed in vacuum to a continuous CO₂ laser radiation at 10-1000 Wt/cm² intensity and removal of the formed TFE by a vacuum pump. PTFE decomposition starts and terminates a few seconds after switching the laser on/off. The crater in the place of PTFE exposure turns to be most heated in the vacuum chamber (about 530 °C). Running of the process in vacuum offers full control over the gas flows and the absence of occasional injections. The laser of 100 Wt power may yield 50-150 g/h of TFE.

Mass spectrometry has shown that thus produced TFE possesses below 1% of the organic fluorine impurities. Evidently, it acquires additional contaminants when passing through the vacuum pump. These contaminants are, however, easily predicted. In case of evacuation by a mechanical pump these are the vapors and aerosols of the vacuum oil, i.e. pure enough paraffins, which do not exert any noticeable affect. Besides, TFE can be made more clean by freezing impurities in cryogenic traps. This method makes it possible to use sintered TFE wastes, in which case the presence of small amounts of metals and oxides does not affect TFE purity.

Notice that, the vacuum pump and pipelines can be filled with air before running the process. A common problem for a number of processes is the requirement for a free from oxygen TFE, which remains even at operation with a gas cylinder. Our method proposes pumping of the inert gas through the vacuum system. Still more efficient is installation of another vacuum pump complying with the system of valves and pipes and exercising an independent evacuation of air from the vacuum chamber.

POLYTETRAFLUOROETHYLENE DECOMPOSITION UNDER CO₂-LASER EXPOSURE

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The aim of the present study is to examine the initial stages of PTFE decomposition under the effect of continuous irradiation of CO₂ laser ($\lambda = 10.6 \mu\text{m}$ or 944 cm^{-1}) in vacuum. The changes in PTFE exposure in $800\text{-}964 \text{ cm}^{-1}$ region under the temperature rise from 300 till 600 K has been studied. The radiation absorption was found to increase 1.4-1.5 times, which is equivalent to the reduction from 280 down to 80 μm of PTFE layer thickness in which 90% of radiation is absorbed. Filming of the process of PTFE fiber growth was made, which has visualized its subdivision into several stages.

During the first stage the polymer is heated up without the signs of fiber formation. A modal structure of the laser beam can be easily detected on the polymer surface. The latent period length turned to be dependent on the radiation intensity, and pressure of the gases in the chamber, making up a few seconds at radiation intensity 80 Wt/cm^2 . This period includes heating and amorphization of PTFE's layer within up to a few hundreds of micrometers, which corresponds to the absorption depth of a greater portion of radiation.

The second stage is characterized by the local formation onset of the fibers in conformity with the modal structure of the beam. Within portions of a second several hundred micrometers long fibers are formed, detach and are carried away from the exposure zone.

At the third stage the gaseous flows from individual parts of the crater get united. The convergence lasts about half a second. The fibers enlarge in size reaching almost a centimeter. The process of fiber formation is comparable to a decelerated burst. The optimum conditions of fiber formation are attained quicker in the center of the crater. The process spreads from the crater's center to its periphery thus bringing about elongation of the fibers starting their growth from the crater's center. This elongation and delamination of the fibers from the polymer melt takes place due to a gas flow generated at PTFE decomposition. The gas isolation constitutes about 8-10 mg/s and its velocity reaches 50-100 m/s. The fibers are carried away from the crater at a speed comparable to that of the gases, i.e. tens of m/s. Having a considerable mass and developed surface, the flowing fibers adhere to those flown beyond the beam bounds earlier and form a thick network. As a result of this process a peculiar corona is formed.

During the fourth stage the crater deepens and acquires a distinct cone shape. The radiation intensity on the walls falls due to, first of all, growth of the wall area and, second, due to increased reflection from the acute angle of incidence.

The increased radiation intensity leads to abrupt decomposition acceleration, all above-described stages being preserved. As it follows from our study, laser-induced decomposition of PTFE is subdivided into a sequence of stages differed in the processes of PTFE decomposition and fiber formation.

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PLASMA POLYMERIZATION OF TETRAFLUOROETHYLENE ON THE CARBON FIBER SURFACE

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The thin polymeric films have found wide application as protective coatings of dielectric layers in microelectronics, filler coats for improved adhesive interaction in polymer composite materials, etc. The thin polytetrafluoroethylene (PTFE) layers can be obtained by the high-energy effect on the fluorine-containing compounds in vacuum, e.g. in the electric discharge plasma. Polymerization in plasma of fluorine-containing gases may follow different modes attracting either molecules, radicals, ions or electrons. It involves just as synthesis of the high-molecular product, so its modification during formation.

The present work studies the composition and structure of the coatings deposited on carbon fibers by plasma polymerization of tetrafluoroethylene (TFE). The research object has been chosen due to the intensive use of carbon fibers as a PTFE filler, as well as perfect adhesive interaction with the polymer matrix thanks to a fluoropolymer interlayer on the surface refining thereby the structure and properties of the composite.

The coating composition on the carbon fabric samples were studied using RFES. The atomic ratio on the carbon fiber surface prior to the plasma treatment made up C : O = 88 : 14. After the treatment in TFE medium fluorine atoms appeared and the ratio changed as C : O : F = 72 : 15 : 9.

Spectral analysis of Cls carbon has shown the reduction of carboxylic groups on the fiber surface after TFE plasma polymerization, and the emergence of 290.9 and 292.3 eV constituents, which are characteristic of $-CF_2$ and $-CF_3$ groups. The spectrum of Cls oxygen before the treatment contained the lines typical for $-C=O$ (532.3 eV) and $-C-O$ (533.7 eV), which shifted till 532.7 and 534.3 eV after the polymerization. This shift can be a result of forming $O-C(O)-CF_3$ and $O-CO-CF_3$ groups, correspondingly. The fluorine line contains those of 688.2 and 689.7 eV, the first of which resulted from overlapping the signals from CF_2CH_2 , $O-C(O)-CF_3$, while the other belongs to PTFE groups $-CF_2-CF_2-CF_2$.

It is shown that along with characteristic of PTFE groups the plasma-polymerized TFE on carbon fibers contains a considerable amount of oxygen-containing groups (carboxylic, ether) and trifluoromethyl ones.

IR spectrum of the film obtained in a HF discharge of TFE medium on a silicone crystal complies on the main with PTFE's spectrum. The absorption band of fluorocarbon groups ($1150-1250\text{ cm}^{-1}$) is somewhat broadened due to plasma polymerization peculiarities. Most often an intricate 3D cross-linked structure is formed in plasma conditions rather than a polymer with a regularly interleaving monomer segments.

The use of carbon fibers with the fluoropolymer coating for PTFE filling has improved essentially structure and physico-mechanical properties of the final composite. The method proposed for depositing fluoropolymer coatings on carbon fibers via TFE plasma polymerization aimed at raising adhesive interaction with PTFE can be employed for other fillers as well. This has proved to ameliorate their processing compatibility with the matrix and achieve high-quality composites.

INFLUENCE OF NONSOLVENT ADDITIVES IN CASTING SOLUTIONS ON STRUCTURE AND PROPERTIES OF FLUORINATED MICROFILTRATION MEMBRANES

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The fluorinated polymers are materials with increasing scientific attention and industrial importance for manufacturing of the microfiltration membranes because of its high thermal and chemical resistance, durability. In the report the structure and transport properties of microfiltration membranes made from tetrafluoroethylene/vinylidene fluoride copolymer F-42 are discussed. The membrane preparation technique include the phase inversion of three-component systems «polymer - solvent - nonsolvent» in water coagulation bath. A wide range of chemical substances were used as nonsolvents: water, inorganic and organic acids, and alcohols. All of the nonsolvents being tested can be divided on two large groups: «soft» ones, which describes by a high precipitation numbers (> 500 g/dl) and "strong", with precipitation numbers in a range from 8.7 up to 30 g/dl. Introduction of any nonsolvent in a casting solution in some critical concentration leads to its phase separation.

It was found, that the rise in the concentration of strong nonsolvent in the casting solution leads to sharp increase of its heterogeneity, which can be fixed on their turbidity. After achievement the binodal there is the "liquid-liquid" phase separation occurs.

The soft nonsolvents doping in the casting solution leads to absolutely different regularities. Compared to strong nonsolvents, the concentration area of homogeneous solutions enlarges. The additives of soft nonsolvent leads to the sharp increase in the viscosity of the solutions. The turbidity does not change significantly. The further increase in concentration of the soft nonsolvent in casting solution leads to system gelation. Gelation is observed in case of ethanol, iso-propalol, acetic and ant acids. The gels obtained represents steady not fluid opalescent systems which are melt at the increasing of temperature. The X-rays analysis of the gels shows that gelation of the solutions is caused by the process of polymer crystallization and formation of a three-dimensional network.

It was established, that the formation of porous permeable films is possible in the limited concentration region of nonsolvent in casting solution. The increase in nonsolvent concentration the hydraulic permeability of membranes pass through a maximum. The strong nonsolvent additives allow to form the large pore membranes with high hydraulic permeability. A film, obtained from the casting solutions with soft nonsolvents are characterized by not developed porous structure and, accordingly, low hydraulic permeability.

The data illustrating the structure and transport characteristics of experimental membranes, as well as the results of comparative testing experimental and commercial membranes (Versapore, Gore) are cited. The application of experimental membranes as air filters for disposable infusions systems are discussed.

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PREPARATION OF LUMINECSENT AND COLOURED POLYTETRAFLUOROETHYLENE IN BLOCKS BY RADIATION CHEMICAL MODIFICATION TECHNIQUE.

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In the recent years, an interest to radiation modification of polytetrafluoroethylene (PTFE) in melt (330-340°C) rose significantly²⁻³. Recently, we have shown that PTFE films (95 μm thick) γ-irradiated at the temperature close to their melting point and preheat treated in vacuo (10⁻³ mm of Hg, T = 340°C) exhibit bright visible fluorescence⁴. Optical centres of various types formed in the polymer as a result of radiation chemical transformation were established to be responsible for their fluorescent properties. The fluorescence intensity, concentration ratio of optical emission centres of various types, and samples colouration are found to depend on the sample irradiation conditions.

In this report, results of spectral luminescence studies of radiation-modified PTFE in large – sized blocks (D ~ 100 mm) are presented. γ-Radiation treatment of the blocks was carried out in the metallic camera heated to the temperature close to the polymer melting point.

The process of optical emission centres formation is different in various parts of the block. This phenomenon is demonstrated in the figure where the photographs of the cylindrical block sections after γ-irradiation in UV – (a) and visible (b) light are presented. It is seen that the colour is different in various areas (areas of equal fluorescence have a view of concentric circles). The central part of the section turned out to be entirely non-fluorescent.



(a)



(b)

The block surface irradiated in air, containing water vapor, grows dark, inner layers retaining a light colour. Samples radiation-treated in the argon atmosphere show brighter fluorescence and practically no change in the colour. So, the colouration and fluorescence are of different nature. The chemical structure of the fluorescence centres has been revealed.

¹ Oshima A. *et al. Rad. Phys. Chem.* 1997, **49**(2), 279-284

² Oshima A. *et al. Rad. Phys. Chem.* 1999, **55**(1), 61-71

³ Lappan U. *et al. Rad. Phys. Chem.* 2000, **59**(3), 317-322

⁴ Khatipov S.A. *et al. Vysokomol. Soedin.* 2006, **48**(2), 263-270

CREEP OF POLYTETRAFLUOROETHYLENE IRRADIATED ABOVE THE MELTING TEMPERATURE OF CRYSTALLITES

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The paper presents the results of a study of the strain properties of polytetrafluoroethylene (PTFE) irradiated at a temperature higher than the melting temperature of the crystalline phase. It is known that the impact of ionizing radiations on PTFE in this temperature region results in an anomalous change of its macroscopic properties.

The films under investigation had the thickness 100 — 200 μ and they were subjected to irradiation with gamma quanta of the ^{60}Co isotope in the temperature range 320 — 360°C with doses of 50 — 300 kGy while varying the medium of irradiation. Presented in the report are study results on the dependence of the value of the unit strain on the time of impact of the static load, as well as the diagrams of tensile strain under variable load.

Based on the obtained results, the conclusion has been made about the qualitative change in the structure of irradiated PTFE. There has been discovered the effect of an anomalously large decrease of the creep (up to 100 times) as compared to the pristine polymer. Shown in Fig. 1 are the time dependences of the unit strain of pristine (Curve 1) and irradiated (Curve 2) PTFE films under static load (11 MPa). It can be seen that not only the value, but also the character of the strain is changed. Under the above-mentioned load, the strain of irradiated PTFE is elastic, whereas in the pristine state, the effect of pseudofluidity is observed.

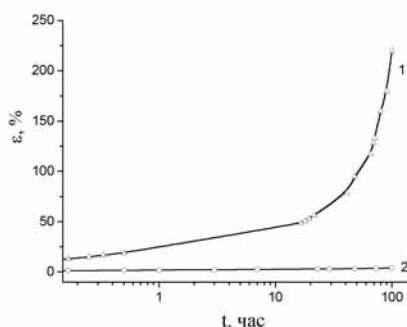


Fig. 1. Unit strain of pristine (1) and irradiated (2) PTFE films in creep mode under the static load 11 MPa.

The change of the plastic strain mechanism is also indicated by the diagrams of tensile strain. Characteristic for pristine PTFE is the high contribution of inelastic strain already at the initial segment of the stress-strain diagrams. The sample elongates uniformly along the full length without the formation of a "neck." Irradiated PTFE elongated with the formation of a neck and, in contrast to the pristine polymer, has a rectilinear segment in the initial part of the diagram. The latter phenomenon is explained by the increase of the intermolecular cohesion of polymer chains.

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HEXAFLUOROPROPYLENE THERMAL TELOMERIZATION REACTION KINETICS AND MECHANISM AT HIGH PRESSURE

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HFP telomerization reaction with perfluoroalkyl iodide at high pressure was not studied earlier. Experiments were conducted on a cylinder-piston high pressure apparatus. [1] Teflon ampoule was served as a reactor. Reaction kinetics was recorded by piston shift measuring with accuracy 0.01 mm.

The experiment lasted for 1 to 24 hours. Reaction mixtures were analyzed by GLC, IR, ¹⁹F NMR and mass spectrometry methods. The molecular weight of oligomers was determined by viscosimetry and cryoscopy methods.

At high telogen concentration (more than 20%) there was liquid oligomers dominance between reaction products (n=1÷4). At low concentration of C₂F₅I molecular weight of products could achieve several thousands. The telomerization reaction speed increased with pressure and temperature growth. The reaction velocity accelerates proportionally to square root of telogen concentration. (Fig.1).

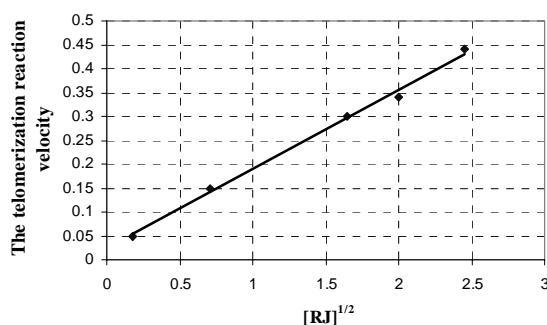
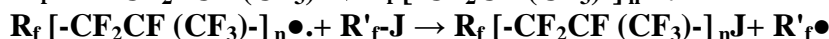
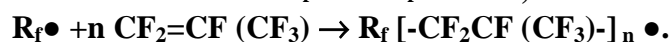


Fig.1 The telomerization reaction velocity - telogen concentration curve.

The calculated value of activation energy E_a was 118,7 kJ/mol.(0,7 GPa). The interesting particularity of HFP reaction with perfluoroalkyl iodide is passing on living radical polymerization mechanism, when separated from reaction mixture telomers can react with HFP again in that reaction conditions: $R_f-J \rightarrow R_f\bullet + J\bullet$;



Thus, as a result of HFP telomerization reaction studies following conclusions were made:

1. Using high pressure method allows to obtain oligomers with high conversion of HFP approximately in ten times faster than under autogenous pressure.[2]

2. The molecular weight of reaction products can be easily regulated by reaction conditions. 3. The telomerization reaction HFP is passing on living radical polymerization mechanism.

¹ Moskvina D.I. et. al. *Zh. Fiz. Khim.* 2004, **78** (5),850.

² Freidlina R.Ch. et. al. *Uspechiu Khimii Polymerov. M.*1966, p.138.

NOVEL FACILE ROUTE TO POLYMERS WITH SiMeR_FO UNITS

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The hydrophobic properties and low refractive indices of fluoro-containing organosiloxanes make them very promising for a variety of applications [1]. Until now, only the complicated four-step preparation of these polymers from diorganodichlorosilanes is well-known [2].

Here, we report the novel facile synthesis of polymers with SiMeR_FO units by hydrolysis of compositions including fluoro-containing organosilicon monomers and 3-aminopropyltriethoxysilane (APTES) (**1**).

The fluoro-containing monomers methyl(3,3,3-trifluoropropyl)dimethoxysilane CF₃CH₂CH₂SiMe(OMe)₂ (**2**), methyl(3,3,3-trifluoropropyl)bis(2,2,2-trifluoroethoxy)silane CF₃CH₂CH₂SiMe(OCH₂CF₃)₂ (**3**) and methyl(1-hydrohexafluoroisopropoxy)methyl-bis(1-hydrohexafluoroisopropoxy)silane (CF₃)₂CHOCH₂SiMe(OCH(CF₃)₂)₂ (**4**) have been prepared by reactions 1 and 2:



4

To our knowledge monomers **3** and **4** have never been reported previously.

The reaction of compounds **2** – **4** with aliphatic amines (Bu^sNH₂, *c*-C₆H₁₁NH₂, Et₂NH, Et₃N) gives complexes (RO)₂MeR_FSi ←NRR'R'' consistent with the IR spectra of the reaction products. These complexes are insoluble in the starting monomers. In contrast, complexes (RO)₂MeR_FSi ←NH₂(CH₂)₃Si(OEt)₃ prepared from APTES are readily soluble in the starting compounds **2** – **4**. In this case, the resulting complexes provide nucleophilic catalysis of the hydrolysis of monomers **2** – **4** and condensation of the silanol groups. Films of good optical quality, absolutely transparent in the UV, visible and near IR regions, can be cast from the compositions at room temperature in the presence of air. The time taken for solid film formation depends on the proportions of the components. All films retain their optical transparency on heating up to 150°C.

Financial support was received under INTAS Grant 03-51-5959, Russian Foundation Grant 05-03-32556, President RF Grant 8017.2006.3 and the RAS Nanotechnology Programme.

¹ Askadskii A.A. *Computational Material Science of Polymers*, Cambridge International Science Publishing, Cambridge, 2003.

² Shamaev E.A. *at al. Russian Chem. Bull* 2004, **10**, 2133-2136.

P-118

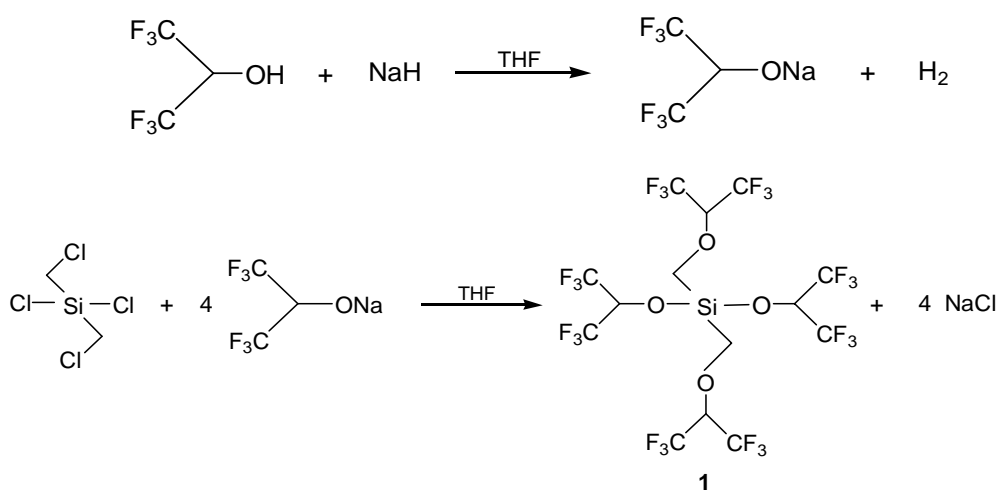
NOVEL MONOMER FOR THE FLUORO-CONTAINING POLYORGANOSILOXANES PREPARATION

T. S. Pozdeeva, E. Yu. Ladilina, V. V. Semenov

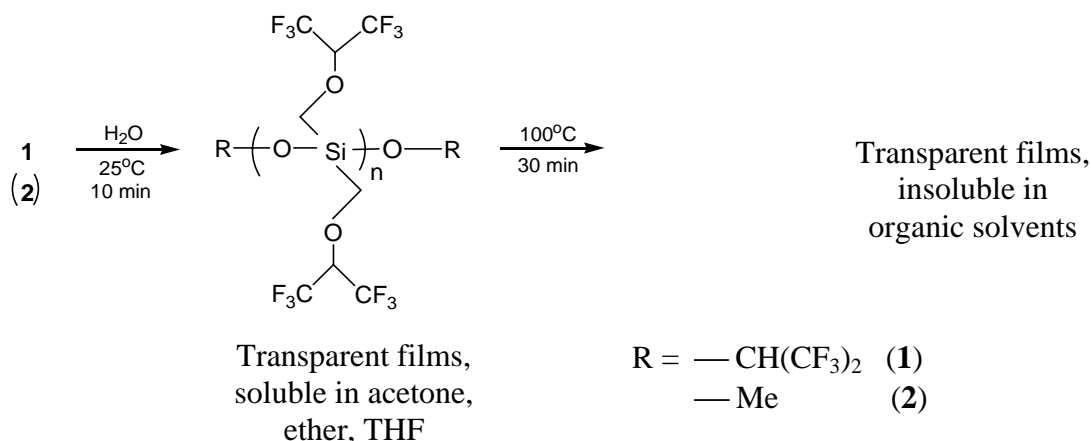
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Bis(1-hydrohexafluoroisopropoxymethyl)bis(1-hydrohexafluoroisopropoxy)silane had been synthesized by the reaction of bis(chloromethyl)dichlorosilane with sodium hexafluoroisopropylate.



The interaction of compound **1** with methanol yields bis(1-hydrohexafluoroisopropoxymethyl)dimethoxysilane ((CF₃)₂CHOCH₂)₂Si(OMe)₂ (**2**). Films of good optical quality can be cast from compounds **1** and **2** at room temperature in the presence of air moisture. The film formation is accompanied with the hydrolysis reaction:



Financial support was received under INTAS Grant 03-51-5959, Russian Foundation Grant 05-03-32556, President RF Grant 8017.2006.3 and the RAS Nanotechnology Programme.

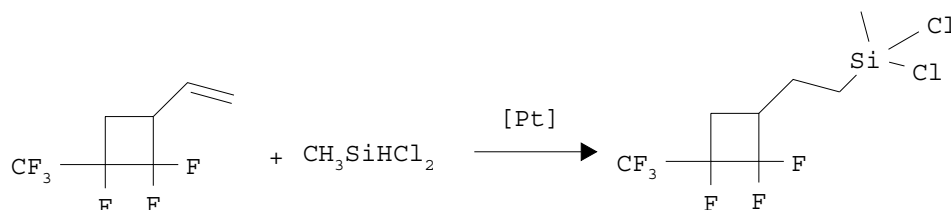
SYNTHESIS OF NEW FLUOROSILOXANE POLYMER BY HYDROSILYLATION

N. K. Skvortsov^a, A. N. Reznikov^a, A.V. Kalinin^b, G. A. Nikolaev^b, R. I. Hvostov^a

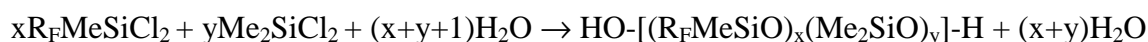
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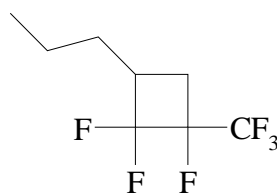
The hydrosilylation of the available 1-vinyl-2,2,3-trifluoro-3-trifluoromethylcyclobutane, the product of cycloaddition of buta-1,3-diene to hexafluoropropene, is applied to the synthesis of the monomer for new fluorosiloxane polymer:



The pattern of the hydrosilylation of fluoroalkene in the presence of bisphosphine complexes of Pt(II) is studied. The synthesis of polymer by hydrolytic copolycondensation of hydrosilylation product with dimethyldichlorosilane allows one to avoid a labour-intensive and power-consuming stage of separation of cyclosiloxanes:



$\text{R}_F =$



The thermostability of obtained oil-and-gasoline resistant polyfluorosiloxane with average molecular weight 606000 exceeds that of the rubber SKTFT-50.

The research was supported financially by Russian Foundation for Basic Research (Project No. 04-03-32632a).

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STRUCTURE OF MODIFIED POLYTETRAFLUOROETHYLENE FORMS. QUANTUM CHEMICAL AND SPECTROSCOPIC STUDY

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Recently the ways of polytetrafluoroethylene (PTFE) modification to perfect properties of its and extend the capabilities of PTFE application are studied deeply. The modification is carried out by various means: by irradiation methods, thermo-treatment, machining, in various technological conditions. The structure of PTFE samples post-treatment can be distinguished from that of standard PTFE. The investigations of such samples by vibration spectroscopy methods showed that with various treatments the new bands arise and some bands change their positions in IR- spectra. These facts reflect the changes in molecular and supramolecular structure of PTFE.

The analysis of IR- spectra of obtained modified PTFE forms showed:

- the new band at 1786 cm⁻¹ arises in IR-spectrum of ultradispersed sample (Forum) obtained by thermo-treatment of PTFE in air atmosphere;
- the electron irradiation of PTFE and ultradispersed sample (Forum) induces the appearance of the bands at 1777 and 1885 cm⁻¹ in IR-spectra of these samples;
- there are not new bands in the spectrum of dispersed PTFE (Tomflon) obtained by irradiation of PTFE with following machining;
- at machining (pressure) of ultradispersed PTFE (Forum) the new band at 986 cm⁻¹ appearances in IR spectra of its.

To understand the nature of changes in microscopic molecular structure of PTFE post-treatment and assign the observed new bands in IR-spectra of modified PTFE samples the quantum-chemical ab initio calculations of stability, structure and vibration spectra of the chaining and branching oligomers of C_nF_{2n+2}, C_nF_{2n} and C_nF_{2n}O (n=5-13) were carried out with using of DFT and HF level of theory. As part of an exploration calculation it was found:

- the optimal molecule structures of chaining oligomers of C_nF_{2n+2} (n>5) are zigzag chains with the bonds of R_{C-C} = 1.53-1.54 Å and R_{C-F} = 1.34-1.36 Å, rolled in spiral with angle of deviation from plane of 17°. The obtained calculation results are in complete agreement with experiments on structure of polytetrafluoroethylene (PTFE);
- the appearance in IR spectrum of PTFE of the bands at 1785 cm⁻¹ and 1885 cm⁻¹ exhibits the presence of -CF=CF₂ and -COF terminal groups in the chain of PTFE, respectively;
- the stretch vibrations of C=C and C=O in the -CF=CF₂ and -COF terminal groups are independent and don't affect on frequencies each of other from seven-fragment molecules on;
- the IR spectra are sensitive to forming of the defects in the oligomer structures resulted by presence of -CF₃ branching groups in the chains. By calculation results, appearance of -CF₃ branching groups in the chain of PTFE results in IR spectrum in the band at 986 cm⁻¹;
- at forming of branches in the chains the sensitive of the frequencies of stretch vibrations of C=C and C=O in the -CF=CF₂ and -COF terminal groups depends on branch place in the chain;
- the chaining configuration of PTFE is more stable then branching one. The difference in energies between the chaining and branching configurations is about 10 kcal/mol. It is a small value. This result shows to possibility of forming of any one of them. The place of radical making by polymer modification determines the place of branch location. The torn loose from chain fragments add to these places.

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THE PECULIARITIES OF THERMAL BEHAVIOUR OF POLYTETRAFLUOROETHYLENES WITH VARIOUS MOLECULAR WEIGHTS

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Ultra-dispersed polytetrafluoroethylene PTFE (trade mark FORUM[®]) prepared by the thermal gas-dynamic method from the products of pyrolysis of fluoroplast F-4 has unusual thermal properties unrepresentative for trade marks of this kinds of the polymers. Such behaviour may be caused by the presence in FORUM's composition some phases with various thermal stabilities that, in turn, may be due to various molecular weights of the macromolecules forming these phases. In order to confirm this suggestion separation of the phases and investigation of their thermal properties are required.

Thermal fractions of the ultra-dispersed polytetrafluoroethylene were prepared by sublimation of FORUM[®] with following condensation of the products in the cooler-receiver. We separated the fraction in the temperature ranges 50-70, 160-180 and at 300°C for our experiments. The previous study of these fractions by the electronic and optic spectroscopy methods indicated to their different morphological structure. The low-temperature fraction consisted of the thin plates. In the powder separated at 160-180°C one could observe multilayer microtubes. The particles of the high-temperature powder were presented as almost calibrated spheres of ~1µm size. It was also shown by the IR spectroscopy method that all the fractions differed by their macromolecules structure. The lines at 1786 and 985 cm⁻¹ were observed in the low-temperature fractions. These lines may be assigned to the presence of CF₃-groups at the ends of the macromolecules and olefins-groups -FC=CF₂. In the high-temperature samples such lines were not observed.

The differential thermal study of the three fractions showed that their temperature properties strongly differed. Thus, the mass loss of the fraction separated at 50-70°C proceed in one stage in the temperature range 60-150°C that indicates to homogeneity of the sample's composition. The differential thermal curve shows endothermic effect with the maximum at 83°C that is related to the fusion of the sample. It means that the thermal decomposition of this fraction proceeds into the melt. In turn, exothermic effect with the maximum at 151°C is related to oxidation of a portion of the products formed.

The sample separated at 160-180°C sublimates in one stage in the temperature range 90-200°C. The type of the thermogravimetric and differential thermogravimetric curves indicates that the mass loss proceeds in one stage. The process is accompanied by wide endothermic effect. Degree of the sample transformation is equal to 99,1%.

The fraction separated at 300°C decomposes in the two stages in the temperature range 90-320°C. Degree of the sample transformation is 100%. The first stage is accompanied by wide endothermic effect (90-225°C). Degree of the sample transformation at this stage is 56%. The second stage proceeds with exothermic effect with the maximum at 267°C that may be explained by oxidation of a portion of the products formed as a result of heating. The more complicated type of the thermogravimetric curve indicates to heterogeneity of this fraction by its molecular weight.

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THE MICROSCOPY STUDY OF FLUOROPOLYMERS

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The different forms of polytetrafluorethylene (PTFE) – monolithic, powder, ultradispersive, fibrous, films- in high- and low molecular states, exposed to radiation, light, mechanical, heat, electron beam – were investigated by electron and scanning probe microscopy. The various forms of PTFE were obtained from monolithic industrial fluoroplastic under certain conditions. The films, isolated from irradiated acetone solution of tetrafluorethylen (TFE) were also studied. All specimens have many-level block structure (see examples - Fig.1., Fig. 2)

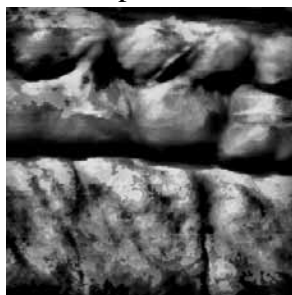


Fig. 1. PTFE fibrous.
1.5×1.5 μm. AFM.

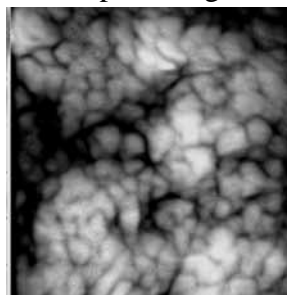


Fig. 2. The films, isolated from irradiated acetone
solution of TFE. 5×5 μm. AFM.

The specimens are different by method of block packing and some from these by macromolecules length. The classification of fluoroplastic materials was proposed.

The composites of UPTFE with the metals were obtained and studied. It was shown that UPTFE forms with metals nanocomposites on level of stirring in one particle of UPTFE.

The films of another (non PTFE) polymers were also studied. The conclusions were made about change of block and porous film structures on nano-level by fluorination. The polymers, for which fluorination most of all changes the surface morphology, were found.

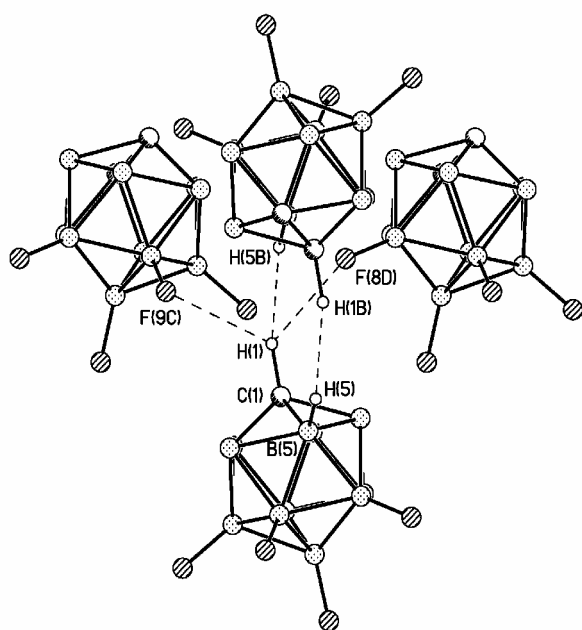
The data obtained were shown the variety of polymer morphology in spite of obtaining method. There are some influences which force TFE or PTFE molecules to collect in nano-films, nano-fibers or nano-particles.

THE COMPETING BETWEEN H...F И H...H INTERACTIONS IN THE CRYSTAL OF 8,9,10,12-TETRAFLUORO-*O*-CARBORANE

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The detailed analysis of the crystal packing of 8,9,10,12-tetrafluoro-*o*-carborane (**TFC**) by the topological analysis of the electron density distribution function was performed and the competing between the F...H and H...H interactions in the crystal was analysed.



The energy of these interactions is in the range of 0.38 - 1.44 kcal/mole with the average value equal to 0.81 kcal/mole. As one could expect from the analysis of the charges, the strongest interaction was found in the case of the hydrogen atom bounded to the carbon atom of the icosahedron (1.44 kcal/mole H...F).

The summation of the energies of all weak interatomic contacts allowed us to obtain the value of the lattice energy for **TFC**, which is equal to 12.95 kcal/mole. This value is slightly lower than the one, found in the case of 1-phenyl-*o*-carborane (**IPOC**) (17.0 kcal/mole) what can be explained by the presence of the phenyl substituent in the latter case, which, in its turn possessing 5 more hydrogen atoms allows the formation of a bigger number of hydrogen bonds. In other words despite the fact

that all H and F-atoms of the **TFC** participate in the formation of the intermolecular H...F interactions their total number is 17 against 25 in **IPOC**.

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MECHANISM OF DIRECT FLUORINATION OF THE FLUORINE CONTAINING POLYMERS.

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Mechanisms of fluorination of fluorine containing polymers and copolymers are discussed. Also, photo destruction of the radicals formed at these processes is considered.

Direct fluorination of polyvinylidene fluoride (PVDF) and the copolymer of tetrafluoroethylene with ethylene (CTE) by molecular fluorine were studied at 35-300 K. The fluorinated polymers were studied by the energy dispersion microscopy (EDAX). According to EDAX data, PVDF has the same content of fluorine before and after fluorination. In contrast, the content of fluorine in CTE increases (~ 2 %) after fluorination. This indicates that only CTE reacts with fluorine under experimental conditions.

Dependencies of the radical formation on temperature and reaction time were obtained by use of electron paramagnetic resonance (EPR) spectroscopy. Primary alkyl radicals formed as a result of the fluorine reaction with a polymer were detected at 35 K. They rapidly react with molecular oxygen producing long-lived (~48 h at 300 K) peroxide radicals. The peroxide radicals when subjected to UV-irradiation ($\lambda < 280$ nm) is decomposed into another radicals which alternation are not stable at $T > 77$ K. Concentration of the radicals produced during fluorination of PVDF at 77-200 K is one order of magnitude less than that of the CTE radicals formed under similar conditions.

Concentration of radicals formed at 77 K during the reaction of CTE with F₂ depends on fluorine pressure and the reaction time. If fluorine pressure increases from 30 torr to 700 torr (F₂ : CTE = 0.15 : 1.0), the radical concentration increases almost 3 times. An increase of the reaction time from 3 to 10 min also leads to the radical concentration increase (2 times). It should be noted that fluorination of CTE granules or films (40 μ m) gives 10 times less radicals than fluorination of highly dispersed co-polymers.

PVDF and CTE polymers have almost similar structures and similar molecular-topological parameters. The ones have only difference, that is, the order of -CH₂- and -CF₂- groups alternation. In PVDF, one -CH₂- group is placed between two -CF₂- groups, and in CTE two -CH₂- groups follow two -CF₂- groups. We have performed quantum-mechanical calculations, which allow to conclude on the mechanisms of these polymers fluorination by way of finding of the structural changes of low molecular analogous of these polymers at fluorination. The structures with a minimal energy for the radicals formed by association of the fluorine and oxygen to above analogous are found.

The mechanism of PVDF and CTE fluorination, most likely, depends on the location of -CH₂- group in the polymer. It has been shown previously that it is necessary to have -CH₂- groups nearby in the polymer chain for successful fluorination of hydrogen-containing polymers.

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KINETIC SPECIFICITIES OF FLUORINATION OF ORGANIC COMPOUNDS*

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Проведен краткий обзор исследований по макро- и микрокинетике газофазных систем фторирования органических соединений с участием F₂ и CF₃OF. Обнаруженные в этих системах закономерности имеют фундаментальное значение для кинетики в целом, и их проявление найдено во многих химических системах другой природы.

Основные из этих закономерностей:

1. Энергетическое разветвление цепей открыто в реакциях фторирования C₁-органических соединений фтором и CF₃OF, но в принципе может являться движущей силой спонтанного протекания в любых системах, где высокая степень химической активации продуктов приводит к размножению радикалов. В случае фторирования, колебательная энергия продуктов RF* высоко экзотермических стадий продолжения цепи типа R+F₂→RF*+F достаточна для их распада на радикалы. Другая возможность реализации химической активации в системах, где R=H, связана с генерацией лазерного излучения.

2. Отрицательное взаимодействие цепей (ОВЦ) по Семенову (рекомбинация не слишком активных в реакциях продолжения цепей радикалов, идущая с образованием относительно стабильных продуктов) может являться причиной квазистационарного протекания разветвленно-цепного процесса. Для реакций с участием CF₃OF такой режим устанавливается при очень низких глубинах конверсии реагентов и сохраняется в течение всего умеренно идущего процесса – за счет квадратичных реакций радикалов: CF₂ и CF₃O*. Анализ кинетических данных по системам с F₂ также показал заметное, хотя и гораздо меньшее, влияние ОВЦ на кинетику процесса. Выяснилось, что ту же природу, благодаря низкой активности пероксидных радикалов, имеет режим медленного окисления углеводородов, воспринимаемый на опыте как период индукции теплового взрыва.

3. В реакциях CF₃OF с галоидметанами ярко проявилась неоднозначная роль кислорода, специально добавляемого в качестве ингибитора или присутствующего как исходная примесь: в недостатке он промотирует процесс, а в избытке – ингибирует. Выяснилось родство этого эффекта с характером влияния кислорода в собственно окислительных процессах и его связь со сложной конфигурацией параметрической области цепного воспламенения системы. Анализ литературы показал, что этот факт часто игнорируется, а условия проведения процесса в относительно стабильном режиме подбираются «вслепую».

Проводится обзор задач, связанных с исследованием механизмов получения фторполимеров, а также природы их реакционной способности и устойчивости к химическим и физическим воздействиям.

Работа выполнена при финансовой поддержке CRDF (the Cooperative Grants Program of the U.S. Civilian Research and Development Foundation) (проект № 15199).

* The authors did not submit an English version.

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ANTI-FRICTIONAL COMPOSITES BASED ON FLUOROPLASTIC MIXTURES

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Today polymer mixtures are becoming extremely promising to serve as binders for anti-frictional materials. To improve structure, mechanical properties and reprocessibility of the materials one can apply combinations of chemically alike polymers, as the closer their chemical nature is the less interface tension and the better their contact in the area of segmental compatibility is, because if chemical interaction between the polymers is possible, it will occur in this very layer.

The presented paper deals with the investigation of the influence induced by fluoroplastic F-4MB on the properties of polymer composite materials (PCM) based on F-4 and magnesium spinel. Application of fluoroplastic F-4 as a modifying agent is conditioned by the fact that it is a co-polymer of tetrafluoroethylene with hexafluorpropylene having a definite amount of adjacent groups of CF_3 . As a rule, co-polymer additives containing rigid and elastic blocks intensify interface adhesion in the interface, which improves the composite's operational properties.

It was shown that after injection of F4MB powder into F-4 fluoroplastic it performs 20-30% improvement in tensile strength, 1.5 to 2 times better ultimate elongation, at the same time wear rate of the composite reduces by 1.5 times. Improvement of strength properties of the composites, especially its ultimate elongation can be explained as follows: F-4MB has less curly and packed spiral conformation due to the adjacent groups of CF_3 , which create defects in the crystal lattice, which reduces rigidity, raises internal mobility and flexibility of the macromolecule chain of F-4. Additional injection of NC into the composition will cause reduction of mass wear by 220 times with preserving other strength characteristics at the level of F-4MB composites. PCM operational properties improving can be explained as follows: injection of F-4-NC polymer into F-4MB causes degradation of the interfacial tension, thermal stresses in the system and intensifies formation of interfacial layers due to its plastifying action. It was shown that F-4 and its compositions with F-4MB wear uniformly under friction conditions, and in case of F-4 with F-4MB and NC adaptation period lasts about 1-1.5 hours, later the tribo-system reaches equilibrium dynamic condition with stable friction characteristics. The very composites perform extremely low friction coefficient and contact temperature, which stems from the fact that the filler particles localize on the friction surface and contribute to reconstruction of the surface layers, which is favorable for the polymer orientation towards friction, thus providing easier sliding.

Therefore, binary fluoroplastic matrix based on the mixture of F-4 and F-4MB can be applied as a binder for anti-frictional composite materials.

INFLUENCE OF SHUNGIT ON POLYTETRAFLUOROETHYLENE PROPERTIES

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The problem of purposeful improvement tribotechnical properties (PTFE), combining excellent frost- and aggressive-resisting properties with low factor of friction remains for today actual. Efficient control its properties is achieved at introduction in PTFE connections nanometric size. However expensive methods of synthesis nanodispersional connections limit their practical application in manufacture of polymeric composite materials (PCM). Search is necessary for creation of profitable manufacture of products from PCM effective fillers on the basis of natural raw material and the new technologies, allowing to transfer natural connections in a highly active condition accessible methods. From among existing technologies on creation new PCM a perspective method of influence on mineral fillers for strengthening of their reactionary ability is mechanical activation. The essence of a method consists in dispersion firm bodies in devices of type planetary mills, thus their translation in a nonequilibrium metastable condition is carried out. Perspectivity of technologies of mechanical activation is connected with low power consumption, ecological safety of process, an opportunity of expansion of a raw-material base.

In work influence shungit on physicommechanical and tribotechnical properties PTFE is investigated. For maintenance of effective interphase interaction on border polymer - filler it is used mechanical activation components of a composite. Activation carried out in a planetary mill firms Fritsch, varying duration and speed of rotation of drums. Thus used as joint (activation of a composite mix), and separate activation of components (activation shungit with the subsequent introduction in a polymeric matrix).

Results of researches show, that under condition of an optimum choice of a mode and reception of activation, mineral additives can become effective modifiers PTFE. Breaking strength at introduction shungit practically was not reduced, and wear resistance in comparison with initial PTFE has increased in 60 times, relative lengthening - in 1,5 times, the module of elasticity - in 2 times.

Thus a result of the lead work perspectivity of use of natural mineral raw material - shungit - is shown as modifier PTFE for development tribotechnical materials, in particular, antifrictional and hermetic purposes. The optimum mode mechanical activation components of a composite for increase tribotechnical characteristics of a material is chosen.

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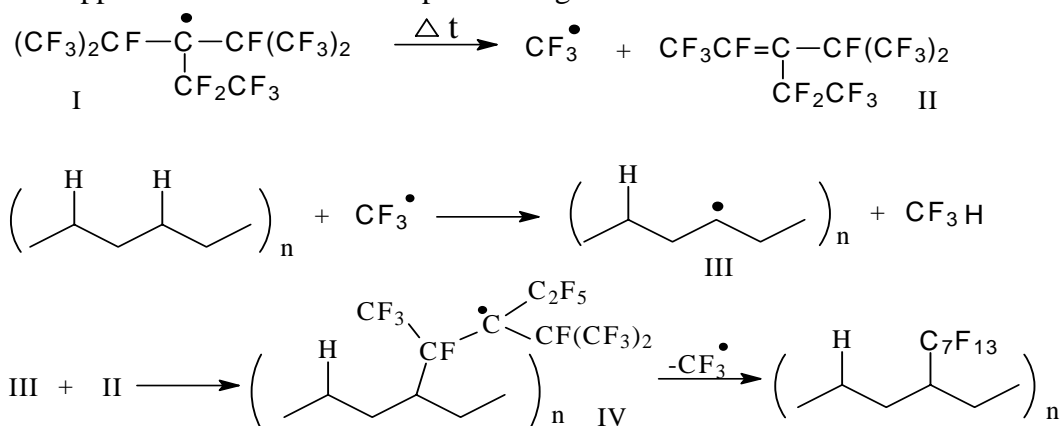
SUPERFICIAL PERFLUOROALKYLATION OF POLYMER MATERIALS

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This work is devoted to a method for modifying polymers and polymer membrane surfaces to decrease their superficial energy, i.e. to impart the more hydrophobic properties to polymer and polymer membrane surfaces without changing the properties of a polymer matrix. Modifying is performed by addition of fluorinated moieties containing trifluoromethyl groups to structure units of a polymer chain. This process is carried out using the stable perfluorinated F-2,4-dimethyl-3-ethyl-3-pentyl radical.³ When polymer materials are treated by a solution of the above radical in an inert solvent at temperature >80°C, perfluoroalkylation of a polymer surface occurs. A supposed mechanism of this process is given below.



As a result, a monolayer is formed on the surface that consists of perfluoroalkyl groups bound with the polymer substrate by covalent C-C bonds. The changes in the properties of the polymers and polymer membrane surfaces were observed. The contact angles of wetting by water and tetradecane for these surfaces have been significantly increased. The X-ray photoelectron spectroscopic analysis of the modified surfaces has shown the presence of an external polymer layer consisting of the fluorinated moieties containing trifluoromethyl groups. Polypropylene, polyethylene, polyethylterephthalate (PETF), polycarbonate, various polysulfones, cellulose derivatives and a number of membranes made of the above polymers have been modified by the proposed technique.

The effect of perfluoroalkylation of the surfaces of PETF films and track membranes (TM) on their chemical stability has been studied. It was shown that

- the contact angles increased from 70 to 95 degrees;
- the alkali solution resistance increased several times.

³Scherer K.V., et al., *JACS*. 1985. **107**, 718-719

HIGHLY CONCENTRATED FLUORINATED EMULSIONS. THEORY AND APPLICATION

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Emulsions with a fluorocarbon (or perfluorocarbon, PFC) phase present interest for their potential biomedical applications. The direct PFC-in-water emulsions are used for in vivo oxygen delivery (blood substitutes) and for diagnosis and therapy, whereas the reverse water-in-PFC emulsions are perspective for encapsulation and sustained release of bioactive substances in cosmetics and medicine.^{1,2,3}

The aim of this presentation is to discuss the colloid aspects of the formulation of reverse highly concentrated emulsions (HCE). These emulsions containing over 90 % of internal water phase, have as continuous phase a swollen micellar L₂ solution of fluorinated surfactants in PFC (Fig. 1). Having the structure of biliquid foams, the HCEs behave as gels manifesting viscoelasticity and plastic (yielding) properties.⁴ Due to higher (with regard to the hydrocarbon surfactants) energy of lateral cohesion in adsorption layers, the fluorinated surfactants lead to higher stability of such emulsions to the phase separation. The cohesion between fluorinated surfactants in the adsorption monolayers may be enhanced by adding multiple OH-groups to the hydrophilic chains of these surfactants.⁵

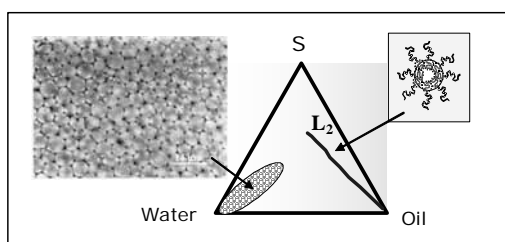


Fig. 1. The region of formation of highly concentrated inverse fluorinated emulsions.

In this work, we have used the complex of physico-chemical methods (SAXS and SANS for characterising the phase diagrams, oscillatory rheology (mechanical scanning), tensiometry of low and ultralow interfacial tension) to study the effect of the molecular structure of the fluorinated surfactants and of physico-chemical parameters on the properties of highly concentrated emulsions (stability to the phase separation, structure formation, efficiency and sustained release of the caffeine). The obtained results have been systematized and explained on the basis of the physico-chemical mechanics of disperse systems, the thermodynamics of microscopic emulsion films, and with the help of the elaborated theory of stability of highly concentrated emulsions.²

⁴ Babak V.G. et al. *Progr. Colloid Polymer Sci.*, 2001, **118**, 216-220.

⁵ Gervits L. L. et al. *Zh. Mendeleev VKhO*. 1985, **30**(6), 578-580.

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SCIENTIFIC BASIS FOR INDUSTRIAL MANUFACTURE OF CHLOROFLUOROCARBONS AND HYDROFLUOROCARBONS BY LIQUID-PHASE METHOD WITH THE SYNTHESIS PRODUCTS RECYCLE

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The ozone layer protection requires the development of full-scale processes for novel transient or non-ozone-depleting fluorinated substances. In order to find a solution of the problem we developed the scientific basis for fluorochemicals full-scale manufacture technologies by liquid-phase methods using computer simulation and the theory of recycle processes.

The liquid-phase method has natural constrains that rule out the possibility to produce some high-fluorinated chemicals. However, we succeeded in expanding the potentialities of the method due to generalization of the results of our studies on as follows:

- impact of the synthesis methods on the structure and activity of the catalysts used in liquid-phase fluorination ¹;
- catalytic activity of hydrogen fluoride applied for a solvent in liquid-phase synthesis ²;
- refinement of the patent information ³ on the catalytic activity of tertiary amines in the reactions of hydrogen fluoride addition to tetrafluoroethylene or hexafluoropropylene;
- development of a general kinetic model for liquid-phase synthesis in the context of the acid-base (electrophilic-nucleophilic) mechanism of catalysis;
- development of some theoretic aspects of recycle processes exemplified by the synthesis of 1,1,1-trifluoroethane, trifluoromethane, and difluoromethane through the development of a general simulator for the synthesis in a capacitive reactor combined with a rectification column; this enables optimization of synthesis and solution of the issues on development and up-scaling with transition to the full-scale integrated reaction unit.

Within the framework of this our approach we developed a continuously-operated laboratory-pilot plant where the reactor was combined with a rectification column. An universal reaction unit is developed that involves the reactor combined with a rectification column so that intermediates are recycled into the reactor by gravity, and a stratification unit intended for hydrogen fluoride separation and recycling by gravity into the reactor ⁴.

¹ Orlov A.P. Abstracts of this conference.

² Orlov A.P. CTAF 97, II Int. Conf., St.Petersburg, 1997. Abstracts P1-24,p.56.

³ Franz R. US Patent 5.969.199 (1999).

⁴Orlov A.P. RF Patent № 2 160 245 (1998).

HOMOGENOUS SYNTHESIS OF FLUORINE-CONTAINING SUBSTANCES CATALISED BY LEWIS ACIDS OR BASES

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Using the results of the study on liquid-phase catalytic synthesis of chlorofluorohydrocarbons and fluorocarbons (methanes and ethanes) for the basis a generalization is made for the mechanisms of catalytic action of Lewis acids and bases on reaction velocities.

The mechanism of the Lewis acids catalytic action is exemplified by the synthesis of difluoromethane (Freon 32) starting with dichloromethane and hydrogen fluoride in the presence of stibium halogenide complexes with hydrogen fluoride.

The mechanism of the Lewis bases catalytic action is exemplified by the addition of hydrogen fluoride to tetrafluoroethylene or hexafluoropropylene in the presence of hydrogen fluoride resulting in pentafluoroethane (Freon 125) or hexafluoropropane (Freon 227ea) formation.

General rules revealed for the complexes' catalytic action may be assigned to acid-base (electrophilic-nucleophilic) catalysis.

It is revealed that the complex catalytic activity grows with its electroconductivity, depending on the complex structure ($\text{SbF}_{5-m}\text{Cl}_m \cdot n\text{HF}$ and $(\text{R})_3\text{N} \cdot n\text{HF}$).

In our studies of the catalytic activity of stibium chlorofluoride complexes we revealed "salt" effect that manifests itself in the uptrend both in the complex catalytic activity and electroconductivity when different salts, e.g., alkali metal fluorides, are added to the initial complex.

The increase in the catalytic complex activity is attended by the unwanted growth of its corrosion action. Our investigation of the relation between the complex structure and its electroconductivity, catalytic action and corrosion activity made it possible to develop technical proposals on the processes realization so that to achieve considerable decrease in the complexes' corrosion effects on construction materials though supporting high rates of the interaction between the reagents.

In our studies on tertiary amines - hydrogen fluoride complexes we established the limit value (that is three) for hydrogen fluoride to amine mole-to-mole ratio that corresponds to the maximal catalytic activity and electric conductivity of the complex.

The methods are developed for kinetic study and kinetic constants calculation using, besides of the analysis data, the results of the reaction mass electroconductivity monitoring over the synthesis process.

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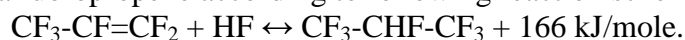
DEVELOPMENT OF HEPTAFLUOROPROPANE SYNTHETIC METHOD

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Heptafluoropropane (CF₃-CHF-CF₃, freon 227ea) is a powerful ozone-non-depleting fire extinguishing agent used instead of ozonedepleting halons - freons 13B1, 12B1, and also apply as a propellant in the medicine.

The main method of heptafluoropropane production is the hydrofluorination of hexafluoropropene according to following reaction scheme:



Gas-phase hydrofluorination of hexafluoropropene possess a number of important advantages as compared with liquid-phase hydrofluorination. Gas-phase hydrofluorination does not require the using of expensive catalysts based on Ta and Nb and long contact time of reaction mixture in the reactor.

Gas-phase hydrofluorination of hexafluoropropene was carried out in fluidized bed of catalyst prepared on the basis of chromium-compounds with using of fluorinated carrier.

The parameters of Arrhenius equation were determined in temperature range 250-325°C: E_a = 73 kJ/mole, lnK₀ = 17,5.

The process was most efficient in the diffusion region at 350-400°C, contact time 7÷20 sec. and molar ratio of the components HF:C₃F₆ = (1÷2):1. In these conditions the conversion of hexafluoropropene was 60-80% with heptafluoropropane selectivity – 97-99%.

DEVELOPMENT OF A METHOD FOR THE SYNTHESIS OF FLUOROMETHANE

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We studied the synthesis of fluoromethane through gas-phase catalyzed hydrofluorination of two raw materials: chloromethane and methanol. Chromium compounds on fluorinated substrate were used for the catalyst.

Our investigation has shown that in the process of chloromethane hydrofluorination even at temperatures exceeding 400°C conversion of chloromethane to fluoromethane was negligible and followed by partial decomposition of the initial raw material.

The reaction constant for chloromethane hydrofluorination is as follows:

$$K = 2.9 \times 10^4 \exp(-E/RT), \text{ m}^3/\text{kmole}\cdot\text{s}$$

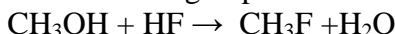
here E is the process activation energy $E=52300 \text{ kJ/kmole}$.

We conducted hydrofluorination of methanol in a nickel reactor with fixed catalyst layer. The catalyst granules were tubes sized: $d=6\div 8\text{mm}$, $h=8\div 12\text{mm}$. The reactor diameter was 0.036m; its height was 1m. The reactor was equipped with a three-section electric heater.

The process was studied at 290÷350°C; the ratio of hydrogen fluoride to methanol was HF: CH₃OH = 2÷3 : 1.

It was shown that at those conditions the conversion of methanol was 40-70%, while the selectivity by fluoromethane exceeded 95%.

When so doing in parallel with the main reaction:



Dehydration of methanol occurs that results in the dimethyl ether formation:



and also methanol conversion to methane by the combined reaction as follows:



The process combines a number of parallel and successive reactions: decomposition of methanol to CO₂ and H₂, water conversion of CO, hydration of CO to methane.

A sample of fluoromethane was produced. Downstream to the reactor the synthesis gas was washed with water and alkali solution, dried with NaA zeolite and condensed into an ampoule cooled with liquid nitrogen. The main impurities in the reaction gas were methane (0.1÷0.5%) and dimethyl ether (up to 1.5%).

Crude fluoromethane contained more than 99% of the main substance. Its further cleaning from acidity and humidity was carried out through adsorption. In order to remove air and residual methane the cylinder was frozen with liquid nitrogen and evacuated. The resulting product contained 99.99% of the main substance.

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PRODUCING OF PERFLUOROETHYLSULFONYL FLUORIDE AND LITHIUM SALT OF PERFLUOROETHYLSULFONIC ACID

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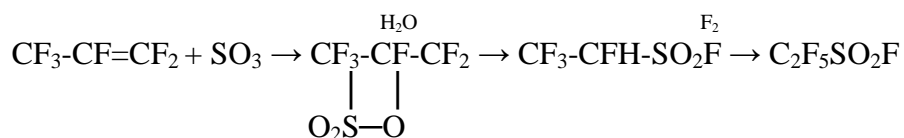
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A process producing of perfluoroethylsulfonyl fluoride (PFESF) and lithium salt of perfluoroethylsulfonic acid by direct fluorination of tetrafluoroethylsulfonyl fluoride formed as a result of hydrolysis of corresponding sultone has been studied:



The process of fluorination is carried out in a tubular reactor at temperature 110–140°C yielding up to 98 %. After purification and distillation PFESF has the purity of 99,95 - 99,99 %. A trial unit for producing PFESF has been set up at OJSC "Halogen".

A process of producing some derivatives of perfluoroethylsulfonic acid, in particular, lithium perfluorosulfonate, has also been studied.



The reaction is carried out at temperature 80-90°C in apparatus with stirrer. After purification the salt contains 99,99 % of the main material.

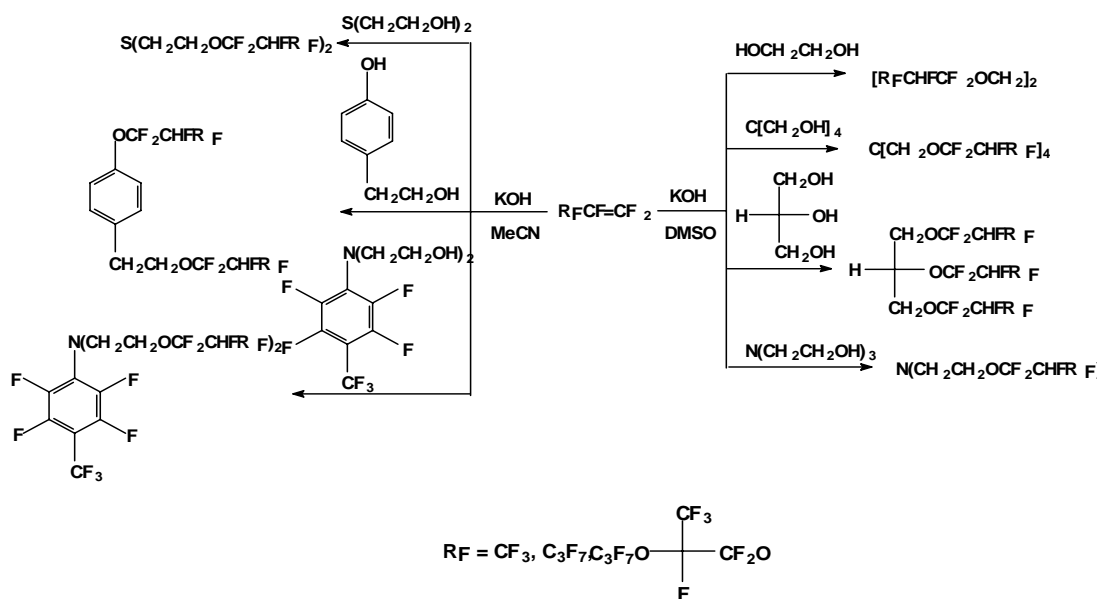
SYNTHESIS AND PROSPECTS OF APPLICATION OF HIGH-TEMPERATURE DIELECTRICS-HEAT-CARRIERS AND LUBRICANTS ON THE BASIS OF PERFLUOROOLEFINS AND MULTINUCLEAR ALIPHATIC ALCOHOLS

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With the purpose of creation of new generation of synthetic nonflammable lubricants, high-temperature dielectrics-heat-carriers and hydraulic liquids prospects of synthesis of such compositions based on interaction perfluoroolefins and multinuclear aliphatic alcohols are investigated. Scientific bases and hardware registration of process of reception in part and completely fluorinated simple dialkyl ethers (direct fluorination F₂ partially fluorinated dialkyl ethers) creations new perfluorinated compounds with high thermal stability and resistance towards oxidants are developed. Are used accessible and industrially let perfluoroolefins and perfluorovinyl ethers, ethyleneglycol, glycerine, pentaerythritol, triethanolamine, etc.



It is established, that greasings on a basis as it is in part and completely fluorinated compounds decrease in friction in kinematic pairs on 30-50 % in comparison with characteristics of the same samples, but working in conditions of dry friction enable. It is revealed, that factor of friction in relative movement of the connected surfaces covered films of them perfluorinated compositions, decreases with increase in speed of relative movement of these surfaces. Perfluorinated dialkyl ethers have been particularly focused on since they are characterized not only by low freezing points, high volatility, improved electrophysical and thermophysical characteristics but also by an excellent lubricating property.

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SYNTHESIS OF MANGANESE TETRAFLUORIDE

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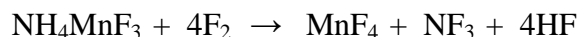
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Manganese tetrafluoride (MnF₄) is of interest due to its powerful oxidative and fluorinating capacities, but nevertheless it still remains an inaccessible compound. At present the world need for this product is small, but the demand for it is growing.

The main methods of synthesis of MnF₄ based on fluorination of two valence manganese (MnF₂, MnCl₂, MnSO₄ and others) and three valence manganese salts by fluorine gas in a fluidized bed of manganese metal powder, requiring high temperatures up to 600°C and high pressures, are inefficient and technologically feasible. The choice of constructional material is a principal matter because of the high chemical aggressivity of fluorine and MnF₄ in gaseous phase. In the well-known methods the synthesis is carried out in nickel reactors or reactors of special-property alloys, which impairs appreciably economic indicators of the process.

In this work the fluorination of a fluorine-ammonium complex, NH₄MnF₃, has been studied to develop an industrial technology for the production of MnF₄. The fluorination process is carried out in two steps: in the first one - at a temperature of 50-70°C, in the second one - at 270-300°C and under a gauge pressure up to 1 kg/cm². The synthesis is effected in an aluminium tubular reactor, in which a tray with fluorine-ammonium complex is placed and fluorine gas is passed.



The developed technology for the fluorination of a fluorine-ammonium complex permits to prepare MnF₄ in a yield up to 90% and use an equipment made of steel or aluminium.

PROCESS FOR PREPARATION OF NITROGEN TRIFLUORIDE

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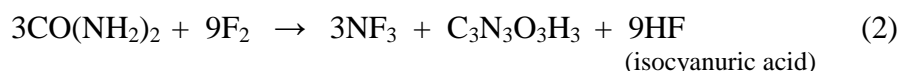
Nitrogen trifluoride has found wide applications in the technologies of semiconducting materials, high-energy lasers and chemical gas-phase deposition, as well as for a fluorinating agent in the technologies of organofluoric compounds. In contrast to elementary fluorine it can easily be transported in a condensed state.

At present the operating industrial technologies are based on a method of the electrolysis of ammonium hydrofluoride melt at a temperature of 100-130°C, at a NH₄F : HF mass ratio of 1:1,1-1,8 and at a current density of 0,05-0,15 A/cm² /1/.

Main drawbacks of the electrochemical synthesis of nitrogen trifluoride are an explosion hazard of the technology and a high corrosivity of the ammonium hydrofluoride melt.

We have developed a high-efficient and safe process for the preparation of nitrogen trifluoride. The method of the nitrogen fluoride synthesis is based on fluorination of a mixture of carbamide and anhydrous hydrogen fluoride by elemental fluorine at a temperature from -20 to 0°C. The content of carbamide in its mixture with anhydrous hydrogen fluoride is 20-50% by weight, which ensures the formation of a solution at operating temperatures. Elemental fluorine with a content of 50-98% F₂ by volume is used for the fluorination.

When carrying out the synthesis in the range of subzero temperatures the reactions (1-2) predominantly proceed, with the reactions (3-4) proceeding slightly.



The process permits to prepare a crude gas containing 40-70 vol.% nitrogen trifluoride and 0,4-2,0 vol.% CF₄ as an impurity. After condensation of nitrogen fluoride followed by purification the product with a content of 99,9-99,99% NF₃ is obtained. The process has been tested under experimental conditions at the plant of a capacity up to 8 t/year with an annual service life of 5000 hours and covered by Russian patent and also patented in the USA, Japan, Korea, China and the EPO countries.

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PROCESS FOR PURIFICATION OF NITROGEN TRIFLUORIDE

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The main field of application of nitrogen trifluoride is the electronic industry, which specifies high requirements for a purity of the product. With a content of the main material being 99,9-99,99% NF_3 , a total content of impurities must not exceed 10-1000 ppm.

The most difficult processing task is a purification of nitrogen fluoride from carbon tetrafluoride, the content of which even in a minor amount causes a serious problem in the etching process of semiconductors because of the formation of solid carbon residues. The difficulty in separating a mixture of NF_3 and CF_4 is due to a negligible difference in their molecular sizes and boiling temperatures, the latter does not exceed 1°.

Currently used processes for the purification of nitrogen trifluoride are labour-consuming, inefficient and expensive. They are based mainly on methods of preparative gas chromatography /1/.

We have developed a process for the purification of nitrogen trifluoride from carbon tetrafluoride, which is realized easily under industrial conditions and characterized by a technological effectiveness and economy. The technology of the fine purification of nitrogen trifluoride is based on adsorption processes on molecular sieves.

A molecular sieve such as erionite with an empirical formula of $(\text{Na,K})_9\text{Al}_9\text{Si}_{27}\text{O}_{72}\cdot 27\text{H}_2\text{O}$ is used for the separation of a mixture of NF_3 and CF_4 . Zeolite is produced on an industrial scale. The sorptive capacity in terms of nitrogen trifluoride is 5-6 g per 100 g of sorbent at room temperature.

The purification process includes the following steps:

- preliminary purification from CO_2 , N_2O , H_2O , NO_2 on zeolite NaA of ball modification;
- selective adsorption of nitrogen trifluoride on erionite KNaE at room temperature;
- removal of (blowoff) carbon tetrafluoride by an inert gas (nitrogen) from the surface of erionite;
- desorption and condensation of the purified nitrogen trifluoride under conditions of the circulation of inert gas in the circuit of adsorption condenser-column at a temperature of -30~-30°C; zeolite in the desorption of NF_3 is not heated, which extends considerably its service life.

The developed process has been tested at the pilot plant with a capacity of 0,72 t of the purified product per year and permits to prepare NF_3 of a purity of 99,9-99,99%, with a content of CF_4 being no more than 10 ppm. The process has been patented in Russia, the USA, Japan, China, Korea and the EPO countries.

¹US Pat. No.3125425 (1991); US Pat. No.5069690 (1991).

GAS CHROMATOGRAPHIC DETERMINATION OF TRACES IN HIGH-PURE NITROGEN TRIFLUORIDE

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The concentration of impurities of electronic grade nitrogen trifluoride must be about 1-10 ppm. For the realization of analysis of nitrogen trifluoride at such trace level, sensitivity of thermal conductor detector, flame ionization detector, thermionic ionization detector and electron capture detector was studied.. Also separating capabilities of activated carbon, porapak Q, polysorb-1, molecular sieve CaA and chromaton AW-HMDS modified with 5% silicon elastomer SE-30 were studied.

Three column separating system shown in the figure 1 below was used..

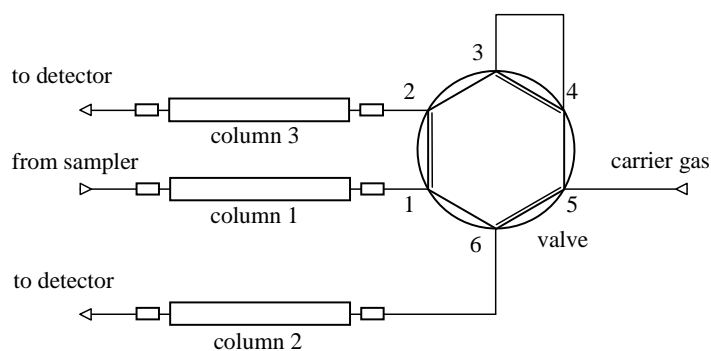


Fig.1. separating system

At first, the sample is passed into the column 1 filled with polysorb-1 where it is separated, and a peak of permanent gases ($N_2 + O_2/Ar + CO$) which elute first passes into the column 3 filled with molecular sieve CaA. Then the valve is switched and other substances pass from column 1 to empty column 2 and then to detector.

Studies of separating capabilities showed that porapak Q and polysorb-1 are the best adsorbents for separating NF_3 -impurity system.

Comparison of sensitivities of detectors gives the result that thermal conductor detector is the best case for determination of all impurities in nitrogen trifluoride in the 1 ppm concentration level.

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PRODUCTION OF HIGH PURITY NITROGEN TRIFLUORIDE

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The modern requirements for chemical products are mainly their low net-cost, production and ecological safety.

Electrochemical synthesis of nitrogen trifluoride allows to get rather pure synthesis-product by the electrolysis of $\text{NH}_4\text{F}\cdot 3\text{HF}$ system on a nickel anode. This method is the most safe and environmental friendly. It allows to produce nitrogen trifluoride with the 70 % current yield. The electrolysis of $\text{NH}_4\text{F}\cdot 3\text{HF}$ system on the nickel anode was studied. The time dependency of concentration of anodic products and the dependency of its concentration were taken off.

It was determined, no impurities emerge at the stage of electrochemical synthesis which are typical with other chemical methods. The synthesis-product was contained from 75 % of the main component, 10 % of both N_2 и N_2F_4 and 5 % of fluoro-, nitrogen- and oxygen-containing impurities.

The estimation of efficiency of different physical-chemical methods of nitrogen trifluoride high purification (up to purity level of microelectronics requirements) was leaded thermodynamically.

It was shown that distilling methods of purification not effective for removal of some impurities from nitrogen trifluoride. The preoxidation stage estimation showed that the products of ammonia partial oxidation oxidize to NFO. But NFO is also the limiting impurity of nitrogen trifluoride. And some impurities which are also irremovable are not oxidizing.

It was proposed to apply a membrane gasseparation for purifying nitrogen trifluoride from the impurities which are irremovable by distillation. The membrane gasseparation is characterized by low energy consumption, simplicity of plant design, purification process realization at ambient temperature, wastelessness and flexibility of production capacity changes.

The values of permeability of impurity components and nitrogen trifluoride were determined. The values of ideal selectivity of nitrogen trifluoride-impurity were calculated. The time dependencies of membrane properties changes i.e. permeability and selectivity were determined on the model gas mixtures of nitrogen trifluoride -impurity.

The possibility of nitrogen trifluoride production with the purity equaled 99,997 % which is required for needs of microelectronics was shown.

FLUOROCARBONS HIGH PURIFICATION BY MEMBRANE GASSEPARATION

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The ability of applying fluorocarbons as reagent for dry etching is connected with its high purity in a process of superscale integration production. Existing distillation purification methods are high energy and money consumption. Therefore lower consumption membrane methods for high purification of fluorocarbons are perspective.

Experimental research of CF₄ (R-14) and C₃F₈ (R-218) high purification by membrane gas separation realized in the radial membrane module with poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane was presented.

It was shown experimentally, that the gasseparation membrane on a base of PTMSP is one of the most permeable membranes for fluorocarbons, but its fluorocarbons selectivity is not high. It was proposed to apply a radial membrane module for increasing the selectivity of the process of fluorocarbons high purification. In order to decrease the influence of longitudinal diffusion on the mass transfer and to increase the separation power the gas flow in the high pressure cavity passes from the periphery to the center.

The selectivity of model gas mixture of CF₄ (R-14) – CHF₃ (R-23) was determined experimentally for optimization of the process of the high purification. The concentration of R-23 was changed in the model gas mixtures from 10 to 0.001 %. The real selectivity (which is equaled to 3.1) was in a good agreement with the ideal selectivity (which is equaled to 3.2). It was determined that the selectivity doesn't depend on the concentration of component in the gas mixture. As a conclusion, it was indicated that the fluorocarbons doesn't change the property of the membrane.

The separation factor of the used radial membrane module was calculated on a base of selectivity. The separation factor is characterized the purification efficiency and in the common case is determined as ratio of the concentrations of impurity component on the inlet and outlet of the membrane module. The influences of gas flows velocity and pressure of the high and low pressure cavities and diffusion on the separation factor were investigated.

The possibility of high purity fluorocarbons production was shown experimentally and theoretically. The PTMSP membrane is provided by high production capacity and the radial membrane module is provided the good selectivity of the process.

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IDENTIFICATION OF IMPURITY STRUCTURE AND THE ANALYSIS OF FLYING FLUORIDES OF TUNGSTEN, NITROGEN AND FREONS 14 AND 218

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Application of fluorides of tungsten, nitrogen and freons 14 and 218 in microelectronics has caused high requirements to their cleanliness. These requirements are accepted by the international gas committee in the form of the SEMI-standard according to which in WF6 the maintenance of impurity O2 is limited, Ar, N2, CO2, CF4, HF, SiF4, SF6, CO at a level 1-20 ppm, and in NF3 - O2, N2, CO2, CF4, N2O, CO, CF4 at a level 1-100 ppm. In freons 14 and 218 maintenance CO2, CO, CxFy, N2, O2, Ar, H2O, SF6, CF2Cl2, CF3H at a level 1-30 ppm is supervised. The specified impurity influence properties of gas, from the point of view of its applicability in microelectronics as they define quality of products. To provide reproduced high quality by manufacture of devices, the reliable quantitative analysis of structure of used gases which allows to supervise their applicability in microelectronics is necessary. The analysis of literary data has shown that the method of a gas chromatography is the highest sensitive, and express.

For revealing genesis impurity structure of fluorides of nitrogen, tungsten and freons 14 and 218 the basic methods of their synthesis have been considered. Impurity structure NF3 which is turning out of as a result most widespread methods: HF, CO, CO2, CF4, N2, N2O, F2, O2, FNO, FNO2, OF2, N2F4, NHF2. The method of direct fluoriding is the most widespread for reception WF6. WF6, received by a method of direct fluoriding can contain following impurity: CF4, CO, CO2, HF, SF6, H2O, CH4, N2, O2. After operation of synthesis freon 14 can have following impurity structure: CO, CO2, N2, O2, H2O, C2F6, F2, C2F3, C2F5H, C2H3F, C2F4, CHF3. Characteristic impurity in freon 218 are CF4, CO, CO2, N2, O2, H2O, C2ClF5, C3F6, CHClF2, CCl2F2.

Concentration of an impurity in tests of fluorides is defined with a method of gas chromatography on chromatograf "Tsvet-800", equipped for work with aggressive substances. Identification of impurity is lead with use of method of chromato-weights-spectroscopy. For realization of gaschromatograf technique of certification NF3, WF6 and freons 14 and 218 on conformity to requirements of the SEMI standard have been investigated dividing ability of columns with porapak Q, HAYESEP Q, chromosorb T and the polychrome modified of 10 % Kel F, polisorb-1 and zeolites CaA, and also sensitivity of detectors heat conductivities (road accident), flame-ionization and constant speed recombination.

As a result of research of dividing ability of columns is established that the most effective sorbent for division of systems on the basis of freons and NF3 is porapak Q or polisorb-1, and for WF6 is the polychrome modified of 10 % Kel F.

For division of impurity in NF3, WF6 and fluorides 14 and 218 is offered to use the multivariate gas chromatography including three columns, the crane-dosator and switching the sixty-course crane.

Thus, quantitative definition of all limited impurity in fluorides of nitrogen and tungsten, freons 14 and 218 at a level 10 ppm is realized.

X-RAY INVESTIGATION OF Nd_{1-x}Te_x(O,F)₂ SOLID SOLUTIONS

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One of the important problems of solid state chemistry and material science is the investigation of interrelation: composition - structure – physical properties for anionconductive fluorite-like solid solutions. Earlier it has been shown, that structural distortions of fluorite-like matrix by introduction in this structure heterovalent ions, lead to formation of the complex defective structure, increasing ionic conductivity. We can suppose, that similar processes will take place in MOF fluorite-like phases (M = REE, Bi) from replacement of M (III) metals with M (IV). Thus as the object of our research the NdOF - TeO₂ system had been chosen. NdOF has fluorite-type hexagonal unit cell which can transform into cubic unit cell when heated above 525°C (but cannot be quenched) or from various defect formation in structure when doped. Tellurium is chosen as the element which has active lone pair, bringing additional distortions in structure and greatly influencing anionconductive properties.

The aim of the present work is synthesis and x-ray investigation of fluorite-like solid solutions in the NdOF – TeO₂ system.

Conditions of synthesis: starting materials - NdOF and TeO₂. During development of the synthesis technique various container materials have been used, temperature and time of annealing were varied over a wide range, modes of initial heating of the start mixes and of cooling. We have found optimum conditions of annealing process: annealing mixes in platinum crucible in vacuumized quartz ampoules at 900°C 60 hours followed with ampoules quenching in icy water. Only such process has allowed to avoid reduction processes of tellurium and oxyfluoride pyrohydrolysis, and also to receive equilibrium samples.

The obtained samples were diagnosed by x-ray powder method. In the system formation of three fluorite-like solid solutions was established, between which are two- phase areas. Phase 1 is a solid solution close to NdOF, it is possible to assume that in this case there is a stabilization of high-temperature cubic NdOF phase, parameters of a unit cell vary within the 5.636-5.56 (2) range. Phase 2 is Nd_{1-x}Te_xO_{1+x}F_{1-x} solid solution (0.33 <x <0.37), parameters of the fluorite subcell vary within the 5.6677 (6) - 5.7073 (7) range. Phase 3 is a solid solution with high quantity of TeO₂, exact borders of this solid solution have not been established yet, the parameter of a fluorite subcell is 5.62 (1) was found for the sample x=0,40 from the 2 phase area x=0,37-0,75.

The work was done under financial support of the RFFI (project №05-03-32719).

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THE SYNTHESIS OF SPECIAL PURITY ZIRCONIUM AND HAFNIUM TETRAFLUORIDES

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By the united laboratory «Fluoride processes and materials» of SSTA and Borekov Institute of Catalysis for three years the chemico-technological model of ZrF_4 , HfF_4 synthesis is created. The model consists of thermodynamic, kinetic data and suggested sublimation purification mechanism. That makes it useful for scientists and engineers.

There are great experimental and technological problems in high pure fluorides obtaining because purification process undergoes high temperatures and influence of aggressive environment. It is important to select construction materials and purification conditions which provide necessary purification degree.

The physical values obtained by calculating of thermodynamic model are assumed for separate purification stages investigation. In the experimental part of model there is kinetic and macrokinetic behavior of sublimation purification. So in the macrokinetic studying we have considered all the three stages of sublimation and desublimation processes:

1. reversible reaction on the crystal surface;
2. transport of gaseous reaction products formed inside the layer, to the surface — inside diffusion;
3. transport of gaseous reaction products from the layer surface to gas flow core — outside diffusion.

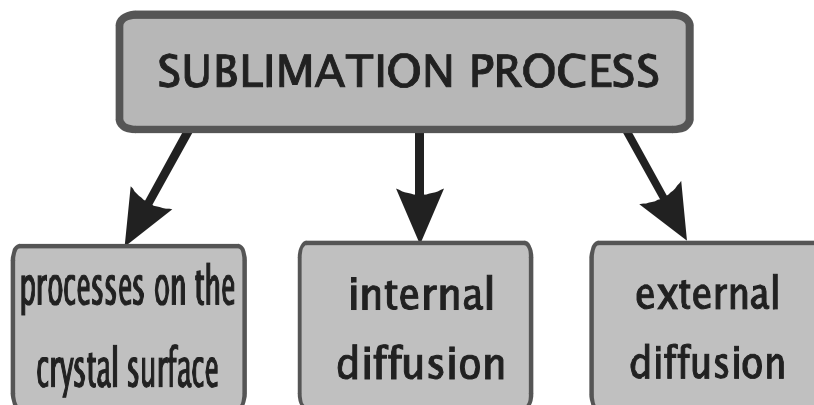


Fig. 1. The three stages of sublimation and desublimation processes

We are investigating a physico-chemical model of sublimation-desublimation process to determine effective ways of sublimation fluorides purification. In the future we plan to make a mathematical model based on this physico-chemical model.

The research was supported financially by Rosatom (Projects No. 3.08-19, 4.08-32).

EFFECT OF "FLOROXAN" ON COTTON-PLANT*

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В Республике Узбекистан культура хлопчатника занимает основные площади посевов. Для стабильного получения урожая хлопка-сырца требуется не только внесение минеральных удобрений, ядохимикатов и внедрение интенсивных болезнеустойчивых высокоурожайных сортов, но и применение регуляторов роста, экологически безопасных и нетоксичных по отношению к человеку и животным. Целью настоящей работы явилось изучение воздействия на хлопчатник фторсодержащего регулятора роста растений – Флороксана.

С целью выявления стимулирующей активности Флороксан испытывался в лабораторных условиях в интервале концентраций раствора $1 \cdot 10^{-1}$ – $1 \cdot 10^{-6}$ %. Биотестом служили семена хлопчатника (сорт С-6524), различные органы проростков и каллусная ткань из гипокотилей хлопчатника. В полевых условиях изучалось влияние препарата на рост, развитие растений хлопчатника и урожайность. Способ обработки – замочка семян перед посевом и опрыскивание в фазу бутонизации.

Так, предпосевная замочка семян хлопчатника в растворе Флороксана в концентрациях 0,001; 0,01 и 0,1% оказывает стимулирующее действие на энергию прорастания и всхожести семян. Оптимальным для прорастания семян хлопчатника оказался 0,1% раствор препарата. При этом энергия прорастания повышалась на 22%, всхожесть семян – на 19% по сравнению с контролем. Фенологические наблюдения, проводимые в течение всего периода вегетации, показали: растения хлопчатника в вариантах с Флороксаном превосходили в развитии растения контрольного варианта. Так, рост главного стебля был на 9,4 см выше контрольного, количество коробочек на кусте увеличивалось на 1,8 штук, площадь листовой поверхности одного растения к концу вегетации – на 292 см², при этом содержание хлорофилла возросло до 40%. Следует отметить, что усиление биосинтеза зеленых пигментов носит недолговременный характер, так как с вступлением в фазу массовой бутонизации хлопчатника количество зеленых пигментов выравнивается с уровнем контроля. Ускорение ростовых процессов, повышение содержания хлорофилла и площади листьев хлопчатника под воздействием Флороксана привели к тому, что цветение и созревание хлопчатника опережает контрольный вариант на 2-3 дня и дает достоверную прибавку урожая на 2,3 ц/га (замочка семян перед посевом) и 2,6 ц/га (при опрыскивании в фазу бутонизации), по сравнению с контролем. Следует отметить, что Флороксан против возбудителя листового гоммоза и корневой гнили неэффективен, так как поражаемость проростков остается на уровне контроля.

Чтобы понять природу регуляторного действия Флороксана, мы попытались изучить характер и уровень действия его в отношении природных фитогормонов. Испытания препарата на ауксиновую, цитокининовую и гиббереллиновую активности не дали положительного результата, что говорит об ином механизме действия препарата Флороксан.

Таким образом, можно предположить, что одним из принципиально возможных путей сохранения плодоорганов и повышения урожайности у хлопчатника может быть регуляция плодоношения путем воздействия регуляторами роста типа Флороксан.

* The authors did not submit an English version.

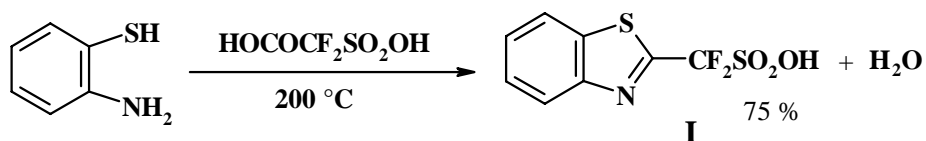
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(BENZOTHAZOL-2-YL)DIFLUOROMETHANESULFONIC ACID

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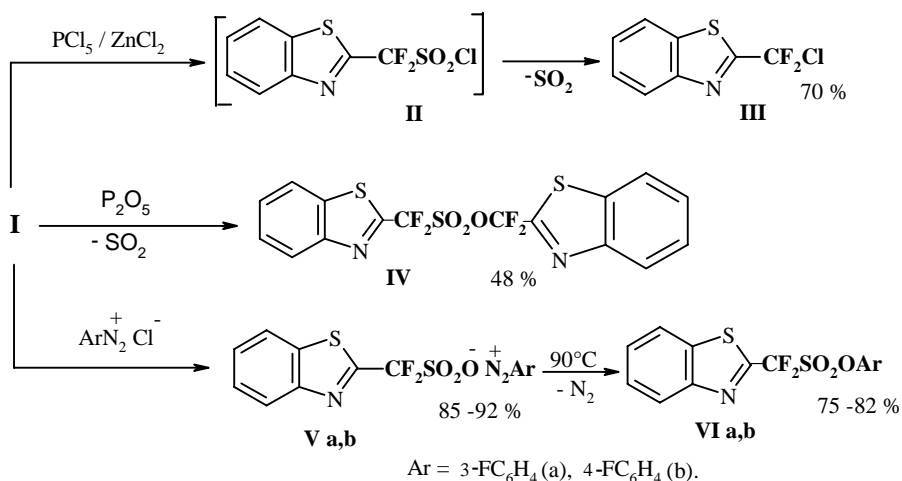
The method of synthesis of unknown (benzothiazol-2-yl)difluoromethanesulfonic acid (I) from accessible $\text{HOCOFC}_2\text{SO}_2\text{OH}$ ¹ and o-aminothiophenole was elaborated.



Interaction of sulfonic acid (I) with $\text{PCl}_5/\text{ZnCl}_2$ led to formation of 2-(chlorodifluoromethyl)benzothiazole (III) instead of expected (benzothiazol-2-yl)difluoromethanesulfonylchloride (II). The reaction of sulfonic acid (I) with P_2O_5 afforded 2-benzothiazolyldifluoromethyl ester of (benzothiazol-2-yl)difluoromethanesulfonic acid (IV).

Individual aryldiazonium salts of (benzothiazol-2-yl)difluoromethanesulfonic acid (Va,b) converts into aryl esters of (benzothiazol-2-yl)difluoromethanesulfonic acid (VIa,b) under heating at 90 °C.

σ_I - and σ_R -constants of (benzothiazol-2-yl)difluoromethanesulfonyloxy group have been determined by the ^{19}F NMR spectroscopy.



¹ Sokol'sky G. A. *et al. Izv. AN SSSR, Ser. Khim.* 1967 (6), 1289-1294.

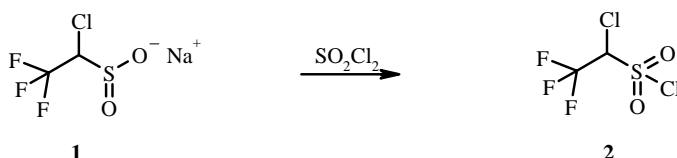
1-CHLORO-2,2,2-TRIFLUOROETHANESULFONYL CHLORIDE

Yu. M. Pustovit, A. N. Alexeenko, N. D. Volkov

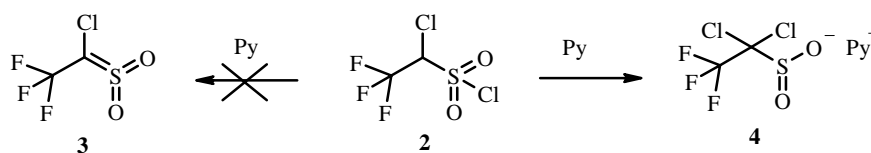
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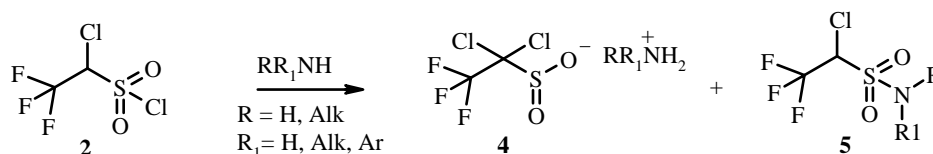
A convenient method for preparation of 1-chloro-2,2,2-trifluoroethanesulfonyl chloride **2** from available^{1a,b} sodium 1-chloro-2,2,2-trifluoroethanesulfinate **1** was developed.



In contrast to previously described² 1,2,2,2-tetrafluoroethanesulfonyl fluoride, sulfonyl chloride **2** in the reaction with pyridine doesn't afford the corresponding sulfene **3**, but yields stable salt 1,1-dichloro-2,2,2-trifluoroethanesulfonic acid **4**.



In aminolysis of sulfonyl chloride **2**, the lower the basicity of primary and secondary amines, the higher the yields of sulfonyl amides **5**.



^{1a} Huang W.Y. *et. al. Acta Chim. Sin.* 1987, **45**(5), 445-449.

^{1b} Dmowski W. *et. al. J. Fluorine Chem.* 2005, **126**, 877-882.

² Ragulin L.I. *et. al. Izv. Akad. Nauk SSSR, Ser. Khim.* 1971 (5), 1045-1049.

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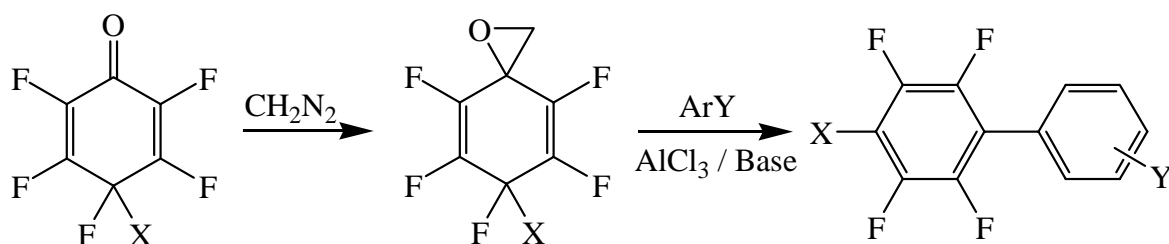
POLIFLUORINATED CYCLOHEXADIENESPIROOXIRANES AS ARYLATED AGENTS

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Fluorinated cyclohexadienones have been shown to be versatile building blocks for the preparation of complex organofluorine compounds. We have shown early that polyfluorinated cyclohexa-2,5-dienones **1a-c**, in contrast to corresponding nonfluorinated cyclohexadienones, reacted with diazomethane at the carbonyl group forming polyfluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2a-c** with good yields¹. Now we have investigated the reactions of these cyclohexadienspirooxiranes with aromatic compounds in the presence of AlCl₃ and obtained the polyfluorinated biaryls. However, the 6-nitro-4,5,6,7,8-pentafluoro-1-oxaspiro[2.5]octa-4,7-diene loses the nitro group with formation of biphenyls **3-6**, being convenient pentafluoroarylated agent. At the same time, oxiranes **2b,c** with such substituent X in 6 position, as OC₆F₅ and Cl, preserve these substituents in the products of reaction biphenyls **7-9**.



1a X = NO₂

2a

3 X = F, Y = H

4 X = F, Y = 2,4,6-CH₃

5 X = F, Y = CH₃

6 X = F, Y = Cl

1b X = OC₆F₅

2b

7 X = OC₆F₅, Y = H

8 X = OC₆F₅, Y = CH₃

1c X = Cl

2c

9 X = Cl, Y = CH₃

Using the bases (pyridine and picoline), it is possible to increase the yields of polyfluorinated biaryls from 20-40% to 45-60%. The ratio of isomeric biphenyls, formed in these reactions, can be indicated, probably, on an electrophilic process.

¹Kovtonyuk V.N. *et al. Eur. J. Org. Chem.* 2005, 1178-1183

SYNTHESIS AND REACTIVITY OF COMPLEX FLUORIDES OF NON-TRANSITION ELEMENTS

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Although complex compounds of transition elements do not belong to number of traditional ones, when the formation of inner coordination sphere with the participation of fluoride ions takes place, in many cases they manifest high thermodynamic and kinetic stability. A lot of compounds of this type have found wide application in a number of important engineering branches¹. In recent years they are used in production of advanced energy converters and accumulators – lithium batteries and supercapacitors². In these cases the quality of output products must meet the high standards, so far as in the mentioned articles they are in contact with reactive compounds for a long period, sometimes for 10-20 years.

The initial foundations for synthesis of complex fluorides of non-transition elements were laid as early as the middle of the last century^{3,4}. In our papers this studies have found further development, some methods are advanced at the level of industrial technologies. The main conception of our developments is the orientation on low-temperature liquid-phase processes running in liquid solvent systems, sometimes in aqueous solutions. In doing so, we use widely the methods of mathematical simulation of complex multi-component systems and identification of their composition by the methods of "Computer Chemistry". The detailed analysis of various factors affecting the system composition enables us to conduct choosing the rational synthesis conditions from the standpoint of product output and purity as well as the minimization of effect of processes upon the environment.

The reactivity of fluorine-acid complexes is governed by the strength of bonds between central atoms and fluoride ion, the composition and properties of reaction medium as well as by the availability of complex-former orbitals for an attack of nucleophilic reagents specifying the mechanism of process. For example, increasing the serial number of a central atom within a period leads to strengthening the acceptability of corresponding Lewis acids and growing the inertness of substitution of fluoride ions by dissociative mechanism. For complexes of the same charge the tendency to realization of associative mechanism grows with the increase of period number resulting in extremum character of the dependence of reactivity parameters (energies and entropies of activation).

The work is performed under the financial support of Deutsche Forschungsgemeinschaft.

¹Isikawa N. *New in Technology of Fluorine Compounds*, 1984, Moscow, Mir Publishing House, 592 p.

²Nasri A. *Lithium Batteries, Science and Technology*, 2004, Kluwer Academic Publishers, 708 p.;

³Ryss I. G. *Chemistry of Fluorine and Its Inorganic Compounds*, 1956, Moscow, Goskhimizdat Publishing House, 718 p.

⁴Schmutzler R. *Fluorides of Phosphorus, Advances Fluorine Chem.*, 1965, **5**, 134-245.

P-150

A NEW HYDROFLUORIDE FLUOROCOMPLEXES OF ZIRCONIUM AND HAFNIUM WITH HETEROATOMIC CATION SUBLATTICE

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The conditions of synthesis are developed and series of new hydrofluoride fluorocomplexes of Zr and Hf with heteroatomic cation sublattice $MM'_4A_3F_{17} \cdot nHF$ ($M = Li, Na; M' = NH_4, Rb, Cs; A = Zr, Hf; n = 1, 2$) is obtained. Hydrofluoride fluorocomplexes of Zr and Hf crystallize from the solution of HF - acid, containing the fluorides of alkali metals, ammonium and zirconium and hafnium oxides with molar ratio 1: 4: 3 according to their compositions. It was stated that all the synthesized compounds were crystallized in monoclinic symmetry and their unit cell parameters were determined. The crystal structures $LiCs_4Zr_3F_{17} \cdot HF$ (I), $LiRb_4Zr_3F_{17} \cdot 2HF$ (II), $NaCs_4Hf_3F_{17} \cdot 2HF$ (III), $Li(NH_4)_4Zr_3F_{17} \cdot 2HF$ (IV) and $Na(NH_4)_4Zr_3F_{17} \cdot 2HF$ (V) were studied. The structures of all five compounds have layer character. The base of layer of the crystals I – V is formed by infinite chains where there are trinuclear fragment consisting of $A(1)F_7 - A(2)F_8 - A(3)F_7$ - polyhedra. Interior to trinuclear fragment coordination polyhedra are united through common edges and between each other through common vertexes. In the structure Li^+ - and Na^+ - cations unite fluoride chains to the layers. In II – V Li - and Na - atoms are surrounded by F - atoms through vertexes of octahedral were the F - atoms of HF - molecules are in axial positions. In the compound I the coordination polyhedron of Li - atom is the distortion square pyramid the base of which is made up of two F - atoms belonging to $Zr(1)$ and $Zr(3)$ polyhedra from different chains, and F - atom of HF - molecule is the vertex of this pyramid. HF - molecules bond the layers of composition $[MA_3F_{17} \cdot nHF]^{4-}_{\infty}$ by strong hydrogen $F - H \dots F$ bonds. Rb^+, Cs^+ and NH_4^+ cations complete the union of the structures to three - dimensional framework.

The IR - absorption spectra ($4000 - 350 \text{ cm}^{-1}$) of the fluorocomplexes synthesized were measured and interpreted. The effect of outer - sphere cation and cation of complexformer on strength of hydrogen $F - H \dots F$ bonds is discussed.

Character of internal movement of ion and molecular groups in the compounds synthesized at the temperature range $170 - 420\text{K}$ was studied by NMR ($^1H, ^{19}F$) method. Modes of movements of the complex ions were determined and the energies of their activations were estimated.

Thermal behaviour of the hydrofluoride fluorocomplexes was studied. It was stated, that dehydrofluorination proceeds at the temperature range $120-270^\circ\text{C}$, which results in decomposition of the substance and formation the fluorocomplexes of zirconium and hafnium with monocation sublattice. Thermolysis of ammonium containing fluorocomplexes after dehydrofluorination proceeds in common circuit.

X-RAY QUANTITATIVE DETERMINATION OF THE POLYTETRAFLUOROETHYLENE PHASE COMPOSITION

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A wide angle X-Ray diffraction study of ultra-dispersed polytetrafluoroethylene (PTFE) was investigated. In all specimens a new amorphous phase was found with scattering localized at 20~40° (CuK_α-radiation). To calculate scatter ability of each phase the Hermans-Weidinger improve approach was applied. For the first time regressive lines for PTFE were received, that allowed to compute scatter coefficients of amorphous phases per crystalline phase. The scatter coefficient of amorphous phase with halo localized at 20~18° was found as 0.69, while the scatter coefficient of amorphous phase with halo localized at 20~40° was 1.46. The X-ray quantitative phase analysis was carried out. For the first time for amorphous component of PTFE with scattering localized at 20~40°, the structure identification was carried out (fig. 1).

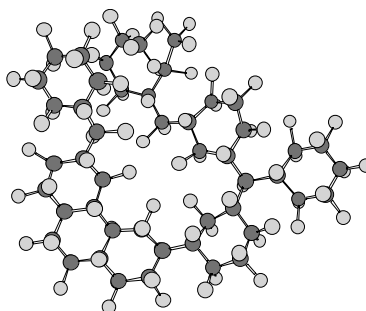


Fig. 1. The structure of amorphous component of PTFE with X-ray scattering localized at 20~40°

The lattice types and parameters of patterns were defined. For cubic lattice type the following parameters were found: $a=0.6961$ nm, $V=0.33736$ nm³ (Forum-1). For monoclinic lattice type: $a=0.5213$ nm, $b=0.4395$ nm, $c=0.3930$ nm, $\beta=108.98^\circ$, $V=0.08514$ nm³; $a=0.5691$ nm, $b=0.4376$ nm, $c=0.2816$ nm, $\beta=119.16^\circ$, $V=0.06124$ nm³ (Forum-2); $a=2.5102$ nm, $b=1.2464$ nm, $c=0.5712$ nm, $\beta=96.23^\circ$, $V=1.7764$ nm³ (PTFE destruction products). This data was compared with technical Teflon (monoclinic lattice type): $a=0.5632$ nm, $b=0.3460$ nm, $c=0.5611$ nm, $\beta=119.59^\circ$, $V=0.09508$ nm³.

The research was supported financially by Russian Foundation for Basic Research (Project No. 05-03-32088).