Journal "Fluorine Notes", Volume # 3(52), May - June 2007

ADDITIONAL FLUORINATION OF PARTLY FLUORINAT ORGANIC COMPOUNDS BY ELEMENTAL FLUORINE AN OBTAINING METHOD FOR PRACTICAL PURPOS FLUORINE MATERIALS

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(continuation)

2. Perfluorinated Organic Compounds Purification

Data listed above allowed us to draw an assumption, that such an approach can be succes deep purification of perfluorinated compounds ("crude materials") obtained using ECF me fluorination method. All known methods are based on destruction of hydrogen containing adr take into account that their content in the reaction mixtures reaches 30%, then these me recognized as wholly satisfactory. Another approach for purification of PFOC (perfluori compounds) is in additional fluorination of hydrogen containing admixtures. This approach implementation allows increasing of yield of PFOC, lowering of waste products, simplifying t and as a result decreasing the cost of target products.

The known method of purification is in high concentration aqua alkali (85-90%) treatment at This method has a number of essential disadvantages, which hampers its application in produc among them are: a need of working under pressure of 13-15 bar, high melting point of high alkali and a related to that danger of blocking armature and communications, and also a ne special alloys for reactor making, as common stainless steel are up to corrosive cracking [58 [59], that water displacement by more major solvents (amines or alcohols) allows decreasing decomposition temperature to 60-80 ^{o}C and working without excessive pressure. We used solutions of KOH, which dissolve forming KF well, for our work.

The process was carried out in the apparatus equipped with stirrer, dosing the crude mate alcohol alkali (1:1:1) accompanied by 14 hour ageing at 60-80^{o}C and further rectification. Proc using such method are characterized as "technical" and their warranty storage period is 6 simplicity of apparatus, the method has been implemented commercially, though it is charact amount of waste. Polyfluorinated compounds practically do not react with gaseous fluorine Above this point we can observe burning, and sometimes explosions. Low molecular polyfluori and soot are the main products of this reaction. Fluorinating using catalysts that is iron, c manganese and nickel fluorides, proved to be more successful. At Fig.2 we can find the i catalytic fluorination of the "crude material", obtained by electrochemical fluorination of tributyla

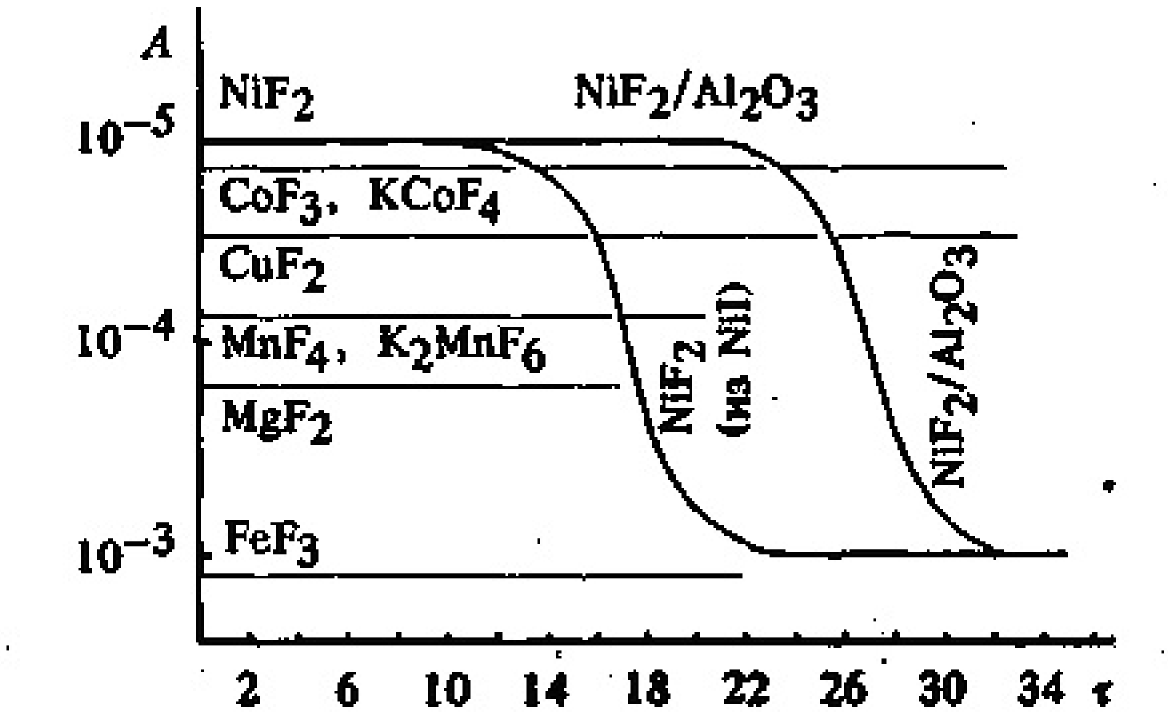


Fig.2. *Catalytic Fluorination of Hydrogen Containing Admixtures of the Perfluorotributy. material" (Temperature 420 ^{o}C, contact period 13 min., A - amount of ion-fluoride bound (process period (h))*

We can see, that fluorination is going in a time gap, at that depending on the nature c fluorination goes with different depth (it was controlled according to the amount of ion-fl Hydrogen containing admixtures fluorination goes at a most full grade when using nickel difluo its activity drops sharply in a few hours time. Cobalt trifluoride properties are close to nicke catalytic activity lasts much longer and is in between the lap of 200 and 350 hours. In Table 1 the results of fluorination using CoF_3 of some of the "crude material", obtained at electrochemi

Table 10. *Parameters of Different "Crude Material" Elemental Fluorine Fluorination Processes*

"Crude Material"	***T(^{o}C)***		***Fluorine consumption (mole/mole)***	***Contact Time (min.)***	***"Crude Material" conte (after) fluorination***		
	vaporizer	***reactor***			***Low-boiling products***	***Target product***	***Hydroge containi products***
C_5F_{10}	60	230-280	3.3	5	4.5 (6.5)	82.5 (93.5)	13.0 (0
$(C_2F_5)_3N$	90	270-330	4.0	5	15.5 (19.4)	74.0 (80.6)	10.5 (0
$(C_3F_7)_3N$	140	320-380	4.9	10	18.4 (24.3)	64.6 (75.7)	17.0 (0
$(C_4F_9)_3n$	200	350-400	6.0	13	23.5 (32.9)	56.5 (67.1)	20.0 (0
$(C_5F_{11})_3N$	250	380-420	5.9	16	34.4 (43.4)	48.6 (56.6)	17.0 (0
$(C_4F_9)_2O$	110	300-350	2.8	6	6.4 (8.2)	83.5 (91.8)	10.1 (0

According to this method we managed to obtain samples of perfluorinated compounds (fluoride equal to (1-3) * 10^{-5} mole/l) which are not absorbed in the area of 200 - 320 nm. Suc be qualified as "pure", their guaranteed shelf life is 20 years and they can be used in techniqu of medical preparations and materials. In Table 11 one can find the characteristic of commer perfluorinated compounds, obtained by additional fluorination of "Crude Material" using eler direct fluorination using cobalt trifluoride as catalyst.

Table 11. *Perfluorinated Dielectrics-Heat-Transfers (PFDT) Developed at Federal State Unit RSC "Applied Chemistry"*

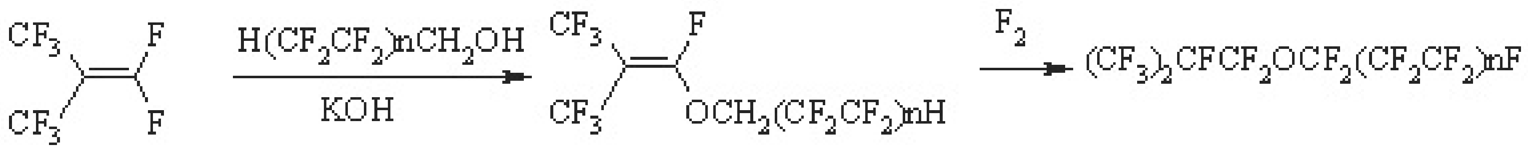
Technical Name	***Main Compound***	***Boiling Point, °C***	***Melting Point, °C***	***d_4^{20}, kg/m³***	***Specific Volume Resistance Ohm*m (20 °C)***	***El Stre KV/***
PFDT-30	C_5F_{12}	25-35	-125	1660	-	-
PFDT-50	$CF_3(C_2F_5)_2N$	45-50	-163	1670	$1.5 \cdot 10^{13}$	3C
PFDT-70	$(C_2F_5)_3N$	65-71	-145	1750	$5.0 \cdot 10^{13}$	3C
PFDT-100	$(C_4F_9)_2O$	98-102	-70	1730	$4.0 \cdot 10^{13}$	46
PFDT-130	$(C_3F_7)_3N$	125-132	-65	1840	$3.0 \cdot 10^{14}$	44
PFDT-180	$(C_4F_9)_3N$	178-185	-55	1890	$4.8 \cdot 10^{14}$	4C
PFDT-205	$(C_5F_{11})_3N$	195-205	about -50	about 1900	-	4C
PFDT-240	$(C_6F_{13})_3N$	235-245	about -50	about 1950	-	-

In our opinion, the major advantage of this approach is the fact, that admixtures do not sep main product, and on the contrary, they transform into useful perfluorinated components, wh not decrease the quality' target product, but also become suitable for use of compositio perfluorinated compounds, they also significantly increase the efficiency of fluorine use. Th waste, which utilization is a very challenging and complicated task, is very important as wel becoming possible to replace the rectification with distillation, that also simplifies the technolog the cost of it.

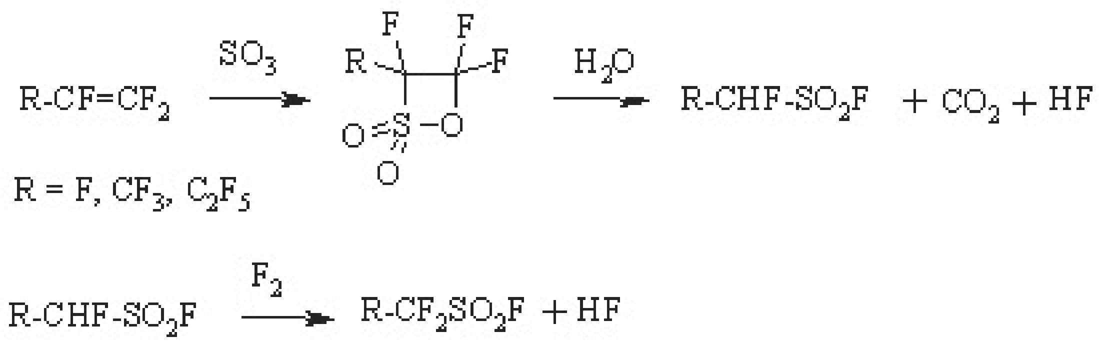
3. Fluorine Containing Semi-Products Synthesis fro Creating of New Generation o and Dielectrics

The semi-products of fluororganic synthesis are of interest of production of new materials such products themselves can find their application, but the base consists of fully fluorinate Here we shall draw a purification of emissions of plants producing fluororganic compounds prod a rule contain high toxic agents, for example, perfluoroisobutylene, as an example. At this d see its transformation into effective liquid dielectric by additional fluorination using elemental flu

Additional fluorination can be carried out using electrochemical fluorination method for compo $(CF_3)_2CHCF_2OC_nF_{2n+1}$ (n= 1-4) [60]. This compound is used as solvent for purificatior systems, chlorine agents, frothers etc.



The second example refers to obtaining of perfluoroalkansulfofluoride, a key semi-product f electrolytes based on lithium bis(perfluoroalkylsulfonylfluoride)imide salt. Here we used obtain cycle opening, decarboxylation and additional elemental fluorine fluorination [61]. Elem fluorination is carried out at temperature ranging from 0 to 30 ^oC, the process goes free f forming of destructive fluorination products with the target product yield reaching 97.5 mass.%



Along with polyfluorinated alkansulfofluorides we have studied the fluorination of alkanesulf yield of perfluoroalkanesulfofluorides is 90% for CH_3SO_2F and 82 % for $C_2F_5SO_2F$. Obtaini perfluoroalkanesulfofluorides provides high yield for target product when using standarc techniques and available raw materials, that gives us an opportunity to implement it on an i Unlike ECF this method provides for period stability of the process and makes the energy cos lower.

4. Production of Ozone-Friendly Chladones

Hexafluoroethane obtaining methods are mainly based on power-consuming processes (pyr CF_2=CF_2). Here we offer hexafluoroethane obtaining method out of tetrafluoroethylene by eler fluorination in the medium of inert solvent [27,62]. Fluorination is carried out in th perfluorocarbon liquid, containing 8-11 (mass.)% of stable perfluoromethyl-2-pentafluoroeth radical at 50-60 ^oC and fluorine : tetrafluoroethylene ratio = 1:1 - 1.1 mole. This approa developing the obtaining method of octafluoropropane by fluorination of hexafluoropropene fluorine influencing hexafluoropropene at temperature ranging from -10 - to +30 ^oC in tl fluorocarbon liquid (perfluorolefines of composition of $(CF_3)_2CFCR^1$=CR^2CF_3, where R^1 = F, C R^2 = F, CF_3, $CF_2CF_2CF_2CF_3$ or linear perfluorinated aliphatic compounds of $CF_3(CF_2)$CF com where n = 5 - 10), containing 3-8 (mass.)%, stable 1,1,3,3-tetraperf pentafluoroethyldifluoropropyl radical [62]. Due to high thermal effect the reaction of direct hexafluoropropene (-658 KJ/mole) was carried out in the liquid perfluorocarbon medium ins designed reactor with combined mixing device. It is stated, that during fluorination of hexafl stable radical is formed, stable at 20 ^oC during one-year storage. The developed octafluoroprop -218, R-218) obtaining method is characterized by as much as five times higher relative pro actual commercial method for gas-cycle fluorination at CoF_3 [28, 63]. The selectivity by hexa amounts to 96-99 %. The method has been implemented at pilot (experimental-industrial) with 200 dm^3 reactor. Low-waste, focused at large-tonnage production gas-cycle elem fluorination technology of hexafluoropropene has been developed. R-218 is applied fo engineering and electronics and is an ozone-friendly product.

n-Perfluoropentane [64] is obtained at high yield by elemental fluorine fluorination of n-pe
Information on fluorination of trichloromethane using metals fluorides in the presence of
catalyst in the solvent medium allowed to come across a trifluoromethane obtaining metho
determined, that fluorination of trichloromethane by alkali metals fluorides in the dimethyl die
ether at 120-150 ^{o}C results generally in total substitution of chlorine atoms for fluorine in a
content of trifluoromethane in gaseous products of fluorination reaches 91.7 % (vol.).

We have conducted a comparative analysis for effectiveness of potassium, sodium, calciur
fluorides in reactions of haloidhydrocarbons fluorination reactions under conditions of phase-trar
We have noticed a small effectiveness of potassium fluorides in the reaction with trichloro
suggested synthesis method and a reactor are successfully approved at an experimental-ind
was determined, that fluorination of trifluoromethane using fluorine, containing oxygen (0.05
over tetrafluoromethane at 100-400 ^{o}C in reactor filled with metallic nozzle made of copp
chrome results in formation of terafluoromethane (products' composition 99.8 % CF_4, 0.2 % C

It allowed increasing the conversion of raw materials and selectivity of the process and lowe
inputs. Tetrafluoromethane obtaining method by fluorinating of different grades of coal conta
carbon (from 5 to 25% mass.) at temperature ranging from 700 to 1200 ^{o}C was developed
mention, that fluorination is conducted either using pure fluorine or anode gas, formed during
KF-2HF mixture and containing up to 10 (mass.) % of anhydrous hydrogen fluoride. It allo
labour-intensive and power-consuming stage of fluorine purification.

At the same time the presence of anhydrous hydrogen fluoride allows to depart from solve
mixture. The availability of anhydrous hydrogen fluoride results in decreasing of excessive hea
fluorinating reaction, improves heat exchange, increases the process selectivity due to lowerin
of concurrent high-molecular perfluoroalkanes.

The use of activated carbon additives decreases the process explosive risk, leads to comb
faster reaching of the stable stage and, therefore to increasing of CF_4 yield. The concentrat
higher than 25(mass.)% makes the method economically irrational.

Conclusion

As can be seen from the data, listed in this review, the conception of synthesis of perfluor
compounds by fluorination using elemental fluorine both in a pure form and in the presence o
found its experimental approval. We also should mark the importance of results of such app
not only and not as much as for obtaining methods of practically necessary perspective
compounds but for economical practicability. Thus, it is manageable to increase the y
perfluorinated compounds sharply, to improve their quality, to increase significantly the ef
fluorine use and to simplify the process itself and obtaining technology of many substances.
showed the urgency and timeliness of setting such a problem and a need for its boosted solv
laid as a foundation of conception mentioned above, proved to be productive and
implementation for commercial production will stimulate a change in the production men's v
regarding the question of using elemental fluorine for production.

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