ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1142–1148. © Pleiades Publishing, Ltd., 2009. Original Russian Text © D.S. Pashkevich, V.G. Barabanov, B.N. Maksimov, 2009, published in Khimicheskaya Promyshlennost', 2009, Vol. 86, No. 2, pp. 82–89.

TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Development and Implementation of Industrial Technologies for Synthesis of Fluorine Compound with the Application of Elemental Fluorine

D. S. Pashkevich, V. G. Barabanov, and B. N. Maksimov

Russian Scientific Center "Applied Chemistry," St. Petersburg, Russia

Received November 11, 2008

Abstract—A survey is given on the application of elemental fluorine in chemical plants and research centers of Russian Federation.

DOI: 10.1134/S107042720906041X

Russian Scientific Center "Applied Chemistry" (former GIPKh, State Institute of Applied Chemistry) is one of advanced organizations in Russia where was developed and practically used the technology of the production of fluorine by the electrolysis of molten potassium bifluoride [1]. As a result the research in the field of elemental fluorine and its application to the synthesis of different fluorine compounds, elemental fluorine became accessible as a raw material; the world capacity of plants producing F_2 reaches 25000 tons per year.

For many years in the Center "Applied Chemistry" are conducted intensive studies on the use of fluorine for producing the fluorine compounds of different designation which meet demand on the world market. This is the so-called "electron gases" utilized in the industry of semiconductors; ozone-safe Freons; the volatile fluorine compounds used in the processes of isotopic enrichment; fluorine compound for medicine; the component of the lithium sources of electric current and others.

The processes of fluorination with the use of elemental fluorine are connected with the very high heat emission and easily transfer into the combustion regime, that lead to heating of the reaction products to several thousand degrees. Under these conditions the majority of the compounds of fluorine are thermolabile. Therefore one of the basic problems at the developing a competitive technology with the application of fluorine as the fluorinating agent is creation of the reactor unit, which ensures maintenance in the zone of fluorination a temperature, at which initial, intermediate and final products are sufficiently thermostable.

In the Center "Applied Chemistry" occurred unique situation from the point of view of the development of effective reactor units for the fluorination by element fluorine. Reactor units for a whole series of the technologies of the production of fluorine compounds with the application of fluorine were developed at the close collaboration of specialists in the technology of fluorine and specialists in the theory and practice of the processes of combustion.

At the creation of highly productive and safe reactor unit for the fluorination by fluorine first of all is necessary to select the thermal condition of conducting the process: stationary or nonstationary. According to [2], exothermic chemical reactions can proceed in the stationary (the rate of heat withdrawal is above or equal to the rate of heat release) and the nonstationary (the rate of the heat withdrawal is lower than that of heat release) thermal conditions. Between these regimes there is a difference, determined by the combination of the parameters of the energy transfer and chemical-kinetic and thermodynamic characteristics of the system.

In the stationary thermal regime the process is close to the isothermal, the reaction rate is relatively low, the volume of the zone of the reaction is relatively large and close to the reactor characteristic volume. It is easy to form this regime in the reaction systems, which possess high heat-transfer coefficient. If the gas (fluorine) is one of the reagents, then such systems are the phase systems: gas-liquid and gas-solid for the dynamic (intermixed, mobile) layers of powder.

In the nonstationary thermal condition the front of combustion or thermal explosion is realized, the process conditions are close to the adiabatic, reaction rate is relatively high and the characteristic volume of the reaction zone usually is substantially lower than the volume of entire reactor (wave localization of the zone of the reaction) [3, 4]. This regime is formed in the phase systems, which possess low heat-transfer coefficient: gas–gas and gas–solid for the stationary (fixed, not intermixed) layers of powder.

Usually the reactor unit working in the nonstationary thermal condition of fluorination is simpler by construction and by industrial operationing. However, in this regime it is expedient either to synthesize sufficient thermostable substances or to perform the processes of low productivity.

At the wave localization of the zone of gas-phase reaction the reactants can be preliminary mixed at the molecular level, and then the reaction proceeds in a homogeneous torch. The composition of fluorination products in this case depends only on the concentration of fluorine.

For the reaction systems gas-liquid and gas-solid is realized diffusion combustion, in this case a chemical reaction often occurs in the diffusion gas-phase torch, since the fluoridated liquid, and in certain cases also solid substances, evaporate, being heated by the liberating heat of reaction. At the diffusion combustion the composition of products can be changed by changing the feed rate of fluorine into the zone of reaction.

A characteristic example of gas-phase fluorination in the homogeneous torch is the synthesis of pentafluoroethane (ozon safe Freon and flame distinguishing agent) and hexafluoroethane (electron gas) by gas-phase fluorination of 1,1,1,2-tetrafluoroethane [5, 6]

$$CF_3CFH_{2 gas} + F_{2 gas} \rightarrow CF_3CF_2H_{gas} + HF_{gas},$$
 (1)

$$CF_3CFH_{2 gas} + F_{2 gas} \rightarrow C_2F_{6 gas} + HF_{gas}, \qquad (2)$$

These processes were realized in the reactor of the "tunnel burner" type with the premixing of components and the stabilization of flame. In this case the complete conversion of fluorine was achieved, selectivity on the pentafluoroethane reached 80%. Basic side reaction is destructive fluorination of fluoroethane molecule with the formation of fluoromethanes. At the conversion of parent 1,1,1,2-tetrafluoroethane to 30% the concentration of fluoromethanes in the gas of synthesis does not exceed 1%. The unreacting raw material is directed into the recycle.

The stage of experimental-industrial checking the developed method has passed the step of installation with the reactor of the "tunnel burner" type of 20 mm diameter and 2.5 m length, with the approximate productivity of the order of magnitude of 50 tons per year on the pentafluoroethane or hexaflouroethane.

At present some producers of semiconductors consider carbonyl difluoride to be an alternative to nitrogen trifluoride and to perfluorocarbons at the etching silicon owing to simplicity of the utilization of its withdrawals. Therefore it was developed a technology of the synthesis of this compound, based on the diffusion combustion of carbon monoxide in fluorine [7]:

$$CO_{gas} + F_{2 gas} \rightarrow COF_{2 gas}.$$
 (3)

The yield of the targeted in the process (3) at the equimolar ratio of initial components exceeds 70%, and at the excess of fluorine reaches 90%. As the admixtures are formed tetrafluoromethane, carbon dioxide and also the traces of trifluormethylhypofluoride.

In the diffusion gas-phase torch combustion of evaporated sulfur in fluorine is carried out the synthesis of sulfur hexafluoride (dielectric for the electrotechnical articles):

$$S_{liq} + 3F_{2 gas} \rightarrow CF_{6 gas}.$$
 (4)

It is known that at the fluorination of sulfur together with SF_6 can be formed also other sulfur fluorides, whose yield must be minimized. On the basis of thermodynamic calculations [8] were revealed the conditions of formation of sulfur hexafluoride as a basic product and is developed a reactor, in which the diffusion torch of the combustion of sulfur in fluorine is formed by feeding the flow of fluorine to the surface of molten sulfur [9]. At the 90% conversion of fluorine the yield of SF_6 reaches 95%. Basic admixtures are SF_4 and S_2F_{10} .

The reactor of 400 mm diameter and 3 m length made it possible to produce 30 tons per year of sulfur hexafluoride. On the developed technology in Russia were created two large-scale plants of sulfur hexafluoride with capacity 500 ton per year on joint stock company "Galogen" and with capacity 450 ton per year on joint stock company "Kirovochepetskii Khimkombinat."

One additional commercially significant sulfur fluoride which is obtained from the elements is SF_4 , the fluorinating agent for the substitution of oxygen in the carbonyl group. According to thermodynamic calculations [8] the maximum content of sulfur tetrafluoride is reached at the temperature of the order of magnitude of 1500 K.

For the realization of this process was developed a falling layer reactor, in which interaction of sulfur and fluorine proceeds in the regime of thermal explosion under the conditions close to the adiabatic [10, 11]. This reactor is the stand pipe, into upper part of which is fed by worm conveyor the solid fluoridated material and fluorine:

$$S_{sol} + 2F_{2 gas} \rightarrow SF_{4 gas}.$$
 (5)

On the created in the experimental plant of the Center "Applied Chemistry" experimental pilot-industrial setup with the reactor 60 mm diameter, sulfur is mixed up with calcium difluoride which absorbs the heat of reactions. On this setup it was possible to achieve the yield of sulfur tetrafluoride 80% of the theoretical yield at the complete conversion of fluorine and at the productivity of reactor about 10 tons per year. Sulfur hexafluoride was a basic by-product.

At the use of the regime of graphite combustion in fluorine was realized the process of the synthesis of tetrafluoromethane (electron gas) [12, 13]:

$$C_{sol} + 2F_{2 gas} \rightarrow SF_{4 gas} + 931 \text{ kJ}$$
(6)

Tetrafluoromethane is one of the most thermostable compounds of fluorine; therefore for its synthesis it is expedient to use a regime of the filtrational combustion of the fixed bed of carbon in fluorine. For this process was developed a reactor with the two-component fuel nozzle of special construction, for feeding with fluorine and gaseous hydrocarbon and shaping the high-temperature zone of reaction at the beginning of the reactor operation. The heat stabilization of the zone of reaction was achieved, selecting experimentally the fluorine consumption to remove heat by thermal radiation on cooled nozzle.

In the State Enterprise "Angara Electrolysis Chemical Plant" on the basis of developments of the Center "Applied Chemistry" was created the production of tetrafluoromethane with a capacity 450 tons per year with three reactors working in the regime of the inverse wave of filtrational combustion with the application of the method of initiating the process as described above. The only product of the realized method of the synthesis is tetrafluoromethane.

In the regime of filtrational combustion in the phase system gas-solid were realized the processes of fluorination of the high-melting metals: tungsten, molybdenum and rhenium whose hexafluorides WF_6 (formation of the films of tungsten in microelectronics), MoF_6 (industry of isotopes) and ReF_6 are sufficiently thermostable [14]:

$$Me_{sol} + 3F_{2 gas} \rightarrow MeF_{6 gas,}$$
(7)
Me = W, Re, Mo.

Just as at the synthesis of tetrafluoromethane the heat stabilization of the zone of reaction is achieved on the basis of thermal radiation; however, the starting of reactor is simpler, since special methods on shaping the hightemperature zone of reaction is not required.

Experimental-industrial production of WF_6 and MoF_6 was realized at the experimental plant of the Center "Applied Chemistry," production WF_6 with capacity 50 tons per year on joint stock company "Galogen."

In the combustion mode were realized the syntheses of boron trifluoride (catalyst of the processes of alkylation, polymerization and isomerizations; the volatile compound of boron, which is used for the rectification enrichment of boron isotope ¹⁰B), phosphorus pentafluoride (raw material for the production of electrolyte for the lithium electric current sources), silicon tetrafluoride (formation of silicon films in microelectronics) and antimony pentafluoride (fluorinating agent) [1, 11]:

$$2O_{3 \text{ sol}} + F_{2 \text{ gas}} \rightarrow BF_{3 \text{ gas}} + O_{2 \text{ gas}}$$
(8)

$$P_{sol} + F_{2 gas} \rightarrow PF_{5 gas} \tag{9}$$

$$Si_{sol} + F_{2 gas} \rightarrow SiF_{4 gas}$$
 (10)

$$Sb_{sol} + F_{2 gas} \rightarrow SbF_{5 gas}$$
 (11)

The feed rate of fluorine was selected to avoid melting of the solid raw material. The industrial producing of boron trifluoride with capacity 15 tons per year was created on joint stock company "Galogen", and pilot plants for the synthesis of phosphorus and antimony pentafluorides and silicon tetrafluoride at the experimental plant of the Center "Applied Chemistry." In the regime of wave localization of reaction zone were realized several industrial processes of producing perfluorocarbons from hydrocarbons by the fluorination of the latter by cobalt trifluoride [15]:

$$R_{H gas} + CoF_{3 sol} \rightarrow R_{F gas} + HF_{gaz} + CoF_{2 sol}, \qquad (12)$$

$$\operatorname{CoF}_{2 \operatorname{sol}} + \operatorname{F}_{2 \operatorname{gas}} \to \operatorname{CoF}_{3 \operatorname{sol}}, \tag{13}$$

where R_H is initial compound, R_F is purposeful perfluorocarbon compound.

The processes of fluorination by cobalt trifluoride and regeneration of cobalt difluoride by fluorine are accompanied by the high heat emission. Therefore in the industrial setups with the steady-state boundary layer of CoF_3 these processes occurred in the regime of the wave of filtrational combustion, where the temperature in the zone of reaction was controlled by the feed rate of fluoridated gaseous compound or fluorine at the regeneration.

In particular, were developed the technologies for producing octafluoropropane C_3F_8 from the hexafluoropropylene [16] and of perfluorodecaline from naphthalene [17]:

$$C_3F_{6 \text{ gas}} + CoF_{3 \text{ sol}} \rightarrow C_3F_{8 \text{ gas}} + HF_{\text{gas}} + CoF_{2 \text{ sol}},$$
 (14)

$$C_{10}F_{8 \text{ gas}} + CoF_{3 \text{ sol}} \rightarrow C_{10}F_{18 \text{ gas}} + HF_{\text{gas}} + CoF_{2 \text{ sol}},$$
 (15)

The octafluoropropane synthesis in the reactors with stationary powder layer was realized at the experimental plant of the Center "Applied Chemistry" with the capacity 10 tons per year, and on joint stock company "Galogen" with capacity 25 tons per year. The technology of the synthesis of perfluordecaline was implemented at the experimental plant of the Center "Applied Chemistry," the capacity reached 1 ton per year.

Also with the application of cobalt trifluoride as a fluorinating agent was developed the technology for the producing carbonyl difluoride [7]:

$$CO_{gas} + CoF_{3 sol} \rightarrow COF_{2 gas} + CoF_{2 sol}.$$
 (16)

In the regime of filtrational combustion at a maximum temperature in the self-propagating reaction zone 400–500°C was observed the practically complete conversion of carbon monoxide. The final product yield exceeded 90%, the basic admixtures were tetrafluoromethane, carbon dioxide and traces of trifluormethyl hypofluoride. The above examples demonstrate production efficiency of the sufficiently thermostable fluorine compounds with applicaton of fluorine in the regime of combustion. In this regime can be obtained also fairly complicated compounds, for example, perfluorodecaline; however, the productivity of reactor unit in this case is relatively low. More thermolabile fluorine compound can also be obtained with the sufficiently high productivity with the application of fluorine. For this it is expedient to use steady thermal (close to the isothermal) state of synthesis, without allowing wave localization of the high-temperature zone of reaction. In this case if the more effective method of removing the heat of reaction is realized in a developed apparatus, then the higher the productivity of this apparatus can be reached. In the reaction system gas-solid the ensuring close to the isothermal regime of synthesis is possible by using a dynamic (mobile, intermixed) layer of powder.

For example, for the reaction system fluor–carbon was developed industrial method of the synthesis of the lowest perfluoroalkanes (electron gas):

$$C_{sol} + F_{2 gas} CF_{4 gas} + C_2 F_{6 gas} + C_3 F_{8 gas} + C_4 F_{10 gas}.$$
 (17)

At the use of reactors with the circulating fluidized graphite bed, with a gas-dust flow down, and with the freely falling layer of powder it was possible to produce a mixture of the listed above substances with the following composition: CF_4 40–45 wt %, C_2F_6 20–25 wt %, C_3F_8 15–20 wt %, C_4F_{10} 10 wt % [18–20]. At the same time in the first case a regime close to the isothermal was created, with removal of the heat of reaction into the wall of reactor. However, in the reactors with the freely falling layer of powder and with the gas-dust flow down the graphite was used not only as a reagent, but also as thermal capacity for consumption of the heat of reaction, and heating of the powder was controlled by a change in its feeding.

At the experimental plant of the Center "Applied Chemistry" was realized a number of low-tonnage technologies for the fluorination of solid substances by elemental fluorine with producing the corresponding fluorides: carbon polyfluoride (component of the cathodic composite of lithium current sources, antifriction material) [21], selenium, tellurium and iridium hexafluorides (isotopic enrichment) [11, 27], selenium tetrafluoride (fluorinating agent for replacing oxygen in the carbonyl groups) [22], iodine pentafluoride (laser technology) [23], manganese tetrafluoride, and potassium

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 82 No. 6 2009

hexafloronickelate (solid-state generators of fluorine) [24], germanium tetrafluoride (isotopic enrichment) [25].

The processes of fluorination were carried out in the regime close to the isothermal in the shelf-type reactors with the productivity hundreds of kilograms per year. The heat removal from the reaction zone was accomplished on the basis of free convection. The industrial production of carbon polyfluoride on the basis of this technology with capacity up to 10 tons per year was created on the State Enterprise "Angara Electrolysis Chemical Plant."

Conducting the fluorination in the regime close to the isothermal is convenient for the reaction system gas–liquid, since in this system it is relatively simple to realize the high intensity transfer processes.

In this phase system was realized the synthesis of 5-fluorouracyl (carcinolytic preparation), which was obtained by the fluorination of powder-like uracil in the medium of acetic acid by fluorine [26]:

$$C_4 N_2 O_2 H_{4 \text{ sol}}[(\text{susp}) CH_3 COOH)] + F_{2 \text{ gas}}$$
$$\rightarrow C_4 N_2 O_2 H_3 F_{\text{sol}} + HF_{\text{liq}}.$$
(18)

Experimental-industrial setup was created at the experimental plant of the Center "Applied Chemistry," its capacity is several tons per year.

In recent years in the Center "Applied Chemistry" by the contracts with limited enterprise "New-Kem," was developed a technology of the synthesis of nitrogen trifluoride by the fluorination of molten NH_4F . *n*HF by gaseous fluorine [28–30]:

$$NH_4F \cdot nHF_{liq} + F_{2 gas} \rightarrow NF_{3 gas} + NH_4F \cdot (n+m)HF_{liq},$$
(19)

$$NH_{3 gas} + NH_{4}F \cdot (n+m)HF_{liq} \rightarrow NH_{4}F \cdot nHF_{liq},$$
(20)

where
$$n \ll m$$

Fluorination is conducted in the non-gradient reactor with the high-speed mixer in the circulation loop, which makes it possible to effectively remove heat on the basis of forced convection and to maintain the isothermal regime of conducting the process, and it also ensures the maximum contact area of gaseous fluorine with the melt. In this method of conducting the process the productivity of the reactor of fluorination reaches 30 g of NF₃ per one liter in a hour with the fluorine conversion up to 95%. This technology at present is implemented on the State Enterprise "Siberian Chemical Plant."

Thus, with the creation of the industrial manufacturing of fluorine compound with the use of fluorine as the fluorinating agent in the dependence on the thermostability of purposeful and parent substances, and also on the productivity of industrial technology, the process of the synthesis can be realized in the regimes of combustion or under the conditions close to the isothermal.

It should be noted that elemental fluorine is used in the chemical-engineering processes not only as the basic fluorinating agent, but also for some other purposes.

At the experimental plant of the Center "Applied Chemistry" was realized the synthesis of perfluoropolyetherpolyperoxide (a component of antifriction liquids) by liquid phase oxidation of hexafluoropropylene by oxygen. At the application as initiator of the fluorine added in amount of a few percents to oxygen the substance obtained had a structure with predominating simple polyether links [31]:

$$C_3F_{6 \text{ liq}} + O_{2 \text{ gas}} (F_{2 \text{ gas}} \sim 100\%) \rightarrow (-C_3F_6O_{-})_{n \text{ liq}},$$
 (21)

The value of n was varied by varying fluorine concentration in oxygen and by changing the method of feeding the gas into reactor [32]. The gaseous products of destruction in the oxidation were practically absent.

Another application of fluorine is use it as a reagent for a combustional work up of withdrawals of tetrafluoromethane with the formation of anhydrous hydrogen fluoride [33]:

$$CF_{4 gas} + nH_{2 gas} + mF_{2 gas} \rightarrow C_{sol} + kHF_{gas}.$$
 (22)

Tetrafluoromethane is one of the most thermodynamically stable fluorine derivatives, and its life time in atmosphere achieves 50000 years. Therewith, its potential of global warming is very high, 6500 [1]. Therefore the development of the method of its utilization to avoid its scattering in atmosphere is important.

As a result of the carried out investigation was shown that at the values n = 0.5 and m = 2.5 can be achieved over 80% conversion of tetrafluoromethane. Therewith, the expenditure index on fluorine is approximately 0.2.

It should be noted that in some regimes of the process (22) was observed high content of tetrafluoroethylene in the reaction products [33, 34] that in perspective can

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 82 No. 6 2009

became an object of separate study.

Fluorine also is explored for the substitution of residual hydrogen in perfluorodecaline [35], in fluorinated tertiary amines [36] synthesized by electrochemical fluorination and in other cases, that allows an increase in chemical stability and in some other performance parameters of these compounds.

To the conclusion, we can resuming that elemental fluorine is widely applied in Russian industry for producing a series of commercially significant fluorine compounds.

REFERENCES

- Maksimov, B.N., Barabanov, V.G., Serushkin, I.L. et, al., *Promyshlennye ftororganicheskie produkty. Spravochnik* (Industrial F;uoroorganic Products. Handbook), St. Petersburg: Khimiya, 1996, 554 p.
- 2. Frank-Kamenetskii, D.A., *Diffuziya i teploperedacha v khimicheskoi kinetike* (Diffusion and Heat Transfer in Chemical Kinetics), Moscow: Nauka, 1967.
- Pashkevich, D.S., Alekseev, Yu.I., Mukhortov, D.A., and Petrov, V.B., *Zh. Prikl. Khim.*, 1999, vol. 72, no. 12, pp., 2007–2011.
- 4. Pashkevich, D.S., Alekseev, Yu.I., and Mukhortov, D.A., *Zh. Prikl. Khim.*, 1999, vol. 72, no. 12, pp. 2000–2006.
- Pashkevich, D.S., Alekseev, Yu.I., Mukhortov, D.A. et al., RF Patent, no. 2115645.
- Pashkevich, D.S., Alekseev, Yu.I., Mukhortov, D.A. Asovich, V.S., and Rozhdestvenskaya, O.V., *Zh. Prikl. Khim.*, 2001, vol. 74, no. 7, pp. 1120–1125.
- Pashkevich, D.S., Moukhortov, D.A., Asovich, V.S., Kambour, M.P., Petrov, V.B., Alekseev, Yu.I, and Kambour, P.S., Abstracts of Papers, 15th European Symposium on Fluorine Chemistry, Prague, 2007.
- Molchanov, O.N., Przheval'skii, I.N., Grigor'eva, I.V. et al., *Otchet o NIR, NPO GIPKh* (Report on Sci. Work of Sci. Center "Applied Chemistry"), no. 203-90, Leningrad, 1990, 191 p.
- 9. Avdulov, G.I., Korolev, V.L., Maslichenko, A.P. et al., USSR Inventor's Certificate, no. 295070.
- Avdulov, G.I., Alekseev, Yu.I., Tsvetkova, L.A, et al., *Otchet o NIR, NPO GIPKh* (Report on Sci. Work of Sci. Center "Applied Chemistry"), no. 203-90, Leningrad, 1990, 191 p.
- Alekseev, Yu.I. and Pashkevich, D.S., Abstracts of Papers, 16 Vserossiiskaya konferentsiia po khimicheskim reaktoram "Khimreaktor-16". Kazan, 2003, p. 201.

- Pashkevich, D.S.and Barabanov, V.G., Abstracts of Papers, II Mezhdunarodnaia konferentsiia "Uglerod: fundamental'nye problemy nauki materialovedenie tekhnologiya" (2nd INt. Conf. "Carbon: Fundamental Problems of Science, Material Science, and Technology"), Moscow, 2003, p. 169.
- 13. Barabanov, V.G., Zh. Prikl. Khim., 2004, vol. 77, no. 1, pp. 96–101.
- 14. Lantratova, O.V., Pashkevich, D.S., Lezhneva, L.V., L.A.Smirnova, L.A., Kalinin, Yu.N., Serdyukov, Yu.M., and Alekseev, Yu.I., Abstracts of Papers, *Tret'ia Mezhdunarodnaia konferentsiai "Khimiya tekhnologiya i primenenie ftorsoedinenii"* (3rd Int.Conf. on Chemistry, Technology and Application of Fluoro Compounds), St. Petersburg, 2001, p. 16.
- 15. Asovich, V.S., Kornilov, V.V., Kostyaev, R.A.et al., Abstracts of Papers, *I Mezhdunarodnaya konferentsiya "Khimiya tekhnologiya i primenenie ftorsoderzhashchikh soedinenii v promyshlennosti"* (1st Int. Conf. on Chemical Technology and Application of Fluoro-Containing Compounds in Industry), St. Petersburg, 1994, p. 15.
- 16. rokudin, I.P., Asovich, V.S., Smirnova, B.M.*et al.*. USSR Inventor's Certificate, no. 1630241, 1984.
- 17. Maksimov, B.N., Asovich, V.S., Mel'nichenko, B.A. et al., *Perftoruglerody Meditsina*, Novosibirsk, 1990, p. 5.
- Alekseev, Yu.I., Pashkevich, D.S., Mukhortov, D.A., V.B., Petrov, V.B., Asovich, V.S., and Shelopin, G.G., *Zh. Prikl. Khim.*, 2004, vol. 77, pp. 1865–1871.
- Shelopin, G.G., Alekseev, Yu.I., Pashkevich, D.S., Mukhortov, D.A., V.B. Petrov, V.B., and Asovich, V.S., *Zh. Prikl. Khim.*, 2006, vol. 79, pp. 950–953.
- Shelopin, G.G., Alekseev, Yu.I., Pashkevich, D.S., Mukhortov, D.A., V.B. Petrov, V.B., Asovich, V.S., *Zh. Prikl. Khim.*, 2006, vol. 79, pp. 1040–1042.
- Kutsenok, Yu.B., Serushkin, I.L., Kaurova, G.I. et al., Otchet o NIR, NPO GIPKh (Report on Sci. Work of Sci. Center "Applied Chemistry"), no. 4-91, Leningrad, 1991, 67 p.
- 22. Lantratova, O.V., Pashkevich, D.S., Alekseev, Yu.I. et al., USSR Inventor's Certificate, no. 2000123346, 2000.
- Lantratova, O.V., Pashkevich, D.S., and Alekseev, Yu.I., . Otchet o NIR, NPO GIPKh (Report on Sci. Work of Sci. Center "Applied Chemistry"), no. 42-98, St. Petersburg, 1998, pp. 9–15.
- Lantratova, O.V., Petrov, Yu.A, and Raitsemring, A.M., Abstracts of Papers, VI Vsesoyuznoe soveshchanie fotokhimii (All-Union Meeting on Photochemistry), Novosibirsk, 1989.
- Lantratova, O.V., Pashkevich, D.S., Alekseev, Yu.I., Karpunin, V.I., Lezhneva, L.V., and Molchanov, O.N., Abstracts of Papers, *II Mezhdunarodnyi sibirskii seminar*

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 82 No. 6 2009

"Sovremennye neorganicheskie ftoridy Intersibfluorine– 2006" (2nd Int. Siberian Seminar on Modern Inorganic Fluorides "Intersibfluorine-2006"), Tomsk, 2006, pp. 146– 147.

- 26. Semenov, S.G., Yufereva, N.M., Serushkin, I.L. et al., *Perftoruglerody Meditsina*, Novosibirsk, 1990, p. 31.
- Pashkevich, D.S., Alekseev, Yu.I., Kambur, M.P., Kambur, P.S., Lantratova, O.V., Mukhortov, D.A., Petrov, V.B., Vasil'eva, L.A., and Predtechenskii. Yu.B., Abstracts of Papers, *III Mezhdunarodnyi sibirskii seminar "Sovremennye neorganicheskie ftoridy Intersibfluorine– 2008"* (3rd Int. Siberian Seminar on Modern Inorganic Fluorides "Intersibfluorine-2008"), Vladivostok, 2008, p. 27.
- 28. Alekseev, Yu.I., Pashkevich, D.S., Mukhortov, D.A., and Petrov, V.B., RF Patent, no. 2256605.
- 29. Pashkevich, D.S., *Khim. Prom.*, 2006, vol. 83. no. 12, p. 576.
- Mukhortov, D.A., Alekseev, Yu.I., Pashkevich, D.S, Petrov, Kambur, M.P., and Lantratova, O.V., Abstracts of Papers, *II Mezhdunarodnyi sibirskii seminar "Sovremennye neorganicheskie ftoridy Intersibfluorine–2006"* (2nd Int. Siberian Seminar on Modern Inorganic Fluorides "Intersibfluorine-2006"), Tomsk,2006, pp. 222–225.
- 31. Shabalin, D.A., Poluektov, V.A., Zakharov, V.Yu.,

Kalashnikov, N.A., and Ryabinin, N.A., *Dokl. Akad. Nauk*, 1990, vol. 313, no. 15, p. 1178.

- 32. Pashkevich, D.S., Mukhortov, D.A., and Petrov, V.B., Abstracts of Papers, *Tret'ia Mezhdunarodnaia konferentsiai* "*Khimiya tekhnologiya i primenenie ftorsoedinenii*" (3rd Int. Conf. on Chemistry, Technology and Application of Fluoro Compounds), St. Petersburg, 2001, p. 11.
- 33. Pashkevich, D.S., Petrov, V.B., Alekseev, Yu.I., Kambur, M.P., Kambur, P.S., and Mukhortov, D.A., *III Mezhdunarodnyi sibirskii seminar "Sovremennye neorganicheskie ftoridy Intersibfluorine–2008"* (3rd Int. Siberian Seminar on Modern Inorganic Fluorides "Intersibfluorine-2008"), Vladivostok, 2008, p. 28.
- Pashkevich, D.S. and Barabanov, V.G., Abstracts of Papers, 15th European Symposium on Fluorine Chemistry, Prague, 2007.
- Kambour, P.S., Pashkevich, D.S., Moukhortov, D.A., Asovich, V.S., Kambour, M.P., Petrov, V.B., and Alekseev, Yu.I., Abstracts of Papers, *15th European Symposium on Fluorine Chemistry*, Prague, 2007.
- Kambur, P.S., Pashkevich, D.S., Mukhortov, D.A., Kambur, M.P., Petrov, V.B., Kaurova, G.I., and Matalin, V.A., Abstracts of Papers, *III Mezhdunarodnyi sibirskii seminar* "Sovremennye neorganicheskie ftoridy Intersibfluorine– 2008" (3rd Int. Siberian Seminar on Modern Inorganic Fluorides "Intersibfluorine-2008"), Vladivostok, 2008, p. 32.