

# THE INFLUENCE OF OXIDATION OF HFC'S AND FC'S ON THEIR FIRE EXTINGUISHING AND EXPLOSION PREVENTING CHARACTERISTICS

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## ABSTRACT

Combustion of some hydrofluorocarbons (HFC's) and fluorocarbons (FC's) in oxygen was investigated in closed vessel at room initial temperature and atmospheric initial pressure. Peculiarities of chemical mechanism of oxidation of HFC's and FC's are discussed in the paper. For the characteristics of fluorinated compounds as agents for fire extinguishing and explosion prevention to be improved, it is necessary to introduce an inhibitor of their oxidation into them. It has been obtained that minimum inertization concentration (MIC) of the mixed agent (mixture of  $C_3H_8$ ,  $C_4H_{10}$  and  $C_3H_6$  with HFC or FC) for methane – air mixtures is substantially lower than for HFC (or FC). Minimum fire extinguishing concentration for the mixture  $C_2F_5H$  – iodinated hydrocarbon is less on 20 % (vol.), than for  $C_2F_5H$ .

## INTRODUCTION

Some fluorinated hydrocarbons (for example,  $C_4F_{10}$ ,  $C_3F_7H$ ,  $C_2F_5H$  etc.) were proposed as ozone friendly replacement for the brominated halons in fire extinguishing and explosion prevention. But they are less effective than the brominated agents [1-3]. According to the conclusions of some papers [4,5], this is due to low chemical activity of HFC's and FC's. But it was showed [1,3] that the fluorinated hydrocarbons decrease the lower flammability limits of hydrocarbon or hydrogen in air and that they may change the mixtures of nonflammable composition to "flammable". It was observed [6,7] that an addition of some fluorinated gases causes an elevation of pressure of a shock wave at detonation in  $C_2H_4$  – air – fluorinated hydrocarbon mixtures due to increase of a heat release at chemical conversion of fluorinated compound. An additional heat release in diffusion flames inhibited by fluorinated agents was found in [8]. The effect of a heat release caused by a chemical conversion of fluorinated hydrocarbons in lean premixed methane – air and hydrogen – air flames has been revealed in [1]. This effect is appeared as a remarkable elevation of maximum explosion pressure and maximum explosion pressure rise rate of gaseous mixtures containing HFC or FC. Thus the experimental results show that HFC's and FC's are not inert diluents; they play an active role in chemical conversion in a flame front. Because all observed phenomena take place in lean combustible mixtures, we can conclude that HFC's and FC's are able to oxidation in the mixtures with hydrogen or hydrocarbon and air and this feature is important for their fire extinguishing and explosion prevention characteristics. At the same time experimental data on oxidation of fluorinated hydrocarbons which are used as replacement for the brominated halons are practically absent. The papers [9-11] should be noted, in which flammability limits as well as other characteristics of combustion of some HFC's and FC's in air and oxygen were determined. So it is interesting to continue the investigations of the peculiarities of oxidation of fluorinated hydrocarbons, because if we know the mechanism of oxidation, we are able to prevent it by introduction of inhibitor of oxidation into fluorinated compound. This approach can be fruitful for the improving of characteristics of HFC's and FC's as agents for fire extinguishing and explosion prevention. This work is aimed on experimental investigation of above mentioned problems.

## EXPERIMENTAL

Experiments were in a set-up "Variant", which scheme is presented in Fig. 1. This set-up is designed for measuring flammability limits, maximum explosion pressure and maximum explosion pressure rise rate in the pressure range 0.1-4.0 MPa. A reaction vessel of the set-up has a spherical form and is made from stainless steel. Its diameter is 20 cm (volume 4.2 l). The set-up has a system for preparing of gaseous mixtures by partial pressures and vacuum pumping system. The required gaseous mixture is formed by partial pressures in the reaction vessel previously evacuated to 0.5 kPa. The gaseous mixtures were ignited in the center of the reaction vessel by fusing a nichrome wire having diameter 0.2 and length 3 mm (ignition energy ca. 10 J). Registration of a flame propagation was made by pressure detector

"Saphire-22" with time constant ca.  $3 \cdot 10^{-3}$  s with recording on a digital storage oscilloscope. It was accepted that flame propagation takes place, if a pressure increase exceeds 30 kPa. The relative error in determination of flammability limits and maximum explosion pressure did not exceed 10 %; for maximum explosion pressure rise rate the error was 20 %. More detail description of apparatus and experimental procedure is given in [12,13]. The following fluorinated substances were used in experiments:  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_{10}$ ;  $\text{CF}_3\text{H}$ ,  $\text{C}_2\text{F}_5\text{H}$ ,  $\text{C}_3\text{F}_7\text{H}$ . Methane was used in some experiments.

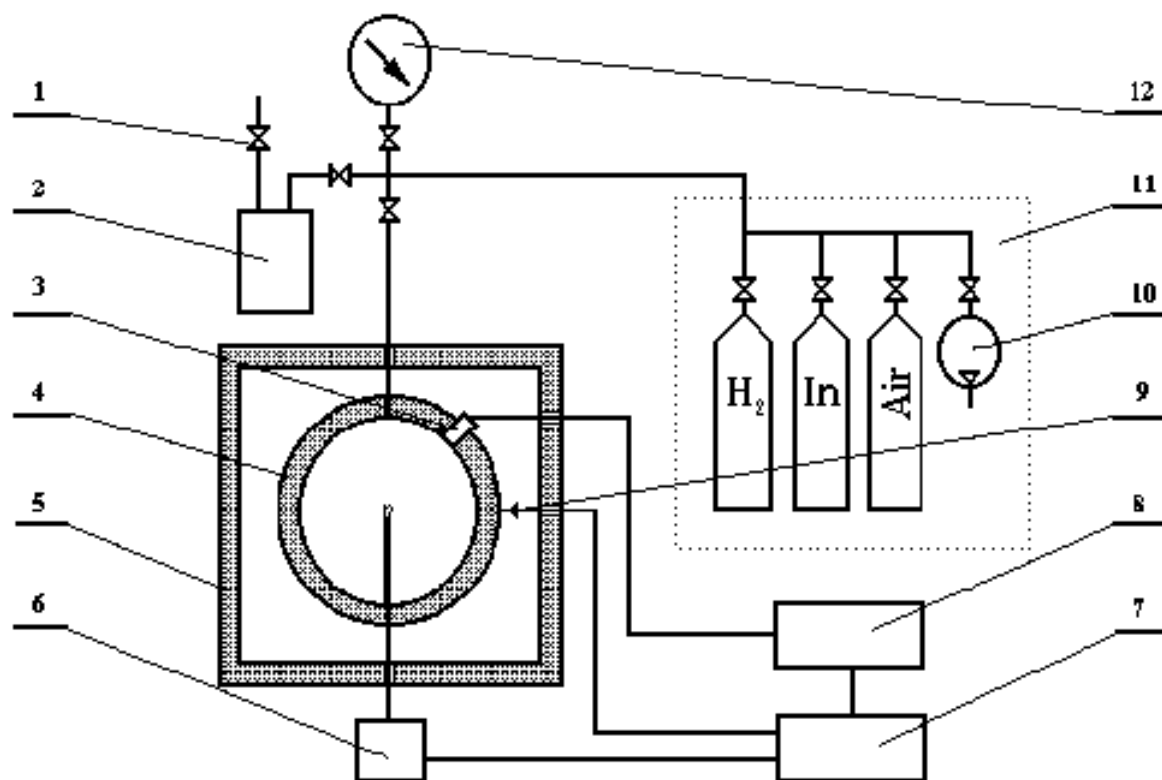


Fig.1. Diagram of the experimental set-up "Variant".

1 - valve; 2 - steam generator; 3 - pressure detector; 4 - reaction vessel; 5- thermostat; 6 - ignition device; 7 - control desk; 8 - oscilloscope; 9 - thermocouple; 10 - vacuum pumping; 11 - system for introducing of gases; 12 - vacuumeter.

## RESULTS AND DISCUSSION

The results of two experimental series are presented in the paper. Combustion of some HFC's and FC's was explored in the first. In the second an investigation of an influence of the mixed agent (fluorinated compound – mixture of alkanes and alkenes) on combustion of hydrogen and methane in air was executed. All experiments were conducted at atmospheric initial pressure and room initial temperature. In Table 1 flammability limits of HFC (or FC) with oxygen are shown. In Figs. 2,3 the dependences of maximum explosion pressure  $\Delta P_{\max}$  and maximum explosion pressure rise rate  $(dP/dt)_{\max}$  are presented.

Table 1. Flammability limits of some fluorinated hydrocarbons in oxygen.

Substance (FC)	Lower flammability limit, % (vol.)	Upper flammability limit, % (vol.)	Substance (HFC)	Lower flammability limit, % (vol.)	Upper flammability limit, % (vol.)
CF <sub>4</sub>	-	-	CF <sub>3</sub> H	-	-
C <sub>2</sub> F <sub>6</sub>	-	-	C <sub>2</sub> F <sub>5</sub> H	22.0	38.0
C <sub>3</sub> F <sub>8</sub>	-	-	C <sub>3</sub> F <sub>7</sub> H	9.0	81.0
C <sub>4</sub> F <sub>10</sub>	36.0	52.0			

You can see from Table 1 that three of saturated fluorocarbons (CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>) and CF<sub>3</sub>H are noncombustible in presence of oxygen. This is in agreement with available literature data [10,11]. But in contradiction with the results of [10] it was found that C<sub>4</sub>F<sub>10</sub> is able to combustion in oxygen. Probably this contradiction is due to difference between experimental conditions in [10] and in the present work. The microburner apparatus was used in [10]; the results of the present work were obtained in a bomb of constant volume.

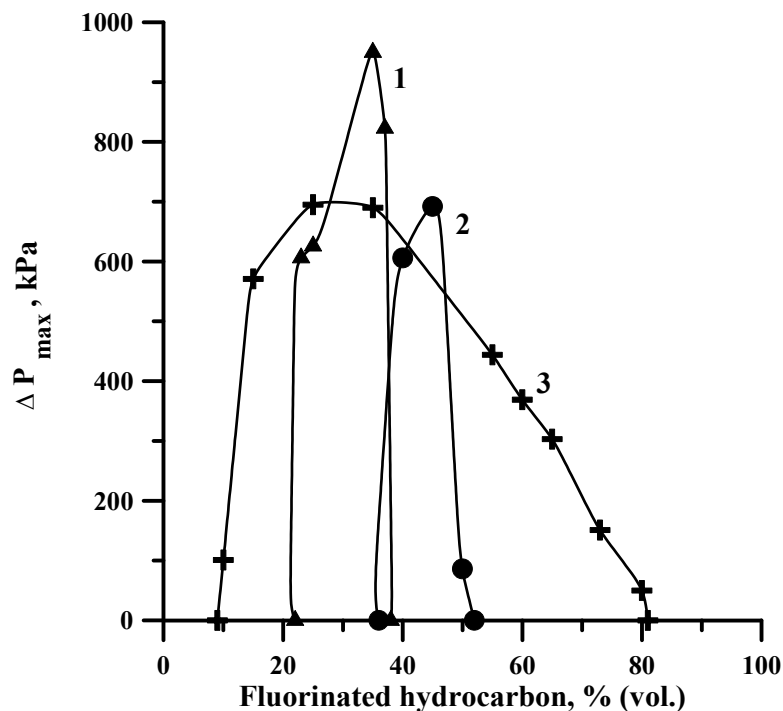


Fig.2. Dependences of the maximum explosion pressure on HFC (or FC) concentration in the mixtures with oxygen.  
1 – C<sub>2</sub>F<sub>5</sub>H; 2 – C<sub>4</sub>F<sub>10</sub>; 3 – C<sub>3</sub>F<sub>7</sub>H.

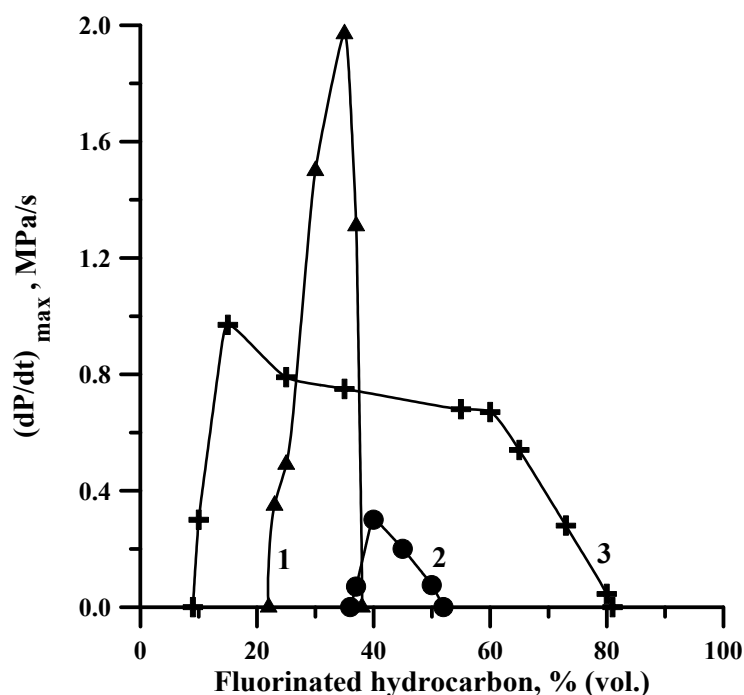


Fig.3. Dependences of the maximum explosion pressure rise rate on HFC (or FC) concentration in the mixtures with oxygen.  
1 – C<sub>2</sub>F<sub>5</sub>H; 2 – C<sub>4</sub>F<sub>10</sub>; 3 – C<sub>3</sub>F<sub>7</sub>H.

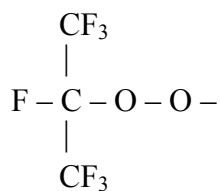
In the case of C<sub>2</sub>F<sub>5</sub>H, C<sub>3</sub>F<sub>7</sub>H and C<sub>4</sub>F<sub>10</sub> we observed their slow combustion (see Fig. 3). It is essentially to note that combustion of C<sub>3</sub>F<sub>7</sub>H essentially differs from combustion of C<sub>2</sub>F<sub>5</sub>H and C<sub>4</sub>F<sub>10</sub>. Its flammability limits in oxygen are essentially wider than for C<sub>2</sub>F<sub>5</sub>H and C<sub>4</sub>F<sub>10</sub>: from 9.0 to 81.0 % (vol.). But the main difference in the experimental results on combustion of these gases in oxygen is concerned with changing of regime of combustion in the case of C<sub>3</sub>F<sub>7</sub>H. It was revealed in our work that intensive soot formation takes place at combustion of mixtures of C<sub>3</sub>F<sub>7</sub>H with oxygen at concentrations of heptafluoropropane from 9.0 to 30.0 % (vol.). When the content of C<sub>3</sub>F<sub>7</sub>H in the mixture is in the range from 9.0 to 15.0 % (vol.), the soot is precipitated at surfaces of reaction vessel and ignition source in a form of flakes. At combustion of C<sub>3</sub>F<sub>7</sub>H at concentrations from 15.0 to 30.0 % (vol.) we observed formation of uniform soot layer at the surfaces of the bomb and ignition source; the thickness of this layer was 0.3-0.4 mm. Extremely high temperatures seem to realize during the combustion of heptafluoropropane in above mentioned concentration area: ceramic insulation of electrodes of ignition source is destroyed after several experiments, such effect doesn't occur at combustion of hydrogen or hydrocarbons. When the concentration of fluorinated substance exceeds 30.0 % (vol.), the transition to another regime of combustion takes place. The low intensity of soot formation and substantially lower temperatures characterize the oxidation of C<sub>3</sub>F<sub>7</sub>H at concentrations from 30.0 to 81.0 % (vol.). Described effects doesn't take place for combustion of C<sub>2</sub>F<sub>5</sub>H and C<sub>4</sub>F<sub>10</sub>. Thus we can conclude that mechanism of oxidation of C<sub>3</sub>F<sub>7</sub>H differs from that of C<sub>2</sub>F<sub>5</sub>H and C<sub>4</sub>F<sub>10</sub>.

Let us consider possible chemical mechanisms of the oxidation of these substances. In the case of HFC's the most probable initial stages of their oxidation are the following:



This sequence is in agreement with the results of the paper [14], in which the conversion of  $\text{CF}_3\text{H}$  in flames was investigated. In particular, it was revealed in [14] that in flames containing fluorinated agents the reaction  $\text{CF}_3 + \text{O}_2$  is important.

In the case of oxidation of  $\text{C}_3\text{F}_7\text{H}$  the reaction (2) gives the following product:



Due to peculiarities of its structure this intermediate substance is essentially unstable and decomposes with rupture of  $\text{C} - \text{C}$  bonds and significant heat release. For the combustion of  $\text{C}_2\text{F}_5\text{H}$  the result of reaction (2) is the compound  $\text{F}_3\text{C} - \text{C} - \text{O} - \text{O} \cdot$ . Radical  $\text{C}_2\text{F}_5\text{OO}$  is substantially more stable than radical  $\text{C}_3\text{F}_7\text{OO}$ . It is possible to assume that it is consumed in slow reactions. Realization of higher temperatures at combustion of  $\text{C}_3\text{F}_7\text{H}$  makes the reactions accompanied with rupture of  $\text{C} - \text{F}$  bonds easier than that for combustion of  $\text{C}_2\text{F}_5\text{H}$ , so we obtain intensive soot formation in the case of  $\text{C}_3\text{F}_7\text{H}$ . But increase of  $\text{C}_3\text{F}_7\text{H}$  concentration in the mixture with  $\text{O}_2$  means appropriate increase of heat losses due to a heating of the agents and reduction of temperature of combustion. The lower temperatures of combustion lead to reduction of the rates of the reactions accompanied with rupture of  $\text{C} - \text{F}$  bonds and increase of stability of radical  $\text{C}_3\text{F}_7\text{OO}$ . Thus the intensity of soot formation decreases.

Above described peculiarities of oxidation of fluorinated hydrocarbons have significant influence on their characteristics as agents for fire extinguishing and explosion prevention. In Fig. 4 the dependences of MIC of HFC's and FC's for combustion of methane on number of C atoms in fluorinated hydrocarbon molecule are presented. As it follows from Fig.4, the MIC of  $\text{C}_3\text{F}_7\text{H}$  is substantially higher than that of  $\text{C}_2\text{F}_5\text{H}$ .

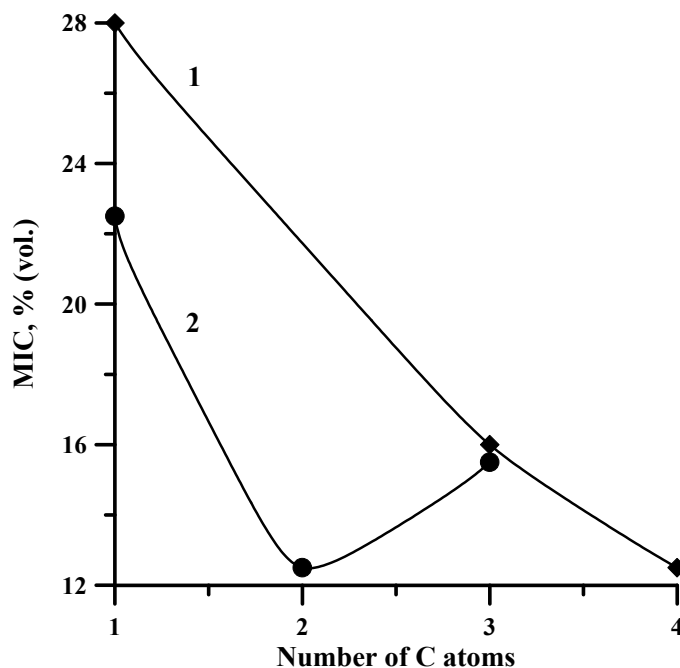


Fig.4. The dependences of MIC of HFC's and FC's for combustion of methane on number of C atoms in fluorinated hydrocarbon molecule. 1 – FC's; 2 – HFC's.

According to [1,15], the main stages of inhibition of combustion by fluorinated hydrocarbons are the following reactions:



or



and then



The rate the reaction  $\text{C}_3\text{F}_7\text{H} + \text{H}$  is higher than the rate of the reaction  $\text{C}_2\text{F}_5\text{H} + \text{H}$  at temperatures of combustion of methane. So it should be expected that heptafluoropropane is stronger inhibitor of combustion than pentafluoroethane. But really we observed reverse situation due to peculiarities of oxidation of  $\text{C}_3\text{F}_7\text{H}$ .

It is necessary to say that the reactions (3) or (4) make the oxidation of fluorinated hydrocarbons easier. It was mentioned above that  $\text{CF}_3\text{H}$  is noncombustible in oxygen. But it was obtained in [1], that an addition of  $\text{CF}_3\text{H}$  to lean methane – air or hydrogen – air mixture causes a remarkable elevation of maximum explosion pressure of combustible mixture due to additional heat release.

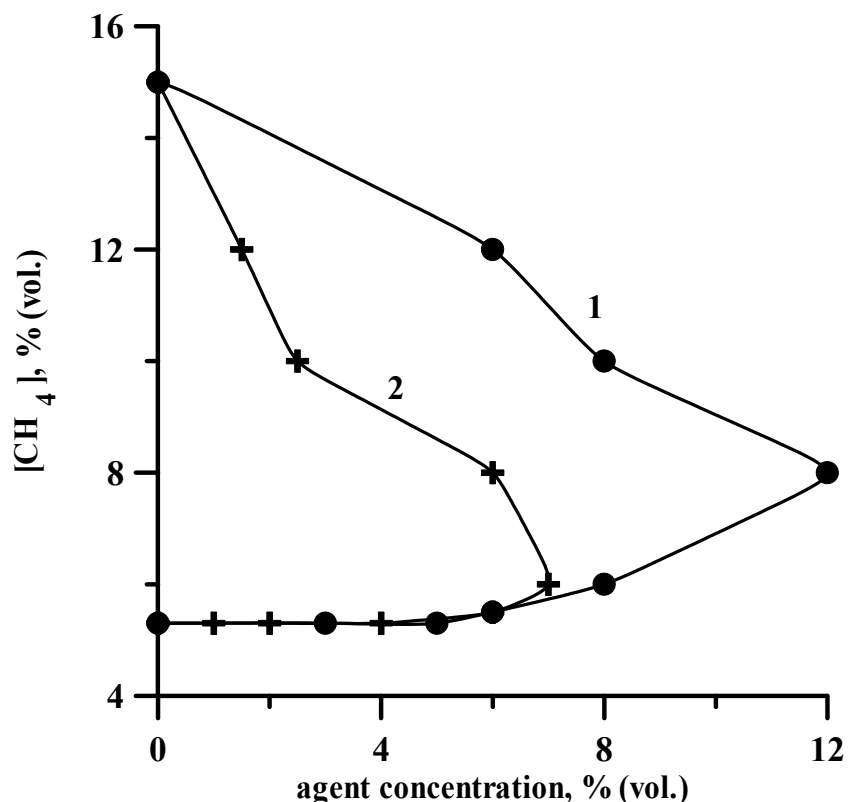


Fig.5. Flammability limits of the mixture  $\text{CH}_4/\text{air}/\text{agent}$  for explosion prevention. Agent for explosion prevention: 1 –  $\text{C}_4\text{F}_{10}$ ; 2 - 41.7 % (vol.) mixture of alkanes and alkenes (40 % (vol.)  $\text{C}_3\text{H}_8$  – 40 % (vol.)  $\text{C}_4\text{H}_{10}$  – 20 % (vol.)  $\text{C}_3\text{H}_6$ ) – 58.3 % (vol.)  $\text{C}_4\text{F}_{10}$

For the characteristics of fluorinated compounds as agents for fire extinguishing and explosion prevention to be improved, it is necessary to introduce an inhibitor of their oxidation into them. In the Figs. 5,6 the results of an investigation of an influence of the mixed agent (fluorinated compound – mixture of alkanes and alkenes (40 % (vol.)  $C_3H_8$  – 40 % (vol.)  $C_4H_{10}$  – 20 % (vol.)  $C_3H_6$ )) on combustion of methane in air are presented. Noncombustible mixtures of HFC or FC with alkanes and alkenes were used in the experiments.

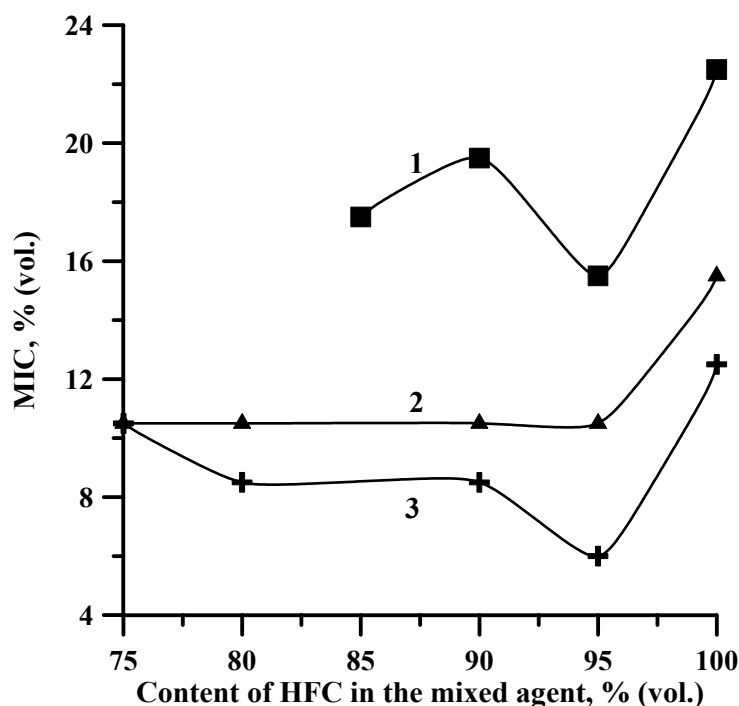


Fig. 6. Dependences of MIC of the mixed agent on content of HFC in it.  
1 –  $CF_3H$ ; 2 –  $C_3F_7H$ ; 3 –  $C_2F_5H$ .

It was shown that addition of above mentioned mixture of hydrocarbons to  $CF_3H$ ,  $C_2F_5H$  and  $C_4F_{10}$  results in substantial reduction of their MIC. For example, it has been obtained that minimum inertization concentration of the mixed agent 41.7 % (vol.) (mixture of alkanes and alkenes) – 58.3 % (vol.)  $C_4F_{10}$  for the combustible system  $CH_4$  – air – 7 % (vol.) (for comparison MIC of  $C_4F_{10}$  for the mixtures of methane and air is 12 % (vol.), see Fig. 5). The same results were obtained for  $CF_3H$ ,  $C_3F_7H$  and  $C_2F_5H$  (see Fig. 6). As it follows from Fig.6, the effectiveness of the mixed agent substantially depends on the ratio between its components. Thus the method for increase of efficiency of existing gaseous tools for explosion prevention has been proposed.

Above mentioned mixed agents are not effective for fire extinguishing due to oxidation of  $C_3H_8$ ,  $C_4H_{10}$  and  $C_3H_6$  in lean combustible mixtures. But it is possible to select another inhibitor of HFC or FC oxidation, for example, iodinated compound. It was showed in [16] that minimum fire extinguishing concentration of the mixture  $C_2F_5H$  with  $C_2F_5I$  is less on 20 %, than for  $C_2F_5H$ .

## CONCLUSIONS

1. Flammability limits of  $C_2F_5H$ ,  $C_3F_7H$  and  $C_4F_{10}$  in oxygen were determined.
2. Intensive soot formation was revealed in combustion of lean mixtures of  $C_3F_7H$  with  $O_2$ .

3. For the characteristics of fluorinated compounds as agents for fire extinguishing and explosion prevention to be improved, it is necessary to introduce an inhibitor of their oxidation into them.

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## REFERENCES

1. Shebeko, Yu.N., Azatyan, V.V., Bolodyan, I.A., Navzenya, V.Yu., Kopylov, S.N., Shebeko, D.Yu., and Zamishevski, E.D., "The Influence of Fluorinated Hydrocarbons on the Combustion of Gaseous Mixtures in a Closed Vessel," *Combustion and Flame*, v. 121, pp. 542-547, 2000.
2. Ohtani, H., "Experimental Study on Flammability Characteristics of Perfluorocarbons," *Fire Safety Science – Proceedings of the Sixth International Symposium*, International Association for Fire Safety Science, Puatier, pp. 245-254, 1999.
3. Saito, N., Tsuruda, T., and Sacurai, K., "Effect of Combustible Vapors in Air on Extinction of Cup Burner Flames by HFC and FC Fire Suppressants," *Fire Safety Science – Proceedings of the Sixth International Symposium*, International Association for Fire Safety Science, Puatier, pp. 411-420, 1999.
4. Noto, T., Babushok, V., Hamins, A., and Tsang, W., "Inhibition Effectiveness of Halogenated Compounds," *Combustion and Flame*, v. 112, pp. 147-160, 1998.
5. Walravens, B., Battin-Leclerc, F., Come, G.M., and Baronnet, F., "Inhibiting Effect of Brominated Compounds on Oxidation Reactions," *Combustion and Flame*, v. 103, pp. 339-342, 1995.
6. Grosshandler, W.L., and Gmurchzyk, G.W., "Suppression of High-Speed Flames and Quasi-Detonations," *Fire Safety Science – Proceedings of the Fifth International Symposium*, International Association for Fire Safety Science, Melbourne, pp. 853-864, 1997.
7. Gmurchzyk, G.W., Grosshandler, W.L., and Lowe, D.L., "Suppression Effectiveness of Extinguishing Agents under Highly Dynamic Conditions," *Fire Safety Science – Proceedings of the Fourth International Symposium*, International Association for Fire Safety Science, Ottawa, pp. 925-936, 1995.
8. Holmstedt, G., Andersson, P., and Andersson, J., *Fire Safety Science – Proceedings of the Fifth International Symposium*, International Association for Fire Safety Science, Melbourne, pp. 853-864, 1995.
9. Lisochkin, Ya.A., and Poznyak, V.I., "Combustibility of the Mixtures of Halons with Air at Elevated Pressures," *Combustion, Explosion and Shock Waves*, #1, v.37, pp. 32-34, 2001.
10. Matula, R.A., Orloff, D.I., and Agnew, J.T., "Burning Velocities of Fluorocarbon-Oxygen Mixtures," *Combustion and Flame*, v. 14, pp. 97-102, 1970.



11. Croomes, E.F., "The Combustion of Hydrocarbons and Fluorosubstituted Hydrocarbons with Nitrogen Trifluoride and Nitrogen Trifluoride – Oxygen Mixtures," *Combustion and Flame*, v. 10, pp. 71-77, 1966.
12. Tsarichenko, S.G., Navzenya, V.Yu., Shebeko, Yu.N., and Lashkin, S.M., "The Set-Up for Investigation of Combustibility Features of Gas – Vapor Mixtures at Elevated Pressures and Temperatures," *Fire Hazard of Substances and Materials Using in Industry*, VNIPO, Moscow, pp. 3-10, 1987 (in Russian).
13. Shebeko, Yu.N., "Burning Velocities and Flammability Limits at Elevated Temperatures and Pressures," *Combustion and Flame*, v. 102, pp. 427-437, 1995.
14. Douglass, C.H., Williams, B.A., and McDonald, J.R., "Low Pressure Flat Studies of  $C_2F_4/O_2$ ," *Combustion and Flame*, v. 107, pp. 475-478, 1996.
15. Babushok V., Noto T., Burgess, D.R.F., and Tsang, W., "Influence of  $CF_3I$ ,  $CF_3Br$ , and  $CF_3H$  on High-Temperature Combustion of Methane," *Combustion and Flame*, v. 107, pp. 351-367, 1996.
16. Baratov., A.N., Zhevlakov, A.F., and Timofeev, E.V. "About Possibility of Improving of Fire Extinguishing Effectiveness of Ozone Friendly Fire Suppressants," *Problems of Combustion and Fire Extinguishing – Proceedings of the 15<sup>th</sup> International Conference*, VNIPO, Moscow, pp. 259-260, 1999 (in Russian).