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Halon Options Technical Working
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Building and Fire Research Laboratory*

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U.S. Department of Commerce
Donald L. Evans, Secretary

Technology Administration
Phillip J. Bond, Under Secretary for Technology

National Institute of Standards and Technology
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ABOUT SUBSTITUTION FOR OZONE-DEPLETING AGENTS FOR FIRE EXTINGUISHING

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ABSTRACT

New ozone-friendly fire extinguishing mixtures based on iodinated halons are proposed in the present paper. They act on a flame both chemical inhibitor and diluent. It was obtained that mixture $\text{CF}_3\text{H}+\text{CH}_3\text{I}$ has value of minimum fire extinguishing concentration (MFEC) which is less on 20 % (vol.) or on 16 % (mass.).

The new method of determination of fire extinguishing concentrations ("cylinder" method) is proposed in this paper. Adequacy of the new method was confirmed by results of large-scale experiments. Experimental results show that values of MFEC for CF_3H , $\text{C}_2\text{F}_5\text{H}$ and CO_2 are less 34, 16, and 30 % respectively, when MFEC was determined according to "cylinder" method.

INTRODUCTION

Up to now brominated halons 1301 and 2402 were the most effective agents for fire extinguishing. But these halons destroy strongly the ozone layer of the Earth, therefore a problem of replacement of these substances by ecologically clean agents arises. Some fluorinated hydrocarbons (HFC's) were proposed in standards [1, 2] as perspective ozone-friendly agents for fire extinguishing. HFC-23 (CF_3H), HFC-125 ($\text{C}_2\text{F}_5\text{H}$) and HFC-227ea ($\text{C}_3\text{F}_7\text{H}$) are the most effective of them. These substances have low toxicity, but they are not chemical inhibitors of the processes of combustion. Their action on combustion is due to dilution of air, so HFC's are less effective than brominated halons (see Table 1). The last circumstance makes the application of HFC's for fire extinguishing substantially more expensive than application of brominated compounds.

Table 1. Comparative efficiency of halons.

Halons	Fire Extinguishing Concentration (FEC)	
	% (vol.)	kg/m ³
HFC – 23	12.9	0,38
HFC - 125	8.7	0,44
HFC - 227ea	6.5	0,46
1301	3,6	0,224
2402	2,0	0,217

It is well known, that fire extinguishing activity of halogenated hydrocarbons drops in the following sequence [3]: $\text{RI} > \text{RBr} \gg \text{RCl} > \text{RF}$ (R - hydrocarbonic radical). The absence of chemical action of chlorinated and fluorinated hydrocarbons on combustion is caused by more

high energies of the chemical bonds C-Cl and C-F in comparison with C-I and C-Br (see Table 2, [4]). According to many works and, in particular, [3], the chemical inhibition of combustion by halogenated compound is realized in reactions with participation of atoms of halogen, which are produced at decomposition of initial halogenated substance. Due to high energies of chemical bounds C-Cl and C-F the possibility of passing of above mentioned reactions becomes very small.

Table 2. Energy of chemical bonds carbon-halogen in halogenated hydrocarbons.

Halogenated hydrocarbons	Products of dissociation	Energy of chemical bound, kJ/mol
CH ₃ F	CH ₃ , F	493.8
CH ₃ Cl	CH ₃ , Cl	335.0
CH ₃ Br	CH ₃ , Br	280.3
CH ₃ I	CH ₃ , I	220.1

It is obvious that iodinated substances will be most effective agents for fire extinguishing due to their strong chemical influence on a flame. This suggestion was confirmed experimentally. It was obtained that fire extinguishing effectiveness of some iodinated inhibitors is substantially higher than that of halons 2402 and 1301. These substances are ozone-friendly, but it is difficult to use them due to their toxicity. For this problem to be avoided we propose to use iodinated inhibitors in a mixture with HFC. It is possible to expect synergetic effect stipulated by combination of chemical inhibition of combustion and dilution of oxidizer. One of the authors of the present paper was the first to offer this direction of creation of gaseous fire extinguishing agents (1961, [3]). Fire extinguishing effectiveness mixed agents (MA) offered in [3] is shown in Table 3.

Table 3 Fire-extinguishing effectiveness of MA on the basis halon 2402 and N₂.

The rate of expenditure of components of MA for extinguishing, % (vol.)		Fire-extinguishing effectiveness of halon 2402, % (vol.)
Halon 2402	N ₂	
0,53-1,19	Hydrogen 35,7-39,5	16,0
0,23-0,40	Petroleum 7,7-10,0	2,5-3,0

As it follows from Table 3, fire extinguishing effectiveness of MA increase up to 3 times in comparison with "pure" nitrogen (for extinction of petroleum flame). This effect is due to effect of synergism. The appearance of the effect of synergism indicates on increase of chemical inhibition by MA at combination of chemically active and chemically inert components in it. An explanation of observed phenomena can be made by the following way. Chemical inhibition of combustion takes place at superequilibrium concentrations of active centers – atoms and radicals – which are responsible for developing of process of combustion. When concentrations of active centers are close to equilibrium, it is necessary to use so large amounts of inhibitor for reducing of their concentrations, that chemical inhibition don't play substantial role in flame extinction. This situation takes place for combustion of hydrogen in air at atmospheric pressure [5]. Thus,

for the effect of chemical inhibition to be increased it is necessary to reduce the equilibrium concentrations of active centers, and it can be reached by cooling of the flame at dilution of air by inert diluent. It is necessary to mean, if temperature of a flame is less, then the superequilibrium concentrations of active centers are higher. The flame becomes more to chemical influence and possibility of chemical inhibition of combustion increases.

Test procedure of determination of effectiveness of gaseous fire extinguishing agents was also investigated in our experiments. Determination of FEC is a complex problem, which requires an investigation of peculiarities of interaction of fire extinguishing substance with diffusion flame of real fire. The standard Cup Burner Test Procedure gives a strong dependence of FEC on a velocity of flow (see Figure 1).

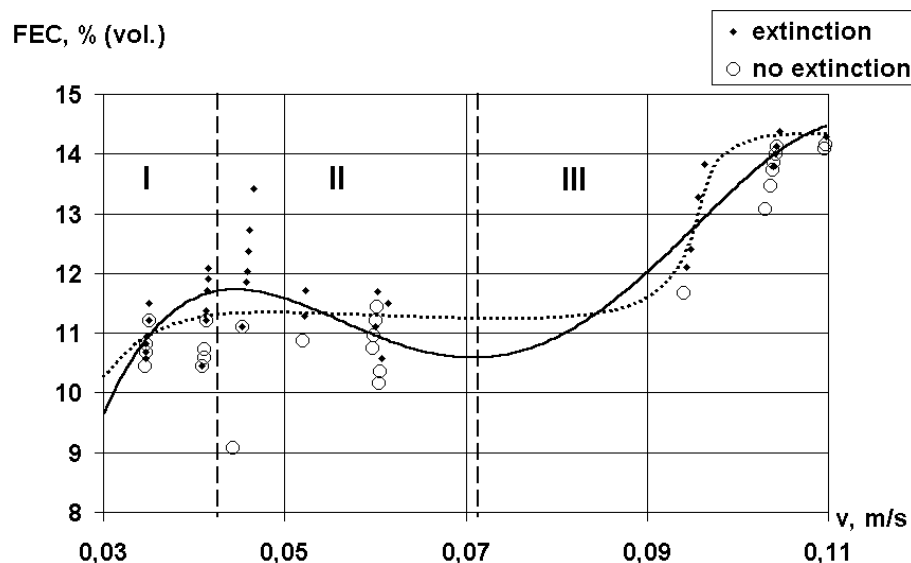


Figure 1. The dependence of FEC CF_3H on the velocity of flow: the continuous curve is built with help of computer analysis of experimental data; the dotted curve is generalized curve.

To our opinion, the "cup burner" method is not enough adequate for real conditions of fire extinguishing. First of all it is necessary to note that flame extinction in this method is realized dynamically in a co-current flow. Thus the rather complex process of extinction of the diffusion flame is influenced by additional factors stipulated by this method. It is easy to see from a Figure 1, that the dependence of FEC on the velocity of the co-current flow has complicated character and it can be divided on three zones. In the first zone the FEC rises continuously with some slowing to the end of the zone. The increase of FEC is concerned with increase of volume of zone of chemical reaction in diffusion flame of fire source under increase of intensity of flow of oxidizer. In this case the intensity of air flow is less than intensity of free convection in the flame. But to the end of the zone I the combustion is slowing down due to increase of content of inhibitor in the flame. In the second zone rates of air flow and flow in the flame are equal and this circumstance makes the conditions of penetrating of fire extinguishing agent into flame zone better. That is why the decrease of FEC takes place. Obviously, the second zone for "cup burner" method corresponds to optimum conditions of fire extinguishing. Flow rate of 0,06 – 0,07 m/s

corresponds to this zone. In the third zone the flow rate of oxidizer exceeds the flow rate of convection in the flame and penetrating of fire-extinguishing agent into flame becomes difficult. Thus, the FEC value increases again in the third zone. It is necessary to underline, that extinction of diffusion flame by air flow with additions of fire extinguishing substance takes place at larger consumption of fire extinguishing agent, than it takes place in immovable environment. In this situation we have increase of consumption of fire extinguishing substances for extinction and increase of price of fire-extinguishing systems. Besides that the modern version of Cup Burner Test Procedure [1, 2] stipulates the determination of an area, in which the FEC does not depend on velocity of the flow. In this case the absence of upper limit of the velocity of air flow leads to extremely large air flow rates. This circumstance indicates that the values of FEC for various fire extinguishing agents will be obtained under different experimental conditions. Another peculiarity of the Cup Burner Test Procedure is the following: increase of concentration of fire extinguishing substance during the experiment is carried out step-by-step up to reaching of extinction. But it was shown in our experiments that in above mentioned case the extinction occurs at larger concentration of fire suppression agent than in the case of setting of total flow rate of the agent. This is probably due to adaptation of diffusion torch in new conditions: in the case of smooth increase of concentration of the agent it is possible to assume that the system passes through the steady-state conditions. Substantial changes take place in the case of fast increase of the concentration of the agent; this effect facilitates the extinction of the flame. This phenomena is distinctly observed at fire extinguishing by nitrogen. In real conditions the increase of agent concentration in a protected enclosure from zero point up to the FEC happens for a short time interval (~ 10 sec.). It is necessary to note that above mentioned circumstances substantially remove the "cup burner" method from real conditions of volume fire extinguishing.

Another important problem at determination of the FEC is the choice of a time of extinguishing. In particular, it is necessary to analyze a relationship between the FEC and the time of extinguishing (τ_E) with the purpose to make practical choice of the FEC value from dependence $FEC = f(\tau_E)$. If we will make the choice on the basis instantaneous extinguishing (the time of extinguishing will tend to zero), the FEC will be too large. If we will demand the greater time of extinguishing, the FEC will be too low. The attempt of the theoretical substantiation of time of extinguishing for determination of the FEC will be given below.

THE THEORETICAL SUBSTANTIATION OF TIME OF EXTINGUISHING

The attempt of an analytical solution of a problem, is based on following assumptions. Supply of inhibitor in flame is made by diffusion transfer in direction of normal to the flame surface. Fire extinguishing realises through decrease of active center's concentration, which is equal C_0 in case of absence of inhibitors. Concentration of inhibitor in the air is assumed equal $C(x,t)$, where x - coordinate, t – time. Then alternation of inhibitor's concentration in the result of diffusion will be:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where D – diffusion coefficient.

Assume that a beginning condition:

$$C(x,0) = C_{\infty} \quad (2)$$

Inhibition of flame is determined by:

$$C_a = C_0 - KC(0,t) \quad (3)$$

where K – constant of reaction rate.

Diffusion flow of inhibitor to flame surface is proportioned to C_a .

Then boundary condition will be:

$$D \frac{\partial C(0,t)}{\partial x} = \alpha(C_0 - KC(0,t)) \quad (4)$$

where α - proportioned coefficient.

Assume the following extinguishing condition:

$$D \frac{\partial C(0,t^x)}{\partial x} = 0 \quad (5)$$

where t^x – extinction time.

In order to solve (1), (2) and (5) we introduce dimensionless variables:

$$\xi = x/l, r = t/t_0 \quad (6)$$

where

l – flame thickness,

t_0 – time scale.

Transform (2) and (5) to the following:

$$\frac{\partial C(\xi,r)}{\partial r} = \frac{Dt_0}{l^2} \frac{\partial^2 C(\xi,r)}{\partial \xi^2} \quad (7)$$

Assume

$$\frac{Dt_0}{l^2} = 1, \text{ that is } t_0 = \frac{l^2}{D} \quad (8)$$

$$\frac{\partial C(0,r)}{\partial \xi} = \frac{\alpha l}{D} (C_0 - KC(0,\tau)) \quad (9)$$

Introduce dimensionless concentration:

$$U = 1 - C/C_\infty \quad (10)$$

Then (7) will be:

$$\frac{\partial U(\xi,r)}{\partial r} = \frac{\partial^2 U(\xi,r)}{\partial \xi^2} \quad (11)$$

and (2) goes into

$$U(\xi,0) = 0 \quad (12)$$

with regard to (10):

$$\frac{\partial U(0,r)}{\partial \xi} + \beta U(0,r) = \psi \quad (13)$$

Where

$$\beta = \frac{K\alpha l}{D}; \quad (14)$$

$$\beta\psi = \frac{\alpha l}{D} \left(K - \frac{C_0}{C_\infty} \right) = \beta - \frac{\alpha l C_0}{D C_\infty} = \beta \left(1 - \frac{C_0}{K C_\infty} \right)$$

where β and ψ - dimensionless complexes.

Extinguishing condition will be:

$$\frac{\partial U(0,r^x)}{\partial \xi} = 0 \quad (15)$$

where

$$r^x = t^x/t_0 \quad (16)$$

and the following solution will be:

$$\frac{\partial U}{\partial r} = \frac{\partial^2 U}{\partial \xi^2} \quad (17)$$

$$U(\xi, 0) = 0 \quad (18)$$

$$\frac{\partial U(0, r)}{\partial \xi} + \beta U(0, r) = \beta \psi \quad (19)$$

$$\frac{\partial U(0, r^x)}{\partial \xi} = 0 \text{ or } U(0, r^x) = \psi \quad (20)$$

You can see from (19) that expressions in (20) are interchangeable.

Solution of the sum (17)-(19) will be:

$$U(\xi, r) = \frac{\beta \psi}{\sqrt{\pi}} \int_0^r H(\xi, v) \frac{dv}{\sqrt{v}} \quad (21)$$

where

$$H(\xi, r) = e^{-\frac{\xi^2}{4r}} + \beta \int_0^\infty \exp\left[-\frac{(\xi + \eta)^2}{4r} + \beta \eta\right] d\eta$$

It is easy to show, that:

$$H(0, r) = 1 + \beta e^{\beta^2 r} \sqrt{\pi r} (1 + \operatorname{erf} \beta \sqrt{r}) \quad (22)$$

where

$$\operatorname{erf} \beta \sqrt{r} = \frac{2}{\sqrt{\pi}} \int_0^{\beta \sqrt{r}} e^{-v^2} dv \quad (23)$$

Then

$$\frac{2\sqrt{r^x}}{\sqrt{\pi}} + \beta \int_0^{r^x} e^{\beta^2 v} (1 + \operatorname{erf} \beta \sqrt{v}) dv = \beta^{-1} \quad (24)$$

Equation (24) is a condition for determination of extinction time t^x .

Mark $\frac{\beta^{-1}}{2\sqrt{\pi}}$ through "A" and $\frac{\beta}{2\sqrt{\pi}} \int_0^{r^x} e^{\beta^2 v} (1 + \operatorname{erf} \beta \sqrt{v}) dv$ through "F", we have:

$$\tau^x = (A - F)^2 \frac{t^x}{t_0} \text{ and } t^x = \tau^x t_0 (A - F)^2 t_0 \quad (25)$$

Diffusion coefficient value of compositions of fluorine- iod-containing substances estimated with help of [4] is $D = 0,07 \text{ sm}^2/\text{s}$. In order to estimate the value of l in the expression (8) we assume that l equals the thickness of light zone of diffusion flame and according to [6] equals approximately 10 mm. Analysis of expressions (24), (25) shows that value of the first factor in (25) is closed to 1. With regard to these assumptions we have from (25) extinction time $t^x \sim 15 \text{ s}$. Assume this with some safety margin $t^x = 10 \text{ s}$. This value is very closed to the tangency point of the dependence "extinction time – fire-extinguishing concentration".

EXPERIMENTAL

Experiments were by "cylinder" method in a set-up, which scheme is presented in Figure 2.

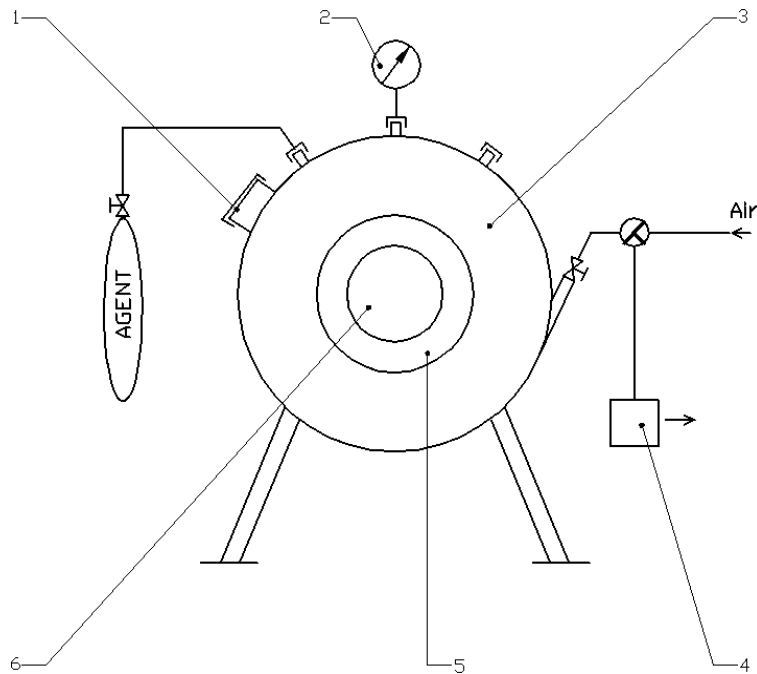


Figure 2. Diagram of the experimental set-up:

- 1 – manhole for input of the model fire source; 2 – vacuummeter; 3 – experimental vessel;
4 – vacuum pumping; 5 – manhole for ventilation; 6 – window

An experimental vessel of the set-up has a cylindrical form and is made from steel. Its diameter is 0.38 m, volume 50 dm^3 . The set-up has a system for preparing of gaseous mixtures and vacuum pumping system. The required gaseous mixture is formed by partial pressures in the experimental vessel previously evacuated to 5-8 mm Hg. Steel cup was used as a fire source. Its

diameter is 40 mm, height 23 mm. Heptane was used as fuel in the experiments. The fire source was ignited and then introduced into the experimental vessel with prepared gaseous mixture in it. The moment of extinction was determined visually. The experimental results are presented in coordinates "time of extinguishing – concentration of fire suppression agent" (typical dependence is shown on Figure 3). The FEC corresponds to the time of fire extinguishing 10 sec.

For an estimation of adequacy of described test method the large scale experiments were conducted. The experiments were in rectangular metal enclosure, which has sizes 1x1x1.15 m and volume 1.16 m³. Fire extinguishing agent was introduced into the enclosure through the nozzle. Cups with diameter 45 mm and length 90 mm were used as fire source. The fire source was made from porcelain. Heptane was used as a fuel in the experiments. The positions of the fire sources in the enclosure were selected so that they were not exposed to the stream of fire extinguishing agent. The time of free combustion with open door of the enclosure was 60 sec. The experimental results were presented in coordinates "time of extinguishing – concentration of fire suppression agent". The FEC corresponds to the time of fire extinguishing 70 sec. This time consists of time of introduction of fire suppression agent (30 sec.), time of distribution of the agent in the enclosure (30 sec.; [7]), and time of extinction (10 sec.).

EXPERIMENTAL RESULTS

HFC-23 and HFC-125 were used as diluents in the experiments; CH₃I was used as chemical inhibitor. The properties of these substances are presented in Table 4.

Table 4. Physicochemical properties of components of MA.

	CF ₃ H	C ₂ F ₅ H	CH ₃ I
Molecular mass	70	120	142
Purity, %	99,9	99,9	99,8
Boiling point, °C	-82,1	-48,5	42,5
Density of liquid, g/ml	-	-	2,28
Density of vapour, kg/m ³	2,9	5,0	5,9

The experimental results are presented in Table 5. Dependence of the time of extinguishing on concentration of fire suppression agent is shown in Figure 3.

Table 5. Fire extinguishing concentration for heptane fire ("cylinder" method).

Substance	Fire extinguishing concentration	
	% (vol.)	kg/m ³
HFC-23 (CF ₃ H)	8,5	0,248
HFC-125 (C ₂ F ₅ H)	7,3	0,360
CH ₃ I	2,0	0,132
CF ₃ H (90 % (mass.)) + CH ₃ I (10 % (mass.))	6.8	0,209
C ₂ F ₅ H (90 % (mass.)) + CH ₃ I (10 % (mass.))	5.1	0,259

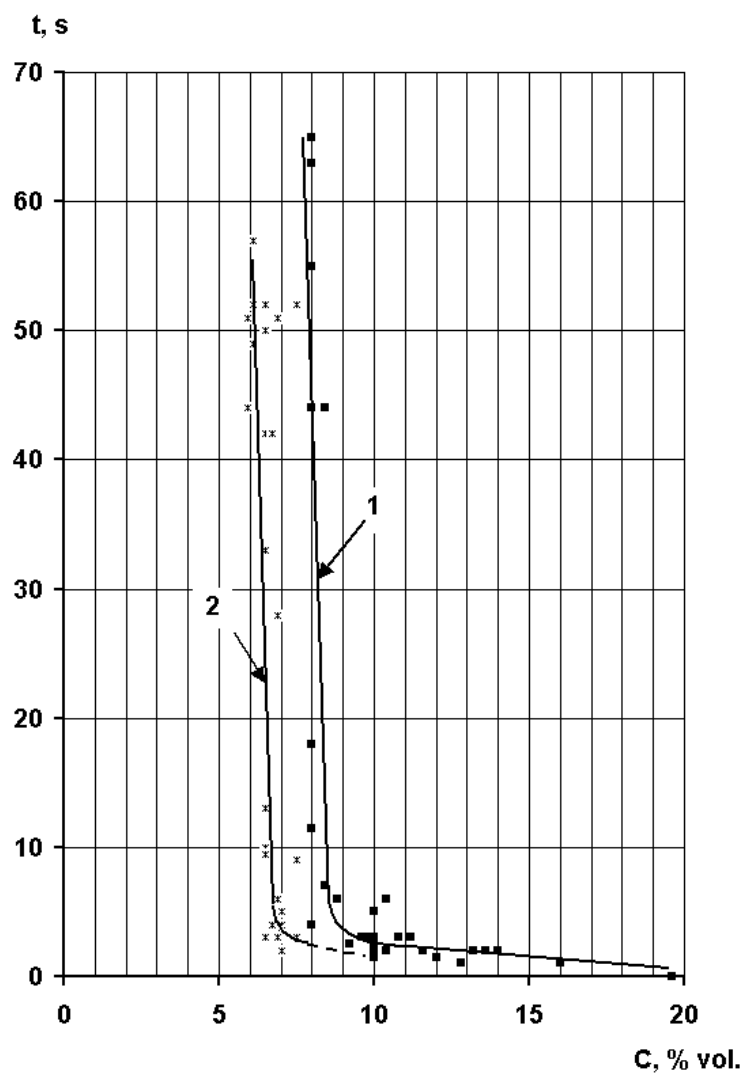


Fig. 3 Dependences of time of extinguishing on a volume concentration OTB:
 1 – CF₃H; 2 - CF₃H (90 % (mass.)) + CH₃I (10 % (mass.))

It is easy to see that the FEC's of CF_3H and $\text{C}_2\text{F}_5\text{H}$, which were obtained by "cylinder" method are less than the FEC's of these agents, which were obtained by standard "cup burner method" (12.9 % for CF_3H , 8.7 % for $\text{C}_2\text{F}_5\text{H}$ [8]). This result is due to above mentioned reasons.

The following positions were used for the choice of ratio between components of MA: mixed agents must have high fire extinguishing ability; safety of the people must be provided at the using of MA. The experimental results show that the highest efficiency of MA takes place at rather low concentration of inhibitor (10 – 15 % (mass.)) in it. This result corresponds to known opinion about action of chemical inhibitor on combustion process [3]. If the LOAEL value for CH_3I is the same as for CF_3I , which is equal to 0.5 % (vol.) at the time of evacuation 30 sec., we obtain the following optimum ratio between components of investigated MA: 90 % (mass.) CF_3H and 10 % (mass.) CH_3I . This composition was patented [9] and has trade mark TFM-18I. According to the data from table 5, fire extinguishing concentration of this composition is 6.8 % (vol.). Concentration of CH_3I in the protected enclosure for fire extinguishing by TFM-18I is ca. 0.4 % (vol.), i.e. substantially below than accepted value of LOAEL. Analysis of the data in Table 5 shows that MA's are effective than HFC-23 and HFC-125 on 20 – 30 %. It is easy to see that concentration of iodinated substance is ca. 20 g/m^3 , so expenses on exploitation of fire suppression systems with using of HFC-23 and HFC-125 will be reduced on 2-3 $\$/\text{m}^3$.

The results of large-scale test show that the FEC of TFM-18I is 6.9 % (vol.), i.e. 0.212 kg/m^3 .

CONCLUSIONS

1. The new method of determination of fire extinguishing concentrations ("cylinder" method) was proposed in the paper.
2. Adequacy of the new method was confirmed by results of large-scale tests.
3. New ozone-friendly fire extinguishing mixture TFM-18I based on iodinated halons was proposed in the paper.

ACKNOWLEDGMENTS

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