

*Теоретично обґрунтована та експериментально доведена ефективність комбінованого впливу бінарної суміші вогнегасного аерозолі та газів CO<sub>2</sub> та N<sub>2</sub> на зниження швидкості полум'я n-гептаноповітряної суміші. Експериментально виявлено, що дія бінарних сумішей на n-гептаноповітряну суміш знижує швидкість поширення полум'я по ній до 6,5 разів у порівнянні з швидкістю поширення полум'я по стехіометричній суміші*

*Ключові слова: флегматизатор, інгібітор горіння, вогнегасний аерозоль, комбіноване гасіння, аерозолеутворювальна сполука*

*Теоретически обоснована и экспериментально доказана эффективность комбинированного воздействия бинарной смеси огнетушащего аэрозоля и газов CO<sub>2</sub> и N<sub>2</sub> на снижение скорости пламени n-гептановоздушной смеси. Экспериментально обнаружено, что действие бинарных смесей на n-гептановоздушную смесь снижает скорость распространения пламени по ней до 6,5 раз по сравнению со скоростью распространения пламени по стехиометрической смеси*

*Ключевые слова: флегматизатор, ингибитор горения, огнетушащий аерозоль, комбинированное тушение, аерозольобразующая смесь*

UDC 614.84

DOI: 10.15587/1729-4061.2017.108427

# EFFECT OF ECOLOGICALLY SAFE GAS-AEROSOL MIXTURES ON THE VELOCITY OF EXPLOSIVE COMBUSTION OF n-HEPTANE

**V. Balanyuk**

PhD, Associate Professor, Colonel of service of civil protection  
Department of postgraduate studies and doctoral studies\*  
E-mail: bagr9111@gmail.com

**V. Kovalyshyn**

Doctor of Technical Sciences, Professor, Head of Department  
Department of fire tactics and rescue operations\*  
E-mail: kovalyshyn.v@gmail.com

**N. Kozyar**

PhD, Deputy Chief, Colonel of the Civil Protection Service  
Main Control service emergencies Ukraine in Kiev  
Volodymyrska str., 13, Kyiv, Ukraine, 01601  
E-mail: Kozyar777@ukr.net

\*Lviv State University of Life Safety  
Kleparivska str., 35, Lviv, Ukraine, 79000

## 1. Introduction

Modern means of volumetric fire suppression, as it is known, do not always provide adequate fire extinguishing efficiency and retardation. That is why quite often there are cases when a fire and an explosion still occur even under condition of protection of the volume with fire extinguishing gases or powders. In such cases, the explosion front might propagate at the corresponding velocity, which may lead to a partial or complete destruction of the equipment through creation, in this case, of the elevated pressure. It is known that the fire extinguishing concentration of CO<sub>2</sub> for most hydrocarbons is about 21 %, and retarding concentration is about 30 % or higher [1–4]. For nitrogen, these values are, respectively, for n-heptane (C<sub>7</sub>H<sub>16</sub>) 33.6 % [4, 5], and retarding concentration of N<sub>2</sub> is 43.9 %, which is 3–4 times as high as the retarding concentration of khladons [5]. In addition, according to the Montreal Protocol [6], CO<sub>2</sub> relates to greenhouse gases, emissions of which are regulated. Often enough, in order to limit the use of CO<sub>2</sub>, it is replaced with nitrogen N<sub>2</sub> as an environmentally friendly fire extinguishing agent. Nitrogen as a fire extinguishing agent is chemically neutral to most substances, cheap and easily available.

Thus, for effective explosion protection, it is required to use enormous amounts of CO<sub>2</sub> or N<sub>2</sub> gases, or khladons, which

in most cases are toxic; in addition, their production and usage are banned because they deplete the planet's ozone layer [7].

At present, an alternative to gas extinguishing agents is the binary mixtures of the specified gases with a fire extinguishing aerosol [4], in which (at certain ratios) fire extinguishing and retarding concentrations of CO<sub>2</sub> and N<sub>2</sub> are considerably smaller than their individual fire extinguishing and retarding concentrations.

In this case, a combination of advantages of the aerosol as a clean, efficient and low-cost fire-extinguishing agent, and benefits of gases makes it possible to obtain a super-effective binary mixture with universal fire extinguishing characteristics. The specified mixture will possess high fire extinguishing capacity, will be environmentally clean, quite cheap and have the capability to effectively suppress explosions or decrease the scale of consequences due to a decrease in the velocity of propagation of the explosive flame front. This will prevent or minimize the effects of explosions.

Thus, at present, there is a lack of effective extinguishing agents, which would provide protection against explosions and fires for sites of chemical, light, petrochemical, nuclear, and machine-building industry. In these industries, there are sites with considerable volumes of circulation and storage of flammable, combustible and explosive substances, which in case of explosion or fire lead to catastrophic consequences.

Such fires cause significant destructions and contamination of the environment as a result of possible explosions and significant volumes of combustion. Thus, over the past few years, there have been several dozens of catastrophic fires. The most devastating of them are the fires that took place in Kuwait in 1990–1992 at oil wells, oil storage depots, in Hemel Hempstead, Hertfordshire, UK; in the village of Kriachki, Kyiv Oblast, Ukraine, on June, 8, 2015, at the oil depot, etc. All of these fires lasted for up to 7 days, the modern means of fire extinguishing were used – fire extinguishing foam, water with wetting agents, and extinguishing powders. The possibility of initiation and lengthy existence of such fires emphasizes the relevance of the specified topic of research.

## 2. Literature review and problem statement

Gas-vapor-air mixtures are known to explode at various velocities of flame front propagation. In general, at an explosion of a homogeneous gas-vapor-air mixture, velocity of flame front propagation is 0.5–10 m/s for deflagrational combustion, 7–12 m/s for kinetic combustion, and 200–3000 m/s for detonational combustion [8]. Under certain conditions, namely, when the walls of a reaction vessel are rough or at large volumes of flammable mixture [8], a combustion of gas-vapor-air mixture abruptly passes into detonational. Detonation is extremely dangerous, because flame velocity rises up to several thousand meters per second, and pressure – up to several thousand atmospheres.

At present, gases and powders are mainly used for the retardation and prevention of explosion. Retardation concentration is known to be 1.4 times as high as a fire-extinguishing concentration; the consumption of fire-extinguishing agents (mixture) for retardation will increase, accordingly, by times. At depressurization of volume, consumption may increase even larger and it is not always possible to create the necessary concentration for effective retardation. Given these characteristics, all known means of volumetric fire extinguishing share a common drawback – devices that implement the retardation method with their use are rather sizeable, gas storage requires a significant number of cylinders, and powder storage requires rather big containers. Fire extinguishing aerosol powder in this case requires regular replacement, as it possesses the ability to cake. In addition, it takes too long to supply the above-mentioned substances, compared with a velocity of explosive front propagation. Therefore, these methods have a number of shortcomings that render relevant the subject matter of explosion safety of homogeneous combustible mixtures.

It is known from an analysis of scientific literature [4, 5] that binary mixtures of fire-extinguishing aerosol and gas-retardants have a high fire extinguishing and retarding efficiency. In a binary gas-aerosol mixture, their effective extinguishing ratios is from 5 g/m<sup>3</sup> of aerosol and from 2.5 % of CO<sub>2</sub> or N<sub>2</sub> gases.

Fig. 1, which shows results of research [9], demonstrates that a fire extinguishing aerosol concentration with the addition of CO<sub>2</sub> rapidly decreases. Thus, when adding CO<sub>2</sub> in a range of concentrations of up to 5 %, fire extinguishing aerosol concentration decreases larger than twice.

The structure of aerosol [9] is known to be constantly changing – from the moment of aerosol formation and its transformation under the influence of flame in the process of

extinguishing. In this case, the first to occur is the process of absorption of CO<sub>2</sub> and N<sub>2</sub> gases with the formation of salts K<sub>2</sub>CO<sub>3</sub>, KCl, KHCO<sub>3</sub>, KOH, which provide a fire extinguishing effect. Such structures will have much more efficient fire-retardant effect due to a combined action of the mixture of inhibitors and retardants [10]. The same indicators will be characteristic for the fire extinguishing aerosol, formed during combustion of the aerosol forming mixture that additionally contain gasifiers – DCDA, DFA, which provide for the formation of CO<sub>2</sub> and N<sub>2</sub> gases. This greatly enhances fire extinguishing effectiveness of the aerosol and is in line with results of papers [9–11]. Thus, article [9] indicated that the addition of CO<sub>2</sub> gases to the fire-extinguishing aerosol, based on potassium salts, leads to reducing its fire-extinguishing concentration for hydrocarbon fuel from 33 g/m<sup>3</sup> to 12 g/m<sup>3</sup> at CO<sub>2</sub> concentration of only 5 %. In article [10], authors also established a significant decrease in the fire-extinguishing concentrations of aerosol at suppression of a diffusive methane flame. Paper [11] reports a significant retarding effectiveness of the specified mixtures for hexane-air media; at 10 % of CO<sub>2</sub>, it is necessary to add only 8 g/m<sup>3</sup> of the aerosol to provide effective retardation. Therefore, the addition of gases to aerosol considerably increases fire extinguishing effectiveness of a gas-aerosol mixture. Effectiveness of the binary mixture increases dramatically at addition of CO<sub>2</sub> to aerosol, probably due to its large thermal capacity, which can be proved by results of the work, given on the diagram in Fig. 1. As for fire-extinguishing gases, we should note that gases-rarefiers, which include in particular carbon dioxide, nitrogen, argon and their mixtures, are non-toxic and do not produce toxic products of thermal decomposition, do not deplete the ozone layer and are more readily available and cheaper than the combustion inhibitors. One of the first gas fire-extinguishing substances, proposed as an alternative to khladons, was carbon dioxide (CO<sub>2</sub>) [12].

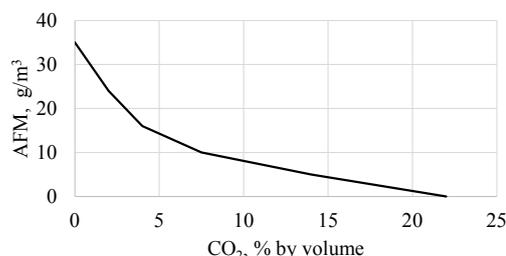


Fig. 1. Effect of CO<sub>2</sub> addition on the fire extinguishing efficiency of aerosol [9]

As for a fire-extinguishing aerosol, its fire extinguishing effectiveness mostly depends on the size of particles. Thus, paper [13] shows that with a decrease in the dimensions of particles from 100 to 20 μm, velocity of flame propagation drops dramatically with the addition of dispersed particles of salt NaCl, K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub> and others to the propane-air mixture. As authors of [13] assume, this happens due to heat absorption and particles evaporation into the flame.

Article [14] shows that there is a direct relationship between dimensions of particles and fire-extinguishing efficiency, flame propagation velocity, which is manifested due to a possible decomposition of these particles in the flame, which provides retardation and inhibition of combustible mixture and the flame.

Thus, paper [15] argues that by using a mixture of free radicals and CO<sub>2</sub> it is possible to decrease the concentration

of fire-extinguishing chemical agents by 3–4 times. The conclusion of the authors [16] indicates that non-combustible gaseous components dilute a combustible system and decrease oxygen concentration. This leads to a decrease in the fire-extinguishing effectiveness of an inhibitor, which, naturally, dramatically decreases the velocity of flame propagation. In article [17], it is indicated that the addition of nitrogen leads to a significant decrease in the fire-extinguishing concentration of hladone 1301, for n-heptane, while maintaining all useful properties of the components. Paper [18] clearly states that the fire extinguishing effectiveness of the mixture of inhibitors and retardants significantly increases due to synergy among them [18–23]. Paper [19] presents calculations of flame temperature at addition of inert gases to a mixture of inhibitor and flegmatizer. They showed a decrease in flame temperature, which in turn provides enhancing of inhibiting effect of the mixture of hladone-1301 and CO<sub>2</sub>. Author of paper [20] pointed out to a substantial efficiency of fire-extinguishing aerosol during extinguishing flammable liquids in the open space with a fire-extinguishing supply intensity of 8 g/m<sup>2</sup>·s. Regarding the influence on living organisms, authors of article [21] note that male rats tolerate a 60-minute influence of aerosol without any significant damage. In this case, a fire-extinguishing aerosol remains in suspension in the air for maximum 40 minutes. Accordingly, it is possible to argue about relative safety of the fire-extinguishing aerosol for living organisms, in particular humans. Combined use of CO<sub>2</sub> and N<sub>2</sub> gases along with fire-extinguishing powders is also known. Paper [22] indicates that the combined fire-extinguishing with powder and inert gases also leads to a decrease in fire-extinguishing concentration of the powder. The same is stated in article [23]. In paper [24], authors emphasize that the additional amount of combustion products in the volume will cause an increase in the activation energy of combustible systems by almost 100 times. Addition of CO<sub>2</sub> and N<sub>2</sub> gases results in a decrease in the velocity of laminar hydrogen flame and low pressures. In this case, the addition of CO<sub>2</sub> has greater effectiveness in contrast to N<sub>2</sub>, the impact of which on the flame propagation velocity is not sufficiently known, which is outlined in paper [25] that notes a somewhat larger significant suppressing effect of N<sub>2</sub> on flame propagation than that expected. Article [26] also highlights a significant impact of CO<sub>2</sub> on the velocity of propagation of laminar flame under conditions of decreased gravity, and emphasizes considerable fire-extinguishing influence of CO<sub>2</sub> under these conditions.

Thus, the use of binary mixtures of fire-extinguishing aerosol and gases-retardants for retarding combustible mixtures is effective, but not completely studied, given the fact that almost all factors of influence are implemented in them – inhibition, cooling, dilution and retardation. In particular, a problem of the impact of these mixtures on flame propagation velocity during explosions of homogeneous gas-vapor-air mixtures was not sufficiently examined.

To determine characteristics of influence of binary mixtures of fire-extinguishing aerosol and CO<sub>2</sub> or N<sub>2</sub> on the velocity of explosive combustion of a homogeneous combustible mixture, it is most expedient to use a vapor-air heptane mixture. Accordingly, determining a dependence of the velocity of flame propagation throughout a stoichiometric heptane-air mixture (SHAM) on additives and parameters of binary gas-aerosol mixture will make it possible to determine conditions of effective retardation and explosion suppression. Obtaining data on the influence of binary gas-aero-

sol mixtures on the velocity of flame propagation throughout a stoichiometric n-heptane-air mixture will make it possible to prevent the emergence of deflagration, kinetic or detonational combustion in homogeneous combustible systems, as well as it will minimize effects of explosions in such cases.

Thus, determining the features of the impact of environmentally safe binary gas-aerosol mixtures on the velocity of explosive combustion of n-heptane will enable us to provide effective fire-retardant and anti-explosion protection of sites of chemical, light, petrochemical, nuclear, and machine-building industry, at which a formation of combustible homogeneous media is possible.

---

### 3. The goal and objectives of research

---

The goal of present research was to provide the minimization of effects of explosions of homogeneous combustible mixtures using ecologically safe binary gas-aerosol mixtures (aerosol and gas CO<sub>2</sub> or N<sub>2</sub>).

To accomplish the set goal, the following tasks had to be solved:

- to establish experimentally the effect of binary gas-aerosol mixtures (aerosol – CO<sub>2</sub> or N<sub>2</sub>) on a stoichiometric n-heptane-air mixture and to determine flame propagation velocity in it;
- to perform a frame by frame analysis and to analyze and identify the features of influence of the addition of binary mixtures of fire-extinguishing aerosol and gases-retardants on an explosion of stoichiometric n-heptane mixtures.

---

### 4. Materials and methods of examining the influence of gas-aerosol mixtures on flame velocity

---

To determine velocity of flame propagation throughout SHAM under the action of binary gas-aerosol mixtures, we used the following materials and devices: aerosol-forming mixture (AFM), consisting of 20 % of iditol (C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>) and 80 % of potassium nitrate (KNO<sub>3</sub>). AFM is prepared by agitating a respective weight of the charge. Nitrogen – N<sub>2</sub> and CO<sub>2</sub> are 99.96 % chemically pure. Viderecording of the explosive combustion was performed by the photocamera Nikon 1 J4, which can take 3-second videos with a frame rate of 1200 per second at a resolution of 416 x 144 p [28].

The base of the plant (Fig. 2) is a thick-walled glass cylindrical vessel of 0.5 l capacity with a powerful electrical ignition source, located inside the cylinder. The upper and lower parts of the cylinder are closed with lids. On the underside lid, there is source of ignition 2, the top lid has a opening, covered with rubber cork 4, and a spiral igniter of AFM 5. The glass housing of cylinder 1 is fixed on the bench on two vertical racks 6. The fasteners of the glass cylinder make it possible to rotate it in the vertical plane. The rubber cork contains a gas pipe, by which gas is fed. Distance from the source of ignition to the top wall of the cylinder is 135 mm, to the bottom wall – 80 mm.

Ignition of the batch of AFM was performed by coil electrical igniter, the amount of gas was measured using a piston measurer with a volume of 100 ml. The experiment was carried out as in the following way: the cylinder was heated up to 50 °C. Then the batch of AFM was combusted in the volume of the cylinder and appropriate amount of nitrogen N<sub>2</sub>, or CO<sub>2</sub> was added, after that, an appropriate amount

of n-heptane was dripped in order to obtain the stoichiometric concentration, the resulting mixture was stirred and ignited by pushing the electrical igniter button 3. Results of the tests were recorded on video under the following states: “explosion”, “failure”, “slow combustion”.

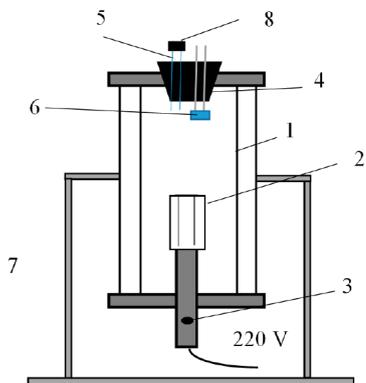


Fig. 2. Plant for determining a retarding concentration of gas-aerosol mixture: 1 – glass housing of the cylinder; 2 – electrical igniter; 3 – electrical igniter button; 4 – rubber cork; 5 – gas pipe; 6 – coil igniter of AFM; 7 – vertical racks; 8 – plug

### 5. Results of study of the effect of additions of gas-aerosol mixture on flame propagation velocity

The frame by frame video recording of the effect of binary mixture on the process of ignition of SHAM, which contains 11 g/m<sup>3</sup> of aerosol and 6 % of CO<sub>2</sub>, is shown in Fig. 3.

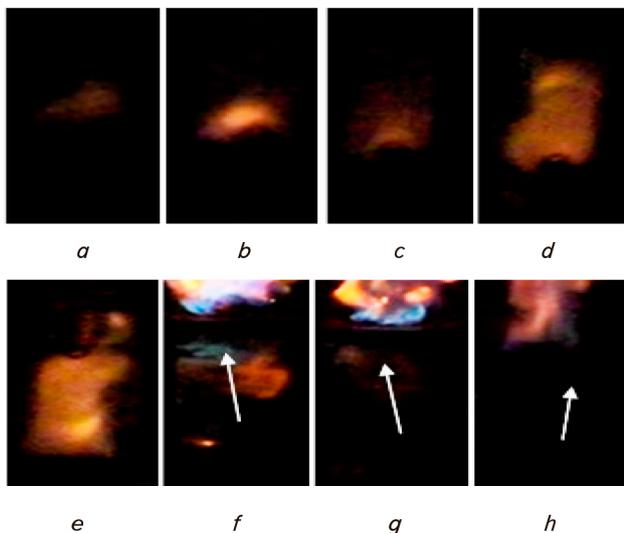


Fig. 3. Frame by frame video recording of the effect of binary mixture of fire-extinguishing aerosol and CO<sub>2</sub> on explosion of SHAM. Aerosol – 11 g/m<sup>3</sup>, gas CO<sub>2</sub> – 6 %.

Velocity – 0.5 m/s; a – 5 ms; b – 50 ms; c – 200 ms; d – 350 ms; e – 500 ms; f – 510 ms; g – 530 ms; h – 540 ms

The frame by frame video recording (Fig. 3) shows that the addition of the binary mixture of aerosol and CO<sub>2</sub> to SHAM leads to a significant decrease in the flame propagation velocity, which is seen by the time of explosion, which is about 530 ms (Fig. 3). In this case, (Fig. 3, a–e), the flame front propagates randomly and in a non-uniform

fashion throughout the combustible homogeneous stoichiometric heptane-air mixture. In the process of combustion of SHAM, not earlier than at millisecond 500 (Fig. 3, e) the flame front increases in size and reaches the walls of the cylinder. At ms 510 (Fig. 3, f), the cork is pushed out (Fig. 3, g) and the flame front is pressed out towards the outside, but at a slight pressure. Then complete combustion of SHAM takes place outside the cylinder (Fig. 3, h).

Thus, based on the results of experiments, we plotted graphs of dependences of the velocity of flame propagation throughout SHAM on concentrations and ratios of the components of the binary mixture (Fig. 4, 5).

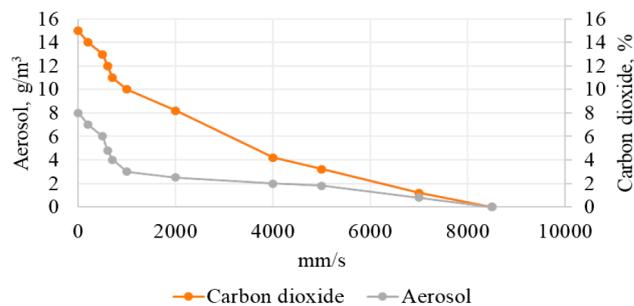


Fig. 4. Dependence of velocity of flame propagation throughout stoichiometric n-heptane-air mixture on concentration and ratio of aerosol and carbon dioxide

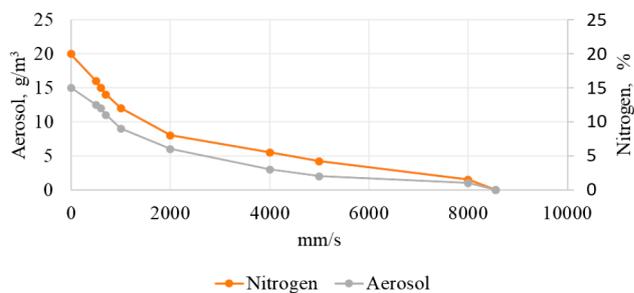


Fig. 5. Dependence of velocity of flame propagation throughout stoichiometric n-heptane-air mixture on concentration and ratio of aerosol and nitrogen

Therefore, it is evident from the results of the experiment that even a slight addition of the binary mixture of aerosol and an inert diluent significantly reduces the normal combustion velocity of stoichiometric n-heptane-air mixture.

Fig. 4, 5 show that the flame front velocity sharply decreases with the addition of even a small amount of mixture of aerosol with gases. In addition, according to the results of theoretical analysis and experiments, binary gas-aerosol mixtures with CO<sub>2</sub> were found to be much more efficient than N<sub>2</sub>-based mixtures. In this case, as it can be seen from graph in Fig. 4, a maximum decrease in velocity occurs within the concentration of aerosol from 8 g/m<sup>3</sup> to 2.2 g/m<sup>3</sup> and at concentration of CO<sub>2</sub> from 16 % to 8.2 %. In this case, the flame propagation velocity was approximately 1.8 m/s. For nitrogen-aerosol mixture, these values corresponded to the amount of aerosol from 15 g/m<sup>3</sup> to 6.5 g/m<sup>3</sup> and of N<sub>2</sub> gas from 20 % to 8.5 %. In this case, flame propagation velocity was also approximately 2 m/s (Fig. 5).

In a number of cases, an incomplete flame propagation for the entire mixture was observed; in this case, the flame front attenuated without propagating throughout the entire

volume of the mixture. Thus, in the case when the mixture of aerosol and  $\text{CO}_2$  was added, such cases were observed at concentrations of  $\text{CO}_2$  from 8.2 %, concentration of aerosol from 2.5  $\text{g}/\text{m}^3$ , and for nitrogen-aerosol mixture, concentration of aerosol was 6  $\text{g}/\text{m}^3$  and of  $\text{N}_2$  – 8 %. Accordingly, a significant increase in pressure was not observed.

### 6. Discussion of results of examining the effect of additions of gas-aerosol mixture on flame velocity

During a fire, part of aerosol after contact with flames loses  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and is carried up by hot convective flows, along with the products of combustion. In addition, a certain portion of aerosol after cooling may settle down on the walls or get outside through the openings and will be brought out of the combustion process, which will lead to a decrease in the total concentration of aerosol. An introduction of relatively cold inert gas ( $\text{CO}_2$  or  $\text{N}_2$ ) with a temperature of 20–24 °C will contribute to a rapid establishment of such thermal mode, under which fire-extinguishing influence of aerosol manifests itself most effectively. The role of the gas phase in terms of improvement of fire-extinguishing effectiveness of aerosols may be explained by the fact that components of the gas phase  $\text{CO}_2$  and  $\text{H}_2\text{O}$  contribute to the formation of carbonate and hydrated forms of solid phase [10]. As it was noted in paper [4], with an increase in humidity, fire extinguishing efficiency of aerosol oxides of metals K, Na increases. During combustion of AFM charge,  $\text{K}_2\text{O}$  is formed, which, as a result of reaction with  $\text{CO}_2$  or with  $\text{H}_2\text{O}$ , leads to the formation of  $\text{K}_2\text{CO}_3$  or  $\text{KOH}$ , or, as a result of simultaneous reaction with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , leads to the formation of  $\text{KHCO}_3$ . In these cases, a volume of the gas phase and, therefore, of the aerosol, slightly decreases, which leads to an increase in the concentration of solid phase in a unit of volume of aerosol.

To prove a combined nature of extinguishing, we can refer to the data from articles [9–12, 20–22], which indicate that the existence of inert gas rarefiers greatly enhances effectiveness of the aerosol. In addition, results of these experiments showed another useful effect of additional use of inert rarefiers along with aerosol, particularly that the existence of  $\text{CO}_2$  or  $\text{N}_2$  slightly increases optical permeability of the aerosol, which coincides with the results from paper [10]. This is especially noticeable at concentrations of  $\text{CO}_2$  or  $\text{N}_2$  of 2 % or larger. At concentrations of components in binary

mixture of  $\text{CO}_2$  from 8.2 %, and of aerosol from 2.5  $\text{g}/\text{m}^3$ , and for nitrogen-aerosol mixture, at concentration of aerosol of 6  $\text{g}/\text{m}^3$  and of  $\text{N}_2$  – 8 %, the flame front in some cases does not propagate around the entire volume of combustible mixture. In this case, flames erratically and asymmetrically propagate in the cylinder to its upper top part at a velocity of approximately 0.01–1 m/s, which can be seen in Fig. 3, *a–e*. A decrease in concentration with a simultaneous increase of fire-extinguishing efficiency corresponds to the results of studies [4, 10], which described the effect of additions of different concentrations of gas-aerosol mixtures on the process of extinguishing of homogeneous combustible systems. It follows from them that, for example, an introduction of 5 %  $\text{N}_2$  allows us to decrease minimum fire-extinguishing mass of the charge of AFM by 3.5 times, in this case, the concentration of oxygen will decrease to 20 % by volume, which is quite a satisfactory indicator when solving practical tasks of evacuating people. If there is a problem regarding extinguishing in volumes where there are no people, the use of  $\text{CO}_2$  is more beneficial than  $\text{N}_2$  without a doubt.

As far as the influence of  $\text{N}_2$  on the combustion propagation velocity is concerned, we, by analyzing the results of paper [27] and using the results of the frame by frame video recording, established a flame propagation velocity under conditions of the performed experiment. Thus, as illustrated by the frame by frame video recording (Fig. 6), explosive combustion of stoichiometric heptane-air mixture (SHAM) can be conventionally divided into two stages. At stage 1 (Fig. 6, *a–g*), the flame front propagates in the cylinder at concentration close to stoichiometric, which is indicated by the intense blue color of the flame front (Fig. 6, *a–j*) for around 42 milliseconds. In this case, the flame front evenly propagates towards both sides to the position (Fig. 6, *f*). Next, out of the top opening, under the influence of the shock wave front pressure, at ms 20, the cork pops out – position *g* in Fig. 6.

Then stage 2 begins, where in the course of explosive combustion (Fig. 6, *h*), combustible mixture, which remained in the lower part of the cylinder, is completely combusted; in this case, flame propagation somewhat slows down and complete combustion takes almost two times as long as the combustion at stage 1 (Fig. 6, *a–f*). In this case, velocity was determined from the moment of flame front origin (position *a*) until the moment it reaches the top of the cylinder (Fig. 6, *g*). The time of explosion in this case was 20 ms while the velocity was 8.5 m/s.

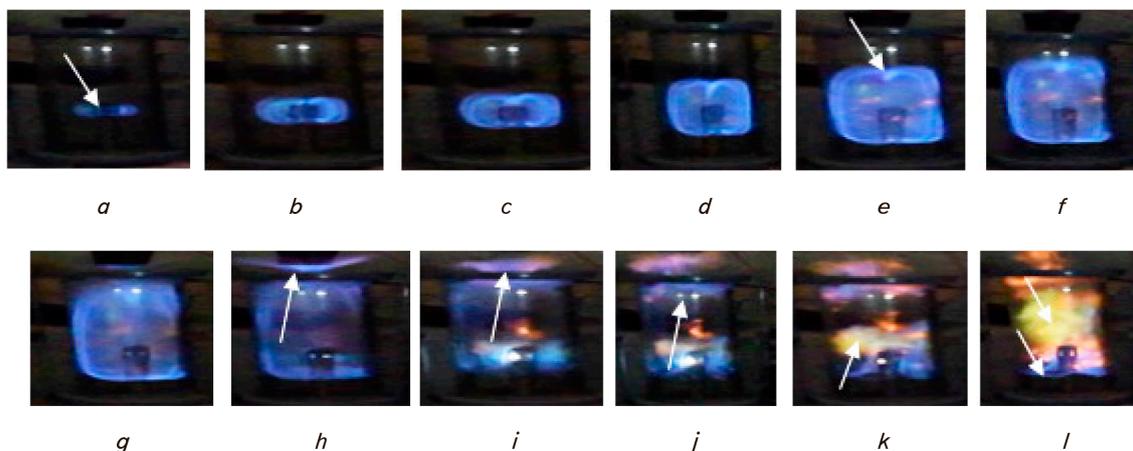


Fig. 6. Frame by frame video recording of the explosion of SHAM. Explosion time:  $\tau_e \approx 20$  ms,  $V=8.5$  m/s [27]:  
*a–g* – 20 ms; *a–j* – 42 ms; *a–l* – 55 ms

By analyzing results of the experiment, conducted in paper [27], and the frame by frame video recording, shown in Fig. 3, it was found that 20 ms elapsed from the start of ignition to the moment of contact of the flame with the top lid of the cylinder. Thus, velocity of the kinetic flame front is about 8.5 m/s.

The same paper [27] showed character of the effect of adding 10 % of nitrogen on the combustible mixture of SHAM. Results of the course of explosion of SHAM with the addition of 10 % of  $N_2$  are shown in the frame by frame video recording of the process in Fig. 7 [27].

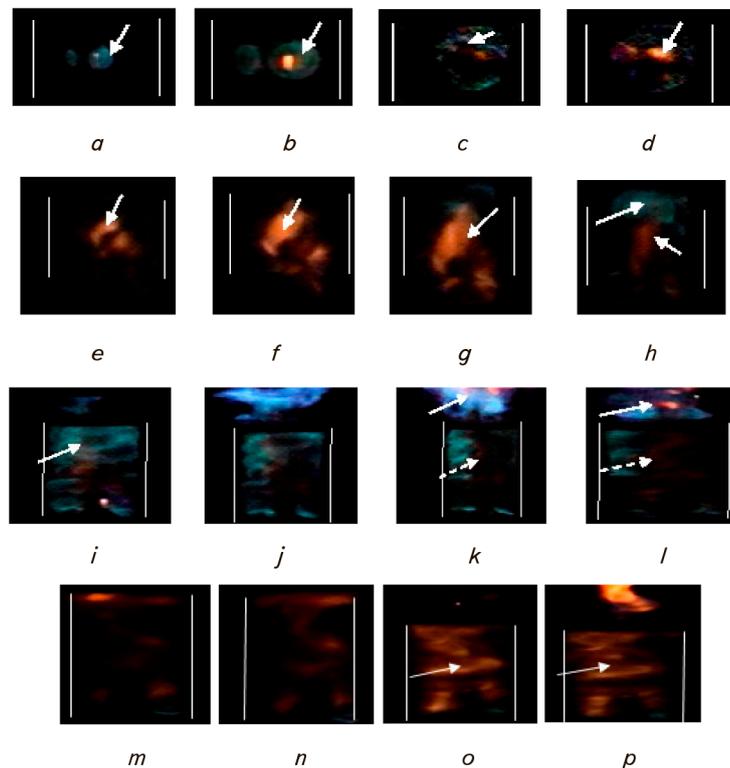


Fig. 7. Frame by frame video recording of the explosive combustion of SHAM with the addition of 10 % of nitrogen. The time of explosion  $\tau_e \approx 210$  ms.  $V=3.5$  m/s. [27]:  $a-f-125$  ms;  $a-c-45$  ms;  $h-i-25$  ms;  $a-p-210$  ms

Taking into account results of paper [27], we draw a conclusion on that the addition of only 10 %  $N_2$  to the combustible mixture greatly increases the time of explosive combustion (up to 220 ms) and, accordingly, decrease flame propagation velocity. The first stage, as the author of [27] points out, which is shown in Fig. 7,  $a-d$ , included the propagation of combustion front; in this case, the flame color changed from blue (Fig. 7,  $a-f$ ) to turquoise (Fig. 7,  $a-d$ ). The time of stage 1, during which the flame was propagating outward until the cork was pushed out from the top opening, was about 5 ms (Fig. 7,  $a-f$ ). Flame front velocity at this stage was 1.36 m/s.

After the cork was pushed out, at the second stage, the flame color drastically changed to turquoise; in this case, in the upper part of the cylinder, where the mixture was in contact with the air, the flame color acquired blue coloring (shown by arrows in Fig. 7,  $j-l$ ), which indicates greater completeness of combustion of the mixture. In addition, after analyzing results of paper [27], it was found that the full time of explosion was 210 milliseconds (Fig. 7,  $a-f$ ). First,

the flame velocity did not change and was about 3.5 m/s (Fig. 7,  $a-f$ ). Time of explosion in this case was 125 ms. Then, when the cork was pushed out outward, the flame velocity increased to 7 m/s (Fig. 7,  $h-l$ ).

An analysis of the frame by frame video recording, given in Fig. 7, shows that the addition of only 10 % of  $N_2$  led to a decrease in velocity of combustion of heptane-air mixture by 2 times, with the period of combustion delay of approximately 45 ms (Fig. 7,  $a-c$ ).

Thus, as we can see, addition of the gas phase significantly influences flame propagation velocity, and its role in the process of extinguishing with binary mixtures of gases and aerosols should be considered equally and simultaneously with the existence of solid phase.

It is known [29–31] that at consumption of AFM starting at  $70$  g/m<sup>3</sup>, due to heat absorption by aerosol mixture, flame temperature may decrease to  $130-200$  °C, reaching in some cases critical values, at which suppression of the process of combustion takes place. In addition, in paper [28], it was indicated that highly dispersed chemical compounds of potassium, which are the base for most aerosol forming compositions, are the most effective among compounds of alkali metals for using as inhibiting components of fire-retardant powders. Other data suggest synergic interaction of gas and powder [31, 32], which leads to a decrease in their fire-extinguishing concentrations. This happens due to the dilution of air with fire-extinguishing gas at a fire-extinguishing concentration of 14–16 % (vol.), which leads to a decrease in the concentration of oxygen in the air. In this case, combustion reactions are inhibited much faster by active particles of fire-extinguishing powder while the interrelated physical-chemical factors of flame suppression are more pronounced.

As we mentioned above, flame propagation velocity, as it was expected for pure heptane-air mixture is 8.5 m/s. With the addition to combustible mixture of 10 % of nitrogen, propagation velocity decreased to 3.5 m/s, and the addition of 10 % of  $CO_2$  decreases velocity to 2.5 m/s. By analysing results of the experiments (Fig. 3, 7), it is possible to argue that with addition of retarding and inhibiting additives, explosive combustion is divided into 2 stages. The first stage is longer and develops rather slowly. In this case, flame front propagation sometimes occurs not in the form of identical and symmetrical hemispheres, but rather as chaotic and irregular flame front (Fig. 3,  $a-e$ ; Fig. 7,  $a-h$ ). In this case, as shown in Fig. 3, 7, the flame front, after supply of electrical discharge, first propagates in the form of semi-circular spheres, after which it is sharply inhibited and starts slowly, randomly and unevenly, propagate in the volume of the cylinder (Fig. 3,  $c-g$  and Fig. 7,  $a-e$ ) at a velocity of approximately 0.5–1.5 m/s to ms 500. Generally, a slow increase in pressure with a low flame propagation velocity in a closed volume is characteristic of all the cases of combustion of a homogeneous mixture in the existence of a binary gas-aerosol mixture, but only until the moment of depressurization – pushing out the cork. After the cork was pushed out, velocity always grew almost instantaneously up to 7 m/s; in this case, the flame color sharply changed from red to blue, indicating

greater completeness of the mixture combustion. At an introduction into the mixture of additions of gas-aerosol with a concentration of aerosol from 2.5 g/m<sup>3</sup> and concentration of CO<sub>2</sub> 8 %, we observed a decrease in the flame velocity, as shown in diagram (Fig. 4), from 8.5 m/s up to 1.8 m/s. When adding more than 4 g/m<sup>3</sup> of aerosol and 3 % of gas, flame propagation velocity decreased more intensively and, in some cases, the flame front did not propagate throughout the entire volume of the mixture.

Thus, a substantial decrease in the original velocity of flame propagation throughout stoichiometric heptane-air mixture from 8.45 m/s to 1.8 m/s or less is the result of the combined effect of the binary gas-aerosol mixture. The combined effect of gas-aerosol mixture involves cooling with aerosol and gas, inhibition and dilution of the homogeneous mixture with the specified components.

## 7. Conclusions

1. It was established experimentally that the influence of binary gas-aerosol mixtures on the stoichiometric n-heptane-air mixture decreases flame propagation velocity by up to 6.5 times compared with the original flame propagation

velocity. In this case, we found dependence of velocity of flame propagation throughout stoichiometric n-heptane-air mixture on concentrations and ratios of components of binary mixtures – aerosol and CO<sub>2</sub> or N<sub>2</sub>, which is in the fact that within a range of aerosol concentrations from 8 g/m<sup>3</sup> to 2.2 g/m<sup>3</sup> and of CO<sub>2</sub> gas from 16 % to 8.2 %, there occurs a maximum decrease in flame propagation velocity. For the nitrogen-aerosol mixture, these values correspond to the concentration range of aerosol from 15 g/m<sup>3</sup> to 6.5 g/m<sup>3</sup> and of N<sub>2</sub> from 20 % to 8.5 %. Maximum flame propagation velocity, which corresponded to the minimum concentration ratios of aerosol and gas, was in both cases about 2 m/s.

2. A frame by frame video recording analysis was performed of the explosions of stoichiometric n-heptane-air mixtures, and special features of effect of the addition of binary mixtures of fire-extinguishing aerosol and gases-reddants were revealed. They are in the fact that with the addition of CO<sub>2</sub> from 8.2 % and of aerosol from 2.5 g/m<sup>3</sup>, or hydrogen from 8 % and aerosol from 6 g/m<sup>3</sup>, there were cases of incomplete flame propagation throughout the entire volume of combustible mixture. In this case, the flame propagation velocity had minimum values of 0.5–3.5 m/s at the start of flame propagation, then it dramatically increased after depressurization of the volume of the explosive cylinder.

## References

1. Linteris, G. T. Clean Agent Suppression of Energized Electrical Equipment Fires [Text] / G. T. Linteris // Fire Technology. – 2009. – Vol. 47, Issue 1. – P. 1–68. doi: 10.1007/s10694-009-0109-5
2. Su, J. Z. Fire Suppression with Inert Gas Agents [Text] / J. Z. Su, A. K. Kim, G. P. Crampton, Z. Liu // Journal of fire protection engineering. 2001. – Vol. 11, Issue 2. – P. 72–87. doi: 10.1106/x21v-yqku-pmkp-xgtp
3. Senecal, J. A. Flame extinguishing in the cup-burner by inert gases [Text] / J. A. Senecal // Fire Safety Journal. – 2005. – Vol. 40, Issue 6. – P. 579–591. doi: 10.1016/j.firesaf.2005.05.008
4. Balanyuk, V. The influence of CO<sub>2</sub> additives on fire extinguishing efficiency of binary aerosol-gas mixture [Text] / V. Balanyuk, N. Kozyar, O. Garasimiyuk, A. Lozinskiy // Pozhezhna Bezpeka. – 2016. – Vol. 28. – P. 6–12.
5. Moore, T. A. Nitrogen gas as a halon replacement [Text] / T. A. Moore, N. Yamada // Halon Options Technical Working Conference, 1998. – P. 330–338.
6. Montreal Protocol on Substances that Deplete the Ozone Layer [Electronic resource] // 1998 Assessment Report of the Technology and Economic Assessment Panel. – Available at: <http://apps.unep.org/redirect.php?file=/publications/pmtdocuments/Technology%20and%20economic%20assessment%20panel-19981871.pdf>
7. United Nations Environment Programme [Text]. – Ozone Secretariat. Scientific Assessment of Ozone Depletion, 2010.
8. Semenov, N. N. Teplovaya teoriya goreniya i zryivov [Text] / N. N. Semenov // Uspekhi Fizicheskikh Nauk. – 1940. – Vol. 23, Issue 3. – P. 251–292. doi: 10.3367/ufnr.0023.194003b.0251
9. Balanyuk, V. Doslidzhennya vplivu Inertnih gazovih rozrizhuvachiv na effektivnist vognegasnih aerazoliv [Text] / V. Balanyuk, B. Grimalyuk // Pozhezhna Bezpeka. – 2004. – Vol. 5. – P. 8–12.
10. Balanyuk, V. Phlegmatisation of flammable gas mixtures by aerosol sprays [Text] / V. Balanyuk, A. Zhurbinskiy // BiTP. – 2013. – Vol. 32, Issue 4. – P. 53–58.
11. Filipczak, R. A. Relative Fxtinguishment Effectiveness and Agent Decomposition products of Halon Alternative Agents [Text] / R. A. Filipczak // Halon Alternatives Technical Working Conference 1993, 1993. – P. 149–159.
12. Ewing, C. T. Flame extinguishment properties of dry chemicals: extinction weights for small diffusion pan fires and additional evidence for flame extinguishment by thermal mechanisms [Text] / C. T. Ewing, F. R. Faith, J. B. Romans, J. T. Hughes, H. W. Carhart // Journal of Fire Protection Engineering. – 1992. – Vol. 4, Issue 2. – P. 35–51. doi: 10.1177/104239159200400201
13. Dewitte, M. Inhibition and Extinction of Premixed Flames by Dust Particles [Text] / M. Dewitte, J. Vrebosch, A. van Tiggelen // Combustion and Flame. – 1964. – Vol. 8, Issue 4. – P. 257–266. doi: 10.1016/0010-2180(64)90079-3
14. Mchale, E. T. Flame Inhibition by Potassium Compounds [Text] / E. T. Mchale // Combust and Flame. – 1975. – Vol. 24. – P. 277–279. doi: 10.1016/0010-2180(75)90159-5
15. Mitani, T. Comparison of Experiment and Theory on Heterogeneous Flame Suppressants [Text] / T. Mitani, T. Niioka // Symposium (International) on Combustion. – 1982. – Vol. 19, Issue 1. – P. 869–875. doi: 10.1016/s0082-0784(82)80262-2
16. Yongfeng, Z. Experimental study of the fire-extinguishing effectiveness of 1-bromo-3,3,3-trifluoropropene/nitrogen mixtures [Text] / Z. Youngferg, J. Xiang, L. Guangxuan, X. Ni // Journal of fire sciences. – 2007. – Vol. 25, Issue 2. – P. 177–187. doi: 10.1177/0734904107067914

17. Lott, J. L. Synergism Between Chemical and Physical Fire-Suppressant Agents [Text] / J. L. Lott, S. D. Christian, C. M. Sliepcevich, E. E. Tucker // *Fire Technology*. – 1996. – Vol. 32. Issue 3. – P. 260–271. doi: 10.1007/bf01040218
18. Saito, N. Fire Extinguishing Effect Of Mixed Agents Of Halon 1301 And Inert Gases [Text] / N. Saito, Y. Saso, Y. Ogawa, Y. Otsu, H. Kikui // *Fire Safety Science*. – 1997. – Vol. 5. – P. 901–910. doi: 10.3801/iafss.fss.5-901
19. Balanyuk, V. M. The effectiveness of open space fire extinguishing with flammable liquid fighting aerosols [Text] / V. M. Balanyuk // *Eastern-European Journal of Enterprise Technologies*. – 2015. – Vol. 5, Issue 10 (77). – P. 4–11. doi: 10.15587/1729-4061.2015.51399
20. Smith, E. A. The Assessment of Toxicity After Exposure to a Pyrotechnically-Generated Aerosol [Text] / E. A. Smith, E. C. Kimmel, J. H. English, R. L. Carpenter // 1995 Halon Options Technical Working Conference, 1995. – P. 521–532.
21. Tischenko, A. M. Kombinirovannoe pozharotushenie inertnyimi gazami s odnovremennym ingibirovaniem ochagov goreniya poroshkovyimi smesyami [Text] / A. M. Tischenko // *Problemy pozharnoi bezopasnosti*. – 1999. – Vol. 6. – P. 159–162.
22. Byikov, S. A. Eksperimentalnoe obosnovanie kombinirovannogo primeneniya azota s oagnetushaschimi poroshkami dlya protivopozharnoy zaschityi ob'ektov [Text] / S. A. Byikov, N. Ya. Otkidach, A. M. Tischenko // *Problemy pozharnoi bezopasnosti*. – 2003. – Vol. 14. – P. 55–59.
23. Blanc, V. Ignition of explosive gas mixtures by electric sparks. I. Minimum ignition energies and quenching distances of mixtures of methane, oxygen, and inert gases [Text] / V. Blanc, G. Guest, G. von Elbe, B. Lewis // *The Journal of Chemical Physics*. – 1947. – Vol. 15, Issue 11. – P. 798–802. doi: 10.1063/1.1746337
24. Chen, Z. Study of Low-Pressure Premixed Dimethyl Ether/Hydrogen/Oxygen/Argon Laminar Flames with Photoionization Mass Spectrometry [Text] / Z. Chen, L. Wei, X. Gu, Z. Huang, T. Yuan, Y. Li, Z. Tian // *Energy Fuels*. – 2010. – Vol. 24, Issue 3. – P. 1628–1635. doi: 10.1021/ef901314r
25. Qiao, L. Extinction of premixed methane/air flames in microgravity by diluents: Effects of radiation and Lewis number [Text] / L. Qiao, Y. Gan, T. Nishiie, W. J. A. Dahm, E. S. Oran // *Combustion and Flame*. – 2010. – Vol. 157, Issue 8. – P. 1446–1455. doi: 10.1016/j.combustflame.2010.04.004
26. Balanyuk, V. M. Specific Nature of Phlegmatizing Air-Heptan Mixture using Aerosol and Nitrogen Binary Mixture [Text] / V. M. Balanyuk // *BiTP*. – 2016. – Vol. 44, Issue 4. – P. 139–149.
27. Nikon 1 J4 [Electronic resource]. – Available at: <http://imaging.nikon.com/lineup/acil/bodies/j4/spec.htm>
28. Balanyuk V. M. Study of fire-extinguishing efficiency of environmentally friendly binary aerosol-nitrogen mixtures [Text] / V. M. Balanyuk, N. M. Kozyar, O. I. Garasyumyk // *Eastern-European Journal of Enterprise Technologies*. – 2016. – Vol. 3, Issue 10 (81). – P. 4–12. doi: 10.15587/1729-4061.2016.72399
29. Agafonov, V. V. Aerosol Extinguishing System: Elements and Characteristics [Text] / V. V. Agafonov, N. P. Kopylov. – Design, Erection and Operation, VNIPO, 1997. – 232 p.
30. Balanyuk, V. M. The usage of gas and aerosol powder extinguishing mixtures for protection of incendiary mixtures [Text] / V. M. Balanyuk, N. M. Kozyar, O. I. Garasim'yuk // *ScienceRise*. – 2016. – Vol. 5, Issue 2 (22). – P. 10–14. doi: 10.15587/2313-8416.2016.69333
31. Balanyuk, V. M. Kombinovane aerazolno-poroshkove pozhezhogasinnya [Text] / V. M. Balanyuk, O. I. Garasim'yuk // *Pozhezhna bezpeka*. – 2015. – Vol. 26. – P. 7–12.