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Possibilities of Using a Fire Extinguishing Substance Based on a Water-Soluble Polymer for Extinguishing Flammable Liquids

Stylyk Igor[1,a*], Kodryk Anatoly[1,b], Titenko Oleksandr[1,c] and Zhartovskyi Sergii[1,d]

[1]Institute of Scientific Research on Civil Protection of the National University of Civil Protection of Ukraine, 60, Centralna str., Dmytrivka village, Buchansky district, Kyiv region, Ukraine, 08112

[a]stylyk_ihor@nuczu.edu.ua, [b]kodrik@ukr.net, [c]titenkoalex1954@gmail.com, [d]zhartovskyi_serhii@nuczu.edu.ua

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Abstract. This study presents the possibilities of using a fire extinguishing agent based on a water-soluble polymer for extinguishing fires at facilities where the fire load is formed by liquid combustible materials. It has been theoretically and experimentally shown that by changing the concentration of gelling additives, the viscosity can be varied, which, in turn, directly affects the characteristics of the protective layer created by applying the gel fire extinguishing agent to the surface of the combustible liquid.. The results of an experimental study of the effectiveness of gel fire extinguishing agents based on a polymer of the ECOFLOC A-18 type are presented. A method for preparing liquid solutions of concentrates of aqueous fire extinguishing agents with a gelling agent concentration of up to 10 %, which are easy to dissolve in water or in a foaming agent, is proposed. It is noted that their concentration should be such that when creating a working solution, the amount of gelling agent in it is not less than 0.05 % for the use of the solution in extinguishing fires.

1 Introduction

Typically, for extinguishing energy facilities of critical infrastructure, a fine spray or compressed foam using aqueous film-forming foam (AFFF) is used [1, 2]. AFFF is a classic foam extinguishing agent consisting of fluorocarbon surfactants, additives and water. The unique chemical structure of AFFF gives it the characteristics of both oleophobicity and hydrophobicity. AFFF can quickly and effectively extinguish Class B fires because it has high fluidity, which promotes film formation. However, these fluorinated compounds have resistance to decomposition, bioaccumulation and toxicity, which hinders its widespread use.

In works [3–5], the issues of developing new foam-forming compositions using water-soluble polymer additives of various nature are considered. It is important to develop and use safe fire extinguishing methods that do not contain fluorine-containing compounds, as well as to strengthen control over their use in industry, maritime transport and nature conservation areas [6].

Hydrophilic polymers [7–9] increase the stability of foam by thickening aqueous solutions. Polysaccharides and cellulose esters, polyacrylates and polyacrylamides, polyethylene glycols, etc. can be added to foaming agent compositions. Polymer complexes formed as a result of the interaction of the composition components contribute to the stabilization of foam films. When choosing the formulation of multicomponent foaming compositions, the use of acrylamide polymers and its copolymers [10–12] is promising. They increase the film-forming ability of water-based foam fire extinguishing compositions, enhance their surface-active properties, stabilize the foam and increase its stability.

Polyacrylamide does not have the ability to bioaccumulate, since it is completely soluble in water. Being a flocculant, it is adsorbed on suspended solids and thus removed from the aqueous phase. The sensitivity of polyacrylamide to ultraviolet rays is well known and described in the scientific literature. Photolysis leads to the destruction of the polymer chain with the formation of smaller molecules (oligomers), which become available for bacterial absorption. The data presented indicate the prospects for the introduction and use of acrylamide polymers and copolymers in the field of fire extinguishing due to the environmental safety of these compounds [9].

2 Main Part

The purpose of this work is to substantiate the possibility of using an aqueous fire extinguishing agent based on a water-soluble polymer of the ECOFLOC A-18 type (hereinafter referred to as a hydrogel based on polyacrylamides or PAA) for extinguishing class B fires (flammable liquids such as transformer oil, diesel fuel, gasoline, etc.), as an alternative to the use of fluorinated foaming agents.

To achieve the set goal, the following tasks were solved in the work:

– determination of the viscosity of fire extinguishing solution concentrates and fire extinguishing solutions depending on the composition and concentration of the compositions;

– determining the influence of compositions and concentrations of fire extinguishing solutions on the stability and multiplicity of the formed foam;

– determination of the fire extinguishing efficiency of the proposed solutions when extinguishing model class B fires in comparison with existing fire extinguishing solutions based on AFFF.

It is proposed to create liquid stabilized concentrates of gel-forming compounds with their subsequent dissolution in water, or with intermediate dissolution in a foaming agent..

As additives to improve the performance characteristics of water-foam solutions of aqueous fire extinguishing agents were used:

– high molecular weight polyacrylamide (M.M.=2×10^5–6×10^6), Ecofloc A-18 series (acrylic acid copolymer crosslinked using polyester derivatives and acrylic acid derivatives (e.g., acrylate salt)), compatible with surfactants and mineral highly dispersed additives, fractionation 20…60 mesh, with a concentration in water from 0.01 % to 0.5 %;

– foamed colloidal silicon dioxide as a suspending agent to regulate the stability and fluidity of the dispersion 0.5 %;

– refined rapeseed oil - as a liquid medium and emulsifier;

– sorbitan monooleate as a surfactant with a low hydrophilic-lipophilic balance to promote the dispersion of dry polymer particles in vegetable oil;

– sodium salt of carboxymethylcellulose as a thickener and to adjust the viscosity of the solution.

General purpose foaming agents and film-forming agents of the AFFF type were used as surfactants (6 %).

Water-soluble polymer additives are used to impart thixotropic properties to water. Such thixotropic mixtures are thinned by shear forces and/or velocity [11, 13] and are easily sprayed using hydrants. As soon as these shear forces are removed, or the velocity becomes close to 0 (when hitting a surface), the mixture thickens, allowing it to adhere to and coat the surface, extinguish the flame, and prevent the spread of fire. When additional water is added to them, both the polymer concentration in the solution and the viscosity decrease. The use of solutions based on such a gel-forming material will be effective for extinguishing Class B fires.

To ensure the homogeneity of the hydrogel structure, the following were additionally used: rapeseed oil, colloidal silicon dioxide according to the recommendations specified in [14].

The basis for measuring the viscosity of a hydrogel-based fire extinguishing agent at values close to the lower limit of the dynamic viscosity range (1.002×10^{-3} Pa×s), which is characteristic of this type of gel at significant values of the shear rate of relative deformations in a liquid medium, is a special method for measuring viscosity, the theoretical basis was the Darcy-Weisbach.

The chosen method consists in measuring the time of full activation of the fire extinguisher while varying the pressure when charging the fire extinguisher and the geometry of the path of movement of the tested liquid by installing inserts of different internal diameters in the path of movement of the solution.

To describe the hydrodynamic processes that occur during the operation of the fire extinguisher in the mode of continuous supply of the tested liquid until full operation, a mathematical model was created, which consists of two blocks of systems of equations that are solved by numerical methods.

The first block consists of a system of equations for calculating the functional dependence of the output velocity on the value of the excess pressure in the fire extinguisher, ω=ω(p):

$$\begin{cases} p = \lambda\left(\mathrm{Re}_1\right)\cdot\dfrac{\rho\cdot\omega_1^2}{2}\cdot\dfrac{L_1}{d_1}+\cdot k_\xi\cdot\lambda\left(\mathrm{Re}_2\right)\cdot\dfrac{\rho\cdot\omega_2^2}{2}\cdot\dfrac{L_2}{d_2}+k_{loc}\cdot\dfrac{\rho\cdot\omega_1^2}{2}+\dfrac{\rho\cdot\omega_1^2}{2} \\ \mathrm{Re}_i = \dfrac{\rho\cdot\omega_i\cdot d_i}{\mu} \\ \lambda\left(\mathrm{Re}_i\right) = \dfrac{64}{\mathrm{Re}_i}\cdot H\left(\mathrm{Re}_{cr}-\mathrm{Re}_i\right)+\left[-2\cdot\log\left(\dfrac{\delta}{3.7}+\left(\dfrac{6.81}{\mathrm{Re}_i}\right)^{0.8}\right)\right]^{-2}\cdot H\left(\mathrm{Re}_i-\mathrm{Re}_{cr}\right) \end{cases}, \quad (1)$$

where, p – pressure value in the fire extinguisher, MPa;

λ(Re) – the value of hydrodynamic resistance, determined by the Reynolds number;

ρ – density of the tested liquid contained in the fire extinguisher, kg/m^3;

κ_ξ – specifying the coefficient of hydrodynamic resistance of the fire extinguisher channel, the value of which is specified during experiments with ordinary water;

ω_1 – speed (flow rate) in the fire extinguisher channel, m/sec;

ω_2 – velocity (flow rate) in the insertion channel, m/sec;

μ – dynamic viscosity of the test liquid contained in the fire extinguisher, Pa×sec;

L_1 – length of the fire extinguisher channel, m;

L_2 – length of the insertion channel, m;

d_1 – diameter of the fire extinguisher channel, m;

d_2 – diameter of the insertion channel, m;

δ – relative roughness of the inner surface of the fire extinguisher channel;

H(Re) – Heaviside function;

Re_{cr} – critical value of the number Re for the transition of the flow regime from laminar to turbulent.

The second block consists of a system of equations for calculating the functional dependence of the full operation of the fire extinguisher tF on the value of the initial excess pressure p, the initial velocity ω and the total volume of the tested liquid VF, tF = f(p, ω, VF):

$$\begin{cases} p(t) = p_0\cdot\left(\dfrac{V_0}{V(t)}\right)^k \\ V(t) = V_0+\displaystyle\int_0^t \omega\left(p(t)\right)\cdot\dfrac{\pi}{4}\cdot d_1^2 dt \\ Q_0 = \displaystyle\int_0^{t_F} V(t)dt \end{cases}, \quad (2)$$

where, t – current time, sec;

p(t) – current pressure value in the fire extinguisher, MPa;

p_0 – initial pressure value in the fire extinguisher, MPa;

t_f - value of full activation time of the fire extinguisher, sec;

ω(p(t))* – current value of velocity (flow rate) in the fire extinguisher channel, m/sec;

d_1 – diameter of the fire extinguisher outlet channel, m;

V_0 – free volume of the fire extinguisher cavity not occupied by the tested liquid, remaining when the fire extinguisher is fully equipped, m^3;

V(t) – the current free volume of the fire extinguisher not occupied by the tested liquid remaining when the fire extinguisher is emptied m^3;

Q_0 – загальний об’єм порожнини вогнегасника, m^3;

k = 1.4 adiabatic index for air.

Figure 1 presents a summary graph of the change in dynamic viscosity versus speed for a number of gel foaming agents from well-known manufacturers and experimental gel foaming agents based on high-molecular gelling agents such as Ecofloc A-18 and its additives.

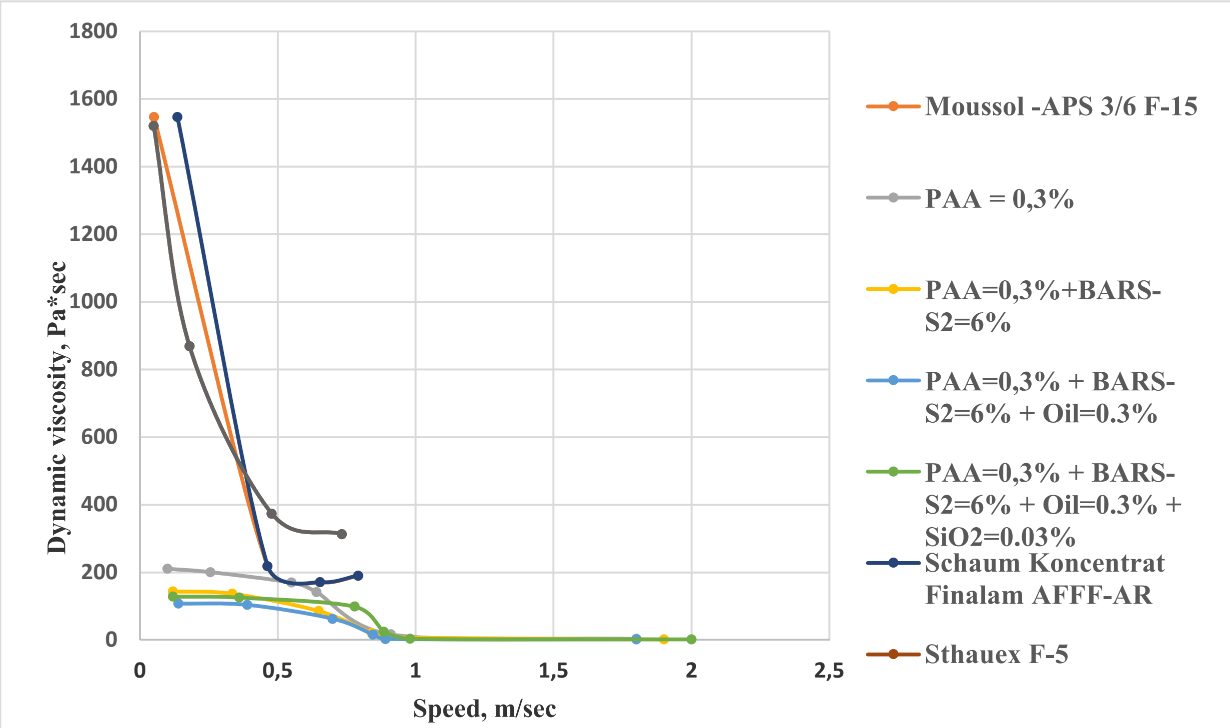

Fig. 1. Summary graph of dynamic viscosity of a number of gel foaming agents of well-known brands and experimental gel foaming agents based on high-molecular gelling agents of the Ecofloc A-18 type and additives to it as a function of speed.

The graph data shows a sharp decrease in the viscosity of the hydrogel (close to ordinary water) with an increase in the rate of supply of water extinguishing agent by existing fire equipment.

The multiplicity and stability of foam obtained from foaming agent solution were investigated when changing the polymer concentration in it.

Figure 2 shows the obtained dependences of the multiplicity and stability of the foam obtained from 3 % and 6 % general purpose foaming agent solution on the amount of concentrate in the solution.

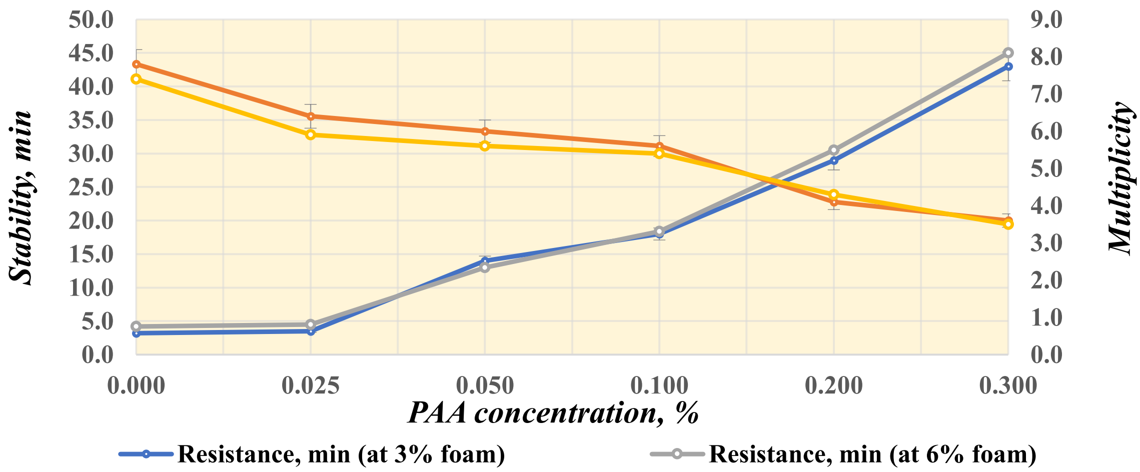

Fig. 2. Dependence of foam multiplicity and stability on the content of polyacrylamide-based concentrate (in terms of polyacrylamide) in an aqueous fire extinguishing agent at 3.0 % and 6.0 % foaming agent.

We see that the use of the proposed concentrate composition at a polyacrylamide concentration of 0.3 % allows you to increase the stability of the foam by almost 10 times while reducing its multiplicity by 2 times. At the same time, looseness was not observed in the resulting foam. The foam is finely dispersed. Figure 3 shows the results of determining the viscosity of a 6 % solution of a general-purpose foaming agent when changing the content of the gel concentrate in the solution.

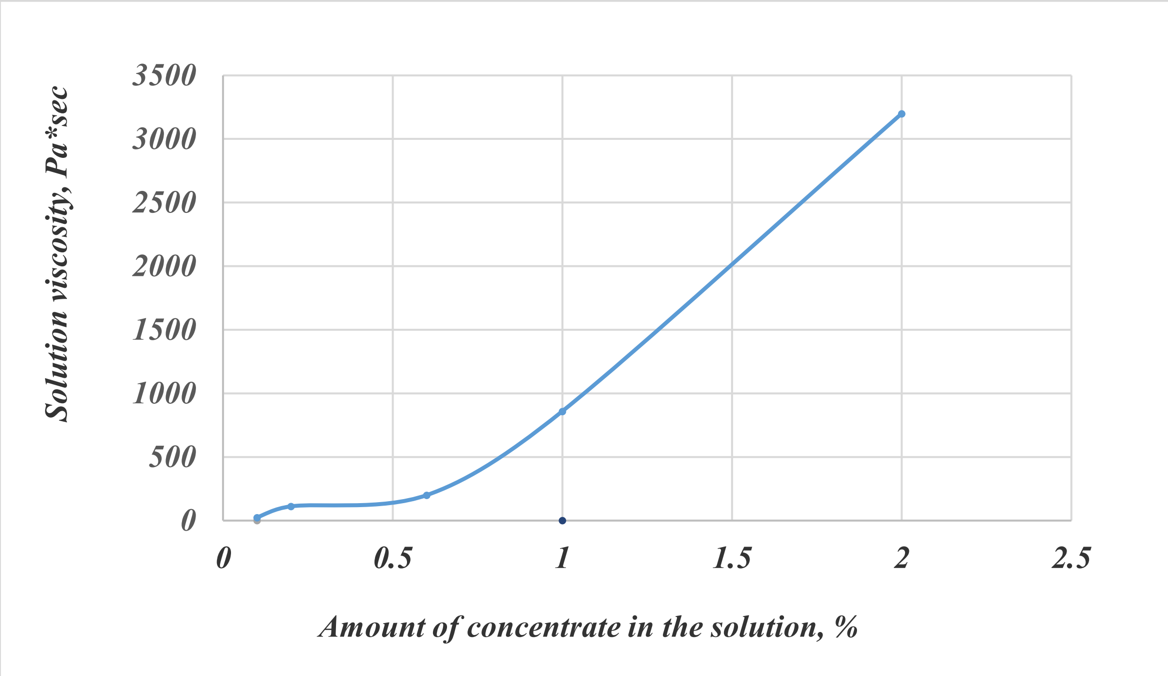

Fig. 3. Dependence on the viscosity of a 6 % solution of a general-purpose foaming agent when changing the content of a polyacrylamide-based gel concentrate in the solution.

The obtained results indicate that even at a concentration of gelling concentrate in foaming agent of 0.15 %, its viscosity is more than 100 Pa×sec, which gives the solution the necessary adhesion to surfaces [9, 15].

Considering the difficulty of dissolving polyacrylamide in water [9–11] and the possible formation of lumps in the solution mass, which occurred during the research, foamy colloidal silicon dioxide was added to dry, single fraction polymer particles (as a suspending agent to regulate the stability and fluidity of the dispersion). The particles were then dispersed in oil with simultaneous mixing and the addition of liquid sorbitan monooleate (Span 80) as a surfactant with a low hydrophilic-lipophilic balance to promote the dispersion of dry polymer particles in vegetable oil.

The obtained concentrate is a solution with a viscosity of more than 100 Pa×sec, with good adhesive properties. As a surfactant, general-purpose foaming agents Bars 2S and film-forming - Bars AFFF 6 % were used in concentrations from 3 % to 6 %. To compare the quality of the obtained characteristics, a high-viscosity foaming agent of the Mousson brand was used as a “standard”.

Fire tests were carried out in accordance with the requirements of [16]. During the study, the following parameters were determined for each fire extinguishing agent to be tested:

– foam multiplicity of medium multiplicity (p. 10.5 [16]);
– medium-density foam stability (p. 10.5 [16]);
– duration of extinguishing with medium-density foam (p. 17 table 1 [16]).

According to the requirements [16], solutions must have:

– medium-density foam multiplicity – not less than 60 (table 1, p. 13 [16]);
– medium-multiplicity foam stability – a regulatory document is established for a specific foaming agent (table 1, p. 14 [16]);
– duration of extinguishing with medium-multiplicity foam – no more than 120 s (p. 17 table 1 [16]).

To determine the multiplicity of medium-multiplicity foam, the working solution of the foaming agent is supplied under pressure to the medium-multiplicity foam generator, and the foam formed on the barrel is directed into a foam collector with a capacity of 200 dm^3. The foam collector together with the stand for its installation, the measuring cylinder and the funnel are weighed first in an empty state, and then after filling with foam. The mass of the solution consumed for the formation of foam is determined by the difference in masses and, knowing the capacity of the foam collector and the density of the working solutions, which is taken as 1 kg/dm^3, the foam multiplicity is calculated by the formula (3):

$$K = \frac{V_n \times \rho_p}{m_1 - m_2}, \tag{3}$$

where: K – foam multiplicity;

V_n – foam volume equal to the volume of the foam collector, dm^3;

ρ_p – density of the working solution of the foaming agent, kg/dm^3;

m_1 – total weight of the frame, cylinder and foam collector with foam, kg;

m_2 – total weight of frame, cylinder and foam collector without foam, kg.

The foam stability indicator is determined by the time interval during which 50 % of the volume of the solution used to form it flows out. In order to determine this indicator, at the moment the foam collector is filled with foam, a stopwatch is turned on and the time interval during which the corresponding volume of solution flows out of it is recorded, which is measured using a measuring cylinder. The test result is taken as the arithmetic mean of the results of two parallel determinations, the difference between which should not exceed 10 % of the arithmetic mean of the results obtained. The test results are given in tables 1–2.

Table 1. Results of studies on determining the multiplicity and stability of medium multiplicity foam formed from the working solution of the foaming agent.

Composition of the aqueous sample solution	Total weight of foam collector, stand and cylinder, [kg]		Foam multiplicity		
	without foam	with foam	Actual value	Average value	Normative value
-Water – 94 %; -Foaming agent Bars AFFF – 6 %	10.13 ± 0.01	13.03 ± 0.01	68.9	68.4	Not less than 60
	10.37 ± 0.01	13.15 ± 0.01	70.8		
	10.20 ± 0.01	13.30 ± 0.01	65.4		
-Water – 95 %; -Foaming agent Mousson AFFF (f-5) – 5 %	10.27 ± 0.01	12.93 ± 0.01	75.1	72.1	
	10.15 ± 0.01	13.03 ± 0.01	69.4		
	10.14 ± 0.01	13.13 ± 0.01	71.5		
-Water – 93.895 %; -Foaming agent BARS -2S – 6 %; - Surfactant concentrate – 0.105 %	10.00 ± 0.01	13.40 ± 0.01	58.0	71.6	
	10.40 ± 0.01	13.62 ± 0.01	62.0		
	10.22 ± 0.01	13.30 ± 0.01	65.0		

Table 2. Results of studies on determining the multiplicity and stability of medium multiplicity foam formed from the working solution of the foaming agent.

Composition of the aqueous sample solution	Total weight of foam collector, stand and cylinder, [kg]		Foam resistance, [sec]	
	without foam	with foam	Actual value	Average value
- Water – 94 %; - Foaming agent Bars AFFF – 6 %	10.13 ± 0.01	13.03 ± 0.01	188.0	186.0
	10.37 ± 0.01	13.15 ± 0.01	182.0	
	10.20 ± 0.01	13.30 ± 0.01	188.0	
- Water – 95 %; - Foaming agent Mousson AFFF (f-5) – 5 %	10.27 ± 0.01	12.93 ± 0.01	234.0	250.0
	10.15 ± 0.01	13.03 ± 0.01	260.0	
	10.14 ± 0.01	13.13 ± 0.01	256.0	
- Water – 93.895 %; - Foaming agent Bars -2S – 6 %; - Surfactant concentrate – 0.105 %	10.00 ± 0.01	13.40 ± 0.01	232.0	230.0
	10.40 ± 0.01	13.62 ± 0.01	228.8	
	10.22 ± 0.01	13.30 ± 0.01	229.2	

The results of determining the duration of extinguishing with samples of water extinguishing agents of the model fire source 55B1 at the working solution supply intensity (0.038 ± 0.004) $dm^3/(m^2 \times sec)$ are given in Table 3.

Table 3. Results of studies on determining the duration of extinguishing with foam of average multiplicity of a model fire source 55B1 using a foaming agent solution.

Composition of the aqueous sample solution	Extinguishing time, [sec]			
	Experiment 1	Experiment 2	Experiment 3	Average value
- Water – 94 %; - Foaming agent BARS AFFF – 6 %	56	59	59	58
- Water – 95 %; - ПУ Mousson AFFF (f-5) – 5 %	45	46	41	44
- Water – 93.895 %; - Foaming agent Bars -2S – 6 %; - Surfactant concentrate – 0.105 %	38	42	37	39

Figure 4 shows a photo of the surface of a model fire extinguished with the proposed gel water fire extinguishing agent. A gel film is visible on the surface, which is formed during extinguishing and acts as a surface insulator, as when using a film-forming foaming agent.

Fig. 4. Protective gel film formed on the surface when extinguishing a model fire 55B1 with a solution based on a gel concentrate of polyacrylamide and a general-purpose foaming agent.

3 Conclusion

1. The fact of a sharp decrease in the viscosity of the hydrogel (close to ordinary water) with an increase in the rate of supply of water extinguishing agent by existing fire equipment has been established, which creates convenient conditions for the design of special fire equipment using hydrogel extinguishing agents.

2. The introduction of a copolymer into the foaming solution, even in very small concentrations (0.01–0.05 %), leads to an increase in foam stability while slightly reducing its multiplicity.

3. To prevent aggregation of polymer particles when introducing it into a solution, it is proposed to first create a polymer dispersion in oil and introduce stabilizers and emulsifiers into the solution.

4. To promote the dispersion of dry polymer particles in vegetable oil, it is recommended to use surfactants with low hydrophilic-lipophilic balance to change the fluidity of the gel.

5. To ensure the stability and flowability of the dispersion, it is recommended to use a suspending agent, such as fumed silica. This allows the dispersion to be introduced into the water supply system in liquid form so that it can be easily applied using standard firefighting equipment.

6. The use of the proposed concentrate of gel-forming polyacrylamide compounds in combination with a general-purpose foaming agent significantly increases the stability of the resulting foam.

7. The composition of a new foaming agent using gel-forming polyacrylamide compounds in combination with a general-purpose foaming agent has been proposed, the mechanism of action of which when extinguishing flammable liquids is similar to the film-forming effect when using fluorinated foaming agents (AFFF), which creates the prerequisites for further significant reduction of the negative impact of such fire extinguishing agents on the ecosystem.

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