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FIRE EXTINGUISHING DEVELOPMENT DIRECTIONS FOR LIQUIDS BASED ON THE FOAM GLASS PRIMARY LAYER

The combustible liquid modulating parameter was established to predict the foam glass fire-extinguishing layer as the primary means for liquids ensuring reliable fire extinguishing in combination with other fire-extinguishing means. The formation peculiarities and buoyancy indicators of dry and wet foam glass in polar and non-polar liquids (alkanes and alcohols) were investigated. It is shown that the foam glass buoyancy increases with an increase in the liquid density. The foam glass buoyancy in polar and non-polar liquids was described depending on the liquid density by an approximate linear dependence separately for dry and wet foam glass. The deviation from the linear trend is explained by the foam glass different wettability, some alcohols water solubility, and liquid mixtures peculiarities. The buoyancy relation with flash point was established, which works separately for n-alkanes, n-alcohols and glycols, which was described mathematically. A formula was developed to describe the relationship between flash temperatures and the liquids density. Correlations with a fire-extinguishing layer of dry foam glass for molar mass, molecule or cluster length, stoichiometric combustion reaction coefficient, burning rate on a free surface, density, flash point, boiling point, autoignition temperature were studied. The forecasting possibility the dry foam glass fire-extinguishing layer based on the description of flammable liquids clusters has been established. Mathematical dependences were obtained for the dry foam glass fire-extinguishing layer depending on the expected clusters length in the liquid and a similar dependence for flash points. The conditions for effective extinguishing of alcohols and alkanes with dry foam glass have been determined. Different modes of extinguishing hydrocarbons with flash temperatures $t_{fp} < 28$ °C and $t_{fp} > 28$ °C are recommended, based on the primary layer of 6 cm of wet foam glass with a fraction of 1.0–1.5 cm, with the possibility of finalizing the extinguishing, if necessary, with an inorganic gel by spraying components with an application rate of 0.2 g/cm².

Keywords: fire extinguishing, flammable liquid, cluster, foam glass, buoyancy, isolation, cooling, gel, consumption

1. Introduction

Worldwide fire statistics show the class "B" fires widespread prevalence. During the war, this problem worsened. Improving facilities fire safety with the circulation or storage of flammable liquids and rescue units ensuring the efficiency during the class "B" fires elimination are work important areas for the SESU. Extinguishing Class "B" fires with a significant free liquid surface area is one of more difficult firefighting problems, both in the case of extinguishing tanks and emergency spills. Such fires are characterized by their duration, significant material and environmental damage, the dangerous factors presence for the human life, and difficult conditions for extinguishing. [1].

The more common ones include fires involving petroleum products of class "B1". Modern technical petroleum products (alcohol-containing gasoline) contain polar additives, which brings their combustion regimes closer to "B2" fires and imposes appropriate restrictions on the fire-extinguishing foams use. The petroleum products main list can be classified as flammable liquids with a flash point of $t_{fp} < 61$ °C. That is, they can

be classified as those that, under typical storage conditions at a certain air temperature and (or) the thermal radiation action, heat up to t_{fp} and independently form vapor which ignition capable. Regulatory requirements allow the installation of tanks with a volume of up to 120.000 m^3 [2], but the means for extinguishing them have disadvantages. Therefore, extinguishing oil products can be attributed to the most large-scale and complex fire extinguishing cases. Currently, extinguishing such fires is carried out using various chemical nature foams. But these means are either not effective enough, expensive, or environmentally unacceptable. Therefore, scientific and practical research continues to search for alternative ways to extinguish class "B" fires.

Thus, the providing fire protection problem with a reliable, inexpensive, environmentally friendly means of extinguishing class "B" fires, which does not contaminate flammable liquids and will be universal for both class "B1" and "B2" fires, both for tanks and for emergency spills, remains unresolved.

2. Analysis of literature data and problem statement

All known extinguishing mechanisms are used to extinguish liquid fires: cooling (of flammable liquid or flame), isolation (including shielding), dilution (of both the gas space and the liquid), flame inhibition [1]. But at present, the existing scientific developments level does not allow replacing foam fire extinguishing in many cases [3]. In this direction, the granular closed-pore solid materials use (as a floating system) turned out to be a promising solution, among which foam glass (FG) has proven itself well in model fires [4]. Granular FG satisfies most of above requirements as a fire extinguishing agent for liquids. But as an individual extinguishing agent, FG works only for high-boiling liquids, and in other cases, the such a solution implementation requires the extinguishing completion by other means. There are many possibilities for stopping combustion weakened by the FG floating layer. These can be both means used to extinguish solid combustible materials, and developments for extinguishing liquids. The only thing that remains is the ban on using a compact water jet to extinguish class "B1" fires.

The main factor in successfully extinguishing liquids fires is ensuring a balance of insulating and cooling properties of the extinguishing material in contact with the burning liquid surface [5]. In practice, this is done without control by feeding either low multiplicity film-forming fluorosynthetic fire-extinguishing foams or medium multiplicity other origin foams [4]. Film-forming foams form a "light water" layer on the liquid surface and isolate the evaporation surface better than other foams, but are expensive, pollute the liquid, and are environmentally unacceptable [6]. Nevertheless, they are currently the dominant foam firefighting technology. Perhaps their use together with FG will significantly reduce their consumption for extinguishing, but this has not been studied. In addition, the polar liquids fire extinguishing problem has not been finally solved, and this depends significantly on their water solubility [7]. Also poorly studied is the medium-multiplicity foams behavior on the granular FG surface, although previous experiments have shown the accumulation and retention possibility of an isolating foam layer on the FG surface. The fire-extinguishing efficiency of medium-multiplicity foams is increased by the urea addition [8], which most likely has an inhibitory effect on the flame, increases the foam stability, and promotes decomposition into non-flammable gases.

Completion of flame quenching above the FG layer can be accomplished by inhibiting, diluting, or cooling the flame. This is usually difficult to implement for extinguishing liquids with a large burning area, but possible for slow burning. That is, it is necessary to create a cloud of water aerosol, pyrotechnic fire extinguishing aerosol, general-purpose

powder, or non-flammable gas that will simultaneously cover the flame entire volume. Flame suppression with aerosol inhibitors is especially relevant for polar liquids, which remains a difficult problem for modern firefighting [9]. However, for a powerful flame, this is difficult to do. Under wind loads, this task becomes more difficult even for a weak flame. Therefore, to extinguish severe combustion in tanks, it is proposed to carry out sublayer combustion of the aerosol-forming composition with simultaneous nitrogen supply [10], the proportionality of the aerosol supply intensity to the reduction in the thermal radiation of alcohols up to extinction defined [11]. But the aerosol part will be lost during the "bubbles" rising and contaminate the liquid, the method is not suitable for emergency spills (i.e., it is not universal), and sublayer agents delivery systems often fail. Therefore, an alternative method of supplying a similar system have developed – directly into the flame under a pressure of 10 atm [12], which can also be implemented for FG. Based on the fire extinguishing agents comparison that supply into the flame volume: non-flammable gases, general-purpose powders, and gas-aerosol agents, researchers concluded that the latter are superior in terms of efficiency, cost-effectiveness, and supply ease [13]. In aerosol fire extinguishing, a new direction has emerged: extinguishing with microencapsulated gel-like liquids, which reduces water loss and provides cooling, dilution, and inhibition effects [14]. In the integrated use case of this agent together with FG, it is easier to overcome powerful convection currents near a developed flame.

Also considered is an extinguishing method with CO₂ granules sublayer supply, which cools the liquid entire volume, not just the surface (this reduces the method effectiveness) and the CO₂ gas phase dilutes the combustion zone [10]. When supplying granules to the liquid surface – they first sink, and then float up when the average diameter decreases to 3 mm (floated by their own gases). It is possible to choose an FG layer that will hold these granules, but the liquid surface cooling will be weakened, but the gasification of the granules will increase. A similar problem will arise in the supplying liquid nitrogen case, which has a certain effectiveness for extinguishing liquids [15].

It is theoretically possible to extinguish liquids with water spray, and it is recommended that for particularly flammable liquids, the droplet dispersion be 0.1 mm, and for others, 0.5 mm [16] to prevent the transformation of a water-insoluble liquid into foam that burns and flows outward. In the FG base layer case on the liquid surface, there is no such problem. On the one hand, the greater water dispersion (small droplets) allows for increased cooling and flame extinguishing efficiency, on the other hand, it is difficult to create a water aerosol with such dispersion simultaneously throughout the flame over a simultaneous burning large area, especially taking into account convection flows near the flame and possible wind loads. Above the FG base layer, when the combustion is weakened, it is easier to provide fire extinguishing conditions, and a coarser aerosol can be applied, which will provide moisture to the FG. The flame extinguishing effectiveness is increased by water fine spraying [17], by adding sodium bicarbonate or other flame inhibitors to the solution [18], by adding film-forming foaming agents (water mist is another way of forming a water film on the liquids surface), and by simultaneously adding an inhibitor and a film-forming agent [19, 20]. In the FG layer presence, the surfactant role changes: it allows for a finer water aerosol and increases FG wetting. The water aerosol fire-extinguishing effect on a flame is well calculated mathematically [21], but in the complex effect case due to certain additives, predicting fire-extinguishing efficiency becomes more difficult.

Regarding specific means of improving the FG fire extinguishing effect, the following can be distinguished. First, it is the FG pre-wetting with water [4]. In this case,

the buoyancy and insulating capacity of FG are reduced, while the cooling capacity increases several times (depending on the liquid temperature), and extinguishing is achieved with a FG smaller layer. But for low-boiling liquids with low density, this worsens the extinguishing effect (the fire-extinguishing layer FG increases), and then another means is required to complete the fire extinguishing.

Secondly, the FG isolating effect enhancement was investigated by applying an inorganic gel, the reaction product between 10 % solutions of calcium chloride and liquid glass, which is carried out during extinguishing, with a feed rate of 0.1–0.2 g/cm² depending on the residual flame intensity above the FG [4]. At the same time, calcium and chlorine ions create an inhibitory effect. For pentane, one of the most volatile non-polar liquids, this reduces the FG fire-extinguishing layer from 50 to 12 cm. The gel allows solving the problem of tank sides cooling efficiency increasing [22], which is usually done by water jets [23]. But the gel, as a water-containing substance (like general-purpose foams), is of little help in extinguishing water-soluble polar liquids: the evaporation delay is reduced from 30 to 3 times. In addition, coating the FG with gel makes it difficult to reuse the FG for extinguishing.

Since the gel use as an additional means when extinguishing class “B” fires has the specified limitations, it is proposed to strengthen the isolation with a FG layer by compacting its surface with solid materials small fractions with low density [24]. This can be FG, perlite or vermiculite with a granule size of up to 5 mm. But this size FG has poor buoyancy – the external open pores proportion increases, so two other materials were investigated. Gasoline extinguishing was achieved with a FG base layer 4 cm. This system all components can be reused. The method is suitable for extinguishing both non-polar and polar liquids.

Inhibitor granules can also be applied to the FG layer, or the FG itself can be treated with flame retardants in a dry powder or liquid state. Researchers have followed a similar path with perlite and vermiculite, which they treat with an inhibitor [25]. But the inhibitor particles possibility from the liquid surface getting into a large flame remains questionable. Therefore, it is more likely to achieve extinguishing if such systems are applied to the FG layer, when the combustion is already weakened due to insulation and cooling.

Liquids extinguishing existing studies by FG-based systems do not focus on the selected extinguishing modes universality for different chemical nature liquids and rely on the t_{fp} indicator, which in some cases gives an extinguishing incorrect expectation. Therefore, it is relevant to conduct scientific research to substantiate the feasibility of selecting one or another means of completing fire extinguishing to create a universal binary means based on FG.

Thus, a considered scientific problem unsolved part is the method improvement the extinguishing of liquids based on the FG base layer by combining it with other means to ensure efficiency, environmental friendliness, and versatility.

3. The purpose and tasks of the research

This work purpose is to establish a modulating liquids parameter for predicting the foam glass fire-extinguishing layer as a base to ensure liquids reliable fire extinguishing in combination with other fire extinguishing means.

To achieve the set purpose, the following tasks solution is provided:

- to determine the foam glass buoyancy as a base layer for the fire extinguishing for polar and non-polar liquids;
- to identify the liquids extinguishing parameters dependence with foam glass on their properties.

4. Research materials and methods

The research object is extinguishing liquids fires with foam glass-based agents.

The research subject is the correlation between the liquids parameters and the foam glass fire-extinguishing layer.

The research hypothesis is the identifying possibility of the such liquids parameter among such as flash point, boiling point, molar mass, combustion reaction stoichiometric coefficient, molecular skeleton length, cluster length, by which the foam glass fire-extinguishing layer can be predicted.

The research method is to conduct an experiment on a class "B" laboratory model fire on the use of dry or wet foam glass for the fire extinguishing, as well as on the extinguishing completion with an inorganic gel, followed by the search for correlations with certain substance parameters.

Foam glass (FG) is investigate as a fire extinguishing agent for liquids. In this research, the FG floating layer is considered as the basic one, which either provides extinguishing or provides for the extinguishing completion by any other fire extinguishing method of surface or volumetric action. For this aim, a comprehensive experiment is planned, which involves establishing the difference in the buoyancy of dry and wet FG in polar and non-polar liquids, operations on wetting FG, experiments on extinguishing liquids with the foam glass, and completing extinguishing by forming the isolating gel layer on the FG layer. For experiments, crushed FG with the following characteristics was selected: granule size 1–1.5 cm, true density 186 kg/m³; apparent density 105 kg/m³; water retention 29±4 %; heat capacity 0.78 kJ/(kg·K). The wetted FG formation was carried out by filling it with water and pressing it with a load for complete immersion under a water layer. After 1 min of holding, the FG was placed on a grid, where 5 min of excess water free outflow, which the external pores were unable to stably hold, was ensured. Under such conditions, the FG absorbs and retains up to 50% of water from its total mass.

The starting components for the gel formation system (GFS) were prepared by dilution. First, a saturated solution was prepared from the technical CaCl₂. After that, a 10 % solution was prepared by the gravimetric method. A 10 % solution of the liquid sodium glass was prepared by the dilution. The solutions concentration was controlled by density using the hydrometric method. Household OP-2 spray guns were used to supply GFS components in aerosol form. The sprayed liquid droplets diameter was 0.2–0.5 mm, and the total flow rate was 0.2 g/cm². The gel forms during the aerosols reaction, settles and adheres to surfaces.

A metal cylindrical container with a diameter of 11.2 cm and $S_{\text{fire}} = 98.5 \text{ cm}^2$ was used as a laboratory model of a class "B" fire. After pouring 250 ml of the flammable liquid into a container, a layer of 2.5 cm was formed. After igniting the fire model, the entire system mass loss was determined using the gravimetric method. Weighing was performed on a "TNV-600" continuous measurement electronic scale with an accuracy of 0.01 g. Measurements were performed at standard atmospheric pressure and ambient temperature of 18±2 °C. After 2 min of the fire model free burning, FG was applied to the liquid surface with a 2 cm layer. After 1 min of steam burning through the FG layer, after the flame size stabilized, the system mass loss was recorded at 30 s intervals for 3 min. The measurements were repeated adding the next 2 cm of FG layer. The measurement results converted into mass burnout rate, g/(m²s). The experiment final result is the FG layer determination at which combustion ceases.

The FG layer relationship with liquids various properties is subject to analysis: flash point t_{fp} , boiling point t_{bp} , molar mass M , combustion reaction stoichiometric coefficient, molecule skeleton length, cluster length.

5. Foam glass buoyancy determination depending on liquid properties

The conducted analysis showed that the t_{bp} of most n-alkanes and n-alcohols fit into a smooth dependence [26, 27]. Therefore, the growth rate of the air vapor pollution zone formation in homologous series should also have a smooth dependence. But t_{fp} , mass burnout rate and other parameters of combustion and substances fire hazard are characterized by oscillation and stepwise nature, which is explained and modeled by us as a clustering consequence in the flame according to the peroxide mechanism with the various supramolecular structures formation in a homologous series [26–28]. Approaches to preventing or stopping the vapor cloud formation and to fire extinguishing may differ slightly for the same liquid. Usually, the extinguishing agent consumption for the liquids fire is divided into several modes depending on the t_{fp} , but a research interesting direction is the search for another criterion for predicting the fire-extinguishing isolating layer, which takes into account possible nonlinearities at hydrocarbons homologous series.

One such parameter may be the mass burnup rate V_m . But the V_m illogical behavior in the n-alcohols homologous series draws attention. It was expected that V_m would be proportional to t_{bp} or t_{fp} . But it turned out that this parameter formation is much more complicated – it is the factors complex action result: t_{fp} , t_{bp} , autoignition temperature t_{ai} , lower flammability limit LFL, molar mass, but this parameter oscillations presence in the homologous series requires taking into account melting point t_{mp} (but the mass evaporation rate does not have oscillations, which indicates a peroxide cluster structure in the flame). According to reference data, n-butanol has a higher V_m , but in the experiment, n-heptanol, which can be explained by better surfaces wettability. Interpretation of experimental results is hampered by the water content in different proportions in different technical alcohols, which is determined by the azeotropy point (the t_{bp} of rectified alcohol is 0.3 °C lower than t_{bp} of chemically pure alcohol). But here too there is an anomaly: it was expected that the water content would reduce the V_m value, as t_{fp} and t_{ai} increase, i.e. the conditions for the formation of the flammable vapor and its ignition worsen (in practice, the opposite is true).

Currently, the extinguishing direction of liquids based on solid floating granular agents, for example, FG, is developing. During burnout, the liquid surface has a t_{mp} , but during insulation, it decreases. If the main mechanism for stopping combustion is the cooling, then the corresponding effect is achieved by cooling the surface to less than t_{fp} . The FG layer same value provides approximately the same surface cooling and evaporation isolation, but these effects determine a different fraction of the t_{bp} and LFL, so the decrease in V_m during the FG layer accumulation is not completely synchronous. The water content creates many slowing factors for the combustion process: t_{fp} and t_{ai} increase, lower LFL, water vapor phlegmatizes the combustion zone, the combustion heat and flame temperature decrease, and can increase the freeboards steel surfaces wetting, which increases the combustion area and V_m (but there is no such effect during FG supply).

For any flammable liquids, there is a FG fire-extinguishing layer, but for more volatile ones, such as pentane, it reaches 70 cm. Therefore, a compromise option for extinguishing is to use FG as a primary fire-extinguishing floating non-combustible layer, above which the weakened combustion still continues. The easiest way to improve the FG fire extinguishing properties is to wet it with water or an inhibitor solution with a single-stage application. This reduces the FG buoyancy, i.e. the non-submerged (insulating) total layer part, and increases the submerged (cooling) part. Wet FG cools the burning liquid surface 5 times better than dry FG, and has a fire-extinguishing layer 1–2 cm smaller. The buoyancy of 0.46–0.76 dry and 0.44–0.74 wet

FG in alcohols is much greater than in alkanes: for dry 0.36–0.58, for wet FG 0.31–0.49 [4], which is proportional to the liquids densities (Fig. 1).

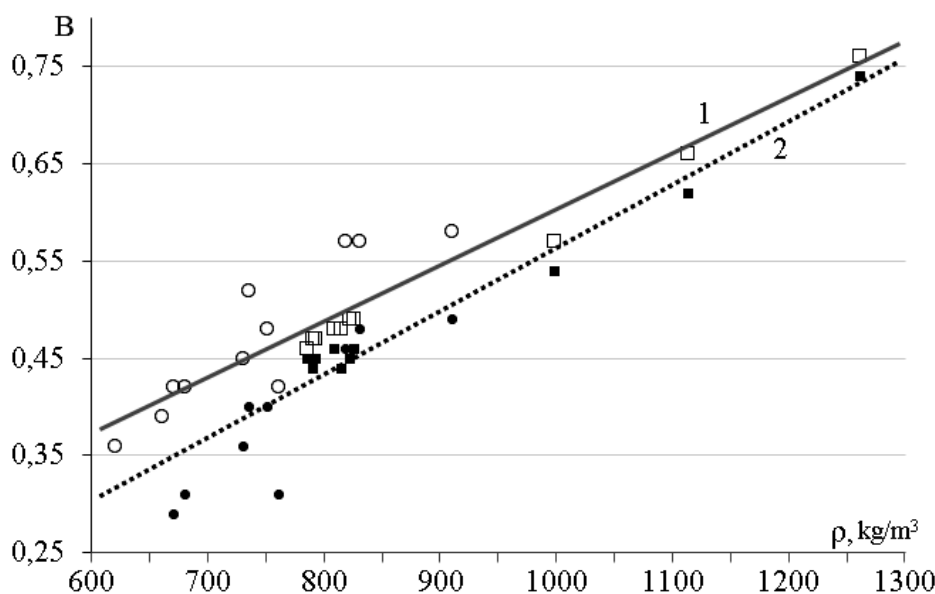


Fig. 1. Foam glass buoyancy depending on the liquids density: 1, ○, □ – dry FG; 2, ●, ■ – wet FG; ○, ● – alkanes, □, ■ – alcohols

Fig. 1 shows the buoyancy in liquids: water; alkanes – pentane, heptane, octane, decane, dodecane, petroleum ether, white spirit, gasoline, kerosene, diesel fuel, engine oil; alcohols – methanol, ethanol, isopropanol, n-butanol, n-pentanol, n-heptanol, n-octanol, ethylene glycol, glycerin. The buoyancy dependence of dry and wet FG on the liquid density in the first approximation is described by equations: $B_{\text{dry}}=0.0006\rho+0.0266$, $B_{\text{wet}}=0.0007\rho-0.1297$.

If we compare liquids with the same molecular skeleton length, then in alcohols the buoyancy is much higher (in butanol – 0.48, in pentane – 0.36), and if we look at the density, then in alkanes the dry FG buoyancy is somewhat higher (in dodecane – 0.48, in methanol – 0.47), and the wet FG buoyancy is somewhat lower (in dodecane – 0.4, in methanol – 0.45). From dependences profile in Fig. 1, white spirit stands out the most, which has a density of 770 kg/m^3 and is an alkanes technical mixture. In pentane, wet FG can be considered non-buoyancy. This shows that the FG wettability by alkanes is greater than that by alcohols with the same density. In addition, the cooling processes of the burning liquid surface by supplying wet FG will vary depending on this liquid temperature: up to $100 \text{ }^\circ\text{C}$ – slow heating of water; up to $120 \text{ }^\circ\text{C}$ – slow boiling; above $120 \text{ }^\circ\text{C}$ – rapid boiling with splashing hot water droplets.

It is also interesting to investigate the relationship between the liquids basic parameter of the fire extinguishing t_{fp} with buoyancy and with the liquid density, as a related parameter (Fig. 2). Since the FG buoyancy determines the mechanism and effectiveness of its use for the fire extinguishing, it seemed promising to obtain common dependencies. No generalized dependencies were obtained, which indicates the conventionality of using t_{fp} as a basic parameter for the FG flow rate normalizing for the fire extinguishing. Nevertheless, there are dependencies within homologous series: for n-alkanes – $B=0.001(t_{\text{fp}}+60)+0.3399$, $\rho=1.1239(t_{\text{fp}}+60)+9.21 \text{ kg/m}^3$; for n-alcohols – $B=0.0003(t_{\text{fp}}+60)+0.4521$, $\rho=0.438(t_{\text{fp}}+60)+763.41 \text{ kg/m}^3$, where " $60 \text{ }^\circ\text{C}$ " is the liquids conditional lowest t_{fp} . Thus, an equation was obtained for the FG buoyancy predicting based on the information on the density or flammable liquid t_{fp} .

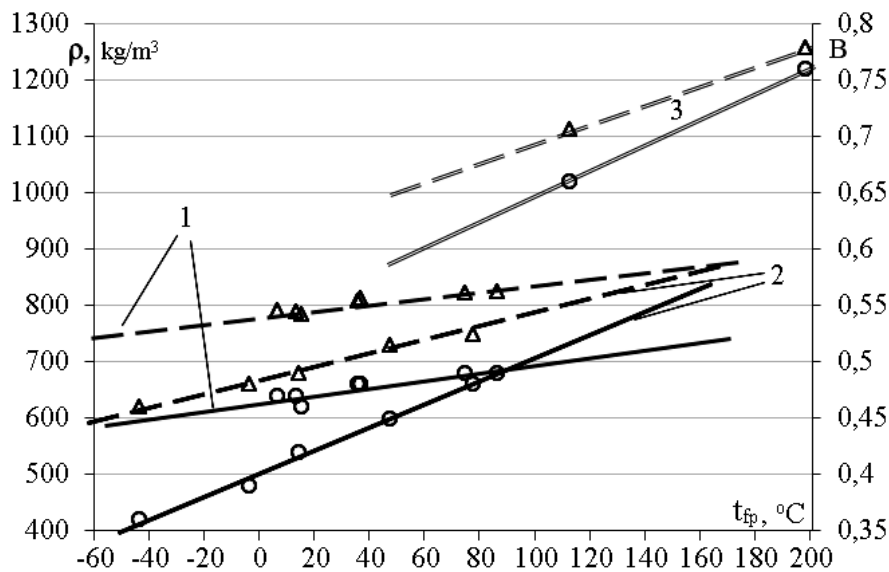


Fig. 2. Relationship between the liquids density (---, Δ) and the dry FG buoyancy (—, \circ) with the liquids t_{fp} : 1 – n-alcohols from methanol to octanol; 2 – n-alkanes from pentane to octane; 3 – polyhydric alcohols (ethylene glycol, glycerin)

The formation of a primary FG layer on a burning liquid creates sufficient conditions for the extinguishing reliable completion by many methods, most of which do not contaminate the liquid. A simpler, more effective and economical solution is to extinguish with a 4 cm wetted FG layer or to complete the extinguishing by applying a gel layer with a consumption of 0.2 g/cm^2 .

6. Extinguishing parameters dependence identification of liquids with foam glass on their properties

The isolating and cooling agents effectiveness in the liquids burning stopping can be assessed by reducing the evaporation mass rates $V_{m(e)}$ and burnout $V_{m(b)}$. If, by cooling, the liquid surface temperature is ensured to be $< t_{fp}$ or a certain fire extinguishing substance isolating layer is accumulated, then the evaporation intensity will become less than the critical one, and the vapor concentration will become less than the LFL, so combustion will become impossible [29]. That is, fire extinguishing by isolating or cooling the surface should slow down evaporation to achieve a vapor concentration less than LFL. Then it is possible to introduce the theoretical evaporation retardation coefficient K_{ev} , which must be provided: for example, for the t_{bp} , the liquids vapor concentration is 100 %, for gasoline LFL $\approx 1 \%$, i.e., it is necessary to slow down evaporation by 100 times.

The dry FG action first effect on the liquid surface is cooling, but for low-boiling liquids it is insignificant – about $5 \text{ }^\circ\text{C}$, which reduces the saturated vapor pressure by only 10–12 kPa and a similar fraction of the concentration. The FG direct isolating effect has 2 components: reducing the evaporation area and slowing down the steam diffusion into the combustion zone, with the first component being the main one. The non-flammable particles presence on the liquid surface reduces, and FG particles wetting with a flammable liquid slightly increases the evaporation area (particles contact points act as capillaries), so the resulting reduction in the evaporation area can be estimated as 50 %. The vapor concentration above the surface decreases proportionally (the $V_{m(e)}$ decreases) and a certain K_{ev} is reached.

For practical use, it is desirable to know which liquid parameter can be relied on to predict the FG reserve for forming a basic fire-extinguishing layer for different ho-

mologous classes liquids. In the foam firefighting practice, this is a liquid t_{fp} . To establish such compliance, it is necessary to conduct a research of the FG fire extinguishing effect for liquids with similar key parameters.

Regarding the extinguishing mechanism, granular closed-pore FG provides effective fire extinguishing only for high-boiling liquids (starting with $t_{fp} > 100$ °C, the dry FG fire-extinguishing layer is 4–6 cm). The FG additional insulating effect is that it shields the liquid surface from flame radiation, with the flame and its heat flux already reduced due to the cooling and isolation stages. Extinguishing gasoline (hexane) requires accumulating a dry FG layer of 0.5 m thick, which is not technologically feasible. Therefore, an extinguishing option with a dry FG base layer 12 cm and extinguishing completion by adding an inorganic gel isolating layer with a total consumption of 0.2 g/cm^2 was developed, which ensures an evaporation slowdown by another 30 times. Then the FG contribution to the reduction in evaporation intensity was 70 % (3.3 times). Wet FG has a greater cooling effect, water vapor dilutes the burning zone, water from the submerged FG layer dilutes flammable water-soluble liquids. Therefore, we recommend extinguishing hydrocarbons with $t_{fp} > 28$ °C with a wet FG base layer 6 cm of fraction 1.0–1.5 cm, which is sufficient to stop the burning or requires the extinguishing completing with an inorganic gel with an application rate of 0.2 g/cm^2 ; for hydrocarbons with $t_{fp} < 28$ °C the wet FG base layer is 12 cm, which is sufficient to stop burning or requires the gel – of 0.45 g/cm^2 .

For a more detailed study of the isolation and cooling contributions by the FG layer, an experiment was conducted on the extinguishing of the polar liquid – n-heptanol, which has an anomalously increased $V_{m(b)}$ through the FG layer among all alcohols [30]), in comparison with the extinguishing of alkanes which have similar t_{bp} , t_{fp} , molar masses M (n-octane, n-decane, n-dodecane) (Tab. 1).

The heptanol anomaly disappears for FG layers close to fire-extinguishing ones: with such a thickness of the FG layer, the burning process already occurs according to the evaporation principle – higher $V_{m(b)}$ through the FG layer are observed for alcohols with lower t_{bp} . A higher t_{fp} simplifies fire extinguishing by cooling the liquid surface with a FG layer. A higher t_{bp} increases the starting surface temperature during extinguishing. A higher t_{ai} is not directly related to the extinction effect, but makes it more difficult to re-ignite from a hot surface. A higher β determines a higher oxygen requirement, which makes combustion more difficult and extinguishing easier. A larger M is related to the factors described, but does not correlate with β molecules with different oxygen contents. For heptanol and dodecane, the main extinguishing mechanism when FG is applied is the liquid surface cooling (according to Tab. 1, a significant decrease in the saturated vapor pressure P_{sv}), and for octane and decane, the evaporation isolation to the combustion zone. There is an effective cooling depth that determines the lowest FG consumption for the fire extinguishing – a layer of 6 cm (≈ 3 cm of the submerged part), which is typical for liquids with $t_{fp} > 100$ °C. Therefore, a 6 cm thick FG layer can be considered basic for the liquid fires extinguishing based on this agent. Based on this layer, it is possible to decide on further tactics for the completing extinguishing: wetting the FG, flame extinguishing agents, adding the FG layer as a floating carrier for inorganic isolating gel or other substances. A FG base layer is sufficient for extinguishing high-boiling liquids.

The residual K_{ev} after the cooling stage the liquid surface by the FG layer is the largest for n-decane, but this did not determine the most difficult conditions for its extinguishing, which can be associated with the large M , and therefore with the slower

diffusion of the vapor through the granular FG layer. The lower the liquid t_{bp} , the greater the residual P_{sv} and the required K_{ev} , the closer the liquid cluster structure will be to the monomeric state (for example, for hexane). That is, the FG isolating capacity is related to the M , and the cooling capacity (in addition to the heat capacity) is related to the t_{bp} and liquid density. Therefore, given the complex action of isolating fire extinguishing means which contact with a surface engulfed in flames, there cannot be a single indicator with which the fire extinguishing ability of a given agent for a substances wide range would be correlated.

Tab. 1. Flammable liquids characteristics [31] and their extinguishing with dry foam glass

Parameter	n- heptanol	n-octane	n-decane	n-dodecane
t_{bp} , °C	176	126	174	216
t_{fp} , °C	74	14	47	77
t_{ai} , °C	275	215	210	202
$t_{bp} - t_{fp}$, °C	102	112	127	139
Δt_{coolFG}^* , °C	14.74	7.73	14.36	24.7
$P_{sv \text{ residual}}$, kPa	64.4	84.1	72.2	54.3
φ_H , %	1	0.9	0.7	0.63
$K_{ev \text{ residual}}$	64.4	93.4	103.1	86.2
M , g/mol	116	114	142	170
ρ , kg/m ³	821.9	680	730	750
β	8	12,5	15,5	18,5
n_{C+OH}	8	8	10	12
n_{Ceq} in liquid	29	16	20	24
n_{Ceq} in flame	12	17	15.5	16.5
B	0.49	0.42	0.45	0.48
h_{FG} , cm	8–10	10–12	7–9	5–6

* – $\Delta t = 4,1e^{0,013t-1}$, °C [5].

There is a FG layer values range within which for the heptanol and octane extinguishing effect may be achieved. At such layers, weak combustion is observed, which may be extinguished either at slightly smaller FG layers or, with a weak flame, will be observed at slightly larger FG layers. The prolonging weak combustion effect with an FG layer increase can be associated with the hydrodynamic resistance disappearance in narrow channels between particles of a FG fraction at low pressures and vapor concentrations of the flammable liquid. Then the final extinction when dry FG is applied is a consequence of the liquid surface shielding by this layer from the flame thermal radiation. This effect will be stronger if the white FG is used. Among the liquids studied, heptanol has the highest density and buoyancy (B) of dry FG; then for it, with the same FG layer, the FG isolating part will be larger.

Close values of t_{fp} for dodecane and heptanol did not result in the same fire extinguishing layer FG (6 cm versus 10 cm), although the t_{fp} is the aim for the surface cooling. Close values of t_{bp} for decane and heptanol brought the $V_{m(b)}$ closer together – for decane, the values are smaller and extinguishing occurs with a smaller FG layer (8 cm). Close values of M for octane and n-heptanol gave a close fire extinguishing layer FG – 10 cm, but they have different extinguishing mechanisms. Also, these compounds have the same molecular skeleton length, which suggests that at the fire extinguishing beginning, when the liquid surface has a t_{bp} , evaporation occurs with the monomer state same characteristics.

It was expected that there might be a correlation of the fire-extinguishing layer for FG or other isolating means for class “B” fires with the $V_{m(b)}$, but it turned out that for

alcohols from methanol to n-heptanol there is an anomaly: instead of this parameter expected decrease, it increases [30]. The parameter $V_{m(b)}$ can be considered as the mass evaporation rate at t_{bp} , but intensified due to the heat flux from the flame to the liquid surface. The evaporation intensity even in one homologous series is also affected by the even-odd molecules phenomenon according to the carbon atoms number in the carbon chain. For example, a zigzag dependence is observed for $V_{m(b)}$ in the homologous series of both alkanes and alcohols [30]. Previously, the various dependencies zigzag pattern in homologous series for certain physicochemical parameters we explained by the cluster structure alternation observed for the solid and liquid states, in flames and aqueous solutions [32]. Tab. 1 shows the molecules predicted framework lengths of studied substances, in liquid and flame. The correlation with the FG fire-extinguishing layer is more noticeable for the molecular state, which can be explained by the fact that the burnout process occurs in a boiling state. But for substances such as glycerin and ethylene glycol, this principle does not work (frame lengths of 5 and 4, and dry FG extinguishing layer – 3 and 4 cm).

In view of the above, an additional study was conducted of the extinguishing process with dry FG of some alkanes, alcohols, glycols and in the presence of water in the liquid in order to find a correlation with supramolecular structures lengths (Fig. 3).

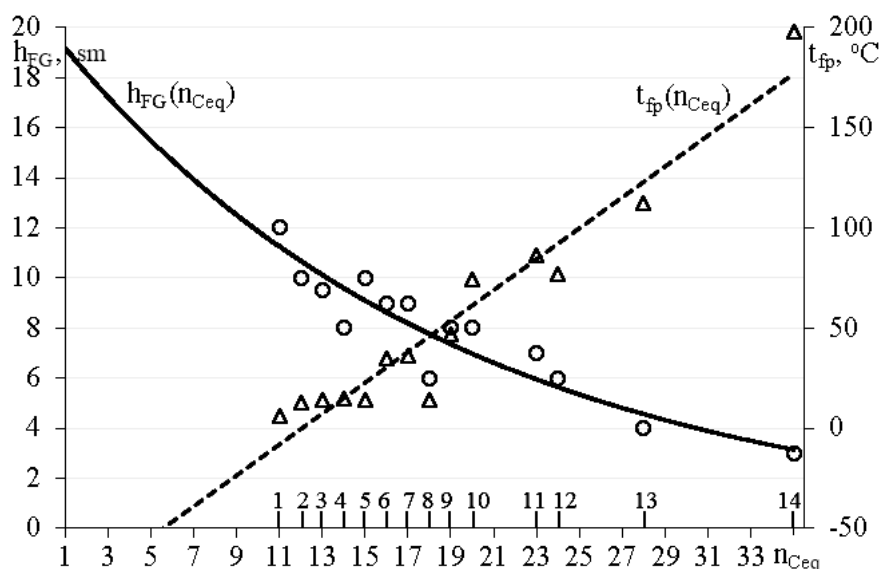


Fig. 3. Correlation of the liquid state clusters equivalent length with the extinguishing layer FG thickness (—, ○) and the liquid flash point (---, Δ): 1 – methanol, 2 – ethanol, 3 – isopropanol, 4 – isopropanol (1.5 % water), 5 – n-octane, 6 – n-butanol, 7 – n-pentanol, 8 – ethanol (4 % water), 9 – n-decane, 10 – n-heptanol, 11 – n-octanol, 12 – n-dodecane, 13 – ethylene glycol, 14 – glycerin

The burnout liquids process is accompanied by a transition from liquid state structures to gaseous state structures with the peroxide complexes formation in the air. Therefore, it is currently not possible to clearly determine which of these structures will predominate in influencing the burnout process. The chosen approach assumes a dimeric structure for alkanes, starting with octane, for alcohols – a tetrameric structure (for methanol – a hexameric), for glycerin and ethylene glycol – a heptameric, for pentane, hexane, heptane – a monomeric, technical ethanol is modeled as a tetramer with the addition of 4 links of intermediate water molecules, technical isopropanol – as an aqueous dimer of an alcohol dimer (a tetramer with 2 additional links of water molecules). It should be noted that spectrometry detects clusters up to the octamer size in alcohols [33]. Based on processing experimental data results on class "B" model fires ex-

tinguishing, a dependence was obtained for the extinguishing layer FG depending on the expected clusters equivalent length n_{Ceq} , as well as the correlation $t_{\text{sp}}(n_{\text{Ceq}})$:

$$h_{\text{FG}}=20.212e^{-0,053n_{\text{Ceq}}}, R^2=0.89. \quad (1)$$

$$t_{\text{fp}}=7.6972 n_{\text{Ceq}}-92.769, R^2=0.93. \quad (2)$$

This method error main component is determined by the fact that modeling principles of the clusters structure are indirect. Technical ethanol, which contains the most water, deviates the most from general dependences. Moreover, the cluster modeling variability does not help here: a small t_{fp} implies a short cluster, a small FG extinguishing layer – a long cluster. The weak correlation of dependencies shown in Fig. 3 in the form of formulas (1) and (2) is also determined by the fact that the extinction moment has a probabilistic component. Depending on the FG particles arrangement randomness in the layer and the channels formation between them, the extinguishing moment may occur with a slightly smaller or larger FG layer.

7. Study results discussion of the extinguishing of liquids by means based on a foam glass

The conducted experimental studies allowed us to establish the extinguishing action proportions of binary means components based on FG and the substance supramolecular structure influence on fire extinguishing. To do this, we relied on the FG buoyancy index in this flammable liquid as a determining factor of its insulating ability, and on the determined cooling effect by the FG layer on polar and non-polar flammable organic liquids artificially heated to different temperatures. This made it possible to establish new relationships between the liquids density, their flash point, buoyancy, the supramolecular clusters length, and the FG fire-extinguishing layer. The fire extinguishing layer FG is inversely proportional to the average cluster length of the flammable liquid during extinguishing, which depends on the primary cooling proportion by the FG layer.

The chosen approach to studying the fire extinguishing of liquids using FG-based means allowed us to clearly separate the successively implemented parts of the cooling and insulating action of FG, the sufficiency and necessity of such action, as well as the additional agent use intensity to the complete fire extinguishing. This result was achieved by introducing a theoretical evaporation retardation coefficient for analyzing the agent effect, the share of which is satisfied by the actual evaporation retardation coefficient due to a certain agent's action component. In addition, previous works [4, 10, 12, 13, 16, 18] did not justify the modulating indicator use, which can be used to select the extinguishing agent supply intensity for different liquids, and by default used the flash point. This paper conducts this issue detailed study and establishes relevant correlations.

At the research first stage, the FG buoyancy in alcohols and alkanes of the normal structure and some of their technical mixtures was determined. Buoyancy determines the amount of isolating and cooling action that an FG layer has, and the second component mass as a binary fire extinguishing system that the FG can hold without immersion in flammable liquid. This can include agents such as foam, vermiculite, perlite, gel, CO₂ granules, etc. The FG buoyancy study showed that in alkanes with a similar molecular length it is smaller than in alcohols, and for liquids with the same density it is larger.

The dependences for the buoyancy of dry and wet FG on the liquid density were obtained and described mathematically with $R^2=0.9$. A similar result was obtained from studies of the relationship between buoyancy and density from t_{fp} . This is partly due to the fact that the technical mixtures under consideration, unlike individual liquids, have disproportionate densities and wettability FG relative to the values for components.

The buoyancy of dry and wet FG does not differ as much as the water weight gained would suggest, because the same external open pores that previously contained the flammable liquid are now filled with water, and the difference in buoyancy is determined by the difference in densities of water and flammable liquid, and the changed flammable liquid contact area with the FG surface. In addition, methanol, ethanol, propanol-2, ethylene glycol and glycerin are infinitely soluble in water, so in the wet FG external pores, part of water is replaced by a flammable liquid. This effect further explains the buoyancy nonlinearity in alcohols and the difference with alkanes. Yes, the water density is less than the density of ethylene glycol and glycerin, so wetting with a lighter component should have slightly increased buoyancy, but this did not happen. The explanation may be the solution formation with water with a higher density than have components. Thus, this work presents the first analytical comparison of FG buoyancy in polar and nonpolar liquids, individual and technical mixtures.

The extinguishing completion with a FG layer is currently more investigated with a non-flammable gel, which is formed by the reaction of 10 % solutions of CaCl_2 and liquid glass. To hold the gel applied at a rate of 0.2 g/cm^2 , the supporting layer of dry FG is 12 cm [3]; CaCl_2 also has an inhibitory effect on the flame. FG immersion by the gel increases the cooled layer thickness of the hot liquid, but hardly changes the heat balance inside the “liquid + FG” layer. That is, there is an effective cooling depth that determines the lowest FG flow rate – 4–6 cm (2–3 cm of the submerged part) for extinguishing only by cooling liquids with large t_{fp} .

It is possible to supply sprayed water or an inhibitor solution to the flame, then in addition to inhibition, cooling of the flame, the FG surface, and the liquid after FG deeper immersion will be involved. It is possible to coat the FG layer with a layer of flame retardant, substances that melt or swell under the flame influence. It is possible to complete the extinguishing with other standard means: medium-multiplicity foams, fire-extinguishing aerosol, general and special-purpose powders, non-flammable gases. Thus, the FG base layer formation on a burning liquid creates sufficient conditions for the extinguishing reliable completion by many methods, most of which do not contaminate the liquid.

At the study second stage, in order to clarify the normalized indicators of the FG use as a extinguishing base layer for liquids, the fire extinguishing mechanism and the modulating indicator of the process as a whole were established. It established that the FG layer has a primary effect in the liquid surface cooling form, which reduces the vapor pressure, its concentration, and the required evaporation retardation coefficient. At the same time, FG isolates the evaporation process by reducing the free surface area and retards the vapor diffusion into the combustion zone. The FG effectiveness is hindered by its wettability by flammable liquid, which increases the evaporation area, i.e. it does not decrease equally with the liquid mirror area occupied by FG particles. In addition, the wettability is not the same for different liquids. It was also previously observed [30] that technical aqueous solutions of methanol and ethanol burn out faster than pure liquids, which implies more difficult extinguishing conditions. In contrast, the fire-extinguishing layer FG for such solutions is reduced [4]. We assume that water-

containing clusters decompose more intensively at t_{bp} and under the flame heat flux influence than clusters of pure alcohol.

Thus, the work investigated the correlations with the dry FG fire-extinguishing layer of such indicators as molar mass, length of the molecular or cluster skeleton, combustion reaction stoichiometric coefficient, burning mass rate from the free surface, density, flash point, boiling point, and autoignition. It turned out that all these parameters work only for some liquids, because each of them does not take into account some factor from the complex that determines the formation of the extinguishing FG layer value. The solution to this problem in this work was to take into account the cluster supramolecular structure of the substance, with the correction that the primary cooling effect for different liquids constitutes a temperature range different fraction of their existence, therefore, a different reduction in saturated vapor pressure is achieved. A smaller effect is observed for low-boiling liquids, therefore it is assumed that their surface has a substance monomolecular state, for other liquids dimeric structures are assumed, for high-boiling liquids – up to heptameric, which corresponds to the cold alcohols spectrometry [33]. This approach for the first time allowed us to obtain mathematical relationships for the dry FG extinguishing layer depending on the expected clusters predominant length in the liquid.

The study results are limited to the homologous classes of alkanes and alcohols, therefore, for other organic compounds classes, separate tests and approximations must be carried out. Moreover, the deviations obtained during the description of physico-chemical and fire-extinguishing properties of studied homologous series indicate the need to improve the experimental processing methodology. The problem with this and other approaches to modulating the FG extinguishing layer is that the extinguishing process by the supplying FG depends on the evaporation process (at different parts of the $t_{mp} - t_{bp}$ range), the FG wettability by the combustible liquid, the vapor diffusion rate through the FG layer, the LFL in the air, the combustion heat, cluster structures in the flame, and have different oxygen requirements for the combustion process. Given such an influencing factors number, it is difficult to achieve greater accuracy in predicting the dry FG extinguishing layer without developing a complex dependence. But the developed approach is sufficient to predict the conditions of the significantly weakened combustion above the FG, which can be extinguished by the vast majority of fire extinguishing means of volumetric or surface action.

Regarding the supramolecular structure consideration as a liquids extinguishing modulating indicator, a clear calculation principle has not yet been developed for determining the equivalent cluster length when describing a certain substance state, including for the liquid actual temperature. $t_{mp} - t_{bp}$ The simplest way is to take into account the residual portion of the temperature range " $t_{bp} - t_{mp}$ (or t_{tr})" after the fire extinguishing agent cooling effect on the surface has been triggered. But, most likely, this part will have to be taken into account in the certain function form, for example, a cube root, as a typical description of non-azeotropic mixtures.

For the studied options for extinguishing polar and non-polar liquids with dry or wet FG and under the condition of the additional coating with the inorganic gel, there are limitations to the method application. Effective extinguishing of alkanes with a dry or wet FG layer up to 8 cm is achieved only for flammable liquids with $t_{fp} > 61$ °C, for alcohols in the dry FG case – for liquids with $t_{fp} > 45$ °C, in the wet FG case – $t_{fp} > 10$ °C. The gel extinguishing is poorly effective for polar liquids due to their water solubility.

Thus, in the field of FG application for the polar and non-polar liquids fire extinguishing, there are still many unexplored combinations with other fire extinguishing

means, which can provide a reliable fire extinguishing effect, cost-effectiveness and environmental friendliness.

8. Conclusions

1. The buoyancy characteristics of dry and wet foam glass in polar and non-polar flammable liquids have been determined. With increasing liquid density, the foam glass buoyancy increases according to a general law close to linear, which is described by approximation formulas separately for dry and wet foam glass, but taking into account both polar and non-polar liquids. The dry foam glass buoyancy in alkanes varies from 0.36 for n-pentane to 0.58, and for wet foam glass from 0.29 to 0.49 (in pentane, wet foam glass can be considered non-floating). The largest deviations from the linear law are observed for alkanes technical mixtures. The dry foam glass buoyancy in alcohols varies from 0.46 to 0.76, and for wet foam glass from 0.44 to 0.74 (the dependence is nonlinear due to the different alcohols water solubility). A relationship between buoyancy and the hydrocarbons flash point has been established, but the dependencies turned out to be individual for n-alkanes, n-alcohols, and glycols, which is described mathematically. A linear relationship between flash points and the liquids density has also been established. The obtained data allow us to predict the foam glass base layer for the binary fire extinguishing.

2. Correlations with the dry FG fire-extinguishing layer of molar mass, length of the molecular or cluster skeleton, combustion reaction stoichiometric coefficient, burning mass rate from the free surface, density, flash points, boiling points, and autoignition were found. The predicting possibility the extinguishing layer of the dry foam glass based on the chemical structure of the molecular and supramolecular states of flammable liquids has been established. An equation for the dry foam glass extinguishing layer depending on the expected clusters length in the liquid, as well as a similar dependence for the flash point, was obtained. Effective extinguishing with dry or wet foam glass of alkanes with a layer of up to 8 cm is achieved only for flammable liquids with $t_{fp} > 61$ °C, for alcohols for the dry FG case – with $t_{fp} > 45$ °C, for the wet FG – $t_{fp} > 10$ °C. It is recommended to extinguish hydrocarbons with $t_{fp} > 28$ °C with a base layer of wet foam glass 6 cm of fraction 1.0–1.5 cm, which is sufficient to stop the burning of most of such hydrocarbons or requires extinguishing completion with an inorganic gel with an application rate of 0.2 g/cm²; for hydrocarbons with $t_{fp} < 28$ °C, the wet foam glass base layer is 12 cm, which is sufficient to stop the burning or requires the gel supply with an application rate of 0.2 g/cm² for some substances.

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НАПРЯМКИ РОЗВИТКУ ГАСІННЯ ПОЖЕЖ РІДИН НА ОСНОВІ БАЗОВОГО ШАРУ ПІНОСКЛА

Встановлено моделюючий параметр горючої рідини для прогнозування вогнегасного шару піноскла як базового засобу для забезпечення надійного пожежогасіння рідин у комплексі з іншими вогнегасними засобами. Досліджено особливості формування та показників плавучості сухого та вологого піноскла у полярних та неполярних рідинах (алканах та спиртах). Показано зростання плавучості піноскла зі збільшенням густини рідини. Описано плавучість піноскла у полярних і неполярних рідинах залежно від густини рідини апроксимаційною лінійною залежністю окремо для сухого і вологого піноскла. Пояснено відхилення від лінійного закону різною змочуваністю піноскла, водорозчинністю деяких спиртів, особливостями сумішей рідин. Встановлено зв'язок плавучості з температурою спалаху, який спостерігається окремо для *n*-алканів, *n*-спиртів та гліколів, що описано математично. Розроблено формулу для опису взаємозв'язку температур спалаху з густиною рідин. Досліджено кореляції з вогнегасним шаром сухого піноскла молярної маси, довжини каркасу молекули або кластеру, стехіометричного коефіцієнту реакції горіння, швидкості вигорання з вільної поверхні, густини, температур спалаху, кипіння, самоспалахування. Встановлено можливість прогнозування вогнегасного шару сухого піноскла на підставі опису кластерів горючих рідин. Отримано математичні залежності для вогнегасного шару сухого піноскла залежно від довжини очікуваних кластерів у рідині та аналогічну залежність для температур спалаху. Визначено умови ефективного гасіння спиртів та алканів сухим піносклом. Рекомендовано різні режими гасіння вуглеводнів з температурами спалаху $t_{сп} < 28\text{ }^{\circ}\text{C}$ та $t_{сп} > 28\text{ }^{\circ}\text{C}$ на основі базового шару вологого піноскла 6 см фракції 1,0–1,5 см з можливістю завершення гасіння за необхідності неорганічним гелем шляхом розпилення компонентів з витратою нанесення 0,2 г/см².

Ключові слова: пожежогасіння, горюча рідина, кластер, піноскло, плавучість, ізоляція, охолодження, гель, витрата

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