

*Designing environmentally friendly protective materials for flammable liquids makes it possible to influence the processes of heat resistance and the physical-chemical properties of a protective coating over a certain time until the emergency is eliminated. Therefore, there is a need to study the conditions that form a barrier for thermal conductivity and to define a mechanism for decelerating the transfer of heat to a flammable liquid by using a foaming agent. Given this, a mathematical model has been built for the process of changing the concentration of a foaming agent when used as a coating. Based on the experimental data, it was established that the foaming layer destruction process took place over 618 s until the achieved critical thickness of the foaming layer made the conductivity cease. According to the derived dependences, the concentration value was calculated at which the critical value of the foaming layer thickness is achieved, which leads to the ignition of a flammable liquid, and is about 25 %. It has been proven that the process of decelerating the temperature involves the decomposition of a foaming agent under the influence of the temperature, with heat absorption and foam release, the insulation of heat at the surface of the flammable liquid. Given this, it has become possible to define the conditions for protecting flammable liquids using foaming agents by forming a barrier to thermal conductivity. Experimental studies have confirmed that under the influence of water evaporation and foaming agent diffusion into a layer of the flammable liquid, the critical amount of the foaming agent reached a minimum in 606 s and only then the flammable liquid ignited. Thus, there is reason to argue about the possibility of using foaming agents to protect the leaks of flammable liquids, capable of forming a protective layer at the surface of the material. It also becomes possible to establish methods for assessing the insulating capacity of a foaming agent that could inhibit the rate of temperature penetration and the release of flammable liquids' vapors*

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## 1. Introduction

The production of high-quality materials, as well as determining their properties, are given special attention at present [1, 2]. Therefore, the effectiveness of fighting fires largely depends on the quality of fire-extinguishing substances and their application technologies [3]. Modern fire-extinguishing substances include water-based fire-ex-

tinguishing substances, in particular foaming agents, which are used to a greater or lesser extent in the practice of fire extinguishing. At the same time, the factors that predetermine the effect of foaming agents include the cooling and insulating of the flammable environment [4].

Knowledge of the physicochemical properties of such substances, their quality indicators, the mechanism of action on flammable materials makes it possible to select them

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# ESTABLISHING REGULARITIES IN THE INSULATING CAPACITY OF A FOAMING AGENT FOR LOCALIZING FLAMMABLE LIQUIDS

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taking into consideration economic indicators, the duration and safety of application, environmental aspects, etc. [5, 6]. The use of coatings makes it possible to decelerate the warming up of the material by forming a protective layer and to maintain its functionality in case of fire over the predefined period [7, 8].

Modern special-purpose foaming agents can create, at the surface of the structures' elements, the heat-insulating shields that withstand high temperatures and direct action of fire, as well as decelerate the release of a flammable liquid's vapors. That is, they are capable of maintaining their functions in case of fire over the predefined period, thereby preventing ignition.

However, the use of solutions of the surface-active substances does not always provide the necessary level of insulating a flammable liquid, which, accordingly, affects the course of fire-preventive measures. Taking into consideration the strict requirements for these indicators, there is a task to determine the properties of foaming agents and to establish their effectiveness.

The above necessitates our research into the conditions of insulating an oxidizer through the formation of a polymeric film at the surface of a flammable liquid in order to substantiate the conditions for protection against the ignition source.

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## 2. Literature review and problem statement

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It is known that combustion occurs in the steam phase in the presence of an oxidant. Therefore, to stop combustion, it is necessary to stop the intake of vapors of the combustible substance or oxidant into the combustion zone or to divide the fuel and oxidant spatially.

Work [9] shows that applying foam to the surface of the burning liquid can reduce the rate of its evaporation by creating a mechanical obstacle for the diffusion and convection transfer of vapors to the combustion zone. However, there remain unresolved issues related to establishing the time of foaming agent operation. Paper [10] demonstrates that to ensure extinguishing it is necessary to continuously supply foam to the surface of the liquid that burns, as it collapses under the influence of the heat flow from the flame. The use of appropriately selected and properly concentrated firefighting foam to extinguish the fire makes it possible to reduce the duration of the fire and its consequences for the environment. However, there remains an unresolved issue related to the resistance of the foam to the flame.

Study [11] reports a new apparatus to assess the impact of foam stabilizers on foam drainage and the property of foam spreading. When choosing foam stabilizers, one needs to deal with factors such as the property to form a film, foam resistance, and the property of foam spraying. The option to overcome the appropriate difficulties may be to determine the insulating capacity of the foaming agent.

The properties of the solution of aqueous film-forming foams containing different content of xanthan gum were examined by varying its mass fraction; the foam properties and the fire extinguishing characteristics of foaming agents were estimated [12]. The results showed that the content of xanthan gum slightly affects the surface tension of foam solutions while the foaming was not impacted. However, it is not known how a given additive affected the burnout of foam.

Work [13] found that water-based film-forming foam is a very important fire-extinguishing agent in case of fires on hydrocarbon fuels. The effectiveness of foam scattering is one of the key factors determining the effectiveness of its extinguishing but there are many parameters that affect the effectiveness of foam propagation. A surface-tension viscosity mode model was used to predict the water film process but the mechanism of foam propagation on a flammable substance was not investigated, making the cited studies inappropriate.

Article [14] reports research into the use of appropriately selected and properly concentrated firefighting foam to extinguish the fire, which reduces the duration of the fire and its effects on the environment. However, the effectiveness of the foam application, its multiplicity, and stability are not shown.

Fluorinated and non-fluoride fire-extinguishing foams are synthesized in work [15]. A variation of the instant foam spread area was analyzed depending on time. The results indicate that a water film at the surface of heptane is observed during the application of fluoride foam but not during the application of the foam that does not contain fluoride. It was established that the rate of spread of non-fluoride foam increases with an increase in the foam flow rate and decreases with an increase. The high surface tension and the high viscosity of the fluoride-free foam solution are important factors leading to its slow propagation. However, no fire extinguishing efficiency of such foam was specified, no stability for other flammable liquids was established.

To determine the foam stability, the authors of [16] conducted experiments to quantify the degradation of foam caused by fuel, the application of foam to liquid fuel and water (for comparison). It was found that foams without fluoride decomposed much faster than AFFF. The video recording of the degradation shows that the propagation occurs mainly due to bubbles near the interface surface, which increase in size with accelerated roughness due to binding. However, there is no mechanism for degradation of foam caused by fuel and its effect on fire extinguishing indicators.

Work [17] suggests the use of cation-anionic surfactant mixtures with short fluorocarbon chains in both cationic and anionic surfactants. The authors examined the distribution rates of its aqueous solution on *n*-heptane, toluene, benzene, cyclohexane, and gasoline, which were positive, and investigated the film propagation, tightness, and foaming. However, the effect of additives on the effectiveness of foam formation and the outflow of foam from a flammable liquid was not established.

The synthesis of new surfactants with a short fluorocarbon chain ( $\leq C4$ ) became a very important technique to resolve the issue of using foaming agents [18]. The authors of this work synthesized a new perfluorobutyl-based foaming agent, investigated the foaming capacity, spreadability, and efficiency of hydrocarbon oils extinguishing. However, no effect of using the most common flammable liquids, particularly gasoline, was determined.

Thus, the scientific literature reveals that foaming agents can be destroyed at the surface of a flammable liquid, thereby losing their insulating capability. All this gives reason to argue that it is appropriate to conduct a study to define those parameters that ensure the resistance to destruction, as well as to elucidate what affects the mechanism of foaming agent action for the protection of a flammable liquid. The need to establish the mechanism of foaming agent action in the elimination of spills, when protecting against ignition, has predetermined our research in this area.

### 3. The aim and objectives of the study

The aim of this work is to identify patterns of insulating flammable liquid with a foaming agent. This would make it possible to substantiate the mechanism of foaming agent action to localize the spills of flammable liquids and their burning.

To accomplish the aim, the following tasks have been set:

- to simulate the process of foaming agent diffusion into a layer of flammable liquid;
- to establish the features of reducing the insulating capacity during the interaction between the foaming agent and flammable liquid.

### 4. Materials and methods to study the insulating capacity of the foaming agent

#### 4.1. Examined materials used in the experiment

Samples of a 3-% solution of the foaming agent So-fir AFF-107 (Ukraine) were used to establish the insulating capacity of the foaming agent. We applied to the surface of gasoline A 92 a foaming agent solution at a flow rate of 0.02 kg/m<sup>2</sup> and tested it for insulating capacity.

#### 4.2. Procedure for determining the indicators of the insulating capacity of the foaming agent

Our study, aimed at simulating the process of insulating a flammable liquid by a foaming agent, was carried out applying the basic provisions of mathematical physics.

Special equipment was used for the experimental research into determining the electrical conductivity of an electrolyte solution (foaming agent) at the surface of flammable liquid. To this end, we applied a cuvette made of plastic, with electrodes, additionally equipped with a device for measuring electrical resistance during tests (Fig. 1). The cuvette was filled with flammable liquid (gasoline), the surface of which was coated with a layer of the foaming agent; then we measured the resistance. Based on the criterion of an insulating capacity loss, no electrical resistance was detected.

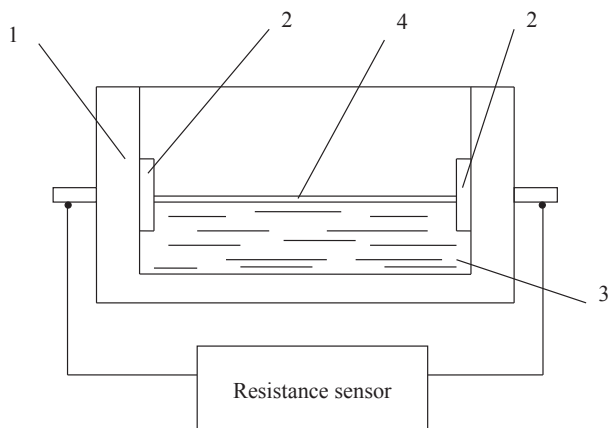


Fig. 1. Schematic determining the foaming agent's electrical resistance: 1 – cuvette made from plastic; 2 – electrodes; 3 – flammable liquid (gasoline); 4 – foaming agent solution

We determined the protective capacity of a foaming agent according to a working procedure, which implied the experimental determination of the insulating capacity of a foaming agent to the ignition of the flammable liquid's va-

pors. At the same time, the flammable liquid sample, poured into the cuvette and coated with a layer of the foaming agent, was exposed to the flame of the burner with the predefined parameters while recording the fuel ignition time.

The model sample was taken into the chamber. The cuvette was filled with a flammable liquid at about 50 g per 1 dm<sup>2</sup> of its surface. We placed a sample of the foaming agent in the amount of 0.02 kg/m<sup>2</sup> at the fuel surface, lit the burner, and kept it in the flame of the fuel during the ignition. The time of the flare-up of the flame was monitored.

### 5. Simulating the process of insulating a flammable liquid with a foaming agent solution

Substance 1, at the initial concentration  $A$ , is in a layer of the thickness  $l < x < 0$ , tangent to the semi-infinite area  $0 < x < \infty$ , which hosts substance 2. From the moment  $t=0$ , substance 1 is chemically decomposed (reaction of the first order), and it diffuses into the semi-infinite area of substance 2, which is in excess and does not penetrate the interface boundary (Fig. 2).

It is required to determine the dependence of the concentration  $C_s$  of substance 1 in the layer  $l < x < 0$  on time. It is assumed that the layer is quite thin so that the dependence of the concentration on the coordinate at  $x < 0$  can be neglected. The process considered is described by the following system:

$$\left( \frac{\partial}{\partial t} - \phi^2 \frac{\partial^2}{\partial x^2} + k \right) C = 0, \tag{1}$$

$$C|_{x=\infty} = 0, \quad C|_{t=0} = 0, \quad C_s|_{t=0} = A, \tag{2}$$

$$l \frac{\partial C_s}{\partial x} \Big|_{x=0} = \phi^2 \frac{\partial C_1}{\partial x} \Big|_{x=0}, \tag{3}$$

where  $C$  is the concentration of a foaming agent at the surface of flammable substance, %;  $\phi = \sqrt{D}$ ,  $D$  is the coefficient of foaming agent diffusion into a layer of the flammable substance, m<sup>2</sup>/s;  $k$  is the constant of the irreversible chemical reaction of the first order, 0,026 min<sup>-1</sup>;  $A$  is the initial concentration, %;  $t$  is the sample stay at the surface of flammable liquid, s.

The solution to system (1) with initial conditions (2) is the following equation [19]:

$$-\phi \frac{\partial C_s}{\partial x} \Big|_{x=0} = e^{-kt} \cdot P^{1/2} \cdot e^{kt} \cdot C_s, \tag{4}$$

where  $P$  is the Laplace operator.

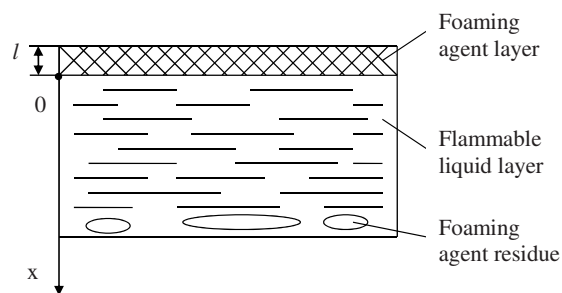


Fig. 2. Diagram of the foaming agent destruction process on the flammable liquid

Considering (3), one can write:

$$\frac{l}{\phi} \frac{dC_s}{dt} + e^{-kt} \cdot P^{1/2} \cdot e^{kt} \cdot C_s = 0. \tag{5}$$

By taking the integral of equation (5) in the range from 0 to  $t$ , that is, by using the  $P^{-1}$  operator, we find a symbolic expression for the desired concentration in the foaming agent layer:

$$C_s(t) = \frac{1}{1 + \delta \cdot P^{-1} \cdot e^{-kt} \cdot P^{1/2} \cdot e^{kt}} \cdot A, \tag{6}$$

where

$$\delta = \frac{\phi}{l}.$$

Taking into consideration the properties of the operator  $P$ , the solution to equation (5) can be represented in the form of a series:

$$C_s = \sum_{n=0}^{\infty} a_n \cdot P^{-n/2} \cdot A. \tag{7}$$

By applying the Laplace transform, one can represent (6) in the following form:

$$P^{-1} \cdot e^{-kt} \cdot P^{1/2} \cdot e^{kt} \cdot f = \frac{\sqrt{p+k}}{p} \cdot f, \tag{8}$$

We find then the average value of the concentration from equation (7):

$$\bar{C}_s = \frac{A}{p + \delta \sqrt{p+k}} = \frac{A}{a-b} \left( \frac{1}{\sqrt{p+k+b}} - \frac{1}{\sqrt{b+k+a}} \right), \tag{9}$$

where

$$a = \frac{\delta}{2} + \sqrt{\frac{\delta^2}{4} + k},$$

$$b = \frac{\delta}{2} - \sqrt{\frac{\delta^2}{4} + k}.$$

Then the concentration value in the foaming agent layer will equal:

$$C_s(t) = \frac{A \cdot e^{-kt}}{a-b} \left( a \cdot e^{kt} \operatorname{erfc} a\sqrt{t} - b \cdot e^{kt} \operatorname{erfc} b\sqrt{t} \right). \tag{10}$$

Using the asymptotic representations of the probability integral, and considering  $b < 0$  at  $t \rightarrow \infty$ ,  $k \neq 0$ , we obtain:

$$C_s = A \left( 1 - \frac{\delta}{\sqrt{\delta^2 + 4k}} \right) \cdot e^{\left[ -\delta \left( \sqrt{\frac{\delta^2}{4} + k} - \frac{\delta}{4} \right) t \right]}. \tag{11}$$

A given dependence can be used to find the value of the concentration of the foaming agent in a given system based on the values of the initial concentration, the film thickness, the coefficient of diffusion, and exposure time.

### 6. Results of determining the insulating properties of a foaming agent

Determining the insulating capacity of flammable liquids using a foaming agent has certain features because at the surface of the flammable liquid there forms a film several millimeters thick. Measuring the film is very difficult. However, given that the aqueous solution of the foaming agent is a solution of electrolytes, it, therefore, is capable of passing electric current. This capability is characterized by the quantity that is reverse to the electrical resistance of the conductor  $R$ ; it is measured in siemens:

$$W = \frac{1}{R}, \text{ Sm}, \tag{12}$$

where  $R$  is the resistance to the foaming agent layer, Ohm.

To establish the time of the foaming agent layer destruction, we studied the change in its electrical resistance during the decomposition at the surface of the flammable liquid (Table 1). Fig. 3 shows the process of determining the time of the foaming agent layer destruction.

Table 1

Results from determining the electrical resistance of a foaming agent

Exposure time, s	Electric resistance value, Ohm	Exposure time, s	Electric resistance value, Ohm
0	58	360	455
30	82	390	489
60	114	420	521
90	143	450	556
120	196	480	585
150	222	510	643
180	256	540	701
210	289	570	767
240	321	600	823
270	347	630	902
300	388	660	984
330	412	690	>1,000



Fig. 3. The process of determining the time of the foaming agent layer destruction

Based on the experimental results, equation (12) was used to calculate the conductivity of the foaming agent solution. Fig. 4 shows the change in the conductivity of the foaming agent layer over time.

It was established that the foaming agent layer destruction process took 618 s whereby the critical thickness of the foaming agent layer was reached and the conductivity was no more.

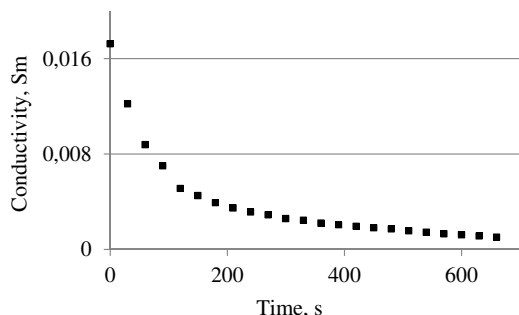


Fig. 4. Change in the conductivity of a foaming agent layer

A given method is limited only to determining the properties of foaming agents, specifically their insulating capacity, since the rupture of the foaming agent’s film leads to the disappearance of conductivity.

Taking into consideration data from the scientific literature, in particular, the value of the diffusion coefficient [20], which is  $0.21 \cdot 10^{-6} \text{ m}^2/\text{s}$ , the thickness of the foaming agent layer, which is 3 mm, we calculated a change in the concentration of the foaming agent. Based on the results reported in [21], we have established the ignition time of the flammable liquid vapors for the foaming agent AFF-107; the formation of the critical thickness of a layer of the foaming agent AFF-107 is about 600 s.

Fig. 5 shows the process of changing the concentration of the foaming agent, which was calculated from equation (11). According to data in Fig. 6, we calculated the concentration value at which the critical value of the foaming agent layer thickness is achieved, which leads to the ignition of flammable liquid; it is about 25 %.

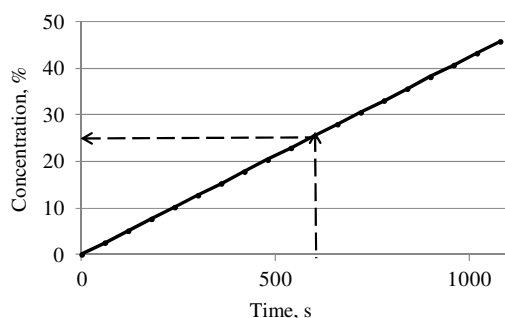


Fig. 5. The concentration of a foaming agent at which the critical value of the thickness of the foaming agent layer is achieved

Given that the process of the ignition of liquid fuel is caused by a variety of sources and their elimination takes time, then, to insulate the surface of the flammable liquid, a foaming agent can be used. To establish the effectiveness of the protection of flammable liquid by a foaming agent, we have performed field tests involving such objects, in particular, as model samples (Fig. 6).

Fig. 6 shows that under the influence of water evaporation and the foaming agent diffusion into a layer of flammable liquid, the critical amount of the foaming agent reached a minimum in 616 s followed by the flammable liquid ignition.

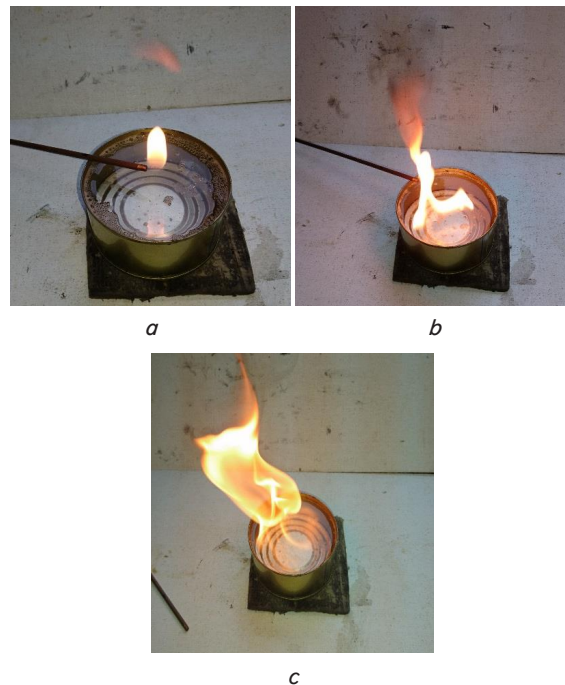


Fig. 6. The process of igniting a sample: *a* – exposure to flame, *b* – ignition of gasoline, *c* – burning of gasoline

### 7. Discussion of results of studying the heat transfer process

When using a foaming liquid to protect flammable liquids from burning, as indicated by the research results (Fig. 5, 6), it is a natural process to insulate flammable liquid, both from the action of temperature and the release of vapors. In this case, a protective layer is formed on the surface, which insulates the release of combustible vapors, and slows down the processes of thermal conductivity. It is obvious that this mechanism of influence exerted by coating the flammable liquid is a factor in adjusting the degree of formation of the protective layer of foam and the effectiveness of thermal insulation of the material. This agrees with the data reported in [10, 12], which also link the effectiveness of thermal protection to the insulation process at the surface of the flammable liquid. Our work fully describes the mechanism of protection of flammable liquids, the movement and implementation of high-temperature insulation but there is also a need to evaluate this process, to build the physical and mathematical model. Unlike the results reported in [11, 14], the obtained data on the impact of the foaming process on the insulation of vapors and changes in the insulating properties allow us to argue the following:

- the main regulator of the process is not only the resistance of foam under the influence of temperature with heat absorption and release of non-combustive gases but also the formation of a layer of foam, which insulates the release of combustible vapors and inhibits the process of transferring heat to flammable liquid;
- significant impact on the process of protection of flammable liquid when using the protective layer of a foaming agent is observed in the direction of reactions in the pre-flame region towards foam formation at the surface of the flammable liquid.

Such conclusions may be considered appropriate from a practical point of view because they make it possible to reasonably approach determining the necessary properties and formulation of the foaming agent. From a theoretical point of view, they allow us to assert the establishment of the protection mechanism against the ignition of flammable liquids, which are certain advantages of this study. The results of determining the insulating capacity of the protected combustible fluid (Fig. 6) indicate the ambiguous impact of the character of the protective means on the change in insulating capacity. Specifically, this implies the availability of data sufficient for the qualitative process of insulating the release of combusting vapors and decelerating the temperature, and detecting, on its basis, the moment at which the drop in heat resistance begins. This finding could make it possible to investigate the surface transformation of the foaming agent layer and identify those variables that significantly affect the conversion mechanism of this process.

Based on our results, one can argue about the presence of an interesting pattern associated with the formation of a foaming agent film, resistant to the flame, and capable of insulating the release of combustible vapors over a certain period. However, there are certain limitations, namely establishing the critical thickness of the film when the insulating capacity falls.

Further research may be aimed at examining the processes of establishing the relationship between the components and properties of foaming agents and their impact on the processes of insulating flammable liquids.

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## 8. Conclusions

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1. We have simulated the process of heat insulation by a foaming agent when it protects flammable liquid; the insulating capacity has been determined; the dependences have been derived to calculate a change in the foaming agent concentration. Based on the experimental data and derived dependences, we have calculated the time it takes to destroy the foaming agent layer on the flammable liquid, through its decomposition; it is about 618 s.

2. Special features in decelerating the process of heat transfer to the flammable liquid, on which the foaming agent layer is applied, are the formation of a heat-protective layer at the surface of the liquid. Thus, at the surface of the sample, the achieved temperature exceeded 600 °C, which is significantly larger than the flashpoint of the flammable liquid vapor, in particular, gasoline, not exceeding –20 °C, but the ignition did not occur.

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