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ВЕСТНИК

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NAS RK is pleased to announce that Bulletin of NAS RK scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of Bulletin of NAS RK in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential multidiscipline content to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабаршысы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабаршысының Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді мультидисциплинарлы контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Вестник НАН РК» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Вестника НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному мультидисциплинарному контенту для нашего сообщества.

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PROTECTIVE COATINGS FOR WALLS AND ROOF OF TANKS MADE OF GRANULAR FUSED NON-COMBUSTIBLE SUBSTANCES AGAINST FIRE EXTENSION

Abstract. As a result of the research, there has been improved the technology of applying new foaming agents and means of limiting the spread of the flame during fires in storage facilities. The analysis of putting out flammable liquids indicates that if the fire is not eliminated at the initial stage, the fire passes to a prolonged stage, where an additional amount of forces and means will be required. To eliminate this stage, an additional amount of forces and means will be required. There have been developed and experimentally tested protective coatings for the walls and roofs of tanks made of granular fusible non-combustible substances as additional passive protection against fire extension. Besides, in laboratory and semi-industrial conditions, there were studied the possibilities of using internal and external coatings. Protective coatings possess fire-resistant properties. They allow reducing the temperature of the walls of vertical steel tanks. The given protective coatings prevent the occurrence of static electricity charges.

Key words: fire protection, fire protection technology, oil products, tank, combustible mixture, granular materials, heat flow, film thickness, foam destruction, highly inflammable liquid.

The program of industrial and innovative development of the Republic of Kazakhstan implies serious structural changes in economic growth due to the development of various sectors of the economy, including those that may present a potential danger to the population, one of which is fire and explosion hazard of the oil and gas industry of the Republic of Kazakhstan. Damage from fires and explosions at refineries has enormous proportions and a tendency of constant growth. As the level of technical equipment of production increases, its fire risk also increases.

Emergencies at oil and gas facilities are often accompanied by fires that cause economic, environmental, material damage to the state. During fires at these sites, a large amount of thermal energy is released, that by means of radiation affects the objects around the fire and forms new fire areas [1].

Fires of flammable liquids in vertical steel tanks are of complex and prolonged nature. The analysis of putting out flammable liquids indicates that if the fire is not eliminated at the initial stage, the fire passes to a prolonged stage, where an additional amount of forces and means will be required. Putting out flammable liquids in vertical steel tanks is very rarely achieved at the first stage. This is accompanied by many reasons, one of which is the poor efficiency of the physicochemical properties of the foaming agent [2].

In case of accidental spills of oil products, when risk of fire arises in storage facilities, it is necessary to assess the degree of danger. Oil products are divided into highly flammable liquids and flammable liquids, the vapors of which can form explosive mixtures with air. In case when the flash point of these oil products is higher or equal, a combustible mixture appears above the open surface of the liquid fuel. If this

mixture is set on fire, the flame will spread across the surface of the liquid fuel at a speed of 1.2-1.4 m/s. In a closed container, the flame spreads at a speed of 0.3-0.7 m/s.

The assessment of the fire hazard of spills is characterized by the following main criteria:

- self-ignition temperature;
- flash point;
- flammability potential;
- concentration limits of explosive mixtures.

The flash point is closely related to the boiling point, i.e. with evaporation. The lighter oil product is, the better it evaporates, and its flash point will be lower. For instance, gasoline fractions have negative flash points (up to – 40 °C), kerosene fractions have flash points within 28-62 °C, diesel fuel fractions – 50-80 °C.

Fire extinguishing and fire prevention equipment that currently exists do not fully ensure the safety of tanks. Systems and devices designed to extinguish fire in tanks do not allow them to be quickly extinguished in a short period of time, leading to an explosion and subsequent fire extension [3].

Theoretical and experimental studies using reliable calculation methods aimed at developing and applying constructive and planning solutions, technologies, devices and means of limiting the spread of fires are still in demand in the oil and gas industry [4].

In this regard, the research aimed at developing a set of fire protection and extinguishing agents for highly flammable liquids technologies is relevant and timely

The development of stable foams is formed on the complex use of foaming solutions of polymeric substances that coagulate when contact with organic solvents and surfactant mixtures, where a special role is given to fluorine-containing compounds with high surface activity [5].

For the research, there was used a wide range of substances produced by industry and synthesized in the laboratory. Fluorinated surfactants were synthesized at the Institute of Chemistry of the Ministry of Education and Science of the Republic of Kazakhstan and K.I. Satpayev Kazakh National Technical University. There were conducted the experiments on extinguishing the flame of oil products and determining the fire extinguishing efficiency of the foam with the subsequent verification of the results of extinguishing fires of flammable liquids in various storage tanks and trays at the chair of operational and tactical disciplines of Kokshetau Technical Institute of the Ministry of Emergency Situations of Kazakhstan.

In modern practice, there are used internal and external coatings, which lower the temperature of the walls of the tanks, prevent the occurrence of static electricity, and also have fire-resistant properties. There is also the possibility of using fusible coatings, which in case of temperature increasing inside the tank during combustion will become liquid and spread over the surface of the liquid in the tank. In this case, high temperature will be an important requirement for these coatings. To determine the range of the required melting point, in table 1 there are given oil and oil products ignition temperatures, as well as the temperature of flame combustion.

Table 1 – Flash point, flash ignition and flame combustion temperature of oil and oil products

Type of the product	Temperature, °C				Notes
	Flash point	Flash ignition	Autoignition	Flame combustion	
Oil	130...320	35...121	300...350	1100...1300	
Gasoline AI-95	39	39	255...370	1300...1400	
Gasoline AI-92	32	39	255...370	1300...1400	
Gasoline AI-80	27	39	255...370	1300...1400	

The range of the melting point at the upper limit is determined by the temperature above 1000 °C. The lower melting limit of the material must be higher than the temperature. Currently, there are many non-combustible materials that can be used as coatings for the inner walls and roof of the tank. There were selected the following materials to compare:

- foam glass;
- sodium liquid glass;

- polybutylene terephthalate;
- silica gel.

Since these coatings will be constantly present on the surface of the inner walls and on the roof of the tank, it is necessary that they should meet the following requirements:

1. Chemical resistance to stored products;
2. Work in the temperature range of the tank service treatment;
3. The melting point is lower than the flame combustion temperature of the product, but higher than the operating temperature;
4. The combustion temperature is higher than the flame combustion temperature of the oil product

Thus, all the given materials, with the exception of polybutylene terephthalate, can be used as coatings to protect the tank. There were developed and experimentally tested two coating schemes: on the walls of the tank and on the roof. The properties of the materials are given in table 2.

Table 2 – Characteristics of the materials for internal coating of the walls and roof of the tank

Characteristics	Foam glass	Sodium liquid glass	Polybutylene terephthalate	Silica gel
Melting point, °C	730	1200	225	1610
Combustion temperature, °C	–	–	–	–
Chemical resistance	High	High	High in temperature range from 20 to 60 °C	High

Thus, all the given materials, with the exception of polybutylene terephthalate, can be used as coatings to protect the tank. There were developed and experimentally tested two coating schemes: on the walls of the tank and on the roof. Both variants are optimal for using. The most effective tank extinguishing system is fire subsurface suppression system, but the speed of this system response does not often allow coping with a rapidly spreading flame. To solve this problem, there was offered to use granular materials with high fire resistance and lower melting point. The design of these coatings is shown in figure 1.

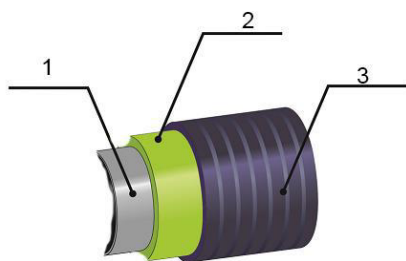


Figure 1 – Multi-layer protective coating:
1 – tank metal; 2 – adhesive layer;
3 – main protective layer

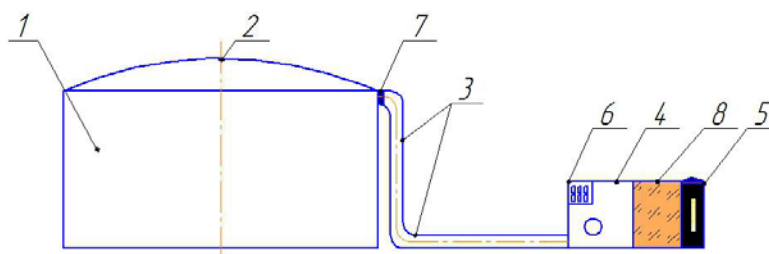


Figure 2 – Scheme of tank fire extinguishing system:
1 – the tank; 2 – tank temperature sensor; 3 – supply pipeline;
4 – injection pump; 5 – nitrogen or carbon dioxide containers;
6 – automatic signal processing system; 7 – valve;
8 – the container with granular material

As it has been noted above, the combustion temperature of oil and oil products exceeds 1000 °C, which enables to choose materials with the required melting point and the missing or sub-missing boundary of combustion. The principle of operation of the given system is as follows: when the temperature in the tank 1 rises, the temperature sensor transmits a signal to the automatic signal processing system 6, which in turn sends a command to start the injection pump 4. The transfer of the granulated substance from the tank 8 is done with the help of using nitrogen or carbon dioxide to prevent oxygen from entering the fire zone. The fire extinguishing system is shown in figure 2.

When the temperature inside the tank rises, the granulated material melts and then spreads over the surface of the burning liquid, thus preventing oxygen from entering the combustion zone. The advantages of fire foam subsurface suppression are the following factors:

- lack of particles catching of burning liquid by granular material;
- the system response speed is much higher than the subsurface suppression extinguishing system due to the absence of need to pass through the volume of burning liquid;

– the possibility of use, both in the presence of an open fire, and in its absence, but with a significant increase in temperature.

Limiting the fire spread in tanks is actual, because when a single tank catches fire, the flame can reach the adjacent tanks, which will lead to an increase in damage to the set of tanks [6].

To limit the spread of the flame in a horizontal position, it is proposed to use horizontal metal grids. Initially, to study the possibility of using this device, it is necessary to determine the heat flux passing through these grids. Since metal grids have a small reflectivity, the decrease in heat flux passing through the grids will be insignificant. The best way the heat flux is shielded by grids with a wire of large diameter and a small grid size. Let us consider the design of the grid as a multilayer wall consisting of two parallel planes located at a short distance from each other. This design is characterized by a change in temperature in the form of a broken line with straight segments, which show the change in temperature in the layers. Thus, the heat flux decreases significantly when passing through several grids [7].

To conduct an experiment to determine the reduction of heat flux, there was offered a construction, as shown in figure 3.

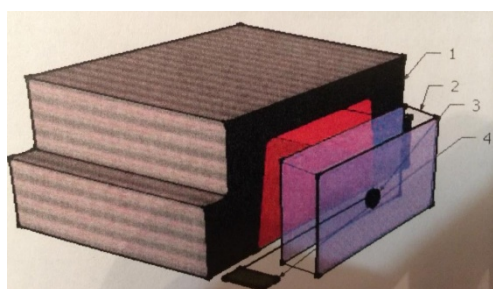


Figure 3 – The construction for determining the amount of heat flux passing through the metal grids:
1 – muffle furnace 1; 2 – grid;
3 – thermocouple TXA; 4 – sensor

The principle of operation is as follows: muffle furnace 1 produces a constant heat flux of 3.5 kV/m^2 , which passes through the grid 2, is fixed by a thermocouple type TXA 3 and sensor 4.

According to the results of the experiment, it was determined that the obstruction of the heat flux by grids located at a distance of 20 cm regarding each other is the most effective, which in turn shows that when the flux passes through a certain medium, its intensity decreases.

There were conducted further studies to determine the dependence of the cell size on the stability of the foam. Studies were conducted to determine the optimal size of the cell structure, so that the foam does not settle inside it and does not go beyond its limits. The tests were carried out for horizontal grid construction with a round shape to install vertical steel grids of various sizes in tanks [8].

To determine the effectiveness of foaming agents, there was chosen an additional foaming agent. «Multipurpose», which is our innovation. In addition to it, there were used the following brands of foaming agents: PO-6SII, PO-6RP, PO-6VAS, « Multipurpose»; as well as the grids of sizes 1,1; 0,9; 0,44; 0,1 and 0,094 mm.

It was determined that the smaller the cell size is, the longer the foam stability in the grid volume and the higher the percentage of filling the volume of the construction. The most optimal cell size – 0,094 mm. See the figure 3.

The next stage in the development of a fire limiting system was a research to establish the optimal foam multiplicity in relation to its stability. Finding the optimal value of the multiplicity at maximum durability depends on the following factors:

- foam agent properties;
- foam agent concentrations;
- method of producing a foaming agent;
- weather conditions;
- other factors.

It has been established that with increasing foam multiplicity, the foam stability time increases, and at the same multiplicity, the foam stability directly depends on the degree of its dispersion. But with increasing degree of dispersion, the film thickness also decreases, which leads to the destruction of the foam. The next research stage of the possibility of using structures limiting the spread of fire was the study of foam stability in a grid structure when exposed to heat flow.

There were carried out the tests to determine the effect of temperature using a tray, and AI-80 gasoline was used as a combustible liquid, poured onto the water cushion with a layer of 10 cm. A grid structure was installed on the top, and free burning was made during 5 minutes, after which there was made filling with mechanical foam, then there was measured time of 50% foam volume destruction. The combustion temperature was 800 °C. The stability time of the average multiplicity foam is higher than that of the high-multiplicity foam; moreover, the resistance time is reduced by 30–35% regarding air tests. However, it should be noted that the “Multipurpose” foam agent has better performance than the widely used foam agents [9, p. 256].

The final stage of the research was the determination of the degree of heat flux retention by the construction filled with air-mechanical foam. Based on the fact that when radiant energy is affected the flammable liquid, there can happen spontaneous combustion, the radiant flux must not exceed the radiation density for this liquid.

The tests consist in measuring the temperature on the outer and inner surfaces of the enclosing structure in conditions close to a real fire. The combustible liquid was AI-80 gasoline that was set on fire and there was allowed open burning. Due to the inhomogeneity of the flame burning, according to the construction area there was defined average temperature on the outer and inner surface of the construction, which was determined using thermocouple TXA at 5 points of the construction in order to achieve reliable results [10, p. 197].

Thus, decrease in temperature is due to the expenditure of heat for heating both the grid construction and the air-mechanical foam. Obviously, with an increase in the amount of combustible material, the maximum temperature and duration of combustion increase.

According to the results of the test, for the effective operation of the enclosing structures, it is necessary to ensure a continuous supply of foam to the grid structure. In addition, to establish the optimal number of sections within the grid structure, there were made tests with round structures of various heights: 450, 500, 550 and 600 mm to establish the time of thermal resistance and the average temperature on the outer surface.

It should be noted that the given horizontal construction for limiting the spread of fire has a high resistance to thermal effects, which allows its use to fight fires in tanks. There was made the analysis of the experiment results using a mathematical model, there was obtained a small discrepancy between mathematical model data and the results of the experiment. But despite this, these results confirm the effectiveness of finding the foam in the protective structure. But despite this, these results confirm the effectiveness of foam presence in the protective structure.

Thus, as the result of the research, there were developed protective coatings for the walls and roofs of tanks made of granular fusible non-combustible substances as an additional passive protection against the fire spread. In the course of the laboratory tests, there was determined that the offered horizontal grid construction for fire extinguishing in a tank, together with the use of the Multi-Purpose foam agent that was developed by us, can prevent fire spreading to the nearest tanks and other structures.

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ӨРТТІҢ ТАРАЛУЫНАН ҚОРҒАУ ҮШІН ТҮЙІРШКТЕЛГЕН БАЛҚИТЫН ЖАНБАЙТЫН ЗАТТАРДАН ЖАСАЛҒАН РЕЗЕРВУАРЛАРДЫҢ ҚАБЫРҒАЛАРЫ МЕН ШАТЫРЛАРЫНА АРНАЛҒАН ҚОРҒАНЫШ ЖАБЫНДАРЫ

Аннотация. Зерттеу нәтижесінде мұнай-газ өнеркәсібі объектілерінің тік болат резервуарларында өрт туындаған кезде жаңа көбік түзетін құрамдар мен жалынның таралуын шектеу құралдарын қолдану технологиясы жетілдірілді. Тез тұтанатын сұйықтықтарды сөндіруге талдау жүргізілді, егер бастапқы кезеңде

өртті жою жүргізілмесе, өрт ұзаққа созылатын сатыға ауысатынын куәландырады. Резервуарлық парктердегі өрт салдарын жою үшін осы кезеңде қосымша күштер мен құралдар қажет болады. Өрт таралуынан қосымша пассивті қорғаныс ретінде түйіршіктелген балқытын жанбайтын заттардан жасалған резервуарлардың қабырғалары мен шатырларына арналған қорғаныс жабындары әзірленді және эксперименталды сынақтан өткізілді. Сонымен қатар, зертханалық және жартылай өнеркәсіптік жағдайларда ішкі және сыртқы жабындарды пайдалану мүмкіндіктері зерделенді. Тік болат резервуарлардың қабырғалары мен шатырларына арналған қорғаныс жабындары отқа төзімді қасиеттерге ие болады. Олар тік болат резервуарлардың қабырғаларының температурасын төмендетуге мүмкіндік береді. Сонымен қатар түйіршіктелген балқымалы жанбайтын заттардан жасалған тік болат резервуарлардың қабырғалары мен шатырларына арналған ұсынылып отырған Қорғаныс жабындары жалынның таралуын шектеуге және оларды оңтайлы оқшаулауына ықпал етеді, сондай-ақ статикалық электр разрядтарынан өрттердің туындауын болдырмайды.

Түйін сөздер: өртке қарсы қорғаныс, өрттен қорғау технологиясы, мұнай өнімдері, резервуар, жанғыш қоспа, жылу ағыны, көбік тұрақтылығы, пленка қалыңдығы, көбіктің бұзылуы, тез тұтанатын сұйықтық.

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ЗАЩИТНЫЕ ПОКРЫТИЯ ДЛЯ СТЕНОК И КРОВЛИ РЕЗЕРВУАРОВ ИЗ ГРАНУЛИРОВАННЫХ ПЛАВКИХ НЕГОРЮЧИХ ВЕЩЕСТВ ДЛЯ ЗАЩИТЫ ОТ РАСПРОСТРАНЕНИЯ ПОЖАРА

Аннотация. В результате исследования была усовершенствована технология применения новых пенообразующих составов и средств ограничения распространения пламени при возникновении пожаров в вертикальных стальных резервуарах объектов нефтегазовой промышленности. Проведен анализ тушения легковоспламеняющихся жидкостей, который свидетельствует, что, если не произведена ликвидация пожара в начальной стадии, пожар перейдет в затяжную стадию. Для ликвидации последствий пожара в резервуарных парках, этой стадии потребуется дополнительное количество сил и средств. В качестве дополнительной пассивной защиты от распространения пожара разработаны и экспериментально апробированы защитные покрытия для стенок и кровли резервуаров из гранулированных плавких негорючих веществ. Кроме того, в лабораторных и полупромышленных условиях были изучены возможности использования внутренних и внешних покрытия. Защитные покрытия для стенок и кровли вертикальных стальных резервуаров будут обладать огнестойкими свойствами. Они позволяют понижать температуру стенок вертикальных стальных резервуаров. Предлагаемые защитные покрытия для стенок и кровли вертикальных стальных резервуаров из гранулированных плавких негорючих веществ будут способствовать ограничению распространения пламени и их успешной локализации, а также предотвращают возникновение пожаров от разрядов статического электричества.

Ключевые слова: противопожарная защита, технология огнезащиты, нефтепродукты, резервуар, горячая смесь, гранулированные материалы, тепловой поток, толщина пленки, разрушение пены, легковоспламеняющаяся жидкость.

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