

Досліджено вплив сухих сумішей покриття з неорганічних та органічних речовин на ефективність захисту деревини від дії полум'я магнію. Встановлено, що сухі суміші на органічній основі з додаванням мінеральних наповнювачів, під дією високої температури виділяють у навколишнє середовище газу, які ізолюють горючий метал від доступу кисню, утворюють покрив та припиняють горіння

Ключові слова: горіння металу, втрата маси, обуглювання, захисні засоби деревини, вогнегасні порошки

Исследовано влияние сухих смесей покрытий из неорганических и органических веществ на эффективность защиты древесины от воздействия пламени магния. Установлено, что сухие смеси на органической основе с добавлением минеральных наполнителей под действием высокой температуры выделяют в окружающую среду газы, которые изолируют горючий металл от доступа кислорода, образуют покров и прекращают горение

Ключевые слова: горение металла, потеря массы, обугливание, защитные средства древесины, огнетушащие порошки

INFLUENCE OF DRY MIXTURES IN A COATING ON THE EFFECTIVENESS OF WOOD PROTECTION FROM THE ACTION OF A MAGNESIUM FLAME

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1. Introduction

One of the most significant risk factors at the objects of storage of explosive products is a fire hazard. Ensuring survivability depends on the choice of fire protection systems for such objects under normal conditions, and in the case of an emergency. Therefore, a problem of the use of combustible materials (wood, plywood, paper) in building structures and packaging products has become more relevant and revealed a low level of operation safety.

The main material for the construction of facilities on military objects is wood. It relates to the group of combustible materials of medium flammability. Fire-retardant treatment by modern effective means can considerably affect or exclude an occurrence of fire and destruction of a structure. In particular, a coating provides wood with the ability to withstand an action of flame and a spread of flame through a surface. It prevents a free access of oxygen, and this contributes to acceleration of a burning process and its subsequent fading.

On February 17, 2016, at approximately 8:20 p. m., explosions started at the ammunition depots in Zaporozhye (Ukraine). Unknown persons dropped inflammatory objects on the territory of the object using an unmanned aerial vehicle. As a result, fire outbreaks appeared, they were difficult to extinguish. Separate magnesium particles fell under wooden crates, which contained ammunition. It was impossible to use water to extinguish fire, because it was ineffective for extinguishing these objects.

It was established that an untreated sample of wood is capable to ignite and spread a flame through a surface after ignition, and this leads to the destruction of a structure [1]. A use of inorganic coatings can slow down heating of a material and maintain its functions during a fire for a given period of time, but it requires significant costs [2, 3].

The effectiveness of fire retardant coatings is aimed at creation of intumescent materials on a surface. Such materials act by the principle of a significant reduction of heat conductivity due to a formation of coatings by them. A moment of ignition of combustible wood constructions and heating of products to unacceptably high temperatures during the set period of time are significantly displaced in time as a result of transformations to cauliflower foam-coked layers due to intense heat effect.

It is necessary to take into account that metal incendiary mixtures, which can evolve temperature above 2,200 °C and ignite combustible materials, in particular wood, are widely used. And as a result, it becomes necessary to protect wood from the effects of such temperatures, to establish the effectiveness of fire protection of coatings, as well as to resolve the problem of elimination of fire outbreaks.

Therefore, studying the effectiveness of extinguishing, as well as the influence of components, which belong to their composition, on this process is an unsolved part of ensuring survivability, it determines the need to develop special fire extinguishers. This necessitated undertaking a research in this field.

2. Literature review and problem statement

A significant amount of explosive fire-hazardous products is stored in wooden containers. Thus, the question is how to prevent a fire and an explosion caused by inflammable substances including metallic incendiary mixtures characterized by high temperatures.

It was established that magnesium alloys are widely used for the manufacture of inflammatory grenades, which provoke an emergence of combined fires (Class A, B, D) [4].

The peculiarity of the fire protection of wooden building constructions by modern means consists of a creation of elements of heat-insulating screens on a surface. They withstand high temperatures and direct action of fire and make possible to maintain their functions for a set period of time [5].

The description of the behavior of swelling coatings at the time of the formation of a porous structure is a separate and complex task, it covers both stages of the process of heat protection: the inflation of a coating, and the subsequent heat transfer, which is formed during swelling [5, 6]. Therefore, it is necessary to study conditions of the formation of a barrier for heat conductivity and to detect a mechanism of action of a coating with the formation of a layer of coke.

Powder compositions of fire extinguishers of special purpose are used for elimination of magnesium flame and its alloys flame. They cover a heat source, and this prevents the access of oxygen to a combustion zone. However, such substances are ineffective and require significant amounts for elimination of an ignition, in addition, an ignition may occur in hard-to-reach places. It was established that it is necessary to develop a complex approach to extinguishing with creation of new methods and ways of extinguishing of magnesium alloys fires and production of appropriate technical means in order to improve the efficiency of extinguishing of magnesium alloys fires [7].

Modern fire protection methods include a use of swelling coatings. They are complex systems of organic and inorganic components. Such coatings have high intumescent potential. A paper [8] shows the effectiveness of the application of organic coatings components. It is shown in a paper that it is possible to influence the formation of a protective foam-coke layer significantly due to the action of fire retardant agents based on polyphosphoric acids and foaming agents. A significant increase in the stability, density and strength of the protective layer is achieved due to the directed formation of certain additives that form high-temperature compounds [9].

Therefore, the promising direction of studies is to increase a fire resistance of building structures with a help of fire protecting means. They are modified by polymeric complexes and fire-retardant agents in most cases, but such coatings relate to easily washable materials and are suitable for indoor spaces [10, 11].

An influence of inorganic fillers on fire retardant coating has shown its effectiveness, however, a function of a coating is not specified and changes in heat conductivity in a transition of a coating into coke are not detected [12, 13]. Authors showed only an analytical model for calculation of heat conductivity of a protective layer of foam coke during functioning of a coating only. It takes into account the forms of pores, but it is unknown what transformations occur at combustion temperatures in material.

We should take into account the following factors during creation of compositions for extinguishing of metals:

- the main substance should not contain an atom of oxygen in the molecule (should not support combustion), as well as adsorbed water and should not come into contact with a metal in the chemical reaction of inhibition;

- powder compositions should have a certain fractional composition, they should not be compressed in the process of storage, which is achieved by an inclusion of hydrophobic additives to a composition.

The main task to achieve a positive result in elimination of combustion of magnesium is a creation of dry mixtures of protective full coating of combustion source, which prevents an access of oxygen to a combustion zone. Such a coating should be sufficiently dense to have required thickness of a powder layer on an entire surface of a combustion source, which is achieved with a defined specific consumption of powder.

The extinguishing of magnesium and its alloys is carried out by pouring a burning magnesium with a large amount of dry graphite, or flux, which is used for melting of magnesium alloys. It is also possible to use boron trichloride to extinguish a magnesium fire, which interacts with burning magnesium, forming magnesium chloride, which isolates a surface from the access of air to a burning surface. Or pouring a burning magnesium with dry dust-like carnallite or sand [14]. Extinguishing powders produced in Ukraine are not suitable for extinguishing fires of magnesium, as well as sand.

Therefore, an important issue is to determine the effectiveness of fire protection at the abovementioned temperatures and the influence of components, which are included to a composition, and to establish a role in a provision of fire resistance. Investigation of mechanisms of interaction of substances with flame of metal will make it possible to develop effective methods and means of extinguishing fires of such classes, and this necessitates a study in this area.

3. The aim and objectives of the study

The aim of present study was to determine features of elimination of magnesium fire with treatment by coatings of different nature, as well as to establish the effectiveness of using dry mixtures for extinguishing a high-temperature combustion of metallic substances.

The following tasks were solved to achieve the objective:

- determination of fire protection features of wood with coatings treatment on a basis of inorganic and organic and mineral substances at a temperature influence;

- establishment of the efficiency of dry mixtures included in a coating for extinguishing a high combustion temperature of metallic substances.

4. Materials and methods of the study

4.1. Studied materials and equipment used in the experiment

The study was carried out with a use of a system of dry mixtures, which consists of ammonium polyphosphate (APPh), melamine, pentaerythritol (PE) and mineral fillers – aluminosilicate microspheres, perlite, basalt scales, metallurgical sludge and ashes.

We prepared experimental samples of wood coatings on the basis of an organic and neogenetic system. They contained 18÷20 % APPh, 12÷1 % melamine, 10÷12 % PE

and astringent, which consisted of 16 % PVA dispersion and water. We stirred the given organic and neogenetic mass, added 10 % of fillers and applied to wooden samples, which were made from wood with a thickness of 19 mm, with an average size of 190×155 mm and a height of 140 mm to create a wood coating. We treated fire protected model samples of wooden containers for the storage of weapons and ammunition with organic coatings with an addition of: aluminosilicate microspheres, perlite, basalt scales, metallurgical sludge and ashes (Fig. 1).



Fig. 1. Model samples of containers for the storage of weapons and ammunition that were treated with an organic coating with an addition of: 1 – aluminosilicate microspheres; 2 – perlite; 3 – basalt scales; 4 – metallurgical sludge; 5 – ashes

We used magnesium chips as a fuel. Combustion of magnesium chips yields a temperature of 2,200 °C [15].

We used a system of dry mixtures, which contained 18 % PFA, 12 % melamine, 10 % PE, to extinguish a model fire of magnesium flame. We stirred the resulting mass, added 10 % of fillers, namely, aluminosilicate microspheres, perlite, basaltic scales, metallurgical sludge and ashes. And we used the obtained dry mass to isolate the magnesium flame.

4. 2. Methodology for determining the parameters of samples' properties

Determination of flame retardant efficiency of wood containers was carried out by a working methodology. Its essence was to determine experimentally the efficiency of fire protection of a wooden structure treated with coating, namely an impact of a magnesium flame on a sample (a model was a solid inflammatory substance) with the given parameters and a recording of burnout and sample mass loss after the test.

We installed pyro-patrons into a container. We placed an incendiary mixture of 10 g per 1 dm² of surface on the lid and under the sample. We fired fuel and kept a sample of wooden container in a fuel flame during the time of burn-up until the absence of self-burning and smoldering. We monitored a time of pyro-patrons' activation.

The criterion for determination of the fire protection efficiency of a container was a correspondence of a value of mass loss parameter of a container, which should be not more than 10 %, as well as the final combustion after the burning out of fuel, the burning out of the material and the time of the pyro-patrons' activation.

Determination of the extinguishing efficiency of dry mixtures coatings was carried out by a working method. Its essence

was the experimental determination of the quantitative parameter of mass loss of powder spent on extinguishing. For example, magnesium flame (a model was solid inflammable substance). We supplied an extinguishing mixture with specified parameters and recorded a time to extinguish and loss of sample mass that went into extinguishing after the test.

We filled a steel round pallet of 80 mm in diameter and 40 mm deep with magnesium chips with a weight of 10 g. The sample was burned from the intermediate igniting composition. We carried out the extinguishing after 90–95 % of the surface area of the sample was inflamed. We poured the investigated composition from the scoop on the burning surface evenly. We determined the powder consumption and the fire source state 5 minutes after extinguishing and calculated the intensity of the extinguishing mixture.

5. Results of study of the influence of dry mixtures coating on the efficiency of magnesium flame

We carried out natural tests on objects in order to establish the effectiveness of fire protection of wood, in particular on model samples of wooden structures.

Fig. 2 shows the results of tests of an untreated sample and wood coatings with the addition of aluminosilicate microspheres, perlite, basalt scales, sludge and ashes.

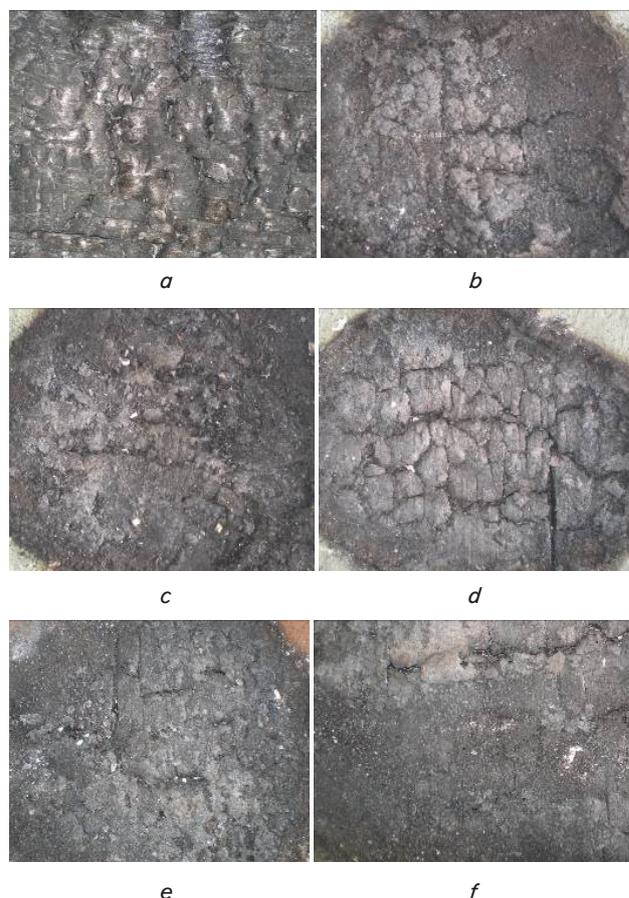


Fig. 2. Results of charring depth of a wooden construction: *a* – untreated; *b* – organic coating with the addition of aluminosilicate microspheres, *c* – organic coating with the addition of perlite, *d* – organic coating with the addition of basaltic scales, *e* – organic coating with the addition of sludge, *f* – organic coating with the addition of ashes

We detected a formation of a slag layer on the surface of the material during tests of combustion of magnesium filings. A process of thermal decomposition of wood continued under a slag layer. And its suspension was going in different ways in dependence on properties of a coating and affected a depth of charring.

Table 1 shows results of mass loss and combustion time of a model fire of wooden container for the storage of explosive products.

Table 1

Results of tests of wooden containers for the storage of explosive products

Model sample of a container for the test treated with a coating with the addition	Sample mass, kg		Sample combustion time, s	Loss of sample mass after testing, Δ m, %	Charring depth, mm
	Be-fore	After			
	the test				
untreated	1.620	0.972	1,301	40.0	16÷20
aluminosilicate microspheres	1.874	1.785	567	4.75	4÷5
perlite	1.861	1.754	783	5.75	5÷6
basalt scales	1.569	1.498	447	4.52	3÷4
metallurgical sludge	1.761	1.671	552	5.11	4÷5
ashes	1.621	1.539	501	5.05	5÷5.5

We found during tests that a depth of charring of untreated wood reached 16÷20 mm. A swelling of a protective coating was observed during the interaction with a flame and charring of wood occurred under a coating layer at a depth of only 5÷6 mm, respectively, for a model sample treated with a protective coating with the addition of mineral substances.

We carried out the study at the extinguishing of magnesium flame with damp sand and established a significant increase in the intensity of combustion (Fig. 3).



Fig. 3. Results of extinguishing magnesium flame with wet sand: a – combustion of magnesium; b – throwing of a wet sand in a magnesium flame

If coating components are able to withstand a flame of magnesium, then they are obviously able to extinguish fires of metals. Appropriate studies were carried out to determine the effectiveness of extinguishing of magnesium flame.

Fig. 4 shows results of tests of a sample of a mixture on organic basis with the addition of mineral substances.

Rate of supply:

$$I = \frac{G}{\tau} = \frac{m}{S \cdot \tau}, \tag{1}$$

where G is the total amount of extinguishing substance consumed during fire extinguishing by a unit of a calculated fire parameter, g/cm^2 ; τ is the time of extinguishing of fire, c , m is the mass of extinguishing substance, g ; S is the area of combustion of fire, m^2 .



Fig. 4. Results of tests of extinguishing magnesium flame with a model sample of dry mixtures coating with the addition of minerals: a – magnesium ignition, b – extinguishing of flame, c – formation of combustible substance of the insulation layer on a surface, d – results of extinguishing

Table 2 gives results of mass loss and time of extinguishing of the model fire.

Table 2

Extinguishing of magnesium flame with mixtures based on organic substances with mineral additives

Mixtures based on organic substances with additives	Sample mass of flame retardant powder, g		Time to extinguish magnesium flame, s	Rate of supply, $g/(cm^2 \cdot s)$	Result of extinguishing (extinguished, not extinguished)
	Before	After			
	tests				
aluminosilicate microspheres	22.1	14.7	3.4	0.034	Extinguished
perlite	22.0	12.1	4.1	0.038	Extinguished
basalt scales	22.2	16.7	2.8	0.031	Extinguished
metallurgical sludge	22.2	10.2	4.6	0.041	Extinguished
ashes	22.1	11.8	4.1	0.039	Extinguished

Results from Table 2 allowed us to state that samples of dry mixtures coating with the addition of aluminosilicate microspheres, perlite, basaltic scales, metallurgical sludge and ashes in the amount of 10 % indicate the intensity of the supply of powder in the extinguishing of magnesium flame in the range $0.034\div 0.041\text{g}/(\text{cm}^2\cdot\text{s})$, which is much lower than the intensity of the supply of sodium chloride, which is $0.044\text{g}/(\text{cm}^2\cdot\text{s})$ [7]. Dry mixing of coatings creates chemical compounds with flammable magnesium and stop the air's access to a burning surface.

6. Discussion of results of study of the effect of dry mixtures coating on the process of extinguishing of magnesium flame

A process of a swelling of a coating is a natural process during functioning of fire retardant coating under a thermal action of a high temperature magnesium flame. Results of studies indicate this (Fig. 2, Table 1). A process of decomposition of dry mixtures coatings with the release of a large number of inert gases and the formation of a heat-insulating layer, which slow processes of heat transfer to the structure of wood and its destruction, goes under the influence of temperature. It should be noted that the presence of 10 % of additives (aluminosilicate microspheres, perlite, basaltic scales, metallurgical sludge, ashes) leads to the crosslinking of the foam coke layer due to the formation of refractory compounds and in accordance with the improvement of magnesium flame resistance. Apparently, such a mechanism of influence of additives is a factor of regulation of the degree of coke resistance and the effectiveness of heat insulation of material. This agrees with the data known from papers [6, 9]. Their authors also associate a change of the process of swelling with the addition of mineral fillers. In contrast to the results of studies [11, 12], the obtained data on the influence of fillers on the process of transition of a coating to a foamed layer of coke and the change of insulation properties gives opportunity to state the following:

- the main controller of the process is not only the formation of a foam coke layer, but also the heat resistance of the fire protection coating;
- a significant influence on the process of phase transition of the fire protection coating into the swelled layer of foam coke provides the correct addition of mineral fillers.

Studies showed that magnesium burns in a humid environment with an explosion. It produces flammable gases and high amounts of heat in contact with water (Fig. 3). Therefore, we

conclude that extinguishing of magnesium requires new extinguishing compositions. Results of determination of the efficiency of extinguishing of magnesium flame with dry mixtures coating (Fig. 4, Table 2) indicate the ambiguous effect of fillers on the change in the supply rate. Such uncertainty cannot be solved within the framework of the above study, as this would require additional experiments to obtain more reliable data. In particular, this implies the availability of data sufficient for the conduction of qualitative extinguishing process and the detection of a time, from which the fall of the flame temperature begins, on its basis. Such detection will give opportunity to investigate the conversion of dry mixtures to a coating that isolates the burning surface of a metal with formation of compounds and to identify those variables that significantly affect the beginning of the transformation of this process.

This work is a continuation of research reported in [1–3], in which the mechanism for the formation of foam-coke, its displacement and the implementation of thermal insulation of high temperature were described in detail.

7. Conclusions

We conducted a study and determined peculiarities of counteraction of substances of different origin to the magnesium flame and established the efficiency of the application of dry mixtures coating to eliminate high temperature of combustion of magnesium, in particular:

- the process of decomposition of dry mixtures coating goes with release of a large amount of inert gases and the formation of a heat-insulating layer during a functioning of the fire protection coating under the thermal action of high-temperature magnesium flame. The charring depth of untreated wood reaches $16\div 20\text{mm}$, the charring reaches a depth of $5\div 7\text{mm}$, respectively, with a protective coating;
- tests on model samples by extinguishing of magnesium flames showed that it releases combustible gases and a large amount of heat in contact with water and humid substances. Instead, samples of dry mixtures coating with the addition of aluminosilicate microspheres, perlite, basalt scales, metallurgical sludge and ashes in the amount of 10 % showed the intensity of the powder supply at extinguishing of magnesium flames in the range of $0.034\div 0.041\text{g}/(\text{cm}^2\cdot\text{s})$, which significantly exceeds the supply rate of sodium chloride, which is used to extinguish fires. In this case, the dry coating mixtures form chemical compounds with combustible magnesium and stop the access of air to the burning surface.

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