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Research of Mechanism of Fire Protection With Wood Lacquer

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Abstract. The effect of the composition on the weight loss of wood protected by a coating based on inorganic and organic substances in the process of thermal exposure, which is a feature of the study of the flame retardant effectiveness of the composition, is investigated. The solution of this problem is carried out by specially developed methods. The influence of fire protection under the influence of high-temperature heat flux on the change in the process of loss of mass of fire-protected wood is determined and the mechanism of kinetics of action of the composition is characterized, which is characterized by a decrease in the speed of flame propagation and mass loss. The results of thermogravimetric studies determined the weight loss of the coatings as a function of temperature, the results of which investigated the activation energy at the temperature decomposition of the coatings and found that for wood it was 36.56 kJ / mol, and in the case of fire protection it increased 2.3 times. which makes it possible to conclude that it is advisable to use lacquer varnish to improve the fire retardant efficiency of wood. Thus, for the specimen of fire-retardant lacquer wood, there is a gradual decrease in temperature, ie, the work of the coating is fixed, and, accordingly, the activation energy is increased during the decomposition of the wood. In order to establish the flame retardant efficiency in the application of high-temperature blowing lacquer, studies were conducted to determine the combustibility index of wood by mass loss, flame spread and temperature increase of flue gases and found that when processing wood goes to the group of combustible materials with a burning index.

1 Introduction

Capital construction and reconstruction of existing civilian, industrial and special purpose facilities related to the use of timber that is sensitive to the effects of high temperature, ie the ability to retain functional properties under operating conditions. Taking into account these problems adopted in the design of the structure of wood should take into account their resistance to thermal impact, as well as carry out the protective treatment of building materials by special means. The reduction of combustibility of wood is solved by the use of fire retardant coatings applied to the surface of structures and materials of wood and impregnation with its flame retardants. However, fire retardant wood surface impregnation, does not provide high fire retardant performance and can create the conditions to achieve the required quality of the protective coating and the duration of safe operation of objects, since flame retardants penetrate to a shallow depth and wash out under the influence of moisture.

2 Analysis of Recent Research and Publications

Today, there are two ways to fire wood. The first is the impregnation with flame retardants, most often based on inorganic salts [1]. When wood is moistened, the flame retardants dissolve in a moist environment and are gradually flushed to the surface, and then the fire retardant effect decreases over time [2]. The second method is to coat the surface of the wood with an organic or inorganic binder [3, 4]. Organic binder has increased smoke and toxicity, so its use is dangerous [5]. It is established that more effective flame retardants based on phosphorus-containing compounds are polymer condensed forms [6], due to the content of ammonium polyphosphate, the coefficient of expansion of the flame retardant composition increases tenfold [7].

The effectiveness of flame retardants for wood and wood materials is determined by their level of flame retardant ability and is determined by [8, 9]: 1 − decomposition of flame retardants under the action of temperature with heat absorption and release of non-combustible gases; 2 − changing the direction of the decomposition of the wood towards the formation of a flammable coke residue; 3 − inhibition of oxidation in the gas and condensed phase; 4 − formation on the surface of the wood heat-protective layer of coke.

Modern fire protection methods include the use of interlocking coatings, which are complex systems of organic and inorganic components. The materials are characterized by high intumescent capacity, but the mechanism of coke formation, phase and temperature transitions of the coating into the coke foam are not shown [10].

In recent years, the proposed research direction known works that are aimed at creating flame retardants, which in the process of heating form a coke insulation layer on the surface of the wood [11].

In [12], a description of the behavior of a flame retardant coating is presented, which is a separate and complex task and covers both the swelling of the coating and the subsequent heat transfer. However, issues related to setting the foam formation temperature remain unresolved. The effect of binder based on vegetable raw materials on the properties of flexible thermal insulation materials is also considered in [13], but the issue of combustibility remains unresolved. In [14], the effect of thermal modification as well as its flame retardant capacity was investigated, and the following characteristics of combustion, such as weight loss, burning rate, maximum burning rate, were revealed, but no chemical changes caused by these factors were indicated. The effectiveness of the application of the components of the coating based on organic substances is shown in [15], where due to the action of flame retardants based on polyphosphoric acids and foamers can significantly influence the formation of the protective layer of foam coke. However, there is a need to investigate the thermal barrier conditions and to establish the effective action of the coke layer.

In [16], the most promising flame retardant compositions of blowing coats are presented, which are complex systems of organic and inorganic components, but the questions regarding the joint action of the coating components during foaming remain unanswered.

A significant increase in the stability, density and strength of the protective layer is achieved by directing the formation of certain additives that form high-temperature compounds [17]. However, no relevant physico-chemical calculations have been provided to confirm this process.

In addition, many coatings have a number of disadvantages, such as the application of individual components, the loss of functional properties with increasing ambient temperature [18]. This means that it is not known how the process proceeds under the conditions of the temperature range of the fire retardant coating.

Studies of protective materials made of organic substances with colemanite ore solution have also been carried out [19]. It is shown that due to the established ratios it is possible to adjust the contents of the components to ensure the process of heat resistance.

However, all aspects of this mechanism are not well defined, so research on the mechanism of fire retardant wood efflux with lacquer remains relevant.

3 The Purpose of this Work

The purpose of this work is to investigate the flame retardant effectiveness of flame retardant wood with lacquer varnish and to establish the mechanism of its flame retardant.

4 Materials and Methods of Research

For the determination of the combustibility of wood, used wood samples, untreated and treated with a composition that forms a colorless film on the surface and is able to create a coke protective layer on the surface of the foam, namely, a roofing impregnation solution based on a mixture of organic and inorganic urea and phosphoric acids and natural polymer in different proportions) (Fig. 1). For pyrolysis, samples of wood of the average size 10×10 mm and 10 mm high were used, which were treated with the fire retardant coating above.

a b c

Fig 1. Model specimens of fire retardant wood: a–untreated; b–treated with blowing lacquer: c– after testing.

In order to determine the temperature range at which thermal degradation of materials is most intense, a preliminary thermogravimetric study of the processes of thermal destruction in dynamic mode was conducted using the derivatograph Q-1500 D. The qualitative and quantitative composition of these mixtures was determined by gas chromatographic method using a gas chromatograph LHM-7A [6]. Examples of sawdust of pine wood, as well as treated with fire-retardant composition in the atmosphere of normal composition (oxygen content – 21% vol.). In all experiments, the sample weight was 190 mg, the heating rate was 5 degrees per minute, the comparison sample was α-corundum powder, the crucible material was allund, the sensitivity of galvanometers: DTA – 250 μV, DTG – 500 μV.

Studies to determine the thermal stability of fireproof wood was performed by the method, the essence of which was to influence the radiation pattern of the wood panel and its ignition, to measure the temperature of the products of combustion and its time, the ignition time and the passage of the flame fronts of the surface sections, the length of the burned part [5]. But according to the obtained data, the dimensionless flammability index is calculated by the coefficient *I*:

$$I = \sqrt{\frac{q \cdot Q}{W} \cdot \frac{\Delta T_{max}}{\Delta T_{но}} \cdot \frac{\tau_{max} - \tau_0}{\tau_0} \cdot \left[1 + \frac{60 \cdot I_г}{I} \cdot \sum_{i=1}^{n} \frac{1}{\tau_i}\right]}, \quad (1)$$

where q – specific heat of gas combustion propane (23630), kDg·l^{-1};

Q – gas flow rate of the inflammatory burner (0.001), l·s^{-1};

W – power of the electric radiation panel, 0,5 kW;
ΔT_{max} – maximum increase in the temperature of flue gases:

$$\Delta T_{max}=T_{max}-T_o,$$

where T_o – ambient temperature, °C;
T_{max} – maximum temperature of flue gases, ° C;
$\Delta T_{но}$ – the maximum increase in the temperature of the heating equipment:

$$\Delta T_{но}=T_1-T_o,$$

where T_o – ambient temperature, °C;
T_1 – temperature of the outlet during operation of the heating equipment, °C;
τ_o – time of ignition of the sample, s;
τ_{max} – time to reach the maximum temperature of flue gases, s;
τ_i – time of passage of the front of the flame of control sites, s;
l – sample length, mm;
$l_г$ – length of sample damage, mm.

In Fig. 2 shows a test chamber for conducting research.

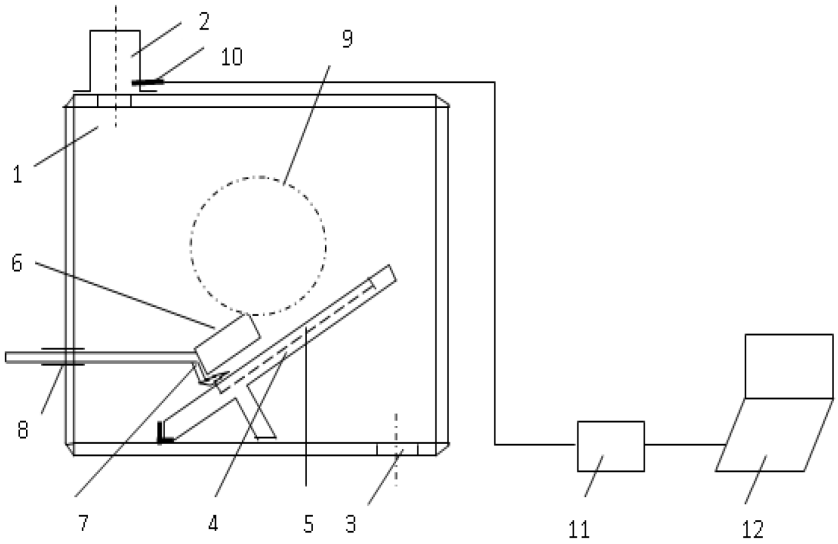

Fig. 2. Test chamber for determining the parameters of ignition and propagation of flame: 1 – test chamber; 2 – exhaust pipe; 3 – vent; 4 – sample holder; 5 – sample; 6 – radiation panel; 7 – ignition device; 8 – adjusting tube; 9 – sight glass; 10 – thermocouple; 11 – analog-to-digital converter; 12 – computer.

5 Research Results

To determine the temperature range at which thermal degradation of wood is most intensive, thermogravimetric study of processes in dynamic mode was performed using the Q-1500 D derivatograph [6].

Specimens of fire-retardant wood lacquer were investigated in an atmosphere of normal composition (oxygen content was 21% vol.). The sample weight is 80 mg, the heating rate is 10 deg/min, the atmosphere is static air, the comparison sample is α-corundum powder, the crucible material is allund, the sensitivity of galvanometers: DTA – 250 μV, DTG – 500 μV, T– temperature curve; DTA – differential thermal analysis curve; TG – mass loss curve; DTG is the mass loss rate curve. In the Table 1 shows the data on the thermal destruction of the coating when adding fillers.

The obtained thermogravimetric parameters make it possible to determine the rate of thermal decomposition of the material at a given temperature and, accordingly, to show a qualitative estimate of thermal effects, but a more important task is to determine the activation energy of thermo-oxidative degradation of coatings.

Calculations of kinetic parameters on the TG curve, which satisfactorily describes the kinetics of the decomposition of solids, are based on the equation [20]:

$$-\frac{dm}{dt} = k \cdot m^n, \tag{2}$$

where m – mass of the sample that reacted to the decomposition, mg;
n – reaction order;
k – specific rate of material decomposition reaction.

Table 1. Test results of thermal decomposition of wood.

Wood						
Mass loss [%] for temperatures						
100 [°C]	200 [°C]	300 [°C]	400 [°C]	500 [°C]	600 [°C]	700 [ºC]
8,4	9,9	33,2	62,1	85,3	92,0	92,6
Balance at 700 [°C]: 9,0 [%]						
Characterization of DTG peak maxima [T_{max}, °C / mass loss rate, % min^{-1}]						
Interval	80 – 655 [°C]					
Peak	100/1,4	225/2,9	310/5,3	330/2,7	425/1,2	525/0,8
Characteristics of DTA effects [T_{max}, °C / effect type]						
Interval	210 – 670 [°C]					
Peak	100/ekzo	225/endo	330/endo	370/ekzo	585/ekzo	
The wood is protected with a lacquer						
Mass loss [%] for temperatures						
100 [°C]	200 [°C]	300 [°C]	400 [°C]	500 [°C]	600 [°C]	700 [ºC]
3,1	8,7	19,3	28,4	40,0	44,8	45,6
Temperature residue 720 [°C]: 53,7 [%]						
Characteristic of DTG peak maxima [T_{max},°C / mass loss rate, % min^{-1}]						
Interval	20 – 580 [°C]					
Peak	110/0,58	265/1,35	350/1,16	390/2,51	475/1,84	
Characteristics of DTA effects [T_{max}, °C / effect type]						
Interval	20 – 390 [°C]			390 – 750 [°C]		
Peak	110/endo	265/endo	355/endo	640/endo		

The dependence of the specific rate of decomposition of the material on temperature is described by the Arrhenius equation:

$$k = A \cdot e\left(-\frac{E}{RT}\right), \tag{3}$$

where A – is the pre-exponential factor;
E – activation energy, kJ / mol;
R – is the universal gas rack, kJ / (mol • K).

For the separated stages of destruction, a possible method of calculating the activation energy is a method in which it is shown that the parameter E, under other equivalent conditions, is a measure of resistance to thermal oxidation degradation of the material.

The following timetable is characteristic of wood:

$$A_{(тв)} \rightarrow B_{(тв)} + C_{(газ)} \tag{4}$$

and determining the rate of decomposition reaction allows the equation:

$$-\frac{dm}{dT} = \frac{A}{V_{нагр}} \cdot e^{-E/RT} \cdot m^n. \tag{5}$$

The calculation of E and n is based on the mathematically processed table. 1 using dependency [10]:

$$\ln\left(\ln\frac{100}{100-\Delta m}\right) = -\frac{E}{R}\cdot\frac{1}{T}. \tag{6}$$

In this equation, Δm – is the mass loss (%) at each temperature in the interval of material decomposition, which is a 1st order process (n = 1) and subject to linearization of dependence:

$$\ln\left(\ln\frac{100}{100-\Delta m}\right) = \ln\left(\ln 100/(100-\Delta m)\right). \tag{7}$$

from temperature T, K.

In Table 2 summarizes the results of calculating the parameters required to calculate the activation energy of the wood.

Table 2**.** The results of the processing of derivatograms.

t, [ºC]	Δm, [%]	Ln[Ln(100/100-Δm))
Wood in normal air atmosphere		
200	9,9	0,878774
250	20,0	0,475885
300	33,2	0,103154
330	45,9	-0,25292
420	66,0	-0,87824
460	77,2	-1,35181
500	85,3	-1,83888
585	92	-2,23234
Covering		
200	8,7	1,052465
300	19,3	0,49778
400	28,4	0,230144
500	40	-0,08742
600	44,8	-0,21945
700	45,6	-0,24174

The value of the activation energy (E) is calculated according to:

$$E = tg\phi \cdot R \quad (8)$$

In Fig. 3 shows a graphical dependence of the speed of destruction of wood from the inverted temperature and the rate of destruction of the coating from the inverted temperature, respectively, and in Table 3 shows the activation energy value.

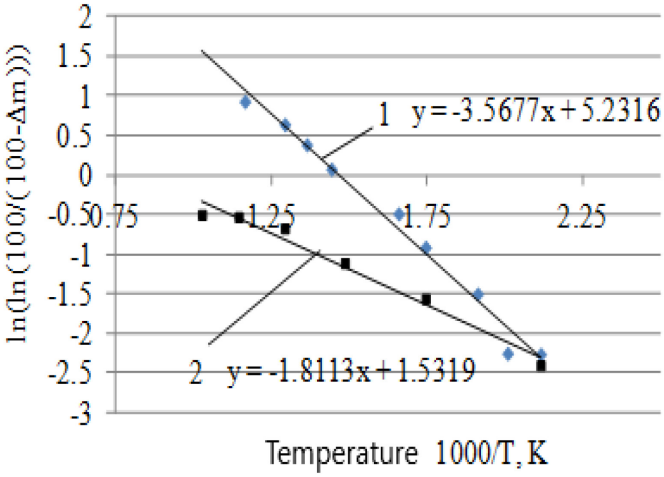

Fig. 3. Graphical dependence of the speed of destruction of wood on the inverted temperature: 1 − untreated; 2 − flame retardant flame retardant.

Table 3. The calculated value of the activation energy in thermal decomposition of the coating with the addition of minerals.

Sample number	Covering	Activation energy, E [kJ / mol]
1	Wood	36,56
2	The wood is protected with a lacquer	84,27

Thus, the calculation revealed that for thermal decomposition of wood protected with lacquer varnish, much more activation energy is required. Therefore, this coating can be effectively used as a fire retardant.

Studies on the determination of combustibility showed (Table 4) that the wood belongs to the combustible materials (the sample after the fire ignited), the flame retardant sample of the wood withstood the temperature influence and belongs to the combustible materials. At the initial temperature of the gaseous combustion products T = 62 ºC, with the action of the radiation panel on the protected sample, the temperature of the gaseous combustion products was T≤120 ºC.

Table 4. Flame front time of control points.

Sample of wood	Flue gas temperature, [°C]		Time to catch up, [s]	Time of passage of the flame front of the sample, [s]									Time to reach maximum flue gas temperature, [s]	Sample burning length, [mm]	Index of grief
	T_1	T_{max}		1	2	3	4	5	6	7	8	9			
Rough	61	329	52	2	8	7	10	6	8	7	6	7	103	294	177,5
The wood is protected with a lacquer	62	114	595	–	–	–	–	–	–	–	–	–	596	18	0,4

Note: – undefined

During the tests of the reed samples it was found that the raw sample was occupied for 52 s, the flame spread throughout the sample for 100 s, the flame retardant specimen was covered by 596 s, the flame spread by the surface only on the first site, the maximum temperature of flue gases was 114 °C over time more than 5 times and the flammability index dropped to 0.4.

6 Conclusions and Perspectives of Further Research

Thus, studies using thermogravimetry and gas chromatography show that the mechanism of flame retardant efficiency is directed toward the formation on the surface of the coke layer. The presence of fire retardant lacquer on wood alters the process of thermal destruction, reduces the amount of combustible gases that are phlegmatized by a large amount of nitrogen and carbon dioxide, which is accordingly confirmed by the results of determination of the flammability index. Obviously, such a mechanism of influence of additives is a factor in regulating the degree of coke stability and the efficiency of thermal insulation of the material.

Further studies will focus on the study of the processes of structure formation of the protective layer, establishing the relationship between the components and properties of coatings and their optimization.

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