

DEEP IMPREGNATION OF BINDER-FREE, LOW-DENSITY WOOD BOARDS WITH FLAME RETARDANTS

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ABSTRACT

This study is aimed at making binder-free low-density wood boards from mechanically activated sawdust by the process of deep vacuum-pressure timber impregnation with aqueous solutions of flame retardants. The thermal decomposition of impregnated boards was examined by thermogravimetric analysis (TGA). Determination of the maximum flame retardant absorption was carried out by a factorial experiment. The SEM/EDX method was used to estimate the distribution of flame retardants across the entire thickness of the board. The fire-proof efficiency of flame retardants was determined as specified in the GOST 12.1.044-89 standards. It was found that the deep impregnation of binder-free boards with a density of 290 kg/m³ makes it possible to obtain a low-combustible material.

Keywords: low-density boards, sawdust, structure of boards, electron microscopy, hydrodynamic processing, fire retardant, wood modification.

INTRODUCTION

Wood-based materials play an important role in the transition to a closed-loop economy. Boards made from renewable, plant-based materials are of particular interest. They reduce the environmental impact, save resources, and significantly contribute to reducing CO₂ emissions (De Luca *et al.*, 2017). In this regard, sawmill and woodworking waste (sawdust, wood chips, and lumps) are highly promising. So far, they have been mainly used to make wood-based panels and provide heat.

The construction industry needs environment-friendly, safe, high-performance materials. Low thermal conductivity, soundproofing, shape stability when exposed to moisture, structural strength, etc., are expected. Currently, low-density wood boards are extensively studied (Monteiro *et al.*, 2019, Pham Van *et al.*, 2021, Sable *et al.*, 2015). Monteiro S. *et al.* obtained chipboard using sour cassava starch as a binder. The properties of such panels are as follows. Density 405 kg/m³; tensile strength: 0.44 MPa; swelling in thickness: 13.2 %. The use of low-density kiri wood (*Paulownia tomentosa*) makes it possible to create oriented chipboard with a density of 400 kg/m³ and a tensile strength perpendicular to the board of 0.52 MPa (Pham Van *et al.*, 2021). The authors Sable I. *et al.* obtained a wood-fiber material based on birch wood with a density of 102 to 120 kg/m³. The interest in such materials arises from the stringent building environmental safety and energy efficiency requirements (Abu-Jdayil *et al.*, 2019).

Wood, with all its clear advantages, is flammable and combustible (Sheloumov, 2017, Maksimenko *et al.*, 2013). The paper lists the most common wood fire resistance

enhancement methods: applying solutions to the wood particles or treatment of finished boards with a flame retardant by applying it to the surface (Leonovich, 2003). The introduction of flame retardants during the manufacturing process increases the fire resistance of wood boards making them low-combustible. However, it reduces the mechanical properties (Zhang *et al.*, 2022, Selamat *et al.*, 2018, Antonov *et al.*, 2012, Ermolin *et al.*, 2015). Zhang B. et al. state that adding fire retardants to wood particles for making 650 kg/m³ chipboard with isocyanate and MUF resin results in a tensile strength reduction from 0.81 MPa to 0.42 MPa and 0.36 MPa, and a thicker swelling: from 5.2 % to 15.1 % and 11.2 % (Dubrulle *et al.*, 2020). Selamat M. E. notes that adding 10 % and 20 % of fire magnesium oxide as a fire retardant to 800 kg/m³ oil palm trunk chipboard decreases the tensile strength from 1.16 MPa to 0.62 MPa and 0.54 MPa, respectively.

The application of fire retardants to the surface of finished boards is intended to prevent flame propagation along the surface. However, the fire retardant is washed away when the board is exposed to a variable moisture environment. It decreases the board fire resistance even after a relatively short service life (Bahrani *et al.*, 2018, Dubrulle *et al.*, 2020). In addition, the lack of a flame retardant inside the material increases its flammability. Therefore, the search for ways of uniform fire protection of boards throughout the entire volume is an urgent task.

Deep impregnation is the most reliable method for solid wood fire protection. The flame retardant is applied through the entire material under overpressure in the autoclave (Ermolin, 1999, Bazhenov *et al.*, 1953). However, the process is not used to protect wood-based composites (Wang *et al.*, 2010). The binder adhesion to the wood chips creates the required physical and mechanical properties of the board, including its low thermal conductivity (Donaldson *et al.*, 1989, Hubbe *et al.*, 2018). As the number of adhesive contacts in wood boards is deficient, they fail under relatively low loads. The autoclave impregnation process uses overpressure or vacuuming. In both cases, mechanical stresses are created at the adhesive contacts between the chips resulting in a loss of strength or complete failure of the board (Panev, 2018). Note that most flame retardants can destroy the supramolecular structures of the cured polymer binder and cause wood swelling. It can also lead to the destruction of adhesive contacts under relatively low external stress. This can be a serious disadvantage in variable humidity conditions (Chudinov, 1984, Shvartsman, 1997).

A possible solution is increasing the number of chip-to-chip contacts without using any synthetic binders. A team from Fraunhofer Institute for Wood Research, Wilhelm-Klauditz-Institut WKI, Braunschweig, developed a manufacturing technology for making a binder-free material called wood foam (Bunzel *et al.*, 2017). They turn wood into thermomechanical pulp (TMP). A wood fiber pulp is foamed by a natural foam stabilizer (e.g., protein) and exposed to air during mixing. The material density ranges from 40 to 250 kg/m³. The 110 kg/m³ pinewood boards have a 0.205 MPa compressive strength and a 0.09 MPa tensile strength perpendicular to the board. The thermal conductivity coefficient of the boards of 0.038 W/(m K) is reached at about 40 kg/m³ (Bunzel *et al.*, 2018).

Our earlier studies (Ermolin *et al.*, 2020, Ermolin *et al.*, 2019, Bayandin *et al.*, 2021) showed that sawdust activated with the hydrodynamic method is suitable for making low-density wood boards without any binder, but with higher physical and mechanical properties and water resistance (Figure 1). The properties of such panels are as follows: density: 250 kg/m³; flexural strength: 1.26 MPa; tensile strength perpendicular to the board: 0.25 MPa; swelling in 24 h: does not exceed 5 %. After drying, the samples return to their initial dimensions and maintain up to 100% of the initial structural strength. The thermal conductivity of the boards at 8 % moisture content is 0.039 W/m·K. Such boards are heat insulators (Namyatov, 2018). The hydrodynamic treatment is based on cavitation. The wood

particles are significantly transformed: the number of macro capillaries and the specific surface increase.

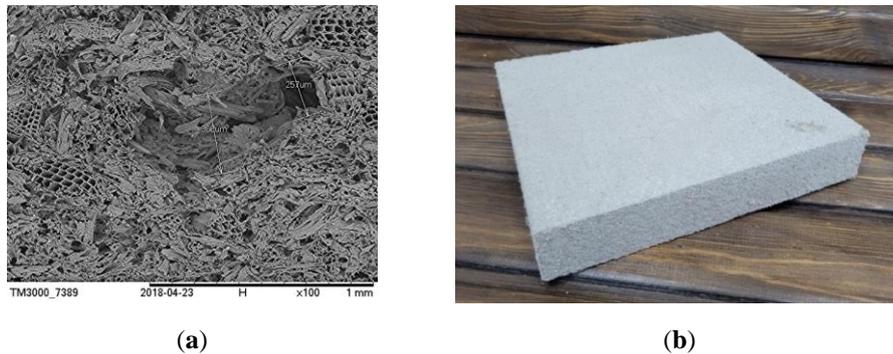


Fig. 1 Low-density wood board without a binder: (a) microstructure, (b) appearance.

Excellent mechanical properties and water resistance make it possible to use deep impregnation flame retardants. The use of this method will ensure maximum absorption of the flame retardant and its even distribution. The purpose of this study is to assess the effect of deep impregnation with fire retardants of low-density, binder-free wood boards on their thermal resistance.

MATERIAL AND METHODS

Materials

We made the sample boards with coniferous sawdust (*Pinus sylvestris*, moisture content $83\pm 12\%$) (Figure 2a), which was collected at the Krasles sawmill (Krasnoyarsk Territory, Russia). The fractional composition of sawdust is shown in Figure 2b. The particle size did not exceed 10 mm. They were separated by mechanical sorting method.

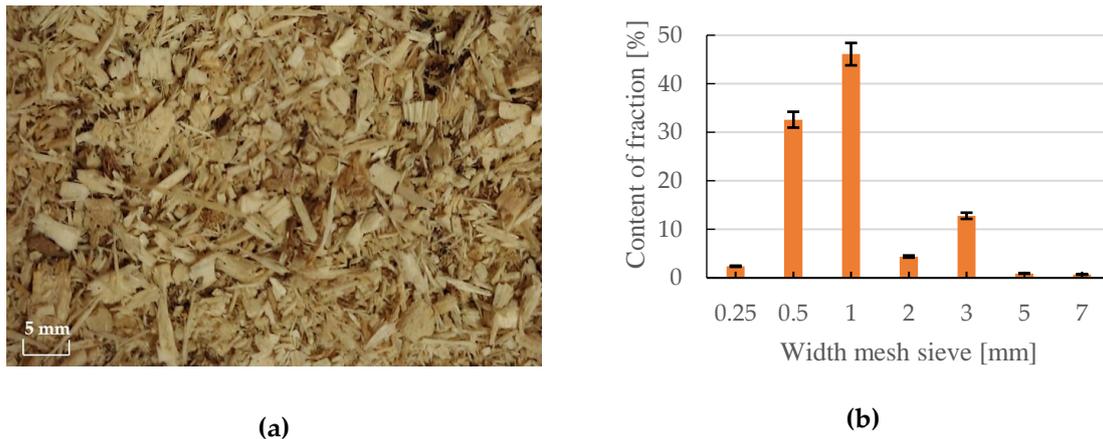


Fig. 2 Sawdust used in the manufacture of wood boards: (a) appearance, (b) fractional composition.

There are many fire retardants available. Analysis of prior information (Sheloumov, 2017, Kulakov *et al.*, 2021, Sivenkov, 2015, Prokopenko, 2019, Kolesnikov *et al.*, 2019) allowed us to identify the following inorganic flame retardant impregnating compounds for surface and deep impregnation, presented in Table 1 and Figure 3. The key fire retardant selection criteria were:

- certified compliance with Group 1 Fire Retardance (in accordance with the GOST R 53292 standard)
- fire retardant as an aqueous solution
- suitability for the fire protection of wood and wood-based materials
- commercial availability.

Tab. 1 Fire retardant properties.

Fire retardant	Appearance	Hydrogen index (pH)	Density, g/cm ³	The composition of the main components
Fire retardant 1	Transparent, slightly colored liquid. Slight mobile precipitation is acceptable.	13.0	1.25	Potassium Carbonate (K ₂ CO ₃) Sodium Fluoride (NaF) (Cheshko <i>et al.</i> , 2016)
Fire retardant 2	Colorless. Some turbidness or small amounts of precipitation are acceptable.	0.8	1.23	Diammonium phosphate ((NH ₄) ₂ HPO ₄) Urea ((NH ₂) ₂ CO) (Andreeva <i>et al.</i> , 2013, Printseva <i>et al.</i> , 2014)
Fire retardant 3	Transparent, slightly turbid liquid; precipitation is acceptable.	7.9	1.02	Diammonium phosphate ((NH ₄) ₂ HPO ₄) (Aseeva <i>et al.</i> , 2007)
Fire retardant 4	Water-soluble, tinted powder.	11.9	1.22	Inorganic salts

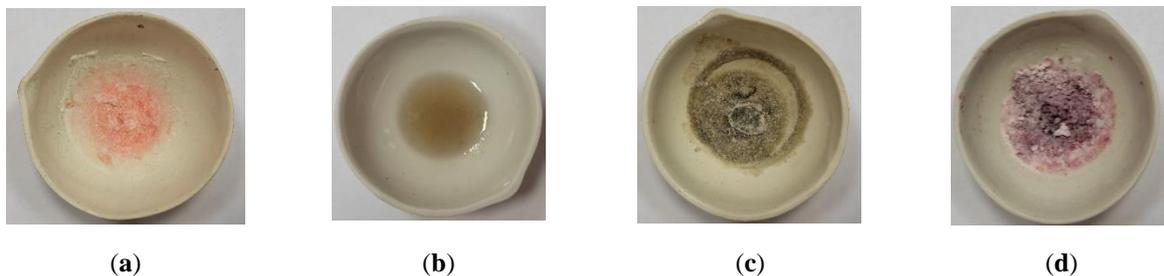


Fig. 3 Fire retardants: (a) fire retardant 1; (b) fire retardant 2; (c) fire retardant 3; (d) fire retardant 4.

The impregnant substance concentration in terms of dry matter was 29.4±0.6%. These substances are extensively used for fireproofing of wood.

Manufacture of low density wood boards

The sawdust was collected at a sawmill. We mixed the sawdust with water at 8 to 10°C. The sawdust content in the mixture was 10% (Ermolin *et al.*, 2017). A lab-grade rotary-pulse hydrodynamic homogenizer was used (Figure 4). After mixing sawdust with water, the apparatus was switched on and repeated mass processing was carried out by passing through the hydrodynamic homogenizer (3) (rotor and stator). The rotation frequency of the rotor was 2950 rev/min. The treatment lasted for 30 minutes.

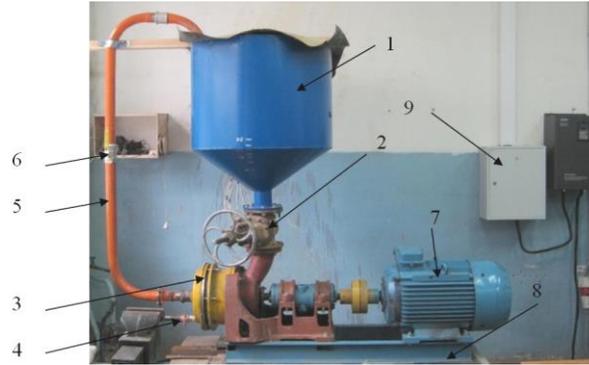


Fig. 4 The general arrangement of the test bench: 1: tank; 2: gate valve; 3: hydrodynamic homogenizer; 4: drain ball valve; 5: circulation pipe; 6: ball valve; 7: motor; 8: support frame; 9: control panel.

A layer of the resulting wood pulp by pouring it into a metal mold with a 250x250 mm mesh bottom and the cell size 1 mm was formed. The molded layer was dewatered by cold pressing at 0.5 MPa. The moisture content of the mass after cold pressing was $200 \pm 20\%$. Then the layers were removed from the mold and placed in a convection air dryer. The drying temperature was 105 ± 5 °C, and the air stream velocity was 2.5 m/s. After conditioning under normal conditions at 65% RH and 23°C for three days, the boards were processed by surface planer and thicknesser to form smooth parallel surfaces. The final size of the boards was $[(250 \times 250 \times 30) \pm 1]$ mm.

The final moisture content of the boards was $8.4 \pm 0.1\%$. The density of the boards was determined as specified in the GOST 17177-94 standard. This is the ratio between the mass loss of a sample dried in a convection air dryer at (105 ± 5) °C to a constant mass, and the mass of the sample after drying. The size of the samples was $[(50 \times 50 \times 30) \pm 1]$ mm. Three samples from the boards were used for each experiment. The board density at this moisture was 290 ± 10 kg/m³.

Deep impregnation of wood boards with flame retardants

Autoclave impregnation of porous materials ensures max absorption and an even distribution of the impregnant. The absorption rate depends on the properties of the impregnated material and the impregnant, pressure, and duration of the impregnation (Krivonogov *et al.*, 2018). The impregnation of wood boards was not previously studied. We performed experiments to determine the conditions for max absorption of the fire retardant. We used low-density board samples (40x40x30 mm, 8.2% humidity). The impregnated substance (composition 4) concentration in terms of dry matter was 27.4 ± 2.5 %. To simulate the impregnation of industrial-size boards, the edges of the boards were insulated with a layer of PF-115 enamel and Akfix P635 sealant (Fig. 5).

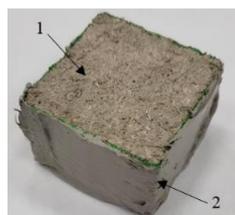


Fig. 5 Waterproofed samples of low-density boards before impregnation: 1: wood panel; 2: waterproof layer.

The experiment followed the Box-Wilson experimental design (Taavitsainen, 2011). The independent variables were the vacuum hold period (t , min) and the underpressure (V , MPa). The board samples impregnated with water were used as a reference (Golubev *et al.*, 2020). The dependent variable was the total flame retardant absorption (P , kg/m³). The experimental impregnation process was as follows. The prepared samples were loaded into an autoclave (Fig. 6). The underpressure and hold periods are indicated in Table 2. Then, still under vacuum, the fire retardant was introduced, the pressure was raised to the atmospheric pressure, and the samples were held for 5 min. Then the fire retardant was removed from the sample surface with filter paper.



Fig. 6 The general arrangement of the test bench: 1: autoclave; 2: compressor; 3: vacuum pump; 4: fire retardant reservoir.

Tab. 2 Wood board impregnation conditions.

Test No.	Initial values	
	Hold period t , min	Underpressure V , MPa
1	15	0.04
2	10	0.04
3	10	0.07
4	5	0.04
5	5	0.01
6	15	0.07
7	5	0.07
8	10	0.01
9	15	0.01

After impregnation, the samples were dried in a Binder ED 23 drying cabinet at 105 ± 5 °C. The boards were subsequently conditioned for three days in normal conditions. The total absorption of flame retardant composition was determined as specified in the GOST 20022.6-93 standard. Absorption P , kg/m³, was determined in accordance with equation

$$P = \frac{m_2 - m_1}{V}, \quad (1)$$

where m_1 - sample mass before impregnation, kg, m_2 - sample mass after impregnation and drying, kg, V – volume of sample, m³.

Thermogravimetrical analysis (TGA)

To determine the effects of flame retardants on the thermal decay of binder-free wood boards, we impregnated the samples by soaking them in the above-listed solutions. We used

low-density board samples $(40 \times 40 \times 30) \pm 1$ mm. Three samples were used for each experiment. For control, three samples were soaked with water.

Since the permeability of this material has not yet been studied sufficiently, after a series of preliminary studies, we adopted the vacuum-atmospheric pressure impregnation method as the most productive. The prepared samples were loaded into an autoclave (Fig. 6) at $t = 2$ min, $V = 0.01$ MPa. Then, still under vacuum, the fire retardant was introduced, the pressure was raised to the atmospheric pressure, and the samples were held for 1 min. Then the fire retardant was removed from the sample surface with filter paper. The samples were then dried at room temperature until their mass did not change anymore. Fig. 7 shows the photos of the samples.

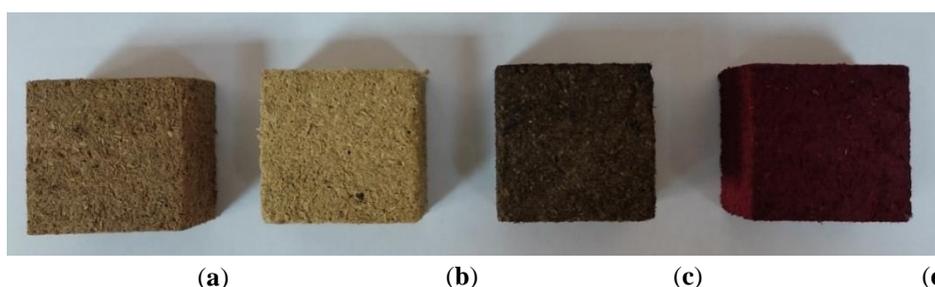


Fig. 7 Samples after the impregnation with fire retardants: (a) fire retardant 1; (b) fire retardant 2; (c) fire retardant 3; (d) fire retardant 4.

After conditioning under normal conditions at 65% RH and 23 °C for three days, the boards were examined by thermogravimetric analysis (TGA) (Azarov *et al.*, 2010).

Thermal analysis was performed on samples weighing 13 ± 0.1 mg taken from the central part of the samples impregnated with flame retardants. Three TGA samples were taken from each impregnated board. A TGA55 thermogravimetric analyzer from TA Instruments (USA) was used. The measurements were taken in an inert nitrogen atmosphere supplied at 45 ml/min in the 40 to 600 °C temperature range and a 20 °C/min heating rate. The TRIOS v. 5.00.44608 software processed the results.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM/EDX microphotography with energy-dispersive X-ray spectroscopy (EDX) was used to study the distribution of fire retardant 4 across the bulk of the boards during impregnation. A Tabletop Microscope Hitachi TM4000Plus was used for microscopic studies. The board samples had a moisture content of $8.4 \pm 0.1\%$ and contained 103.8 ± 1.4 kg/m³ of fire retardant 4 on a dry matter basis. The dust-free sample was placed on a table (without additional sample preparation). During the image capturing process accelerating voltage of 15 kV and backscattered electron were used. Vacuum modes were "Conductor" and "Standard". Element mapping was carried out with an X-ray energy dispersion spectrometer BRUKER XFlash 630Hc coupled with a microscope. Accelerating voltage: 20kV.

Determination of fire-retardant efficiency

To determine the flammability, we used a ceramic box according to the GOST 12.1.044-89 standard (Fig. 8). We prepared three samples: 30x60 cross-section, 150 mm long, $8.4 \pm 0.1\%$ moisture content. The samples were impregnated with fire retardant 4. The absorption in terms of dry matter was 103.8 ± 1.4 kg/m³.

The sample (5) was fixed in the holder (6). The position of the sample relative to its vertical axis was checked using a template. The temperature recorder (10) with a measurement accuracy of 2.5 °C was turned on, the gas burner (2) was lit, and the gas flow rate (4) was

adjusted so that the temperature of the gaseous combustion products controlled for 3 minutes was $(200 \pm 5) ^\circ\text{C}$. The holder with the sample was inserted into the chamber (3) for no more than 5 seconds and tested for (300 ± 2) seconds or until the maximum temperature of the exhaust gaseous combustion products of the material was reached. After that, the burner was turned off. The sample was kept in the chamber until complete cooling (room temperature), then removed from the chamber and weighed.

According to the value of the maximum temperature increment Δt_{max} (formula 2) and mass loss Δm (formula 3) materials are classified as:

- low-combustible - $\Delta t_{\text{max}} < 60 ^\circ\text{C}$ and $\Delta m < 60 \%$;
- combustible - $\Delta t_{\text{max}} \geq 60 ^\circ\text{C}$ or $\Delta m \geq 60 \%$.

The maximum temperature increment (Δt_{max}) is calculated by the formula

$$\Delta t_{\text{max}} = t_{\text{max}} - t_0, \quad (2)$$

where t_{max} - the maximum temperature of gaseous combustion products of the material under study, $^\circ\text{C}$;

t_0 - the starting test temperature ($200 ^\circ\text{C}$).

Mass loss Δm , %, is calculated:

$$\Delta m = \frac{(m_1 - m_2) \cdot 100}{m_1}, \quad (3)$$

where m_1 - sample mass before testing, m_2 - sample mass after testing.

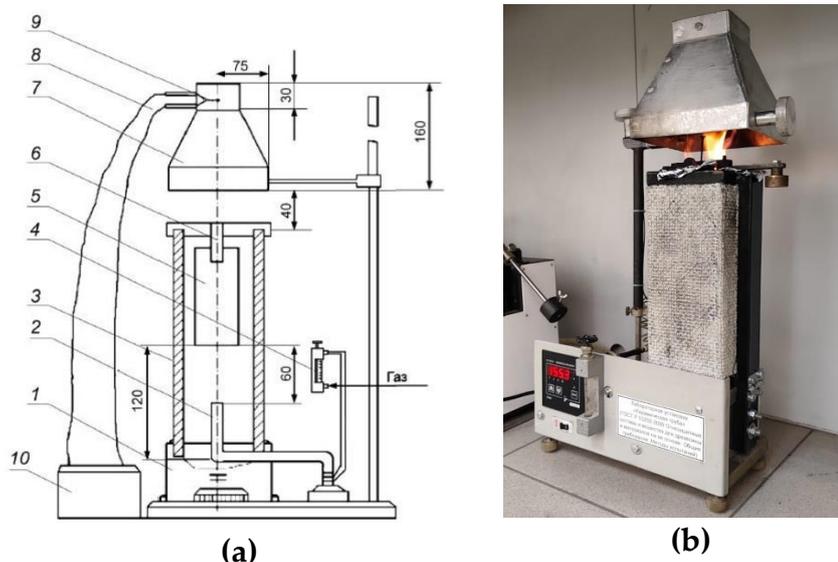


Fig. 8 The general arrangement of the ceramic box: (a) installation diagram: 1 – stand; 2 – gas burner; 3 – ceramic box; 4 – rotameter; 5 – sample; 6 – sample holder; 7 – exhaust hood; 8 – thermoelectric converter; 9 – exhaust duct; 10 – automatic potentiometer; (b) appearance.

Statistical processing

Microsoft Excel 2010 for Windows 8 was used for statistical processing. Each test was repeated three times. The mean value, standard deviation and confidence intervals were calculated. The significance level was 0.05.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA)

Table 3 shows that for the reference samples of water-impregnated boards at the max temperature t_{max} 314.94 °C at the thermogravimetric peak the weight loss was 44.4 %. A further temperature increase in the reference samples resulted in the formation of 0.2 % ash residue. The chemical theory explains the properties of fire retardant compositions, such substances change the pyrolysis of wood by increasing charring and formation of less volatile and combustible gaseous products of wood decomposition (Levan *et al.*, 1990). The thermogravimetric analysis results for the fire retardant-impregnated samples are consistent with this theory. It was noted that the pyrolysis of samples occurred at lower temperatures than for the reference samples.

Tab. 3 Intensive decomposition temperatures for the wood board samples impregnated with fire retardants.

Fire retardant	t_{max} *	DTG $_{max}$ *	Massloss, %	Ashcontent (%) at 560 °C
Reference sample soaked in water	314.94	12.130	44.4	0.2
Fire retardant 1	229.2	0.356	15.1	60.5
Fire retardant 2	251.5	0.638	25.2	45.1
Fire retardant 3	253.97	0.660	27.8	32.4
Fire retardant 4	206.28	2.464	17.3	59.8

* Where t_{max} is the max temperature at the DTG curve, °C; DTG $_{max}$ is the max mass loss rate, %/°C.

The max decomposition temperature (t_{max}) of the boards impregnated with fire retardant 1 was 85.7 °C lower than that of the reference samples. The weight loss of the samples impregnated with fire retardant 1 at max was 15.1%. The ash residue after the max thermal impact was 60.5 %. Fire retardant 3 showed the highest t_{max} = 253.97 °C. Upon reaching this temperature, the weight loss was 27.8%. The ash residue was 32.4%, which may indicate a relatively low fire-retardant effect (Uner *et al.*, 2016). The thermal analysis results of the boards impregnated with fire retardant 2 are similar to those of fire retardant 3 (Table 3, Figure 9).

Fire retardant 4 applied to wood boards significantly changes the wood thermal destruction: the rate of destruction decreases, the DTG $_{max}$ peak shifts to lower temperatures (t_{max} = 206.28 °C).

Our results are consistent with that presented in (Bezzaponnaya *et al.*, 2017): for efficient fire protection, it is advisable to lower the initial swelling temperature of the flame retardant to reduce the heating rate of the base material. The higher weight loss rate compared to fire retardants 1-4 is associated with the fire-retardant decomposition at the max temperature (t_{max}) resulting in the release of gases that inhibit combustible products of thermal oxidation (Antsupov *et al.*, 2011).

For comparison, Fig. 9 shows the thermo gravimetric and differential thermogravimetric curves (TG and DTG) of the wood boards impregnated with fire retardant 4 and water.

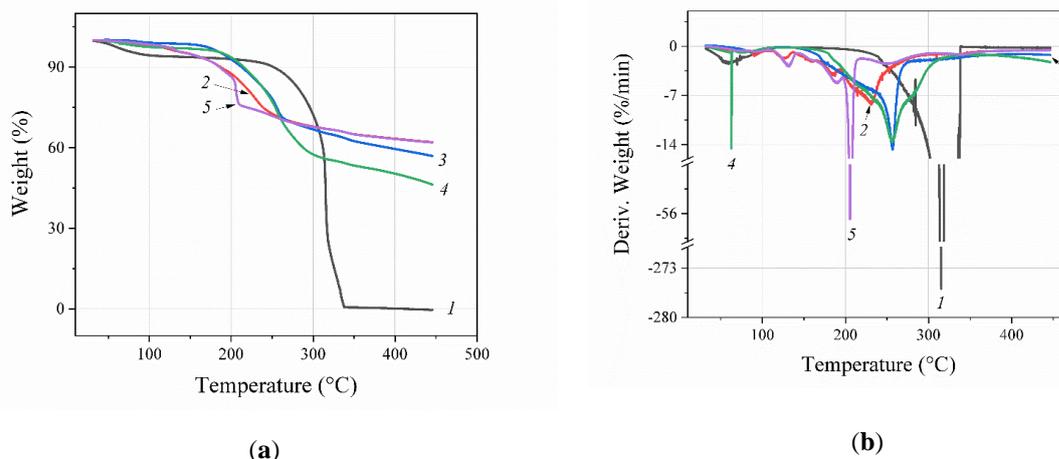


Fig. 9 Thermo gravimetric curves of the original low-density board (1) and the fire retardant-impregnated board: 1 (2), 2 (3), 3 (4), 4 (5): a: TG; b: DTG.

Fig. 9a shows that thermogravimetric curves of the original low-density board (1) and the fire retardant-impregnated board (5) have different forms. Thermal degradation of the reference boards impregnated with water occurs in three stages, as typical for wood (Sinha *et al.*, 2000). In the first stage (temperature up to 200 °C) the reference boards evaporate the bound moisture and remove the volatile components. Hemicelluloses are decomposed in the second stage (200 to 320 °C). In the third stage, (up to 440°C), cellulose and lignin are degraded. Note that the reference samples at 440 °C had an ash residue of 0.2 %, while for spruce wood this value was about 20 % (Hagen *et al.*, 2009). The difference is probably due to the high porosity of the boards with a higher amount of trapped air. It contributes to a more complete thermal decomposition of wood (Brosse *et al.*, 2010).

The thermogravimetric curve for the boards impregnated with fire retardant 4 is broadly consistent with previous results (Tang, 1967). The impregnated board samples began to lose weight at about 50 °C with an intermediate peak at 131 °C, followed by a rapid weight loss increase with a peak at 206.28 °C (Fig.9b). This can be explained by wood dehydration, partial thermal destruction of hemicelluloses, and decomposition of the fire retardant. At a subsequent heating from 215 °C the weight loss slows down. A possible reason is that the thermal decomposition of the fire retardant inhibits the effect of volatile substances released during the decomposition of hemicelluloses. They intensify the cellulose decomposition. It was also found that at about 500 °C the samples of fire retardant-impregnated boards showed a 60 % weight loss.

Therefore, fire retardant 4 was selected to study the binder-free wood board impregnation conditions.

Deep impregnation of wood boards with flame retardants

The results indicate that the absorption of the fire retardant 4 per dry matter ranges from 103.8 ± 1.4 to 288.4 ± 3.1 kg/m³ (Table 4). This is probably due to the large porous volume, where the fire-retardant solution can penetrate and stay.

Tab. 4 Experimental matrix.

Test No.	Normalized factors		Absolute factors		Total absorption of flame retardant on initial board volume
	X ₁	X ₂	Hold period t, min	Underpressure V, MPa	P, kg/m ³
1	1	0	15	0.04	111.6 ±8.2
2	0	0	10	0.04	164.9 ±2.0
3	0	1	10	0.07	268.6 ±7.9
4	-1	0	5	0.04	134.2 ±2.6
5	-1	-1	5	0.01	103.8 ±1.4
6	1	1	15	0.07	269.3 ±3.5
7	-1	1	5	0.07	288.4 ±3.1
8	0	-1	10	0.01	116.8 ±1.2
9	1	-1	15	0.01	107.9 ±2.8

To estimate the effects of the control variables (AA and A: quadratic and linear effects of the vacuuming time on the absorption value; BB and B: similar effects for the underpressure; AB: combined effect of the two factors), we drew a Pareto diagram (Fig. 10) using a regression analysis in the STATGRAPHICS Centurion 18 software.

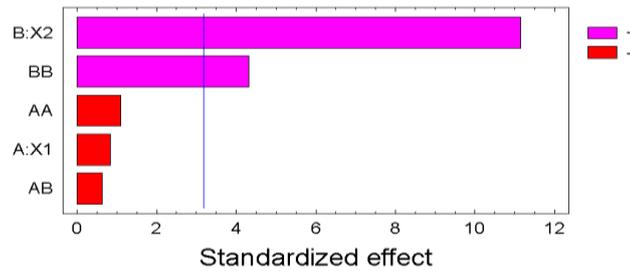


Fig. 10 Pareto chart of standardized effects.

The results indicate that the underpressure has the greatest influence on the absorption value. There are just two significant factors: B and BB. Such a high significance of B can be explained as follows: the material contains a larger number of air-filled pores. The air is replaced by the flame retardant during impregnation. It is known that overpressure during the impregnation of such materials, including wood, reduces the air volume and increases its pressure. This slows or even stops the fluid transfer in the material (Shamaev *et al.*, 2013). The vacuum removes some of the air and promotes the fluid transfer to fill the free volume of pores across the sample with the flame retardant, as the results show. The high significance of BB is probably because the material has pores of different pores with poor transport between the pores. It does not allow for air removal at an underpressure of less than 0.04 MPa to increase the absorption of the flame retardant.

Eq. (4) is the regression model (96.04 %, representativeness) which includes the effects shown in Fig. 10. The response surface in Fig. 11 shows that the nonlinearity is largely caused by the underpressure (mainly represented by the quadratic BB effect).

$$P \text{ (kg/m}^3\text{)} = 146.39 - 6.27 \times X_1 + 82.97 \times X_2 - 14.23 \times X_1^2 - 5.80 \times X_1 \times X_2 + 55.57 \times X_2^2 \quad (4)$$

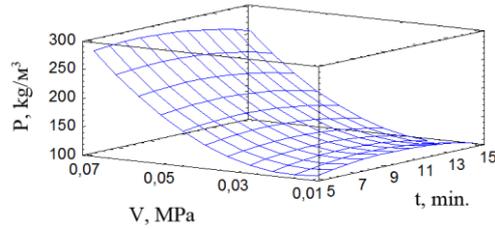


Fig. 11 Impregnation substance absorption vs. hold period and underpressure.

The relationship is non-linear. It can be seen that underpressure is the limiting factor. The max increase in absorption (more than twofold) was found as the underpressure was increased from 0.04 to 0.07 MPa for virtually the same hold period. The max flame retardant absorption of $288.4 \pm 3.1 \text{ kg/m}^3$ is achieved at the underpressure up to 0.07 MPa.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Test results of the control samples' central part surface obtained with the aid of scanning electron microscopy (SEM) and EDX indicate a potassium (K) exposure near 1%, which is due to inferiority of the accepted sample preparation technique (Fig. 12a). In addition to it, the elemental composition of the considered part of the sample's surface includes carbon (C) about 50% and oxygen (O) about 30 % (Table 5).

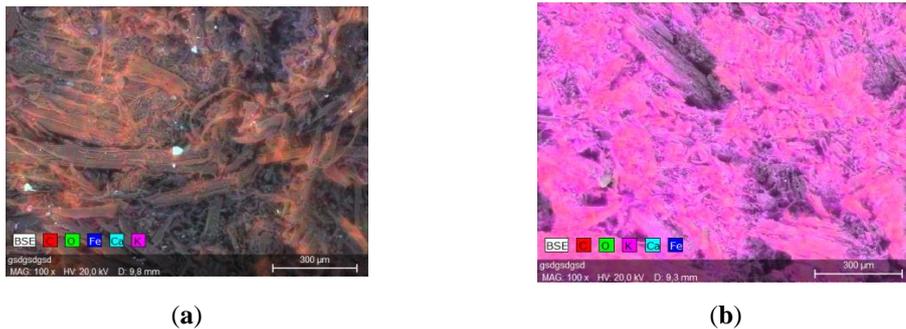


Fig. 12 SEM-micrography and visualization of potassium (K) distribution using EDX (a) reference sample, (b) sample impregnated with flame retardant 4 (magnification = 100X).

Tab. 5. Elemental chemical composition of the boards.

Elements	Weight, %	
	Control sample	Slabs treated with flame retardant 4
Carbon, C	57.77	35.08
Oxygen, O	35.07	32.76
Potassium, K	1.06	31.73
Iron, Fe	4.82	0.30
Calcium, Ca	1.28	0.30

The autoclave impregnation process allowed the distribution of flame retardant 4 through the entire volume of the wood panels. A sample impregnated with flame retardant 4 (Fig.12b) contains 31.34% of potassium (Table 5). The presence of potassium in such a significant amount may indicate that the working substance in the flame retardant

composition is potassium carbonate (K_2CO_3). Since the purpose of flame retardants is to prevent, delay ignition and reduce the consequences of fire, achieving deep penetration of the impregnating flame retardant will increase the level of fire protection of the material under study (Elvira-León *et al.*, 2016).

Determination of flame retardant efficiency

The results of inflammability tests and appearance before and after testing are presented in the Table 6 and in the Figure 13 respectively.

During the test, there was no temperature increase in gaseous combustion products (Δt_{max}). The temperature of the gaseous combustion products (Δt_{max}) decreased from 201.7 ± 1.5 °C to 60.9 ± 9.2 °C for (300 ± 2) seconds. The obtained data are consistent with that presented in (Seo *et al.*, 2017), where it is noted that wood samples undergone vacuum impregnation with an aqueous solution of flame retardants (diammonium phosphate and potassium carbonate) show less heat formation than samples after surface treatment.

As known, a smaller mass loss of the sample during the fire tests indicates a high resistance to thermal destruction under fire. As a result of using flame retardant, when exposed to fire, the mass loss of the sample averaged 29.0 ± 6.9 %.

Studies conducted on fiberboard (Özdemiretal, 2013) have shown that adding 9% of dry ammonium polyphosphate (APP) fiber to UF resin reduces weight loss by 37.3 % compared to the control sample. Ibragimov *et al.* (2020) achieved a 1.3...3.2-fold reduction in mass loss when burning heat insulating material samples of cotton, linen fibers, and wood chips by adding coke-forming flame retardants (sodium carbonate (Na_2CO_3) or aluminum trihydrate (Al_2O_3) in amounts of 30 % of plant filler) to the binder.

Such patterns of mass change can be explained by the fact that after putting the test sample into the chamber of the experimental installation, the flame retardant swelling began with gas release and foam coke formation. The carbonized layer helps to limit the spread of gaseous decomposition products of the sample, as well as oxygen access to its surface. An increase in the spread of carbonized products and the volume of the foam-coke layer reduces the number of gaseous products entering the combustion zone, reduces the rate of heat transfer to the layers located at the bottom of the coating. (Levan *et al.*, 1990, Khalturinskiy *et al.*, 2011, Chuang *et al.*, 2010).

Tab. 6 Combustibility tests of samples.

Sample No	The temperature of the soaking chamber before testing the sample, °C	Temperature of gaseous combustion products at the end of the test, t, °C	Maximum temperature of gaseous combustion products, t_{max} , °C	sample mass, g		Maximum temperature increment (Δt_{max}), °C	Mass loss, Δm , %
				before testing	after testing		
1	200	62.9	200	117.9	87.1	0	26.1
2	202	69.0	202	111.4	70.3	0	36.9
3	203	50.9	203	114.3	86.9	0	24.0
Average	201.7 ± 1.5	60.9 ± 9.2	201.7 ± 1.5				29.0 ± 6.9



Fig. 13 Sample of fire-proof board before (a) and after (b) testing.

The experiment proved that deep impregnation with flame retardants increases the fire resistance of binder-free wood boards making them low-combustible. Indeed, the temperature of the combustible gases released as the material is heated has decreased ($\Delta t_{\max} < 60$ °C), the mass loss rate does not exceed 60%. It means the material has a higher thermal resistance. In accordance with the GOST 12.1.044-89 standard, it matches the criteria for “hardly combustible materials”.

CONCLUSIONS

This study was aimed at estimating the binder-free wood board fire protection efficiency. The autoclave impregnation process allowed making them low-combustible material when tested as specified in the GOST 12.1.044-89 standard. Such boards are not commercially available now, but are of great research interest, as evidenced by similar studies. Boards made of activated wood particles have a wide range of absorption capacity ($103.8 \pm 1.4 - 288.4 \pm 3.1$ kg/m³). It enables their modification by deep impregnation with fire retardant and other liquid compositions. This approach is new and requires a comprehensive study since it expands the possibilities of obtaining binder-free materials with specified properties. Modified panels can be used in construction, e.g., for the manufacture of enclosing structures. To further improve the fire protection processes of binder-free low-density wood boards, it is necessary to study the effect of autoclave impregnation on their physical and mechanical properties.

REFERENCES

- Abu-Jdayil, B., Mourad, A. H., Hittini, W., Hassan, M., Hameedi, S., 2019. Traditional, state-of-the-art and renewable thermal building insulation materials: An overview. *Construction and Building Materials*, 214, 709-735.
- Andreeva, E. D., Printseva M.YU., Cheshko I.D., 2013. Application of infrared spectroscopy method for the flame-retarded wood. *FireSafety*, No. 4, 69-73.
- Antonov, A.V., Petrusheva, N.A., Alashkevich, Yu.D., 2012. Obtaining fire-proof fiberboards. *News of Higher Educational Institutions. Forest Magazine*, No. 4 (328), pp. 99-103.
- Antsupov, E. V., Rodivilov S. M., 2011. Flame retardants for porous materials // *Fire and explosion safety*. - T. 20. - №. 10. - C. 25-32.
- Aseeva R. M., Serkov B. B., Sivenkov A. B., 2007. Efficiency and action mechanism of two flame-retardant systems for wood *Fire and explosion safety*, V. 16, № 5, 23-30.
- Azarov, V.I., Burov, A.V., Obolenskaya, A.V., 2010. *Chemistry of Wood and Synthetic Polymers: Textbook*, 2nd ed.; Lan, Saint-Petersburg, Russia, p. 624. Lan: electronic library system. Available online: <https://e.lanbook.com/book/4022> (accessed on: 12.10.2022).

- Bahrani, B., Hemmati, V., Zhou, A., Quarles, S. L., 2018. Effects of natural weathering on the fire properties of intumescent fire-retardant coatings. *Fire and Materials*, 42 (4), 413-423.
- Bayandin, M.A.; Ermolin, V.A.; Ostryakova, V.A., Namyatov, A.V., 2021. Study of the properties of mechanically activated wood pulp for the production of adhesive-free wood boards. Actual problems and prospects for the development of the timber industry: Materials of the IV International Scientific and Practical Conference, Kostroma city, Russia, 08-11 September, 2021. Editors: Titunin, A.A., Vakhnina, T.N., Kostroma: Kostroma State University, pp. 10-13.
- Bazhenov, V. A., Moskaleva V. E., 1953. On the permeability of sapwood and pine kernels by liquids and the possibility of its regulation // Tr. Institute of forests of the USSR Academy of Sciences. Vol. 9. P. 205–216.
- Bezzaponnaya, O.V., Golovina, E.V., Mansurov T.K., Akulov A.Y., 2017. Application of the thermal analysis method for a comprehensive study and improvement of intumescent flame retardants. *Tekhnosfernaya bezopasnost'*, V 2, No. 15, pp. 3-7.
- Brosse, N., EL Hage, R., Chaouch, M., Petrissans, M., Dumarcay, S., Gérardin, P., 2010. Investigation of the chemical modifications of beech wood lignin during heat treatment. *Polymer Degradation and Stability* 95(9): 1721-1726.
- Bunzel, F., Ritter, N., 2017. Wood Foam. In *Cultivated Building Materials* (pp. 100-107). Birkhäuser.
- Bunzel, F., Kowalik, T., Scholz, S., Hohlfeld, J., 2018. Wood Foam and Metal Sponge Hybrid Material. *Lightweight Design worldwide*, 11(6), 32-37.
- Cheshko I.D., Printseva M.Yu.; Mokryak. A.Yu. Pariyskaya A.Yu. 2016. Possible applications of scanning electron microscopy and X-ray microanalysis in solving forensic fire examination. Saint-Petersburg university of State fire service of EMERCOM of Russia, 84-92.
- Chuang, C.S., Tsai, K.C., Wang, Y.C. et al., 2010. Impact of wetting and drying cycle treatment of intumescent coatings on the fire performance of thin painted red lauan (*Parashorea* sp.) plywood. *J Wood Sci* 56, 208-215. <https://doi.org/10.1007/s10086-009-1089-2>
- Chudinov, B.S. Water in wood [Text]: monograph / B.S. Chudinov; ed. A. Bazhenov ; Academy of Sciences of USSR, Siberian Branch, Institute of Forest and Wood named after Suchechev. V. N. Sukachev. - Novosibirsk: Nauka. Siberian Branch, 1984. - 272 c. Bibliography: pp. 263-269.
- De Luca, P., Carbone, I., Nagy, J. B., 2017. Green building materials: A review of state of the art studies of innovative materials. *Journal of Green Building*, 12 (4), 141-161.
- Donaldson, L.A., Lomax, T.D.1989. Adhesive. *Fibre Interaction in Medium Density Fiberboard. Wood Science and Technology*, vol. 23, iss. 4, pp. 371–380. <https://doi.org/10.1007/BF00353254>
- Dubrulle, L., Zammarano, M., Davis, R. D., 2020. Effect of Fire-Retardant Coatings and Accelerated-Weathering on the Flammability of Wood-Based Materials in Wildland-Urban Interface (WUI) Communities. *NIST Tech. Note*, 2094, 1-30.
- Elvira-León, J. C., Chimenos, J. M., Isábal, C., Monton, J., Formosa, J., Haurie, L., 2016. Epsomite as flame retardant treatment for wood: Preliminary study. *Construction and Building Materials*, 126, 936-942.
- Ermolin, V. N., 1999. Fundamentals of increasing the permeability of coniferous wood liquids: Monograph; Siberian State Technical University. Krasnoyarsk.
- Ermolin, V.N., Bayandin, M.A., Kazitsin, S.N., 2020. Water resistance of wood slabs obtained without the use of binders. *News of Higher Educational Institutions. Forest Magazine*, No. 3 (375), pp. 151-158. <https://doi.org/10.37482/0536-1036-2020-3-151-158>
- Ermolin, V.N., Bayandin, M.A., Kazitsin, S.N., Namyatov, A.V., 2019. Structure formation of low-density boards from hydrodynamically activated soft wood waste. *News of Higher Educational Institutions. Forest Magazine*, № 5 (371), pp. 148-157. <https://doi.org/10.17238/issn0536-1036.2019.5.148>
- Ermolin, V.N., Kazitsin, S.N., Bayandin, A.V., Namyatov, A.V., 2017. Developing the mode for hydro dynamic activation of wood particles for adhesive-free panels production. *Conifers of the Boreal Zone*, V. 35, No. 3-4, pp. 79-83.
- Ermolin, V.N.; Ermolina, A.V., 2015. Increasing the fire resistance of heat-insulating wood slabs. *Conifers of the Boreal Zone*, V. 33, No.1-2, pp. 82-86.

- Golubev, E., Dyageleva, A., Smirnova, A., 2020. Methods of modification of wood with the use of chemical means of protection. *Norwegian Journal of Development of the International Science*, No. 43-1, pp. 3-6.
- GOST 12.1.044 - 89 OSSS. Fire and explosion hazard of substances and materials. Nomenclature of indicators and methods of their determination (ISO 4589-84).
- GOST 17177-94. Materials and products of thermal insulation construction. Test methods. Interstate Scientific and Technical Commission for Standardization, 1994.
- GOST 20022.6-93 Interstate standard. Wood protection. Methods of impregnation. Introduction 1995-01-01. Minsk: Gosstandart of Russia, 1993.
- GOST R 53292–2009 Flame retardants and substances for wood and materials based on it. General requirements. Test methods. Moscow City, Publishing House of Standards, 2009, p. 18.
- Hagen, M., Hereid, J., Delichatsios, M. A., Zhang, J., Bakirtzis, D., 2009. Flammability assessment of fire-retarded Nordic Spruce wood using thermogravimetric analyses and cone calorimetry. *Fire Safety Journal*, 44 (8), 1053-1066.
- Hubbe, M.A.; Pizzi, A.; Zhang, H.; Halis, R., 2018. Critical Links Governing Performance of Self-Binding and Natural Binders for Hot-Pressed Reconstituted Lignocellulosic Board without Added Formaldehyde. A Review. *BioResources*, vol. 13, no. 1, pp. 2049–2115. <https://doi.org/10.15376/biores.13.1.Hubbe>
- Ibragimov, A. M., Vachnina, T. N., Susoeva, I. V., 2020. Use of Mineral Flame Retardants to Reduce the Combustibility of Thermal Insulating Board Composites from Plant Waste. In *IOP Conference Series: Earth and Environmental Science* (Vol. 459, No. 6, p. 062115). IOP Publishing.
- Khalturinskiy, N.A., Krupkin, V.G., 2011. On mechanism of fire retardant intumescent coating formation. *Fire and Explosion Safety*, 20(10), 33-36.
- Kolesnikov, G.N., Kantishev, A.V., Zaitseva, M.I. et al., 2019. Analysis of wood impregnation as a capillary-porous material. *Resources and Technology*, V. 16, No. 2, pp. 141-151. <https://doi.org/10.15393/j2.art.2019.4722>
- Krivosogov, A. S., et al., 2018. Theoretical substantiation of the process of fluid movement in capillary-porous media in the context of increasing the strength characteristics of the material. *Systems. Methods. Technologies*, No. 3, pp. 130-135. <https://doi.org/10.18324/2077-5415-2018-3-130-135>
- Kulakov, V.S, Krashennnikova, N.N, Sivenkov, A.B., 2021. Reduction of fire hazard of wooden building structures by the method of deep impregnation of wood with a fire and biological protection composition KSD-a (mark 1). *Fire and Explosion Safety*, V. 21, No. 3, pp. 31-38.
- Leonovich, A.A. 2003. Physico-chemical bases of the formation of wood slabs. Chemizdat, Saint-Petersburg, Russia, p. 192.
- Levan, S.L.; Winandy, J.E., 1990. Effect of fire-retardant treatments on wood strength: A review. *Wood and Fiber Science* 22 (1): 113-131.
- List of certified fire safety equipment. *Fire and Explosion Safety* 1998, No. 1, pp. 104-118.
- Maksimenko, S.A., Krivtsov, N.A., Maksimenko, N.A. et al. 2013. Fire hazard of new types of timber. *Fire Safety*, No. 2, pp. 74-77.
- Monteiro, S., Martins, J., Magalhães, F. D., Carvalho, L., 2019. Low density wood particleboards bonded with starch foam—study of production process conditions. *Materials*, 12 (12), 1975.
- Namyatov, M.A., Bayandin, S.N., Kazitsin, S.N., Ermolin, V.N., 2018. Investigation of the properties of boards, small density from mechano-activated wood chips without adhesives. Structure, properties and quality of wood: Materials of the VI International Symposium named after B.N. Ugolev, dedicated to the 50th anniversary of the Regional Coordinating Council on Modern Problems of Wood Science, Krasnoyarsk city, Russia, 10-16 September, 2018. Krasnoyarsk city, Publishing House of the Siberian Branch of the Russian Academy of Sciences, pp. 149-151.
- Özdemir, F., Tutuş, A., 2013. Effects of Fire Retardants on the Combustion Behavior of High-Density Fiberboard. *BioResources*, 8(2).

- Panev, N.M., 2018. Analysis of the use of flame retardant compositions for wood and development of methods for monitoring their availability. Dissertation for the degree of Technical Sciences Candidate, p. 148.
- Pham Van, T., Schöpfer, C., Klüppel, A., Mai, C., 2021. Effect of wood and panel density on the properties of lightweight strand boards. *Wood Material Science & Engineering*, 16(4), 237-245.
- Printseva M.Yu., Cheshko I.D., 2014. Thermal analysis and infrared spectroscopy of gaseous products of thermal destruction in the expert research of flame-retarded wood. *Fire Safety*, № 3, 96-101.
- Prokopenko, V.A., 2019. The effect of the depth of impregnation on the fire resistance of low-density wood slabs without binders. *Young scientists in solving urgent problems of science: A collection of materials of the All-Russian Scientific and Practical Conference of students, postgraduates and young scientists, Krasnoyarsk city, Russia, 25-26 April, 2019, Krasnoyarsk: Federal State Budgetary Educational Institution of Higher Education Siberian State University of Science and Technology named after Academician M.F. Reshetnev*, pp. 245-247.
- Sable, I., Grinfelds, U., Vikele, L., Rozenberga, L., Zeps, M., LUGUZA, S., 2015. Thermal insulation from hardwood residues. In *IOP Conference Series: Materials Science and Engineering* (Vol. 96, No. 1, p. 012027). IOP Publishing.
- Selamat, M. E., Hui, T. Y., Hashim, R., Sulaiman, O., Haafiz, M., Kassim, M., STALIN, N. J., 2018. Properties of Particleboard Made from Oil Palm Trunks Added Magnesium Oxide as Fire Retardant. *Journal of Physical Science*, 29 (1).
- Seo, H. J., Hwang, W., & Lee, M. C., 2017. Combustion Characteristics of Fire Retardants Treated Domestic Wood. *Journal of the Korean Society of Combustion*, 22(2), 9-18.
- Shamaev, V.A., Nikulina N.S., Medvedev I.N., 2013. *Wood Modification: Monograph*. Moscow, FLINTA Publ., 448 p.
- Sheloumov, A.V., 2017. (Saint-Petersburg). Technology of environmentally sound fire-proof wood boards using phosphorus- and aluminum-containing binders. Specialty 05.21.05 Wood science, technology and equipment of wood processing: abstract of the dissertation for the degree of Doctor of Technical Sciences, p. 22.
- Shvartsman, G.M. 1997. Production of chipboard [Text]: Tutorial / G.M. Shvartsman, D.A. Shchedro. - M.: Forest Industry, 320 p.
- Sinha, S., Jhalani, A., Ravi, M.R., Ray, A., 2000. Modelling of pyrolysis in wood: a review. *SESI Journal* 10(1): 41-62.
- Sivenkov, A.B., 2015. The influence of physico-chemical characteristics of wood on its fire hazard and fire protection efficiency. Specialty 02.00.06 High molecular compounds: abstract of the dissertation for the degree of Doctor of Technical Sciences, p. 22.
- Taavitsainen, V.-M.T., 2011. *Experimental Optimization and Response Surfaces*; IntechOpen: London, UK.
- Tang, W.K., 1967. Effect of Inorganic Salts on Pyrolysis of Wood Alpha Cellulose and Lignin Determined by Thermogravimetry, FPL 71, Madison Wisconsin; US Department of Agriculture, Madison, Wisconsin.
- Uner, I. H., Deveci, I., Baysal, E., Turkoglu, T., Toker, H., Peker, H., 2016. Thermal analysis of Oriental beech wood treated with some borates as fire retardants. *Maderas. Ciencia y tecnología*, 18(2), 293-304.
- Wang, F., Wang, Q., Wang, X., 2010. Progress in research on fire retardant-treated wood and wood-based composites: A Chinese perspective. *Forest Products Journal*, 60 (7-8), 668-678.
- Zhang, B., Yu, L., Zhang, Q., Li, D., Tu, Y., Xiao, G., Liang, J., 2022. Effects of fire retardants on mechanical properties and water resistance of pinusmassoniana particleboard. *Wood research*, 67(3), 411-422.

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