Influence of modifiers on coked foam structure and properties formed with thermal decomposition of wood

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Abstract. Wood is a material that forms a surface layer of coke when burning. Properties of the coke layer significantly impact the fire resistance of structures due to the change of the structure working section reduction rate. This paper discusses the research of how the wood surface layer modifiers influence the structure and properties of the coke layer formed with thermal decomposition of wood. As modifiers have been used phosphorus flame-retardants. To evaluate how the modifiers influence the coke layer formation process, the source and modified samples of pine have been analyzed before and after thermal decomposition using the element analysis, electron microscopy, and adsorption. Thermal analysis has been accomplished using the thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry. To evaluate the fire protection efficiency of the modified wood, fire tests have been accomplished. Such tests were tests to determine the magnitude of weight loss during combustion, flame spread index and the coefficient of smoke-ability. Based on the acquired data, it was identified that when the modifiers are used, and these modifiers enter into efficient superficial chemical reaction with wood under mild conditions, the thermal decomposition occurred under mild conditions - the first stage of thermal decomposition transits to the lower temperatures zone. This reduces the thermal effect of thermal decomposition reaction. There is a decrease in weight loss during thermal decomposition. This results in formation of the strong and structured, thermally stable surface, which is less adsorption ability, specific surface area and porosity reduction. This explains high rate of fire protection and low smoke-generating capacities.

1. Introduction

Wood is natural construction material. Nowadays wooden architecture is of great importance in Russia. Wood is easily accessible. Its processing and production of wooden construction materials are quite cost saving. An important feature of wood is environmental friendliness. Staying in buildings where wood was used as building structures or finishing materials is good for human health. It is possible to recycle waste from the production of wooden building materials [1, 2].

Native wood is very fire hazardous [3-6]. Stages of wood thermal decomposition have been studied in many investigations. In the low-temperature area, wood loses moisture, and a sample loses about 7% in weight. There is no carbonization of wood at this stage. We know that the first stage of wood thermal decomposition starts at a temperature of 300-320°C. A wood sample burns out by more than 60%, and wood surface is carbonized. At a temperature over 420°C, further burnup of the sample takes place. Weight loss in this area is 25%. The limit of fire resistance of wooden, in particular
vertical, structures is characterized by the time of reaching the limit cross section during burning. At that, material burns out layer by layer. Thermal decomposition of deeper wood layers occurs with partial decomposition and mechanical destruction of the outer layers. We know that the carbonized layer of wood features high porosity compared to wood before thermal decomposition; it is fragile, nevertheless such a layer can ensure resistance of the bottom layer to high temperatures. Increasing the wood surface layer resistance when exposed to flame is a factor of increasing the fire resistance limit [7-8].

One of the most effective ways of changing structure and properties of wood surface is surface adsorption-chemical modification. Wood modification occurs when we apply reactive solutions (10-30%) of organo-element compounds (phosphorus-, silicon-containing, boron-nitrogen ones) under normal conditions (t = 20-25°C, P = 1 atm) to the surface. Impregnation depth is 0.5-1 mm.

2. Materials and methods of research
The subject of the study is sapwood. 20% solutions of alkyl esters of phosphorus acids (DMF, DEF, DFF and ammonium polyphosphate APF-1 (n>1,000)) were used as modifiers [9, 11]. The compositions were applied on the surface under normal conditions in three layers with consumption of 300 g/m2.

To assess the effectiveness of the modifying effects of the selected compounds, we made an elemental analysis using Quanta 200 scanning microscope with Apollo 40 elemental analysis accessory using energy dispersive spectroscopy [12].

Influence of modifiers on thermal decomposition of wood was investigated by thermal analysis using Netzsch STA 409C device. This device allows obtaining data on thermogravimetry (TG), differential thermogravimetry (DTG) and differential-scanning calorimetry (DSC) [13, 14].

Analysis of the original wood carbonized layer surface and modified one after thermal decomposition was carried out by scanning electron microscopy [15, 16].

Studying properties of the porous structure of the original and modified wood layer was carried out by sorption of water vapor before thermal decomposition and by capillary adsorption of nitrogen after thermal decomposition [17-20].

3. Results
Figures 1-3 show data on thermal decomposition of the original wood (graph 1), as well as wood modified with DMF (graph 2), DEF (graph 3), DFF (graph 4), APF-1 (graph 5). Thermogravimetric (TG) graphs are shown in Figure 1. It shows dependence of the sample weight loss with a uniform increase in temperature (10°C/sec).
The data of differential thermogravimetry (DTG) given in Figure 2 show characteristic peaks of thermal decomposition. The data of differential-scanning calorimetry given in Figure 3 show thermal effects of thermal decomposition.

**Figure 2.** Differential thermogravimetry of the original and modified wood

**Figure 3.** Differential-scanning calorimetry of the original and modified wood

Figures 4-12 show the results of electron microscopy: images of the carbonized surface of the original and modified wood at magnification of 200 times and 10000 times, respectively.
**Figure 4.** Carbonized surface of the original wood at magnification of x200

**Figure 5.** Carbonized surface of the wood modified by DMF at magnification of x200

**Figure 6.** Carbonized surface of the wood modified by DEF at magnification of x200

**Figure 7.** Carbonized surface of the wood modified by DFF at magnification of x200

**Figure 8.** Carbonized surface of the wood modified by APF-1 at magnification of x200
These changes in the porous structure before and after thermal decomposition are shown in Figure 13 and in Table 1. Based on the test using the method of vapor sorption, we obtained data about specific surface area of the wood porous structure shown in Figure 13. In nitrogen adsorption test, we obtained distribution of pores in the surface carbonized layer of wood. The data obtained were summarized in Table 1, which shows the specific volume of pores of the carbonized layer of the original and modified wood, depending on the pore radius.

**Figure 13.** Specific surface area of the carbonized layer of native and modified wood
### Table 1. Surface carbonized layer pores distribution for native and modified wood

| Pore radius, Å | Original wood | DMF | DEF | DFF | APF-1 |
|---------------|--------------|-----|-----|-----|-------|
| 18.12–18.20  | 0.0161       | 0.0185 | 0.00706 | 0.00768 | 0.0177 |
| 21.36–21.49  | 0.0278       | 0.0339 | 0.0125 | 0.01309 | 0.0336 |
| 25.65–25.78  | 0.0375       | 0.0467 | 0.0157 | 0.0165 | 0.0471 |
| 31.57–31.84  | 0.0446       | 0.0582 | 0.0179 | 0.0186 | 0.0586 |
| 40.56–42.12  | 0.0478       | 0.0663 | 0.0184 | 0.0203 | 0.0686 |
| 56.21–59.07  | –            | 0.0717 | –     | –     | 0.0711 |
| 89.95–92.26  | –            | 0.0752 | –     | –     | –     |
| 1575         | –            | 0.0757 | –     | –     | –     |

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### 4. Discussion

The experimental data show that the first stage of thermal decomposition when wood is modified with phosphorus-containing modifiers is shifted to lower temperatures area (220-240°C), and intensity of thermal decomposition is significantly reduced in comparison with the original wood. The second stage of thermal decomposition with modification is shifted to higher temperatures area (510-530°C) compared to the original wood (450°C). The DSC graphs show that exothermic effects of the thermal decomposition reaction are significantly less for wood modified with phosphorus-containing compounds. At that, in case of using diethylphosphite as a modifier, thermal decomposition in the first stage occurs without pronounced exothermic peaks. In case of the original wood, as well as wood modified with the rest of modifiers, the first stage of thermal decomposition occurs with two exothermic peaks.

When analyzing images obtained with a 200 times magnification electron microscope, we can see that in case of using DMF modifier, a film is formed on the wood surface, probably from the modifier decomposition products, with open capillaries outlets. If we use DFF and APF-1 modifiers, structure of the carbonized layer is unstable. If we use DEF modifier, the fibrils are lined with the modifier, the carbonized layer structure is ordered. With magnification of 10,000 times, we can see the following: in case of using DMF, the pictures show the film mentioned above. If we use DFF and APF-1, particles of the modifier are found on the surface of the carbonized layer. If we use DEF, a pronounced strong carbonized structure is observed.

When evaluating properties of the wood porous structure before and after thermal decomposition, the largest pores are observed when DMF is used as a modifier. In case of using DEF, a structure with the smallest pores by volume and radius is formed in the carbonized layer. At that, the smallest specific surface area of the samples (Figure 7) is also characteristic for the carbonized layer of wood modified by DEF.

### 5. Conclusions

Based on the data obtained, we can make the following conclusion. It is obvious that characteristics of wood thermal decomposition may influence the surface carbonized layer structure. The shift of the first stage of thermal decomposition into the lower temperatures area has a key effect on the carbonized layer structure and fire resistance of wood. Carbonization of wood at lower temperatures in
case of using phosphorus-containing modifiers ensures that this process proceeds without significant damage to the original structure of wood. At that, if we use DEF, we have "soft” thermal decomposition: this process goes without significant exothermic effects, and the resulting carbonized layer has a stronger structure. Strength of the carbonized layer in this case is confirmed by the smallest pore size and even surface structure.

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