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COMBUSTION, EXPLOSION,  
AND SHOCK WAVES

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# The Mechanism of Action and the Synergistic Effect of Nitrogen- and Phosphorus-Containing Fire Retardants in Fire Protection and Wood and Peat Fire Suppression

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**Abstract**—The factors exerting a significant influence on the termination of the combustion of natural materials (wood and peat) were studied with the use of synthetic nitrogen- and phosphorus-containing fire retardants with different efficiencies. With the use of a mathematical experimental design method, it was confirmed that the inhibition of gas-phase radical processes by volatile nitrogen-containing products is the predominant process of combustion suppression. It was found that the synergism of the nitrogen–phosphorus flame retardants is determined by their complex action: phosphorus mainly enters into organomineral structures in a the condensed phase, and nitrogen inhibits reactions in a gas phase.

**Keywords:** flame retardants, fire retardant efficiency, fire protection mechanism, natural combustible materials, wood, peat, mathematical design of experiments

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The combustion of natural combustible materials (wood and peat) occurs in the diffusion mode [1] with the following basic mechanisms of burn termination [2]: the isolation of combustible mixture components from atmospheric oxygen; a decrease in the inflow rate of volatile combustible decomposition products into the flame zone; and the cooling of the combustion zone as a result of the inhibition of radical processes in a gas phase. After burn termination in the gas phase, the continuation of smoldering combustion processes in surface layers [3], which can change to flame combustion, is typical of solid fuel materials.

In the literature, there is no information on the processes that make a prevailing contribution to the inhibition of the combustion of natural fuels, and the mechanism of the synergistic and inhibiting action of nitrogen- and phosphorus-containing fire retardants is unclear. According to the most conventional point of view [4, 5], the fire-extinguishing action of chemical substances in cellulose materials is based on the mechanism of dehydration catalysis caused by cellulose decomposition predominantly a carbonized residue and water. As a result of this, the yield of volatile combustible products decreased and the formation of a coke cap insulates the lower layers of wood from a heat flow and changes the conditions heat and of mass transfer between the flame zone and the condensed phase. However, reliable data on a correlation between the efficiency of fireproofing compounds and the

amount of coke formed are absent from the literature, and the influence of the inhibition of gas-phase chain processes on the flame failure of cellulose materials was considered only in a few publications. The mechanism of the inhibition of peat combustion with the aid of chemical agents was not described in the literature.

It is possible to determine which of the various processes that occur in condensed and gas phases exert a predominant effect on the flame failure of combustible solid materials with the availability of comparative data on the efficiency of fire-retardant systems and the qualitative and quantitative composition of products, which become distributed between these phases on the thermal decomposition and combustion of fuels in the presence of fireproofing compounds with different efficiencies. We synthesized readily available nitrogen- and phosphorus-containing fire retardants—the phosphates of bivalent and trivalent metals and ammonium (MAPs), which are convenient models for determining the reason for their different fire-retardant efficiency. This is caused by a wide range of the physicochemical and thermal properties of MAPs, which depend on the conditions of their synthesis, the nature of the metal-containing and neutralizing agents, and a ratio between them [6, 7].

In order to determine factors that make a predominant contribution to the inhibition of wood and peat combustion and are responsible for the synergistic

**Table 1.** Chemical composition and fire retarding properties of FEAs with respect to wood and peat

FEA no.	Weight ratios between the main components: Al <sub>2</sub> O <sub>3</sub> : ZnO : MgO : CaO : P <sub>2</sub> O <sub>5</sub> : B <sub>2</sub> O <sub>3</sub> : SiO <sub>2</sub> : NH <sub>3</sub> : K <sub>2</sub> O : SO <sub>3</sub> : HCl	Fire-retardant efficiency with respect to wood $\Delta m$ , %	Fire-retardant efficiency with respect to peat $\Delta m$ , %	Complex fire-retardant and fire-extinguishing efficiency $\Sigma\Delta m$ , %
1	1 : 2.4 : 0 : 0 : 17.3 : 0 : 1 : 3.9 : 0 : 0 : 0	8.6	5.8	14.4
2	1 : 2.4 : 0 : 0 : 30.3 : 0.41 : 1 : 8.9 : 0 : 0 : 0	10.0	5.1	15.0
3	0.3 : 0 : 0 : 0.7 : 14.8 : 0 : 1 : 7.0 : 4.5 : 0 : 2.5	4.2	1.8	6.0
4	0.2 : 0 : 0 : 0 : 8 : 0 : 1 : 2.5 : 5.6 : 5.9 : 0	18.8	2.9	21.7
5	0.2 : 0 : 0.5 : 0 : 11.8 : 0 : 1 : 4.5 : 3.5 : 0 : 2.5	8.7	1.1	9.8

Weight losses in the initial wood and peat samples, 39.1 and 46.6%, respectively.

action of the nitrogen- and phosphorus-containing fire retardants, we studied the physicochemical properties of MAPs and the flame resistance and thermally stimulated transformations of wood and peat fireproofed by compounds of different efficiencies with the simultaneous determination of the residual nitrogen and phosphorus contents of the solid heat-treatment products. The fireproofing and fire extinguishing of wood and peat were carried out with the synthetic dispersions of ammonium metal phosphates, which were obtained at different ratios between the components of the total cationic and anionic composition:  $[\text{NH}_4^+]$ ,  $[\text{Me}^{2+}/\text{Me}^{3+}]$ , and  $[\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-/\text{PO}_4^{3-}]$ .

## EXPERIMENTAL

The fire-retarding properties of the synthesized products with respect to wood and peat were determined in accordance with *GOST* [State Standard] 16363 and based on weight loss upon the combustion of fireproofed peat samples, respectively [8]. The height of foam layers formed upon the heating of fire-extinguishing agents (FEAs) to temperatures of 300–350°C in a fixed time interval was taken as the heat-insulating ability of these agents. The shielding properties of FEAs at the same temperatures were determined according to *GOST R50045* [9]; FEA-1 was used as a reference composition (Table 1). The temperature range was chosen in accordance with data on temperatures in the preflame zone of a condensed phase at the first stage of the thermal decomposition of natural combustible materials.

In the course of the calorimetric studies of the initial synthesized products, sawdust, and peat and also the above materials fireproofed with the same amounts of each of the test FEAs performed by differential scanning calorimetry (DSC) with the use of a Netzsch STA 449C instrument (10°C/min; air), we determined the total endo or exo heat effects ( $\Sigma Q_{\text{endo}}$  and  $\Sigma Q_{\text{exo}}$ , J/g) in a temperature range of 20–600°C. The calculation was performed with the aid of applica-

tion software based on the areas of complex peaks due to effects in the processing of the DSC curves. The amounts of nitrogen and phosphorus in the unheated samples of the above fireproofed materials and in the solid products of their heat treatment were determined by microchromium and spectrophotometric methods, respectively [10, 11]. The release of volatile nitrogen- and phosphorus-containing compounds into the gas phase on the combustion and thermal decomposition of fireproofed wood and peat in a temperature range of 200–500°C was evaluated by difference between the concentrations of these elements in the unheated and heat-treated samples. In data processing, the conversion of the concentrations of nitrogen and phosphorus was carried out with consideration for the weight losses of analyzed samples upon heating. For obtaining comparative data, we converted the concentrations of the test elements per unit weight of an analyzed sample.

## RESULTS AND DISCUSSION

The test FEAs were suspensions with a dispersed phase of the amorphous phosphates of bivalent and/or trivalent metals and ammonium and silica distributed in a solution component, which contained ammonium and/or potassium phosphates and/or chlorides (sulfates) depending on the starting reagents used. Furthermore, the presence of nanosized particles, supposedly, the hydrolysis products of metal- and silicon-containing constituents of the dispersed phase, in the solution component was detected. Tables 1 and 2 summarize the weight ratios between the main components and the fire-retarding, physicochemical, and thermal properties of the synthesized FEAs.

FEA-3 and FEA-5 exhibited the highest fire-retarding efficiency; in this case, FEA-3 and FEA-5 were the most efficient agents for wood and peat, respectively (Table 1). Based on a comparison of the physicochemical and thermal properties of individual FEAs and wood samples treated with them (Table 2), we assume that the high efficiency of FEA-3 can be caused, on the one hand, by the low heat emission of

**Table 2.** Physicochemical and thermal properties of FEAs and fireproofed wood and peat

FEA no.	Height of solid FEA foam, mm	Flowability of molten FEA	Total endo heat effects in the DSC of FEAs, $\Sigma Q_{\text{endo}}$ , J/g	Total exo heat effects in the DSC of flame-retarded materials, $\Sigma Q_{\text{exo}}$ , J/g		Total losses* of nitrogen and phosphorus in flame-retarded materials (content in an unheated sample), g			
						wood		peat	
				wood	peat	N	P	N	P
With no FEA	–	–	–	7429	–	1.98	–	–	–
With no FEA	–	–	–	–	9951	–	–	2.52	0.83
1	2.5	1.0	168	3017	–	16.42 (8.53)	2.95 (13.5)	–	–
2	1.3	1.25	189	–	5773	–	–	19.4 (8.1)	2.9 (14.7)
3	2.0	1.3	416	1596	6327	17.8 (8.04)	3.1 (10.4)	5.27 (5.03)	1.06 (5.24)
4	4.1	0.91	418	3526	3477	8.8 (4.13)	0.23 (6.25)	4.5 (4.98)	0.25 (4.06)
5	4.0	1.03	345	2769	3541	6.95 (4.34)	1.83 (8.75)	7.29 (5.5)	3.7 (4.7)

\* Data are given in terms of a 100-g sample.

the fireproofed wood (1596 J/g), which was likely due to the screening effect of the resulting low-viscosity fusion and foamed heat-insulating structure. On the other hand, the most significant release of volatile nitrogen- and phosphorus-containing inhibitors of combustion into the gas phase FEA-3, as compared with the other FEAs, should be noted.

FEA-5 exhibited a higher fire-extinguishing efficiency for peat. According to the data of Table 2, FEA-5 manifested a high framework-forming ability and a significant decrease in heat emission on the thermal decomposition of peat in the presence of this fireproofing compound. At the same time, the same properties are inherent to FEA-4; however, its efficiency as applied to peat was much lower, and this is consistent with the low quantitative release of volatile nitrogen-containing products into the gas phase. In the case of FEA-2, the release of a large amount of volatile inhibitors of combustion into the gas phase without a considerable decrease in heat emission in the condensed phase did not lead to an increase in the fire-retarding efficiency.

It is important that, regardless of the nature of a polymer and the fire-retardant and fire-extinguishing efficiencies of the test combustion inhibitors, a considerable difference in the total quantitative release of volatile nitrogen- and phosphorus-containing products into the gas phase was observed: the amount of volatile nitrogen-containing products formed upon the thermolysis of fireproofed samples in a temperature range of 200–500°C was greater than that of phosphorus-containing products by a factor of 5 to 10 (Table 2). This fact is indicative of different mechanisms of the fire-retarding action of nitrogen and

phosphorus. From the comparative experimental data, it follows that, for the inhibition of the combustion of natural fuels, it is important to affect the processes that occur both in the preflame zone of a condensed phase and in the gas phase. In this case, it is problematic to unambiguously assert which of the tested factors is predominant.

In order to obtain additional information on the role of factors that make a predominant contribution to the inhibition of the combustion of natural polymer materials (wood and peat), we constructed mathematical models for adequately describing the fire-retardant and fire-extinguishing efficiency characteristics of the synthesized products with the use of a mathematical apparatus for optimum experimental design [12–15]. To determine the adequacy of the obtained mathematical models of observations, we applied the criterion of adequacy of the models to repeated observations at each full factorial experiment (FFE) point [13]:

$$\frac{(N - n)(m \bar{Y} \bar{Y} - N \|\hat{\theta}\|^2)}{(n - p)(Y Y - m \bar{Y} \bar{Y})} \leq F_{\alpha; n-p, N-n} \quad (1)$$

where  $n$  is the number of different points in the FFE,  $m$  is the number of repeated observations at each point of FFE,  $p$  is the number of unknown model parameters,  $\bar{Y}$  is the vector of the mean observed values at each point of the spectrum of FFE,  $F_{\alpha; n-p, N-n}$  is the quantile of the significance level  $\alpha$  of Fischer's distribution with  $n - p$ ,  $N - n$  degrees of freedom. In case of the implementation of inequality (1), the model was recognized adequate to the obtained observations at the level of significance  $\alpha$ .

The significance of coefficients in the mathematical models was determined with the use of Student's test [13]. The coefficient  $\theta_j$  is significant if

$$\frac{|\hat{\theta}_j|}{s\sqrt{c_{jj}^{1/2}}} > t_{\alpha, N-p}, \quad (2)$$

where  $t_{\alpha, N-p}$  is the quantile of the level  $\alpha$  of Student's distribution with  $N-p$  degrees of freedom,  $c_{jj}$  is the  $j$ th diagonal element of the inverse matrix  $(X'X)^{-1}$ , and  $s^2$  is the unbiased estimate of the variance of equally accurate observations. For FFE,  $c_{jj} = 1/N$ , the value of  $sc_{jj}^{1/2}$ , is calculated by the appropriate Excel statistical function, and  $t_{\alpha, N-p}$  is the quantile of the level  $\alpha$  of Student's distribution with  $N-p$  degrees of freedom.

The synthetic dispersion of the ammonium-containing phosphates of bivalent and trivalent metals (FEA-3), in which a natural metal silicate was used as a starting reagent, was chosen as a test material that possesses complex fire-resistant capability (the fire extinguishing of peat and the fire protection of wood). Previously, it was found that the formation of foamed structures was observed in the course of the thermolysis of flame-retarded wood and peat at the temperatures of the preflame zone of a condensed phase (200–500°C) due to the presence of a metal silicate. These foamed structures impede the further pyrolysis of combustible solid materials and simultaneously hamper the release of volatile combustible products into the gas phase. Therefore, varied factors such as the phosphorus content of the FEA formula (factor  $x_1$ ), the metal silicate content (factor  $x_2$ ), and the nitrogen content (factor  $x_3$ ) were chosen as the basic components capable of substantially influencing the fire-resistant properties of FEAs for wood and peat. The numerical values of these components (in g/100 g FEAs) for the best FEA in terms of efficiency were the following:  $x_1^{(0)} = 6.09$ ,  $x_2^{(0)} = 2.8$ , and  $x_3^{(0)} = 6.09$ . The fire-extinguishing efficiency with respect to peat ( $y_{\text{peat}}$ ) and the fire-retarding efficiency with respect to wood ( $y_{\text{wood}}$ ) were chosen as response functions to characterize the effectiveness of the application of fire-retardant and fire-extinguishing means. In the course of two experiments at these parameters, the following results on the fire-extinguishing efficiency with respect to peat were obtained:  $y_1 = 2.2\%$  and  $y_2 = 1.45\%$  (the average value  $\bar{y}_{\text{peat}}^{(0)} = 1.825\%$ ). The fire-retardant efficiency with respect to wood was the following:  $y_1 = 4.284\%$ ,  $y_2 = 4.541\%$ ,  $y_3 = 4.247\%$ , and  $y_4 = 3.808\%$  (the average value  $\bar{y}_{\text{wood}}^{(0)} = 4.22\%$ ).

Because peat and wood are combustible solid materials of different nature, and it is very difficult to experimentally find a combination of the values of influencing factors at which the extremums of both of the response functions of interest are reached simulta-

neously, we used the following approach to improve the fire-retardant and fire-extinguishing properties of FEAs simultaneously with respect to peat and wood: Initially, we constructed an adequate mathematical model to describe the influence of the selected factors on the fire-extinguishing effectiveness of FEAs with respect to peat. Then, this response function was minimized according to the Box–Wilson method [13, 14] with the simultaneous condition of an increase in the fire-retardant efficiency of FEAs with respect to wood.

For determining the influence of the chemical composition of FEAs on the fire-extinguishing efficiency with respect to peat, the test FEA-3 was chosen as the center of the type  $2^3$  FFE plan. As a phenomenological model of the fire-extinguishing efficiency of FEAs with respect to peat, we decided on the following regression model with pairwise interaction coefficients:

$$E\{y\} = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3, \quad (3)$$

where  $E\{y\}$  is the average expected value of the fire-extinguishing efficiency  $y$ .

In the coded variables  $X_i$  with a given 10% variation interval of  $x_i^{(0)}$ , regression equation (3) takes the form

$$E\{y\} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3. \quad (4)$$

For estimating the unknown parameters of models (4) in accordance with the FFE, in each of the eight corners of a cube in coded variables  $X^{(1)} = (-1, -1, -1)$ ,  $X^{(2)} = (-1, -1, 1)$ ,  $X^{(3)} = (-1, 1, -1)$ ,  $X^{(4)} = (-1, 1, 1)$ ,  $X^{(5)} = (1, -1, -1)$ ,  $X^{(6)} = (1, -1, 1)$ ,  $X^{(7)} = (1, 1, -1)$ , and  $X^{(8)} = (1, 1, 1)$ , we performed double observations, the results of which are given in Table 3.

In a matrix form, the model of observations (4) can be written as

$$E\{Y\} = X\theta, \quad (5)$$

where  $Y$  is the observation vector of dimension 16,  $X$  is the experiment planning matrix of dimension  $16 \times 7$ , and  $\theta$  is the vector of unknown parameters of dimension 7. Because the experiments were conducted in accordance with the FFE, in this case, the experiment planning matrix  $X$  is a matrix with mutually orthogonal columns; then, the effect of the multicollinearity of factors does not appear and the best linear unbiased estimator [13] is

$$\hat{\theta} = X'YN^{-1}, \quad (6)$$

where  $X'$  is the transposed matrix  $X$ , and  $N$  is the total number of experiments.

**Table 3.** Plan of the  $2^3$  full factorial experiment and the results of experiments on the optimization of FEA formulations for peat

Experiment no.	Factors in a natural scale			Factors in coded variables			Response function $y_{\text{peat}}$ , %
	$x_1$	$x_2$	$x_3$	$X_1$	$X_2$	$X_3$	
1	5.48	2.52	5.48	-1	-1	-1	$y_{11} = 3.62; y_{12} = 3.98; y_{13} = 3.80$
2	5.48	2.52	6.7	-1	-1	1	$y_{21} = 2.71; y_{22} = 3.06; y_{23} = 2.89$
3	5.48	3.08	5.48	-1	1	-1	$y_{31} = 2.68; y_{32} = 3.13; y_{33} = 3.10$
4	5.48	3.08	6.7	-1	1	1	$y_{41} = 1.35; y_{42} = 1.17; y_{43} = 1.18$
5	6.7	2.52	5.48	1	-1	-1	$y_{51} = 3.51; y_{52} = 2.61; y_{53} = 2.80$
6	6.7	2.52	6.7	1	-1	1	$y_{61} = 2.51; y_{62} = 2.37; y_{63} = 2.48$
7	6.7	3.08	5.48	1	1	-1	$y_{71} = 1.64; y_{72} = 1.91; y_{73} = 1.70$
8	6.7	3.08	6.7	1	1	1	$y_{81} = 1.06; y_{82} = 0.83; y_{83} = 0.94$

Using the statistical functions of Excel spreadsheets, we obtained the estimates of the parameters of model (4):

$$E\{y\} = 2.3838 - 0.3288X_1 - 0.663X_2 - 0.501X_3 - 0.033X_1X_2 + 0.1388X_1X_3 - 0.118X_2X_3. \quad (7)$$

In the determination of the adequacy of the obtained model observations (7) after the verification of the significance of its coefficients, we found that the model is adequate at the level of significance  $\alpha = 0.05$ , and the coefficients at  $X_{12}$ ,  $X_{13}$ , and  $X_{23}$  are insignificant at a level of 0.05. If they are not taken into account, model (7) becomes very simplified, and it poorly describes the real phenomenological effect of fire-extinguishing efficiency due to a small number of experiments ( $N = 16$ ), which does not allow us to estimate all of the seven significant coefficients of model (7). Therefore, to obtain more information in the estimation of unknown parameters at each point of the FFE spectrum, we carried out additional experiments to obtain data for  $y_{13}$ – $y_{83}$  (Table 3).

After the re-evaluation of the coefficients of model (7), the determination of the adequacy of a new model at the significance level  $\alpha = 0.05$ , and the removal of an insignificant coefficient at  $X_{12}$ , we obtained the following adequate model of observations with all relevant coefficients:

$$E\{y\} = 2.3763 - 0.3463X_1 - 0.6521X_2 - 0.4971X_3 + 0.1654X_1X_3 - 0.1388X_2X_3. \quad (8)$$

Upon going to natural variables, model (8) appears in the form

$$E\{y\} = 19.95178 - 3.27493x_1 - 4.60345x_2 - 7.31x_3 + 0.4455x_1x_3 - 0.81235x_2x_3. \quad (9)$$

Model (9) describes the phenomenological effect of a change in the average expected value of the efficiency of fire-extinguishing means with respect to peat

under changes in the formula of the initial fire-retardant and fire-extinguishing composition in the neighborhood of a point with the values  $x_1^{(0)} = 6.09$ ,  $x_2^{(0)} = 2.8$ , and  $x_3^{(0)} = 6.09$ .

Models (8) or (9) were used to increase the fire-protective and fire-extinguishing efficiency of the original FEA-3 with respect to both peat and wood by the Box–Wilson gradient descent method [13]. According to the condition, the smaller  $E\{y\}$ , the higher the fire-protective and fire-extinguishing efficiency of FEAs. To formulate a new FEA composition, which is more efficient simultaneously to the two combustible test materials, we assumed that the anti-gradient of function (8) at the FFE center is the three-dimensional vector  $g = (0.3463, 0.6521, 0.4971)$  and made a transition from the plan center to a new point ( $X^{(i)} = \alpha_i g$  at  $i = 1, 2, 3, \dots$ , where  $\alpha_i > 0$  is the step motion parameter) in the direction of vector  $g$ .

In the chosen direction of  $g$ , sequential motion was performed with the steps  $\alpha_1 = 0.2$  and then  $\alpha_2 = 0.4$  with a transition to the first point with the coordinates  $X_1^{(1)} = 0.0693$ ,  $X_2^{(1)} = 0.1304$ , and  $X_3^{(1)} = 0.0994$  (in natural variables,  $x_1^{(1)} = 6.13$ ,  $x_2^{(1)} = 2.84$ , and  $x_3^{(1)} = 6.15$ ) and then to a point with the coordinates  $X_1^{(2)} = 0.1385$ ,  $X_2^{(2)} = 0.2608$ , and  $X_3^{(2)} = 0.1988$  (in natural variables,  $x_1^{(2)} = 6.17$ ,  $x_2^{(2)} = 2.87$ , and  $x_3^{(2)} = 6.21$ ). For each of the two new FEA formulas, which correspond to coordinates in natural variables, we carried out five experiments for the determination of the fire-retardant and fire-extinguishing efficiency with respect to peat and wood. Table 4 summarizes the results of the experiments and the average values of the vectors  $y_{\text{peat}}$  and  $y_{\text{wood}}$ .

Every time we went to a new formula, we observed a simultaneous improvement in the fire-retardant and

**Table 4.** Values of the vectors of observations (fire-retardant and fire-extinguishing efficiency of FEAs) on going from the FFE plan center in the direction of the vector  $g$  with the step  $\alpha$ 

$\alpha$	Factors in natural variables			Values of the vectors of observations	
	$x_1$	$x_2$	$x_3$	$y_{\text{peat}}, \%$	$y_{\text{wood}}, \%$
0.2	6.13	2.84	6.15	$y_{\text{peat}}^{(1)} = (0.78; 1.55; 0.78; 1.15; 0.85);$ $\bar{y}_{\text{peat}}^{(1)} = 1.02$	$y_{\text{wood}}^{(1)} = (3.09; 3.85; 3.75; 2.5; 5.84);$ $\bar{y}_{\text{wood}}^{(1)} = 3.81$
0.4	6.17	2.87	6.21	$y_{\text{peat}}^{(2)} = (0.40; 0.41; 0.01; 0.31; 0.04);$ $\bar{y}_{\text{peat}}^{(2)} = 0.23$	$y_{\text{wood}}^{(2)} = (2.55; 2.52; 2.25; 3.07; 3.87);$ $\bar{y}_{\text{wood}}^{(2)} = 2.85$
0.6	6.22	2.91	6.27	$y_{\text{peat}}^{(3)} = (3.37; 1.53; 2.89; 2.22; 1.83);$ $\bar{y}_{\text{peat}}^{(3)} = 2.37$	$y_{\text{wood}}^{(3)} = (5.41; 5.92; 4.61; 4.27; 4.67);$ $\bar{y}_{\text{wood}}^{(3)} = 4.97$

fire-extinguishing properties of FEAs with respect to both peat and wood. Because further motion in the selected direction of  $g$  at  $\alpha_3 = 0.6$  led to a FEA composition whose fire tests showed lower results in terms of fire-extinguishing and fire-retardant efficiency with respect to the test materials (Table 4), the previous FEA formula with the parameters  $x_1^{(2)} = 6.17$ ,  $x_2^{(2)} = 2.87$ , and  $x_3^{(2)} = 6.21$  was adopted as the improved formulation. The ratios between the main components of the optimized FEA formula (wt %) are the following:  $\text{Al}_2\text{O}_3 : \text{CaO} : \text{P}_2\text{O}_5 : \text{SiO}_2 : \text{NH}_3 : \text{K}_2\text{O} : \text{HCl} = 0.33 : 0.8 : 15.1 : 1 : 7.3 : 4.5 : 2.5$ . The application of a mathematical experimental design procedure made it possible to optimize the FEA formula and to increase the retardant and fire-extinguishing efficiency simultaneously with respect to peat and wood, as compared with that of the initial formula.

Based on adequate model (9), we made conclusions on the effects of the chosen factors  $x_1$ ,  $x_2$ , and  $x_3$  on the fire-retardant and fire-extinguishing efficiency with respect to peat and wood. The coefficients at  $x_1$ ,  $x_2$ , and  $x_3$  determine the levels of these factors in terms of the fire-retardant and fire-extinguishing efficiency of FEAs. The absolute values of the coefficients of regression (9) indicate that the nitrogen content of the formulation ( $x_3$ ) exerts the greatest effect on the fire-retardant and fire-extinguishing efficiency of FEAs. This circumstance was also confirmed by the fact that nitrogen additionally enters into pairwise interactions with phosphorus ( $x_1$ ) and a metal silicate component ( $x_2$ ) in the obtained model. This fact confirms our previous experimental data [16] that ammonium-containing metal phosphate fire-retardant systems manifest a complex mechanism of fire-extinguishing action to slow down the thermolysis reactions of materials in a condensed phase and to simultaneously inhibit combustion processes in a gas phase. In this case, the volatile nitrogen-containing products of the thermolysis of FEAs play a predominant role in their fire-retardant

action; this correlates with the experimental data on the quantitative release of volatile nitrogen compounds into the gas phase [16–18].

## CONCLUSIONS

Recognizing that polymer compounds are complex systems characterized by supramolecular structure, moisture content, deviation from average chemical composition, and the presence of impurities and additives, we can state that the kinetics and the detailed mechanism of combustion and inhibition of these materials are still unclear [4, 19]. In this work, we confirmed and detailed the mechanism of the fire-retardant and fire-extinguishing action of synthetic inorganic nitrogen- and phosphorus-containing fireproofing compounds with the use of a mathematical experimental design method for the selection of a formula of the most effective fire retardant for wood and peat. We found that the inhibition of radical processes by volatile nitrogen-containing products in a gas phase is the prevailing process as applied to the termination of the combustion of natural fuels. We demonstrated that the synergism of nitrogen- and phosphorus-containing fire retardant agents is determined by their complex action: phosphorus mainly facilitates the formation of heat-insulating organomineral structures in a condensed phase, and nitrogen inhibits reactions in a gas phase.

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