STUDY OF THE FIRE RETARDING MECHANISM OF NITROGEN AND PHOSPHORUS CONTAINING INHIBITORS IN NATURAL COMBUSTIBLE MATERIALS

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1 Introduction

From an economic point of view, nitrogen and phosphorus containing flame retardants (FR) are the most perspective fire extinguishing agents for natural combustible materials (wood, peat). Due to the fact that the specificity of burning of solid combustible materials (SCM) in the presence of FR consists in occurrence of several concurrent transformations of the combustible material, flame retardant, products of their decomposition interacting both in the condensed and gas phases, up to the present time, there is no information in literature about the mechanism of the synergistic inhibitory action of nitrogen–phosphorus FR. This, in turn, impedes directed development of extinguishing agents and SCM fire suppressants meeting the contemporary requirements.

To understand why the developed flame retardants exhibit different flame protective properties, the present authors have previously investigated evolution of volatile flame retardants (nitrogen and phosphorus) into the gaseous phase and properties of the preflame zone formed in the condensed phase melts and foam protective structures [1–4].

In order to obtain more information about the role of the factors that introduce the dominant contribution to inhibition of burning natural polymeric combustible materials (wood, peat), the mathematical models that adequately describe the FR and fire-extinguishing efficiency have been developed using the mathematical apparatus of optimal experiment planning [5–8].

2 Experimental Technique

Fire extinguishing efficiency of FR with respect to peat was determined by the method, described in [9], according to which the relative weight loss of a peat sample (in %) after firing tests was measured. The fire retardant efficiency with respect to wood was assessed, following the State Standard 16363, by weight loss (in %) by a fire protected wood sample displaced in a "ceramic pipe" over a gas burner flame. Flame retardant composition (FRC) is considered to be efficient when $\Delta m \leq 25\%$. To assess the adequacy of the obtained observations to mathematical models, the criterion of adequacy of the models was applied to repeated observations at each full factorial experiment (FFE) point [8]:

$$\frac{(N-n)\left(m\overline{Y}'\overline{Y} - N\|\hat{\theta}\|^2\right)}{(n-p)\left(Y'Y - m\overline{Y}'\overline{Y}\right)} \leq F_{\alpha;n-p,N-n} \tag{1}$$

where n is the the number of different points in the FFE; m is the the number of repeated observations at each point of FFE; p is the the number of unknown model parameters; $\overline{Y}$ is the vector of the mean observed values at each point in the spectrum of FFE; and $F_{\alpha;n-p,N-n}$ is the quantile of significance level α of Fischer distribution with $n-p$, $N-n$ being the degrees of freedom. In case of implementation of inequality (1), the model was deemed adequate to obtained observations at the level of significance α. Significance of coefficients in the mathematical models was determined with the use of Student's t criterion [8]. Coefficient θ_j is a significant factor if

$$\frac{\left|\hat{\theta}_j\right|}{s\sqrt{c_{jj}}} > t_{\alpha,N-p}$$

where $t_{\alpha,N-p}$ is the quantile of the level α of Student distribution with $N-p$ degrees of freedom; c_{jj} is the jth 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 $s\sqrt{c_{jj}}$, counts on the appropriate aggregate function Excel; and $t_{\alpha,N-p}$ is the quantile of the α level of Student distribution with $N-p$ degrees of freedom.

3 Results and Discussion

The synthetic dispersion of ammonium-metalphosphate (bi- and trivalent metals) which has a complex fire-retarding effect (peat fire-extinguishing and wood fire-protection) was selected as an object of research. Natural metallosilicate (bentonite) was used as one of the synthesis starting reagents [10]. Previously, it was found that during thermolysis of fire-retarded wood and peat at temperatures realized in the preflame zone of condensed phase (200–500 °C), formation of foam structures preventing further SCM pyrolysis and evolution of volatile combustible products into the gas phase were observed. Therefore, such variable factors as the contents of phosphorus (factor x_1), bentonite (factor x_2), and nitrogen (factor x_3) in the formulation of FRC were selected as the main components that can significantly affect the fire-retarding properties of extinguishing and flame retardant compositions for wood and peat. Numerical values of these components (g/100 g) for the best FRC efficiency are as follows: $x_1^{(0)} = 6.09$, $x_2^{(0)} = 2.8$, and $x_3^{(0)} = 6.09$. The efficiency of peat extinguishing (v_{peat}) and the efficiency of wood fire-protecting (v_{wood}) were selected as response functions that characterize the effectiveness of fire-resistant, fire-extinguishing means for peat and wood burnout (FRC).

In fire tests, averaged data on extinguishing and fire-protecting properties of FRC were obtained: $\overline{y}^{(0)}_{\text{peat}} = 1.825\%$ and $\overline{y}^{(0)}_{\text{wood}} = 4.22\%$. In order to determine the influence of the FRC chemical composition on its fire-extinguishing efficiency with respect to peat, the FRC analyzed was chosen as the center of the type 2^3 FFE plan. As a phenomenological model of the FRC fire-extinguishing efficiency with respect to peat, the regression model with pairwise interaction coefficients was chosen:

$$E\{y\} = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 \qquad (2)$$

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

In the coded variables X_i with given variation interval of $x_i^{(0)}$, equal to 10%, the regression equation (2) takes the form:

$$E\{y\} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3\,. \qquad (3)$$

In order to estimate the unknown parameters of the model (3) 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 $X^{(8)} = (1,1,1)$ double observations have been performed, results are presented in Table 1.

In the matrix form, the model of observation (3) can be written as

$$E\{Y\} = X\theta$$

where Y is the observations vector of dimension 16; X is the experiment planning matrix of dimension 16×7; and θ is the vector of unknown parameters of dimension 7.

Since the experiments were conducted in accordance with the FFE, the experiment planning matrix X is a matrix with mutually orthogonal columns; in this case, the effect of multicollinearity factors vanishes and the best linear unbiased estimator [8] is equal to

$$\hat{\theta} = X'YN^{-1}$$

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

Table 1 Plan 2^3 FFE and the results of experiments to optimize FRC formulations for peat

No. of experiment	Factors in the natural scale			Factors in the coded variables			Response function, y_{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, the estimates of the parameters of the model (3) were obtained:

$$E\{y\} = 2.3838 - 0.3288X_1 - 0.663X_2 - 0.501X_3 - 0.033X_1X_2 + 0.1388X_1X_3 - 0.118X_2X_3\,. \quad (4)$$

In determining the adequacy of the observation model obtained (4), after verification of the significance of its coefficients, it has been established that the model is adequate on the level of significance $\alpha = 0.05$ and the coefficients X_{12}, X_{13}, and X_{23} are not significant at the 0.05 level. If they are not taken into account, the model (4) will be very simplified and poorly describe the real phenomenological effect of extinguishing efficiency due to a small number of experiments ($N = 16$), which does not allow all the seven significant coefficients of model (4) to be evaluated. Therefore, to get more information for estimating the unknown parameters, at each range of FFE, another additional experiment has been conducted and data for y_{13}–y_{83} obtained (see Table 1). After revaluation of model (4) coefficients, determining the new model adequacy at a significance level $\alpha = 0.05$, and removing the insignificant coefficient of X_{12}, the adequate observation model with all relevant coefficients was received:

$$E\{y\} = 2.3763 - 0.3463X_1 - 0.6521X_2 - 0.4971X_3 + 0.1654X_1X_3 - 0.1388X_2X_3\,. \quad (5)$$

Upon transition to natural variables, model (8) looks as follows:

$$E\{y\} = 19.95178 - 3.27493x_1 - 4.60345x_2 - 7.31x_3 + 0.4455x_1x_3 - 0.81235x_2x_3\,. \quad (6)$$

Model (6) describes the phenomenological effect of changing the composition of initial fire-resistant, fire-extinguishing mixture in the vicinity of points with values $x_1^{(0)} = 6.09$, $x_2^{(0)} = 2.8$, and $x_3^{(0)} = 6.09$ on changes in the average expected value of FRC efficiency in peat extinguishing. Because peat and wood are the solid combustible materials of different nature and it is quite difficult to find a combination of values of the influencing factors which provide extremums of both response functions of interest, therefore, to improve the fire-extinguishing and protective properties of FRC simultaneously with respect to peat and wood, the following approach was used. Initially, an adequate mathematical model was built that describes the influence of the selected factors on the effectiveness of FRC fire extinguishers for peat, then, this response function was minimized by the Box–Wilson method [6, 8], with additional condition of increasing the FR efficiency for wood.

Models (5) or (6) were used to increase the fire-protective and fire-extinguishing efficiency of the original FRC with respect to peat and wood by the Box–Wilson method of steepest descent [8]. According to the condition, the effectiveness of a fire-resistant, fire-extinguishing FRC is the higher, the smaller $E\{y\}$. To formulate a new FRC composition, more efficient simultaneously to the two combustible materials studied, the present authors have assumed that antigradient function (5) at the FFE center is 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 $i = 1, 2, 3, \ldots$ where $\alpha_i > 0$ is the setting step motion) in the direction of vector g. In the chosen direction g, a consistent displacement was performed at step $\alpha_1 = 0.2$ and then at step $\alpha_2 = 0.4$ with transition to the first point with 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 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 FRC pertaining to the coordinates in the natural variables, five experiments were conducted to determine the efficiency of flame-retarding and fire-extinguishing of peat and wood and which furnished the experimental results, as well as average values of vectors y_{peat} and y_{wood} listed in Table 2. Thus, the new recipe made it possible to improve extinguishing and fire-resisting properties of FRC for both peat and wood. Inasmuch as further displacements in the selected direction g at $\alpha_3 = 0.6$ has led to an FRC, fire tests of which showed lower fire-extinguishing and fire-protection efficiencies (see Table 2), the previous FRC with parameters $x_1^{(2)} = 6.17$, $x_2^{(2)} = 2.87$, and $x_3^{(2)} = 6.21$ was adopted as the best formulation. Application of the mathematical method of experiment planning allowed to optimize the FRC and increase its fire-retardant and fire-extinguishing efficiency with respect to both peat and wood as compared to the initial recipe. The conclusions about the influence of the

Table 2 Values of the vectors of observations (fire retardant and fire-extinguishing efficiency of FRC) changing with transition from central plan FFE in direction of vector g with increments α

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

selected factors x_1, x_2, and x_3 on fire-protection and fire-extinguishing efficiency for peat and wood were drawn based on the adequate model (6). Coefficients of these factors determine how fast the FRC fire-extinguishing and fire-protective effectiveness changes. Absolute values of the regression coefficients (6) indicate that the nitrogen content in the formulation (x_3) exerts the greatest effect on the FRC fire-extinguishing and protective effectiveness. Preemptive effect of nitrogen on FRC fire-extinguishing and fire-protective properties is also confirmed by the fact that the model includes nitrogen additionally in pair interactions with phosphorus (x_1) and bentonite (x_2).

This fact confirms the present authors' experimental data [11] that metal phosphate ammonium-containing FR systems exhibit a complex mechanism of fire-fighting action, slowing down the thermolysis reaction of material in the condensed phase and simultaneously inhibiting the combustion processes in the gas phase. Thus, the dominant role in fire-retardant action of basically belongs to the volatile nitrogenous products of their thermolysis, which correlates with the experimental data on the quantitative admission of volatile nitrogen compounds in the gas phase [1–3].

4 Concluding Remarks

Application of the mathematical experiment planning method to find the factors that exert the decisive effect on the fire-resistive and fire-extinguishing effectiveness of the synthetic nitrogen and phosphorus containing FR for wood and peat allowed to confirm and refine the mechanism of their action. It is found that the dominant process in termination of burning of natural materials is the inhibition of radical processes in the gas phase by volatile nitrogen-containing products. It is shown that the synergism of nitrogen-, phosphorus-containing FR is due to their complex action: phosphorus is mainly involved in formation of organic mineral structures in the condensed phase, and nitrogen is an inhibitor for reactions in the gas phase.

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