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Mathematical Modeling of Fire-Proof Efficiency of Coatings Based on Silicate Composition

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Abstract. The paper analyzes the scientific work on fire protection, fire resistance, mathematical modeling of fire-proof properties, mathematical planning of experiments. The factors determining the efficiency of fire-proof coating have been determined. The experimental technique for determining fire-proof efficiency as an output parameter was selected. A factor space was constructed, and an experimental plan was drawn up. Experimental studies of the fire-proof effect of the coating based on the xerogel of the gel-forming system at all points of the factor space were carried out. A regression equation was obtained that describes the effect of the qualitative and quantitative composition of the coating on its fire-proof efficiency.

1. Introduction

Currently, the most common building material traditionally still remains wood and wood products. However, along with the advantages that distinguish it from other building materials, wood also has disadvantages, the main of which are flammability and combustibility. In this regard, the problem of fire-protection of wood in various ways is of great importance in a systematic approach to ensuring the safety of objects [1]. The most effective are flame retardant coating and impregnation with special compounds. One of the protection methods is applying a coating layer on the surface of the material to be protected, the effectiveness of which is determined by the physicochemical properties of the coating. With local exposure to a short-term ignition source, fire-protective coatings hinder the burning of wooden structures, make it easier to extinguish fire, and in some cases exclude the possibility of its occurrence.

2. Unresolved Issues

Earlier, the problems of algorithm for the development of solution areas in a linear multidimensional space of hazardous factors [2], the influence of thermodynamic processes on the physicochemical characteristics of substances [3], the physicochemical principles of the transformation of compositions under various environmental conditions [4], the effect of high temperature on the chemical composition of the porous layers of the compositions have been solved [5].

The experimental-computational method is effective for calculating the characteristics of building structures [6]. Before that, a study had been conducted to determine the effectiveness of building materials testing under different conditions [7].

In previous works, the methods of applying a gel-forming system were selected that provide good adhesion of the coating to the wood surface and the absence of cracking and peeling of the coatings in the course of drying. Comparative tests of fire retardant coatings based on xerogels and other certified fire retardants of various types were conducted. Studies have shown that the resulting xerogel layers exhibit high flame retardant properties. It was also found that xerogel layers obtained on the basis of sodium silicate and salts of divalent and trivalent metals are not prone to swelling.

Slight swelling is only possible with significant excess of sodium silicate. To achieve high fire retardant properties of such coatings, the application of thick layers is necessary.

In case of using monovalent metals as a gelation catalyst, silica gel is the reaction product. Thus obtained coating is capable of significant expansion. In some cases, the expansion coefficient reached 20.

3. Main Part

The aim of this work is to establish the quantitative composition of fire retardant coatings for wood. Qualitative composition of the coating: sodium silicate, potassium carbonate, asbestos, vermiculite. Therefore, experimental studies were conducted to determine the effect of coating components concentration on its fire retardant efficiency.

According to the results of preliminary studies, it was found that four factors have the greatest influence on flame retardant efficiency: the concentration of K_2CO_3 solution, the content of asbestos and vermiculite in the sodium silicate solution, and the ratio of the applied gel-forming and gel-forming catalysts rates. Taking into account the chemical compatibility of the coating components, the conditions of rapid gelling and the possibility of application, the levels of these factors variation were determined (Table 1).

The plan matrix of type 2^4 experiment was composed as follows: for x_1 levels alternate in each experiment, for x_2 – after two experiments, for x_3 – after four, for x_4 – after eight. The plan matrix is presented in table. 2. The above plan allows an independent assessment of the regression equation coefficients. It is an expanded matrix, so it has columns that allow to evaluate the regression coefficients in the interaction of factors.

Table 1. Factor Variation Levels

Factors	Code designation	Level zero $x_i = 0$	Interval varying	Maximum level $x_i = 1$	Minimum level $x_i = -1$
Asbestos content, [$g \cdot l^{-1}$]	x_1	45	15	60	30
The content of vermiculite, [$g \cdot l^{-1}$]	x_2	55	15	70	40
Concentration K_2CO_3, [%]	x_3	36	6	42	30
Ratio of rates	x_4	2	1	3	1

Tests of each composition were carried out on 3 samples. Those were made from straight-layered air-dried pine wood with a density of 400 to 550 $kg \cdot m^{-3}$ in the form of a rectangular bar with a cross section of 30×60 (mm^2) and a fiber length of 150 mm. Deviations from sample sizes should not exceed ± 1 mm. Wood samples must have a moisture content of (8±2) % before applying the fire retardant. For this purpose, the samples were conditioned in a desiccator with a saturated solution of 6-hydrous zinc nitrate at a temperature of (23±5) °C. The conditioning of the wood samples was stopped when the change between the two subsequent weighings after 24 hours was not more than 0.2 g.

The fire retardant composition was applied using pneumatic spraying according to (Table 1), the coating thickness was 1.5 mm.

Before testing, the treated and dried wood samples had been conditioned under the conditions indicated above and weighed with an error not exceeding 0.1 g. After drying, the samples were examined on a thermogravimetric assembly (Fig. 1). During the assembly setup the previously known sensors of increased accuracy described in [8, 9] were used to measure the temperature.

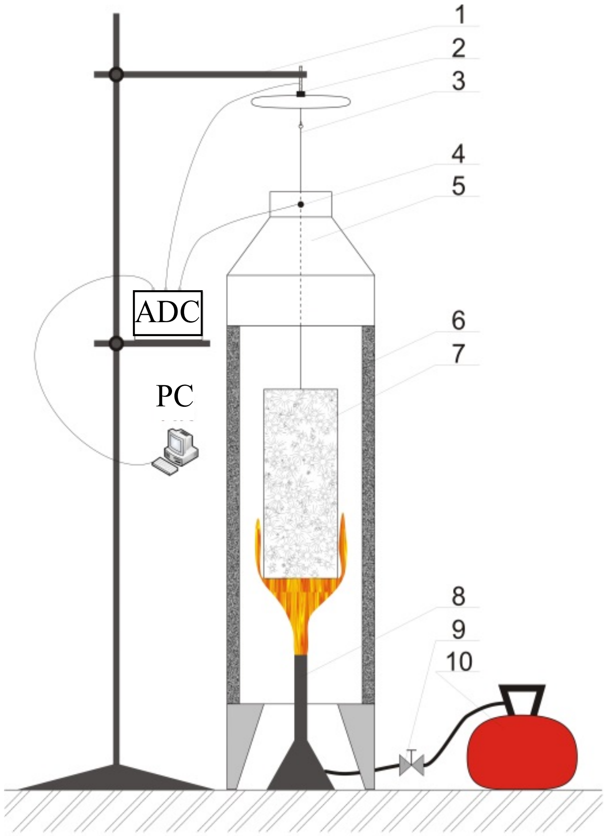

Fig. 1. The assembly for thermogravimetric studies of fire protection means efficiency for wood fire protection: 1 – tripod; 2 –dynamometer sensor; 3 – thread for sample suspension; 4 – thermocouple sensor; 5 – canopy; 6 – ceramic pipe; 7 – sample; 8 – burner; 9 – gas regulator; 10 – gas cylinder; ADC – analog to digital converter; PC – Personal Computer

The essence of this method of samples research is to synchronously study changes in the temperature of the flue gases in the upper part of the umbrella and the mass of the wood sample treated with a fire retardant under test during fire exposure.

Before testing, a gas burner was ignited and the gas flow was adjusted so that the temperature in the upper part of the umbrella was equal to (200±5) °C for 5 minutes. Upon reaching the temperature of (200±5) °C, the test sample fixed on the steel thread of the dynamometer sensor was lowered into a ceramic box and at the same time the measurement program was launched. The sample was kept in the burner flame until the flue gas temperature at the top of the burner reached 205 °C. The test time was recorded.

The criterion for fire protection efficiency of this method is the time necessary for the flue gas to reach the initial temperature before the test sample is placed in a ceramic pipe (200 ± 5) °C. This criterion was chosen because the moment of heating, when the wood becomes flammable, is determined by the release of combustible thermal decomposition products. It is under this condition that the temperature of the flue gases exceeds the initial (200 ± 5) °C.

The efficiency of fire protection was taken as the time from the moment of placement of a wood sample treated with flame retardant in a ceramic pipe and until the flue gas reaches its initial temperature, i.e. 205 °C.

The assembly consisted of a ceramic pipe with a gas burner in the lower part. At the top of the pipe there was a temperature sensor. The assembly was heated up to a stable temperature of 200 °C, after which a treated sample was placed in the pipe. The time necessary to reach the temperature of 205 °C was recorded. This indicated that the wood undergoes a process of thermal degradation with the release of combustible products. The combustion of these products in a burner flame gives an energy effect. As a result, the temperature rises above the initial value.

The obtained results processing was carried out using the experimental design theory methods [6, 7] (Table 2).

Table 2. Conditions and results of experiments on the study of fire retardant action of coatings based on a gel-forming system $K_2CO_3 + Na_2O{\cdot}2.71SiO_2$

x_1	x_2	x_3	x_4	$x_1 x_2$	$x_1 x_3$	$x_1 x_4$	$x_2 x_3$	$x_2 x_4$	$x_3 x_4$	F
-1	-1	-1	-1	+1	+1	+1	+1	+1	+1	195
+1	-1	-1	-1	-1	-1	-1	+1	+1	+1	210
-1	+1	-1	-1	-1	+1	+1	-1	-1	+1	211.5
+1	+1	-1	-1	+1	-1	-1	-1	-1	+1	270
-1	-1	+1	-1	+1	-1	+1	-1	+1	-1	297.5
+1	-1	+1	-1	-1	+1	-1	-1	+1	-1	240
-1	+1	+1	-1	-1	-1	+1	+1	-1	-1	270
+1	+1	+1	-1	+1	+1	-1	+1	-1	-1	370
-1	-1	-1	+1	+1	+1	-1	+1	-1	-1	205
+1	-1	-1	+1	-1	-1	+1	+1	-1	-1	260
-1	+1	-1	+1	-1	+1	-1	-1	+1	-1	305
+1	+1	-1	+1	+1	-1	+1	-1	+1	-1	250
-1	-1	+1	+1	+1	-1	-1	-1	-1	+1	310
+1	-1	+1	+1	-1	+1	+1	-1	-1	+1	300
-1	+1	+1	+1	-1	-1	-1	+1	+1	+1	310
+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	340

The error estimation of the experiment was carried out according to the results of 7 parallel experiments in the center of the plan (Table 3). The average value of the experiments results in the center of the plan is 280.71.

Table 3. The results of experiments in the center of the plan for the study of fire retardant effect of the coating based on a gel-forming system $K_2CO_3 + Na_2O{\cdot}2.71SiO_2$

Experience Number	1	2	3	4	5	6	7
Result	280	270	275	290	285	265	300

The hypothesis about the significance of quadratic effects in the model was tested using the inequality:

$$\left|\overline{F}_{\text{c.p.}} - b_0\right| < t_{(0.05;6)} \cdot s_y \cdot \sqrt{\frac{n_0 + N}{n_0 \cdot N}}, \tag{1}$$

where $\overline{F}_{\text{c.p.}}$ is the average value of the experiments results in the center of the plan; b_0 is the estimate obtained by the experiment results in the core of the plan, equal to 271.5; s_y – assessment of the variance of experimental errors, which was determined by the results of seven parallel experiments in the center of the plan; $t_{(0.05;6)}$ is the Student's coefficient value at 6 degrees of freedom;
N is the number of computational procedures for the plan 2^4; n_0 is the number of experiments in the center of the plan.

For s_y = 12.05 and $t_{(0.05;6)}$ = 2.45, inequality (1) holds; therefore, the quadratic effects are not statistically significant. Therefore, the mathematical model can be represented as an incomplete quadratic equation.

After calculating the values of the regression coefficients and evaluating their significance according to the Student's criterion [5], the following regression equation was obtained:

$$F = 271,5 + 8,5 \cdot x_1 + 19,3 \cdot x_2 + 33,2 \cdot x_3 + 13,5 \cdot x_4 + \\ + 8,2 \cdot x_1 \cdot x_2 - 7,6 \cdot x_1 \cdot x_4 + 16,5 \cdot x_1 \cdot x_2 \cdot x_3 - 16,9 \cdot x_1 \cdot x_2 \cdot x_4. \quad (2)$$

Verification of the obtained model adequacy by the Fisher test gave a positive result.

The analysis of expression (2) showed that at zero values of all factors, the fire retardant efficiency factor is 271.5 s. An increase in concentration values of the first three coating components leads to an increase in the response function. In this case, a change in K_2CO_3 concentration makes the greatest effect. The concentration of vermiculite also has a significant effect on the factor under study. This is confirmed by the fact that the estimates for interaction of factors are higher where x_2 is present.

Let's test the expression (2) for the extremum and note down the partial derivatives with respect to all variables

$$\frac{\partial F}{\partial x_1} = 8,5 + 8,2 \cdot x_2 - 7,6 \cdot x_4 + 16,5 \cdot x_2 \cdot x_3 - 16,9 \cdot x_2 \cdot x_4; \quad (3)$$

$$\frac{\partial F}{\partial x_2} = 19,3 + 8,2 \cdot x_1 + 16,5 \cdot x_1 \cdot x_3 - 16,9 \cdot x_1 \cdot x_4; \quad (4)$$

$$\frac{\partial F}{\partial x_3} = 33,2 + 16,5 \cdot x_1 \cdot x_2; \quad (5)$$

$$\frac{\partial F}{\partial x_4} = 13,5 - 7,6 \cdot x_1 - 16,9 \cdot x_1 \cdot x_2. \quad (6)$$

Equating the right-hand sides of the obtained expressions to zero, we obtain a system of equations whose solution is a point with coordinates (6.25; -0.32; 0.59; 1.25).

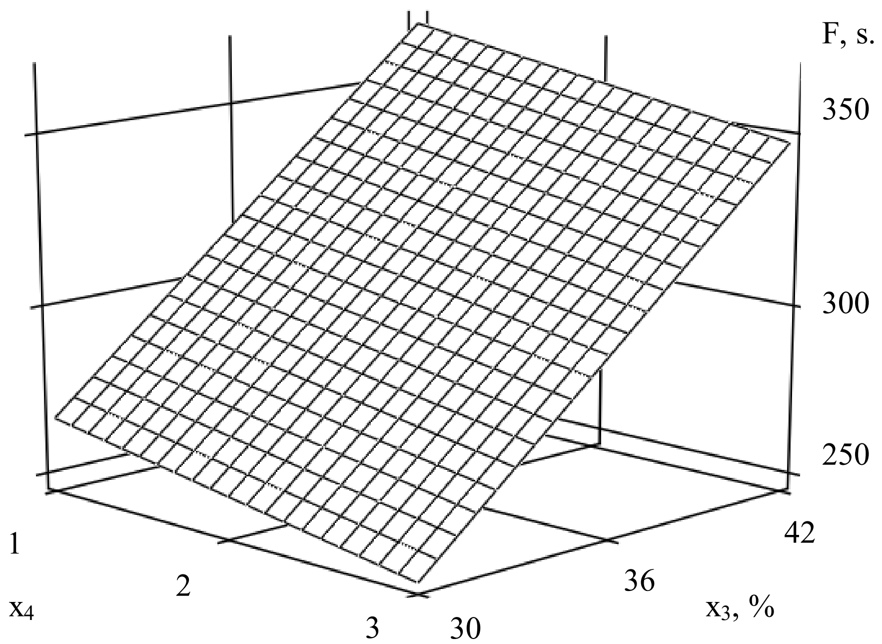

Fig. 2. The dependence of flame retardant efficiency on the concentration of K_2CO_3 and the ratio of gelling components rates

Since the values of the first and fourth coordinates are greater than unity, the stationary point is outside the domain of model definition (2). To search for the extremum, function (2), let's perform a step-by-step search procedure for all four coordinates. The calculations found that the maximum time until the loss of 9% of the initial mass of a sample treated with a fire retardant coating is achieved at the maximum values of the first three parameters and the minimum value of the fourth (Fig. 2).

4. Conclusion

Based on the analysis of existing methods for studying fire retardant efficiency, a method has been developed that allows to study fire retardant agents of increased efficiency, detecting the beginning of the release of combustible thermal destruction products.

The mathematical dependence of the quantitative composition of a flame retardant based on a gel-forming system $K_2CO_3 + Na_2O \cdot 2{,}71SiO_2$ was determined

A quantitative relationship has been established between the flame retardant efficiency and component concentrations. To increase the fire retardant ability of the gel-forming system, it is advisable to increase the concentration of potassium carbonate, and taking into account the conditions of gelation from K_2CO_3 and $Na_2O\ SiO_2$ solutions, the ratio of their volumes should be 1:1.

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