Fire protection of timber building structural units by mono- and di-ethanolamine-(N→B)- phenyl borates

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Abstract. Fire protection of timber is represented by the combination of methods and techniques that allow maintaining bearing and other design properties of building structural units when exposed to fire during certain period of time. The variety of factors, such as an access of oxygen, air draft, and projected fire intensity should be taken into account while choosing efficient methods and techniques of fire protection. Along with that, when applying various methods of fire protection, it's crucial to preserve natural properties of timber determining comfortable indoor climate. Within this context, "soft" timber modification is preferable. Thus, finding methods lowering combustibility of timber, while preserving its unique natural properties, represents the goal of this study. The present paper studies fire-proof efficiency of compounds based on mono- and di-ethanolamine-(N→B)-phenyl borates by means of 'ceramic pipe' method. Durability of shielding effect of the designed compositions was assessed by the method of determining ageing resistance. It was established that "soft" surface modification by the compositions based on mono- and di-ethanolamine-(N→B)-phenyl borates allows upgrading timber to the class of flash-resistant materials and enables to increase fire resistance significantly (period of fire resistance accounts for 90 min), along with that, protective effect remains after accelerated ageing of timber.

1 Introduction

Fire protection serves as the key element of the system of methods for fire safety of wooden buildings and structures. The principal goals of fire protection are defined as follows: fire outbreak prevention, putting a stop to an early stage of fire development, creation of 'passive' fire control measures, descent of hazardous factors of fire, increasing the capabilities of application of innovative advanced design solutions [1, 2]. The known methods of fire protection are numerous. They comprise the design methods allowing creation of various heat shields on the element's surface, as well as physical and chemical and technological approaches lowering contribution of construction products to the propagation of fire [3-5]. Depending on the specific features of structures' resistance to thermal exposure during a fire case, the character of their performance when loaded, their functional requirements, various

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methods and approaches to fire protection could be distinguished. Those methods could be applied separately or in multiple combinations [6-8]. Thus, fire protection of building structures could be defined as a combination of methods and approaches which allow maintaining bearing and other design properties when exposed to fire during certain period of time. There are many aspects to consider such as an access of oxygen, air draft, and projected fire intensity depending on the presence of flammable substances in the premises [9-11]. Those aspects should be taken into account while selecting efficient fire protection methods. Efficiency of applied fire-retarding compositions could be divided according to the time of withstanding thermal exposure. The methods of fire protection of wooden structures and elements of light guard groups have their specific features related to the physical nature of timber, peculiarities of behavior and thermal exposure fracture and lead to reducing probability of burning action. The special compounds – flame retarders – are used for fire protection of wooden structures. The particular defined concentration of flame retarders in timber eliminates its burning in the absence of the fire source. Current methods of fire protection are considered efficient provided they enable to obtain non-flammable or flash-resistant building materials. In this case, bearing structures could be regarded as protected against fire and heat. Thus, development of efficient protective methods for wooden structures is of crucial importance [12-14]. Of special interest is so-called ‘soft’ modification of base sheet surface that allows preserving unique natural properties of wooden compound material preconditioning comfortable indoor climate.

Reported works [15, 16] have proved high efficiency of boron-nitrogen compounds for lowering combustibility of pine timber. However, it cannot be regarded as ‘soft’ modification as the satisfactory output is achieved only by the use of high-level modifier’s solutions. In the present paper we pursued the objective to lower modifier’s concentration while maintaining high fire protective efficiency. It was realized when mono- and di-ethanolamine borates had been replaced by mono- and di-ethanolamine phenyl borates.

2 Materials and Methods

As fire proof compositions were used the composite materials on the base of mono- and di-ethanolamine (N→B) phenyl borates and water: 10% solution of mono-ethanolamine (N→B) phenyl borate (compound 1), 5%- solution of mono-ethanolamine (N→B) (compound 2), 5%- solution of di-ethanolamine (N→B) phenyl borate (compound 3). The assessment of fire-proof efficiency of the compounds on the base of boron-nitrogen compositions was carried out in compliance with the All-Union State Standard GOST P 53292-2009 clause 6.1. For the tests, 10 samples of sapwood were used with a cross section of 30x60 mm and a length along the fibers of 150 mm. The sample fixed in the holder was lowered into a ceramic box, including a stopwatch, the bumbershoot was moved to the working position and held in the flame of the burner for 2 minutes. The gas consumption remained constant. Then, the gas supply to the burner was stopped and the sample was left in the apparatus for cooling. The loss of sample mass P_i ,%, was calculated from formula (1):

$$P_i = \frac{(m_{1i} - m_{2i})}{m_{1i}} \cdot 100\% \quad (1)$$

where m_{1i} - mass of the sample before the test, g;

m_{2i} - mass of the sample after the test, g;

i - sample number.

Lasting quality of fire-proof efficiency was assessed by the accelerated ageing method according to the All-Union State Standard GOST P 53292-2009 clause 6.3. The tests were carried out on 6 samples. Three of them have been randomly selected as the base samples,

the remaining three have been considered as test specimen. The mass loss of three test specimen was determined in accordance with the formula (1). Arithmetical average of three measurements P_K , %, was defined. It was admitted that while carrying out tests of protecting coat simultaneously with the purpose of defining ageing resistance and fire-proof efficiency, the test result obtained according to the method of determination of fire-proof efficiency was taken as the result of test specimen.

Three base samples were subsequently kept in the drying oven for 8 hours at the temperature $(60 \pm 5)^\circ\text{C}$, another 16 hours in the desiccator filled with water with relative air humidity equal to 100% at the temperature of $(23 \pm 5)^\circ\text{C}$, then 8 hours in the desiccator at the temperature of $(60 \pm 5)^\circ\text{C}$, 16 hours at the temperature $(23 \pm 5)^\circ\text{C}$ and relative air humidity $(65 \pm 5)\%$. All these manipulations compose one full cycle (48 hours). The tests included seven cycles implemented under the scheme mentioned. Throughout the test process, the samples state was duly monitored. At the end of the period indicated the samples were conditioned. The mass loss of three base specimens was determined by the formula (1). Arithmetical average of three values P_0 , %, was determined. The difference $(P_0 - P_K)$ rounded to integer percentage number was taken as the test result.

The protecting coat applied is stated to pass the aging test successfully if fire-proof coating integrity remains intact (no cracks, scaling, blistering, flaking or other deterioration) and for all the samples the equalities (2) and (3) are functioning:

$$P_0 - P_K \leq 3 \text{ at } P_K \leq 9; \quad (2)$$

$$P_0 - P_K \leq 5 \text{ at } 9 \leq P_K \leq 25; \quad (3)$$

where P_0 - arithmetical average of mass loss of three base samples, %;

P_K - arithmetical average of mass loss of three test specimen, %.

Sample preparation was implemented in concordance with the clause 6.3.3.2 of the All-Union State Standard 53292-2009. The samples were made of straight-grained, air-dried pine wood with moisture content varying from 8 to 15% and density ranging from 400 up to 550 g/m^3 in the shape of rectangular blocks with the cross-section of 30x60mm and the along-the-grain length of 150 mm, when dimensional deviation didn't exceed 1 mm. The samples were made of sapwood lacking visible flaws and resin flecks. Side surfaces of samples were surfaced; the edges were sawn and treated with the polishing stone.

Before applying protecting coat, the wood samples were conditioned in the desiccator in the sole solution of 6-aqueous zinc nitrate at the temperature of $(23 \pm 5)^\circ\text{C}$. The conditioning was stopped when the mass change of samples between two consequent weighing operations implemented after 24 hours didn't exceed 0.2 g; the obtained result was rounded to 0.1 g. The protecting coat was applied on all sides of conditioned samples followed by samples drying. Total consumption of the protecting coat applied on the wood sample was determined by summing up the consumption after each layer's application and was compared to the surface area. Protecting coat consumption after each application was determined by the weight-change method according to the mass difference of samples before and after application of a flame-retardant compound.

When treated with dipping compounds, the samples were weighed as soon as leaking unabsorbed solution off the sample surface had stopped. A residual coat was removed from the sample's edge by filter paper. The surface of timber samples was treated by brushing method with the protective compounds 1, 2, 3, consumption 320, 338 and 258 g/m^2 correspondingly, then after complete desiccation the samples were tested in compliance with the rules and regulations mentioned above.

3 Results and Discussion

Test data are represented in the tables 1 and 2.

Table 1. Test data in compliance with the All-Union State Standard P 53292-2009 clause 6.1. of timber samples with the compounds 1-3 applied

NN	Sample mass, g		Mass loss, g/m ² of protection	Sample mass loss		Average sample mass loss	
	before burning	after burning		g	%	g	%
Compound 1							
1	152,1	135,1	320	17,0	11,2	21,7	15,2
2	133,3	108,0		25,3	19,0		
3	150,8	127,7		23,1	15,3		
4	132,7	109,3		23,4	17,6		
5	134,8	110,3		24,5	18,2		
6	148,2	122,7		25,5	17,2		
7	141,7	120,9		20,8	14,7		
8	139,0	121,1		17,9	12,9		
9	150,7	128,7		22,0	14,6		
10	157,1	139,3		17,8	11,3		
Compound 2							
11	165,4	141,6	338	23,8	14,4	26,3	18,5
12	157,7	132,1		25,6	16,2		
13	155,4	125,6		29,8	19,2		
14	123,4	101,5		21,9	17,8		
15	126,7	104,7		22,0	17,4		
16	152,1	118,8		33,3	21,9		
17	137,6	111,9		25,7	18,7		
18	130,2	101,0		29,2	22,4		
19	153,9	123,7		30,2	19,6		
20	124,5	102,8		21,7	17,4		
Compound 3							
21	149,2	120,3	258	28,9	19,4	24,8	17,7
22	154,4	132,6		21,8	14,1		
23	128,7	103,4		25,3	19,7		
24	133,9	106,8		27,1	20,2		
25	137,0	115,5		21,5	15,7		
26	146,8	120,5		26,3	17,9		
27	158,7	133,3		25,4	16,0		

28	127,9	100,9		27,0	21,1		
29	123,1	106,9		16,2	13,2		
30	145,3	116,7		28,6	19,7		

Table 2. Test data in compliance with the All-Union State Standard P 53292-2009 clause 6.3.3.1. of the fire-proof compound 1 for ageing resistance

Samples	NN	Sample mass, g		Overall consumption, g/m ²	Average sample mass loss	
		before burning	after burning		g	%
check samples	1	—*	—*	320	21,7	15,2
	2	—*	—*			
	3	—*	—*			
base samples	4	155,7	126,5		28,5	19,1
	5	134,7	107,3			
	6	157,6	128,8			

*- Samples mass before burning and after burning are given in accordance with the All-Union State Standard P 53292-2009 clause 6.3.3.1. The data of the average mass loss are taken from the table 1.

According to the All-Union State Standard 53292-2009 clause 6.1., the following groups of fire-proof efficiency of the compounds have been distinguished depending upon the value of mass loss of samples: the class I of fire-proof efficiency (the value of mass loss is not exceeding 9%), timber treated by such a compound is considered non-flammable; the class II of fire-proof efficiency (the value of mass loss is greater than 9% but not exceeding 25%); the class III of fire-proof efficiency doesn’t guarantee fire protection and is not regarded as fire-retardant (the value of mass loss is greater than 25%). It has been affirmed that treatment under the First class of fire-resistance enables to save wooden structures from burning for the period up to 150 minutes. In our case, the developed protective compounds are classified as the second class of fire-proof efficiency. Timber treated by such compounds becomes a flash-resistant material; the period of fire resistance is extended up to 90 minutes. The compound 1 could be regarded as the most efficient as when applied to the sample, the registered mass loss is the lowest (see table 1).

Lasting quality of fire proof efficiency for the compound 1 was assessment by the method of ageing resistance subject to the All-Union State Standard P 53292-2009, clause 6.3. Summary of test method includes assessment of lasting quality of fire proof efficiency of the flame-resistant finish obtained on the base of flame-retardant composition, after accelerated ageing by means of alternate exposure of samples to fluctuating temperature and humidity in a successive order. The applied fire-resistant finish undergoes the test for ageing resistance successfully if integrity of fire-resistant coat remains intact (no cracks, chippings, flaking, blistering and other deteriorations permitted by the technical specification for fire-resistant materials) for all the samples and inequalities $P_0 - P_k \leq 3$, when $9 \leq P_0 - P_k \leq 5$, when $9 < P_k \leq 25$ are applicable, where P_0 – arithmetic middling of the mass loss value for three base samples, %; P_k – arithmetic middling of the mass loss value for three check samples, %. The difference $(P_0 - P_k)$, rounded to the nearest whole number on a percentage base, was taken as the test result. The results of tests are presented in the table 2.

From the data presented in the table 2 it appears that after having undergone long-term ageing, the samples show mass loss corresponding to the class II of fire-proof efficiency. Fire-resistant compound 1 has passed the tests successfully as the integrity of fire-resistant coat on its base had remained intact. Thus, 'soft' surface modification by the compounds on the base of mono- and di-ethanolamine (N→B) phenyl borates allows upgrading timber to the class of flash-resistant materials and enables to increase fire resistance significantly (period of fire resistance accounts for 90 min), along with that, protective effect remains after accelerated ageing of timber.

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