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Study Of Phosphorus-Containing Oligomeric Antipyrenes

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Abstract

Synthesized a new polyfunctional oligomeric a phosphorous flame retardant based on epichlorohydrin adduct with urea and inorganic compounds of silicon, called a conditional ADj-1, ADj-2 and ADj-3. The physico-chemical characteristics of flame retardant compositions. The effect of the interaction of the molecule on the physicochemical properties of the oligomeric flame retardant, fire wood and polymer materials. In this paper we used the methods of impregnation oligomeric flame retardant according to GOST 16363-98. Accelerated test method used for the control of fire-retardant effectiveness of fire protection, passed classification test. The dependence of the oxygen index composite sample grades ADj-10, ADj-11 and ADj-12 on the polymers according to GOST 21793-76.

Keywords*: Oligomeric flame retardant, the oxygen index, polyethylene, weight loss, the flame-retardant efficiency.*

Introduction

In modern conditions, it is important to widely use flame retardants [1], which should be provided by a new generation of environmentally friendly [2], cost-effective flame retardant compositions with high performance [3]. The compositions used for this, after applying them [4] to the surface of combustible materials, increase their fire resistance [9].

New fire safety problems also arise in connection with the accelerated construction of residential [5], industrial and public buildings [6]. The likelihood of a fire can be reduced [7], using materials that are difficult to combustible in buildings [10], protecting them with special firefighting structures [8].

The test procedure was carried out as follows: test samples of pine wood were suspended vertically on a ceramic box with an external size of 120 × 120 × 300 mm and a wall thickness of (16 ± 2) mm. A flame of a gas or alcohol burner was placed under the sample protruding from the box (an alcohol burner was used in our tests). The distance from the upper edge of the burner to the sample was 60 mm. The exposure time of the sample in the flame of a gas burner is 1 min., And in the flame of an alcohol burner 1 minute. 30 seconds After the burner was removed, the duration of self-burning and smoldering of the sample was recorded.

This experiment was performed according to GOST 16363-98. The essence of the methods lies in the determination of the mass loss of wood treated with the coatings or impregnating compounds under test during fire tests under conditions conducive to the accumulation of heat. The classification method is used to determine the group of flame retardant efficiency and when conducting certification tests. The method of accelerated testing is used to control the fire retardant effectiveness of fire protection products that have passed the classification tests.

A solution of oligomeric flame retardant was prepared as follows: in warm (water temperature 323-333K) water (30% dry composition and 70% water) was thoroughly dissolved (solubility of oligomer up to 90%) the calculated amount of flame retardant. The prepared solution was thoroughly mixed and filtered through a dense gauze, folded in two layers.

New polyfunctional compositions based on the products of the interaction of phosphorus, boron, and silicon containing compounds were created, and the properties of the flame retardants of the ADJ-10, ADJ-11 and ADJ-12 grades were studied [11].

The ADJ-10 IR spectrum contains absorption bands in the regions of 2850-1470 cm-1, confirming the presence of -CH2 groups, and absorption bands in the regions of 1650 cm-1, confirming the presence of the -CONH2 group in the free state.

The IR spectrum contains absorption bands in the regions of 3200-3350 cm-1, primary — CONH2 groups and absorption bands in the regions of 3440 cm-1, secondary — CONHR groups.

Absorption bands in the regions of 780–672 cm– 1 confirm the presence of –NH2 groups. For solid and liquid polymeric hydroxyl substances, there is only one wide band in the region of 3450-3200cm-1. On the IR spectra, absorption bands are usually present, in the regions of 1460-1300 cm-1, there are absorption bands confirming the presence of C = S groups, and absorption bands in the regions of 1300-1250 cm-1 and 1180-1040 cm-1 confirming the presence of organic phosphates P = O and P-O-C groups.

The deformation vibrations of all active groups are manifested in the form of strong narrow bands between the usual bands of deformation vibrations –CH2 – CO– in the region of 1465–1380 cm – 1.

Absorption bands in the regions of 800 and 1600 cm-1 confirm the presence of –NH2 groups. In addition, narrow low-intensity bands containing boron bonds and metal containing compounds appear in the IR spectrum in the regions of 600-800 cm-1 and 1460 cm-1.

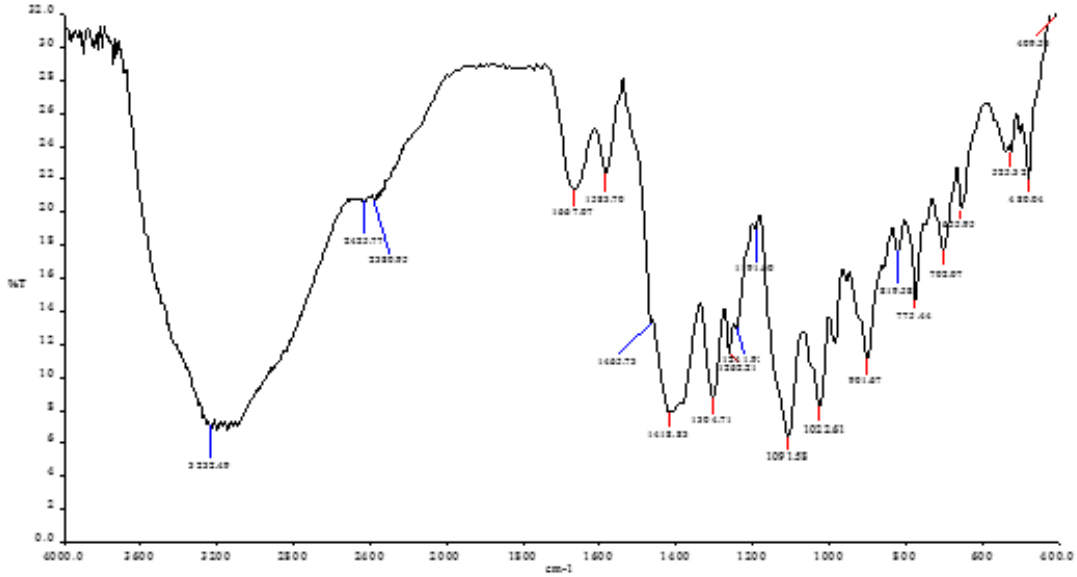

Fig.1. IR spectra ADJ-10.

The structure of the composition ADJ-11 was also studied by IR spectroscopy and the IR spectrum of ADJ-11 was taken. The IR spectrum contains absorption bands in the regions 3200-3350 cm-1, corresponding to the primary –CONH2 groups and absorption bands in the regions 3440cm-1, corresponding to the secondary –CONHR groups. Absorption bands in the regions of 780–672 cm – 1 confirm the presence of the –NH2 group.

For solid and liquid polymeric hydroxyl substances, there is only one wide band 3450-3200cm-1. The IR spectrum contains absorption bands in the regions of 1460–1300 cm– 1; there are absorption bands confirming the presence of organic phosphate P = O and P-O-C groups. The deformation vibrations of all active groups are manifested in the form of strong narrow bands between the usual deformation vibration bands –CH2 – CO– in the region of 1465–1380 cm– 1. Absorption bands in the regions of 800 and 1600 cm-1 confirm the presence of –NH2 groups.

In addition, narrow low-intensity bands containing bonds of metal-containing compounds appear in the IR spectrum in the regions of 600-800 cm-1 and 1460 cm-1.

The IR spectrum contains absorption bands in the 1487 and 1353 cm-1 regions, confirming the presence of the B-NHR group and absorption bands in the 704 cm-1 regions, confirming the presence of this group. There are also new absorption bands at 1487 cm-1, corresponding to - NH2 + groups for quaternary bonds of hexamine with epichlorohydrin. (Fig. 2).

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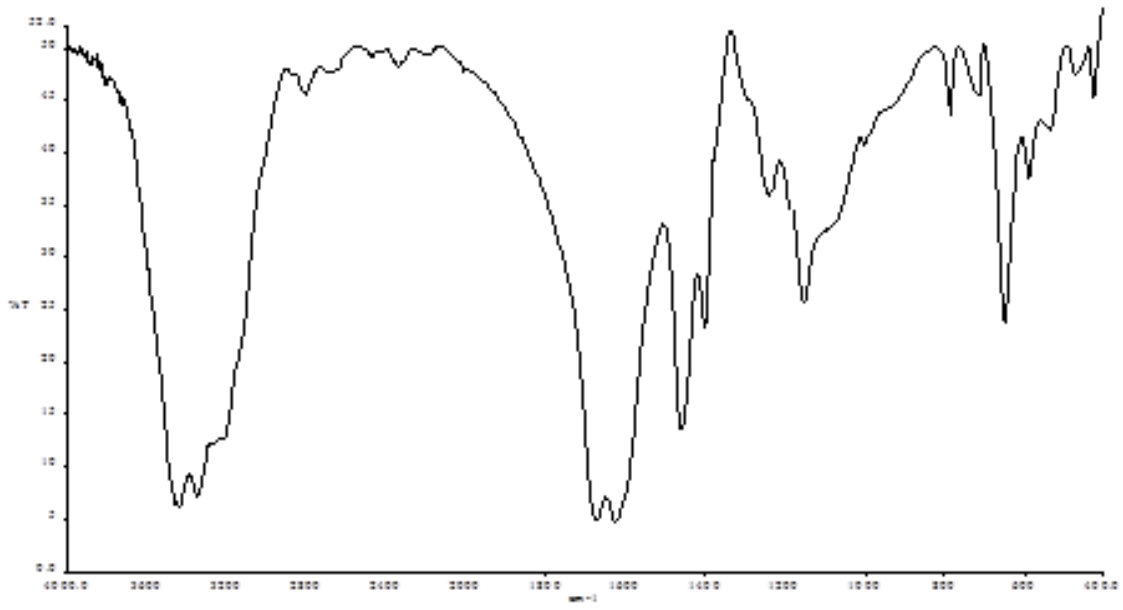

Fig.2. IR spectra ADJ-11.

On the IR spectrum of ADJ-12, new specific absorption bands appear, due to the stretching vibrations of P-O-C bonds of 1016, 1042, and 1146 cm – 1. Also, the deformation vibrations of all active groups are manifested in the form of strong narrow bands between the usual deformation vibration bands –CH2 – CO– 1465 - 1380 cm-1. Absorption bands in the regions of 800 and 1600 cm-1, confirming the presence of –NH2 group. For shifts of carbonyl groups, a wide band of 3400 - 3200 cm-1 is observed. In the presence of groups containing phosphorus P = O and P – O – C is very intense. In addition, there appear narrow low-intensity bands at 1000 - 1250 cm-1. The IR spectrum containing bonds of boron and magnesium appears in the regions of 600–800 cm – 1 and 1401 cm – 1 (Fig. 3).

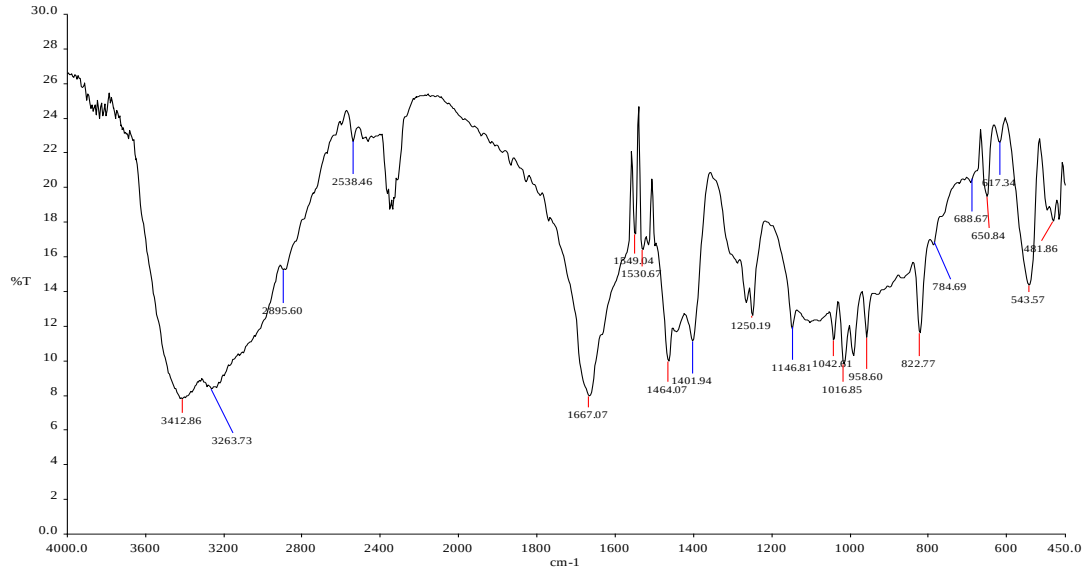

Fig.3. IR spectra of oligomeric flame retardant grade ADJ-12.

The physicochemical characteristics of the synthesized oligomeric antipyrins of the ADJ-10, ADJ-11, and ADJ-12 samples were determined by various methods [12]. Investigated the effect of flame retardants on the refractive index, density, viscosity and solubility. The research results are presented in table 1. We studied flame retardants ADJ-10, ADJ-11 and ADJ-12. obtained by condensation of ammophos with urea, magnesium oxide and water glass in a weakly alkaline medium, followed by neutralization of the reaction mixture with phosphoric acid.

Table 1Physico-chemical characteristics of oligomeric flame retardants.

Title	Refractive index 20°C	Density, g/cm3	pH	ή$_{xb}$ Viscosity	Output %	State of aggregation	Solubility
АДж-10	1,402	1,06	7,0	0,044	86	White solid matter	Soluble in water
АДж-11	1,353	1,01	7,0	0,048	82		
АДж-12	1,354	1,02	7,0	0,048	92		

New polyfunctional oligomeric flame retardants were synthesized based on the products of the interaction of phosphorus-boron-containing compounds, and the properties of the flame retardants of the ADJ-10 and ADJ-11 brands were studied.

The effect of fire retardants is based on the fact that if there is a certain concentration in the wood, they prevent it from burning without a source of flame. When wood is exposed to fire, various physicochemical processes take place, and fire retardants have a fire retardant effect on it.

Investigations of flame retardant effectiveness were carried out on wooden elements. The application of the composition to the treated surface was carried out by the method of spraying. The application was made in layers (2 layers). In two steps, 450 g / m2 of the composition was applied. The interval between treatments was at least 12 hours. The results of the study of the compositions of ADJ-10 showed that, on average, the mass loss of the sample was 6.9%, that is, the flame retardant composition provides the I group of flame-retardant efficiency, according to GOST 16363-98 (Table 2).

Table 2 Fireproof efficiency of ADJ-10.

Sample number	Time, sec	Mass, gr	Weight loss			
	Self burning	Smoldering	Before the test	After the test	gr.	%
1	Missing	Missing	135,66	125,84	9,82	7,24
2			139,04	128,59	10,45	7,52
3			136,72	127,58	9,14	6,69
4			134,19	124,88	9,31	6,94
5			138,58	129,13	9,45	6,82
6			136,33	127,43	8,90	6,53
7			134,85	125,62	9,23	6,85
8			136,97	126,46	10,51	7,68
9			133,89	125,39	8,50	6,35
10			137,41	128,37	9,04	6,58
		Average		6,9		

The results of the study of the compositions of ADJ-11 showed that, on average, the mass loss of the sample was 8.2%, that is, the flame retardant composition provides the I group of flame-retardant efficiency, according to GOST 16363-98 (Table 3).

Table 3 Fireproof efficiency of ADJ-11

Sample number	Time, sec		Mass, gr		Weight loss	
	Self burning	Smoldering	Before the test	Self burning	Smoldering	Before the test
1	Missing	Missing	137,41	124,85	12,56	9,14
2			133,89	123,49	10,40	7,77
3			136,97	125,63	11,34	8,28
4			138,85	128,23	10,62	7,65
5			138,33	127,46	10,87	7,86
6			138,58	127,86	10,72	7,74
7			134,19	122,76	11,43	8,52
8			136,72	125,8	10,92	7,99
9			139,04	126,36	12,68	9,12
10			135,66	124,83	10,83	7,99

From these impregnating compositions ADJ-10, ADJ-11 and from those given in table 4, one can see that oligomeric flame retardants belong to the I group of flame retardant efficiency. Solutions of oligomeric compositions penetrate inwards, wetting the surface layer of wood. After the carrier water evaporates, the flame retardant remains among the fibers of the fiber, thereby creating a protective layer.

Table 4 Impact of impregnation for wood fire protection

The name of the material	Application technology	Consumption, kg / m2	Fire retardant efficiency group
АДж-10	Brush, roller, spray	0,45	I
АДж-11		0,40	I

The flame retardant efficiency of the compositions ADJ-10 and ADJ-11, with a weight loss, was 6.9 - 8.2%. Analysis of ways to improve fire retardant impregnating compositions, their use in construction to increase the fire resistance of structures and wood products showed that priority is given to compositions that can provide the required fire resistance parameters at minimal cost without reducing and impairing the operational properties of wood. Such a wide range of requirements for modern fire protection obliges researchers to constantly expand scientific research.

In the study of flame retardant properties of flame retardants, the flammability index is determined, which determines the minimum volume percentage of oxygen in the oxygen-nitrogen mixture, in which there is an independent burning of a vertically positioned sample ignited from above and possibly candle-shaped burning of the material under special testing conditions. It also characterizes the fire hazard of polymers, fibrous materials, fabrics and other combustible materials.

In this regard, we studied the oxygen index, the obtained flame retardant compositions with polyethylene brand F-0220 in an amount of from 10 to 60 mass. %, the calculated oxygen index, turned out to be 28 and 44% for ADJ-10, respectively. Typical for PE compositions were observed in ADJ-12, which is an oxygen index equal to 48% at a mass ratio of 40:60 PE and ADJ-12. The results of the study of the compositions of ADJ-10, ADJ-11 and ADJ-12 with polyethylene are shown in Table 5.

Table 5 The dependence of the oxygen index on the content of the flame retardant

The name of the flame retardant	Fire Retardant concentration, mass, %	Oxygen index, %
-	0	18,0
АДж-10	10	28
	40	37
	60	44
АДж-11	10	29
	40	40
	60	46
АДж-12	10	28
	40	41
	60	49

Findings

Compositions have been developed, based on phosphorus-containing compounds, and have been tested on wood and polymeric building materials. It is established that oligomeric flame retardants have high flame retardant properties for fire resistance and fire safety, which provides the compositions of group I with fire retardant efficiency.

Thus, the analysis of the work performed shows the prospects for the development and use of composite materials of oligomeric flame retardants as flame retardants for wood and polymeric building materials.

Bibliography

[1] Sapaev, Kh. Kh. The development of fire-resistant plasticised polyvinylchloride// International Polymer Science & Technology; - 2012., - Vol. 39 Issue 12, p. 59.
[2] Joseph, P., Mcnally, S.T. Reactive modifications of some chain- and step-growth polymers with phosphorus containing compounds: Effects on flame retardance: A review// Polym. Adv. Technol. 2011, -Vol. 22, pp. 395–406.
[3] Shen, Y.M., Kuan, F.C. Preparation, characterization, thermal and flame retardant properties of green silicon containing epoxy functionalized grapheme Nano sheets composites// J. Nanomat. -2013., pp. 1–10. doi: 10.1155/2013/747963
[4] Котенева И.В. Боразотные модификаторы поверхности для древесины строительных конструкций. Москва. МГСУ. 2011. 191 с.
[5] Ненахов С.А., Пименова В.П., Пименов А.Л. Проблемы оценки ресурса работоспособности огнезащитных вспучивающихся покрытий //Пажаровзрывобезопасность.-2009.-Т.18,№8.-С.46-49.
[6] Каблов В.Ф., Кейбал Н.А., Рубенко К.Ю., Блинов А.А., Мотченко А.О. Влияние волокнистых наполнителей на адгезионные и теплозащитные свойства эластомерных композиций // Известия ВГТУ., -2015. -№7. -С.178-181.
[7] Kajiwara N., Desborough J., Harrad S., Takigami H. Photolysis of brominated flame retardants in textiles exposed to natural sunlight// Environ. Sci. Process. -2013., pp. 653-660. Impacts 15 (2013)
[8] Абдурагимов И.М. О механизмах огнетушащего действия средств пожаротушения // Пожаровзрывобезопасность. - 2012. -Т. 21, №4. -С. 60-82.
[9] Корольчинко А.Я. Проблемы определения горючести веществ // Пожаровзрывобезопасность. - 2015. -Т. 24, №12. -С. 6-8.
[10] Кейбал Н.А., Каблов В.Ф., Бондаренко С.Н. Состав для огнезащитной обработки синтетических волокон. Патент РФ №2418898, 20.05.2011.

[11] Джалилов А.Т., Нуркулов Ф.Н., Вофаев О.Ш., Каримов М.У. Способ получения олигомерного антипирена. Патент UZ №05216, 28.04.2016г.

[12] Нуркулов.Ф.Н., Джалилов А.Т. Фосфор-борсодержащие олигомерные антипирены для древесины и древесных композиционных материалов // V Международная конференция-школа по химии и физикохимии олигомеров: Сборник тезисов докладов. (Волгоград, 1-6 июня -2015). Москва-Черноголовка-Волгоград. - 2015. - С. 241.