

# CHEMICAL CELLULOSE-BASED FIBERS OF DECREASED FLAMMABILITY

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The studies reported here have made it possible to determine the optimal ways of fire protection, in which the samples of modified complexite have reduced flammability. The sample with the ions of molybdenum (VI), treated with phosphoric acid, had the highest magnitude of oxygen index among five modified samples of the fiber. This is the most fire-protected sample, which contains three types of flame retardants: nitrogen (amidoxime groups of complexite, phosphorus (treatment with phosphoric acid) and molybdenum (VI). The obtained data indicate the chemical interaction of flame retardant with complexite.

The morphology of fibers and the process of their destruction are influenced by the introduction of flame retardants. Scanning electronic microphotographs show the existence of a morphological change of the surface at modification of the complexite samples with flame retardant. The introduction of flame retardant into complexite affects the process of thermal destruction of the samples in the air and argon media. At the same time, the introduction of molybdenum (VI) significantly reduces the thermal stability of fibers. It is likely that processes of thermal destruction can be catalyzed by metals both in the air medium and in the argon medium. The magnitudes of order of reaction of thermal decomposition at the transition from a fiber sample treated only with acids to the samples of complexite containing molybdenum (VI) decreases up to 0.38. At the same time, the values of activation energies  $E$ , kcal/mol, and the enthalpy of the process of thermal destruction of complexite  $DH$ , kcal/mole also decrease. The mechanical properties of fibers at the introduction of flame retardants into the fiber composition change insignificantly. Depending on the composition of flame retardants, rupture load decreases by 6–11 %, lengthening of the samples decreases by 6–16 %.

Thus, there are some grounds to suggest that it is possible to create fibrous materials based on cellulose with predetermined properties of reduced flammability

**Keywords:** fire protection of cellulose fiber, flame retardants, thermal destruction, scanning electron microscopy

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## 1. Introduction

Cellulose-based fibers are the most important materials in the textile industry. Like other types of fibers, cellulose fibers are easily ignited, have a high rate of combustion, and their flame spreads rapidly. In this case, toxic gases and smoke are released [1]. Scientists around the world are conducting research aimed at reducing the flammability of natural and synthetic fibers, and there appear new types of fire protective compositions or substances – flame retardants, and treatment methods.

Flame retardants, which modify cellulose fibers, can suppress or delay ignition, the appearance of flames, and delay or reduce the rate of their combustion [2]. The use of such low-flammability textiles excludes the possibility of ignition of materials from low-calorie ignition sources. The ability flame propagation around the surface, the smoke-forming ability, and toxicity of decomposition products decrease as well [3, 4].

It is known that the most promising flame retardants for cellulose fibers are phosphorus-containing compounds in the mixture with nitrogen-containing substances [4], as well as

the introduction of metal ions into the structure of the matrix of the chemical fiber [5]. At the same time, the existence of functional groups of different nature in cellulose fibers makes it possible to carry out such a modification. This ensures an effective decrease in a fire hazard.

Thus, the problem of giving fire retardant properties to cellulose fibers and further research into the properties of obtained materials with decreased flammability is becoming increasingly relevant.

## 2. Literature review and problem statement

Treatment with flame retardant or combustion retardant is the most effective and common way to obtain fire-protected fibers and materials based on them. At the same time, the number of effective combustion retardants is small due to the complexity of the processes accompanying the thermal oxidizing decomposition of cellulose, the toxicity of the used flame retardant, and insufficient studies of chemical inter-

action of flame retardant with protected fiber. Therefore, further research and testing of new substances for fire protection of cellulose fibers are necessary and relevant.

A large amount of material was accumulated in the field of creating cellulose-based low-flammability materials. However, there are not enough effective flame retardants to produce a variety of fire-protected cellulose materials, as evidenced by a wide range of studies in this area [2–4]. It is known [4] that phosphorus-containing, nitrogen-containing flame retardants are used effectively in the fire protection of cellulose fibers. The issues of reducing the flammability of cellulose fibers by modifying them with the ions of transient and other types of metals are studied not enough. At the same time, the complexes of the ions of metal with the functional groups of complexite are formed [5–7]. According to paper [8], the effect of such flame retardant is manifested both in decreasing the number of combustible compounds and in the protection of, for example, cellulose fiber, by the charred layer from burning flames [4] with an increase in coke formation of the polymer.

Different methods are used to give fire protection to cellulose fibers. Thus, the authors of [2] modified cotton fibers by the padding method, including the treatment of fiber samples with an aqueous solution of epoxy flame retardant Afflamit KWB, with further treatment with phosphoric acid, washing, and heat treatment. The authors determined the optimal conditions of treatment with the flame retardant while maintaining good physical and mechanical properties, and established the chemical interaction of a flame retardant with cellulose fiber.

One of the modern ways to reduce the flammability of cellulose fibers is to use the new surface technologies based on nanoparticles, sol-gel, and layered depositions [8, 9]. Thus, the authors of paper [9] applied a hybrid flame retardant containing the elements of phosphorus, silicon, and nitrogen using the sol-gel method to modify cellulose fibers. As a result, the authors were able to obtain excellent fire-retardant properties of cellulose fiber, characterizing its structure, morphology, and thermal stability. This approach and the obtained data expand the possibilities of the use of silicon-phosphorus gel for fire-resistant cellulose fibers. Applying a similar method, the authors of [10] obtained a fire-proof cellulose fiber using industrial pyrovatex flame retardant and metacryloxyethylorthophosphortetraethylidiamide (MPD) by examining the structure of the samples.

Modern methods for reducing the flammability of cellulose fibers also involve the use of whole systems of fiber-burning retardation. Thus, the authors of paper [11] used two fire retardant systems at the same time – molecules of chitosan, silicon dioxide, and ammonium polyphosphate (APP). The chitosan–APP pair is a system similar to the swollen one, in which chitosan can act as a source of carbon and foam-forming agent, while the APP produces phosphoric acid at high temperatures, contributing to the formation of semi-coke. On the other hand, the silica–APP pair uses the joint effect of phosphoric acid, generated by the APP, which causes polymer carbonation, and thermal-insulating properties of the ceramer, such as silica. The two systems under study were responsible for an overall increase in fire resistance. Indeed, both coatings were able to suppress the afterglow phenomenon and leave a noticeable residue after flammability testing. When it comes to chitosan, the residue looked more coherent than silica residue. In addition, the silicon dioxide/APP system showed a significant increase in the time before ignition and a strong decrease in overall heat release during the conic calorimeter tests. From the practical point of view, such methods cause experimental difficulties

conducting both the experiment itself and the study of the structure of obtained fibers and the mechanism of interaction with the flammability decreasing system.

The source data on the thermal behavior of flame retardant are very important for pre-selection of systems. Paper [12] studied the thermal decomposition of two symmetrical bisphosphoramidates, tetraphenylethan-1,2-diilbis (phosphoramidite) 1 and tetraphenylpropan-1.3-diilbis (phosphoramidite) for their use as flame retardant.

Studies [7, 14] revealed a decrease in the flammability of fibers based on cellulose and polyacrylonitrile complexite NAG [15, 16] modified by fire retardants of phosphoric acid, ions of copper (II) and nickel (II), depending on the magnitude of constants of  $\lg K_{res}$  resistance. The experimental data obtained by the authors are of interest. Therefore, it is interesting to study the influence of the metal forming the most resistant complexes with complexite of CG [5], for example, with ions of molybdenum (VI), additionally varying the treatment of such complexes by phosphorus-containing flame retardant. The above-mentioned studies have practical significance. At the same time, the potential success of modification of the surface of cellulose-based fibers depends on a number of factors, including the physical and chemical properties of the fiber, required minimal fire resistance level, the concentration of flame retardant, and durability requirements. Any successful treatment should have a minimal effect on other properties of fiber and fabric and, of course, be cost-effective and rubbing resistant.

Thus, the unresolved problems in the study and creation of materials with decreased flammability are studying the mechanism of interaction between fibers and flame retardant, the search for factors that influence the fire protection method.

That is why there are some grounds to argue that when studying the processes of decreasing the flammability of fibrous cellulose-based materials, it is advisable to consider the entire range of factors arising in the system of flame retardant – cellulose fiber. At the same time, it is necessary to apply different methods for studying both original and modified fibers. This necessitates research in this direction.

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### 3. The aim and objectives of the study

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The aim of this work is to study the features of decreasing flammability and properties of modified fibrous complexite.

To accomplish the aim, the following tasks were set:

- to establish the optimal factors of modification of fiber samples, affecting the fire protection of fibrous complexite;
- to establish the effect of flame retardant on the morphology, thermal destruction of samples of modified fiber;
- to assess the impact of modification of complexite by flame retardant on mechanical properties.

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### 4. Materials and methods for studying the features of decreasing flammability and the properties of modified fibrous complexite

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#### 4.1. Materials for studying the modification of complexite samples by flame retardants

The samples of fibrous complexite (CG complexite) were used as the objects of the study. Fiber is a grafted cellulose co-polymer and polyacrylonitrile (CPAN) with the groups of hydroxamic acid and amidoxime. The nature of the reaction centers, the physical and chemical properties of complexite

CG – ion exchange, solvation, protolytic complexite of the CG are shown in paper [17].

Five different methods for treatment by flame retardant were used to study a decrease in the flammability of CG complexite and to obtain fire-protected fiber samples. 15–30 % aqueous solutions of the industrial flame retardant methylphosphonamide and urea were used as the substances decreasing the flammability of fiber samples with the following fixation of fiber samples by 0.1 n solution of phosphoric acid (sample 1). The following methods for modifying fiber samples included the treatment by phosphoric acid (0.1–0.15 n) (sample 2) and phosphonic acid (0.2 n) (sample 3). The fourth kind of fiber modification implied obtaining complexes of CG complexite with ions of molybdenum Mo (VI) in an acidic medium (sample 4). To do this, we obtained the fiber complexes by the maximum saturation with molybdenum ions from 0.1 n of aqueous solutions of molybdenum salt  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  by the method described in [5]. The fifth kind of modification of fiber samples for the purpose of studying the obtaining of fire protection involved the flame retardant treatment of the samples of CG complexite with ions of molybdenum Mo(VI) by water solution of phosphoric acid (sample 5).

In experiments, the batch of fibers was 0.5 g. At the same time, the optimal parameters of the treatment time and concentrations of flame retardants were selected.

#### 4. 2. Methods to study the decreased flammability of fibrous complexite

The methods of oxygen index, infrared spectroscopy (IR-spectroscopy), scanning electron microscopy, differential thermogravimetry, and differential thermal analysis, determining rupture load and relative lengthening of fiber samples were used.

##### 4. 2. 1. Methods for studying fire retardant properties of fibrous samples

The oxygen index method (OI, vol. %) indicates a decrease in the flammability of the CG complexite samples modified in different ways. Oxygen index is the minimum oxygen content in the oxygen-nitrogen mixture, at which candle-like combustion of material under conditions of special tests is possible. The essence of the method for determining the oxygen index is finding a minimum concentration of oxygen in the flow of oxygen-nitrogen mixture, at which there is independent combustion of a vertically located sample, ignited from above. The studies were carried out using the method described in [18].

The system of mixing and regulation of gases before entering the reaction chamber allows changing the oxygen concentration at the pitch of not more than 0.2 % vol. At the same time, the means of measuring and controlling the oxygen concentration in the gas mixture had a margin of error of no more than 0.5 % vol, the concentration regulation had a margin of error of  $\pm 0.1$  %. Oxygen index, % vol. was calculated according to [18].

The IR-spectra of the obtained modified fibers were recorded on the "Specord M-80" spectrophotometer (Germany). To do this, the samples of fibers were carefully ground in an agate mortar and pressed in the form of tablets with KBr (1:30).

##### 4. 2. 2. Methods to study the morphology of CG complexite samples

The morphology of fiber samples was studied using a scanning electron microscope with thermal emission Hitachi S-3400N.

##### 4. 2. 3. Methods to study the thermal properties of fiber samples

The data of thermogravimetric (TG) differential-thermogravimetric (DTG) analysis of modified CG complexite samples were recorded at a derivatograph – the synchronous TGA/DTA/DSK analyzer SDTQ600 (SDT-Simultaneous Differential Technics, USA). The samples weighing 5–10 mg were placed in an open platinum dish, heated from 50 to 600 °C in the air and in the argon medium. The heating rate was 6 °C/min. The temperatures of the beginning of weight loss (determined at the weight loss of 5 %), as well as the temperatures of the maximum weight loss, were determined.

The kinetic parameters of the destruction of the studied samples of cellulose fibers were calculated from the data of the curves of differential-thermogravimetric (DTG) and thermogravimetric (TG) analysis. To do this, we used the technique described in paper [19]. The DTG curve was split by the lines parallel to the ordinate axis. Further, a decrease in the weight of the sample of fibrous CG complexite was determined for each temperature.

##### 4. 2. 4. Methods to study the mechanical properties of the samples of fibers with decreased flammability

To determine the rupture load and relative lengthening of the samples of CG complexite fibers, we used a special device intended to determine the strength at stretching and lengthening of the rupture of fibrous materials. The samples of fibrous material to determine rupture load and relative lengthening were prepared according to the method for determining rupture load and lengthening at rupture in the part of the technical tissues. The velocity of the movement of a lower clamp was constant and corresponded to 10 mm/min.

The relative error of the data of the rupture load was 1–2 %, and the error of the lengthening readings was 1 mm.

## 5. Results of studying cellulose-based chemical fibers

### 5. 1. Results of studying a decrease in the flammability of CG complexite samples

The data given in Table 1 indicate a decrease in the flammability (OI data, %) of the CG complexite samples.

It should be noted that the presented data are arithmetic mean results of measuring the OI magnitudes of at least three samples of the CG complexite. The samples of the CG complexite with decreased flammability were obtained taking into consideration the pre-studied optimally effective conditions of sorption interaction of fibers with flame retardant. To do this, we examined the sorption capacity of the CG complexite samples by a flame retardant under statistical conditions. The ratio of flame retardant, kept by the fiber batch after one washing to the concentration of flame retardant, kept by the fiber batch after modification, was calculated.

In order to determine the character of the interaction of a flame retardant with the samples of the CG complexite, the IR-spectra of fiber samples before and after their treatment with flame retardant were taken. The spectrum of the CG complexite was discussed in study [17]. In the CG spectra, absorption at 3,600–3,200  $\text{cm}^{-1}$  refers to valence oscillations of NH and ON groups in the amidoxime and hydroxamic groups of complexite. At 1,680–1,650  $\text{cm}^{-1}$ , valence oscillations of C=O, NH<sub>2</sub>, C=N bonds in monosubstituted amines are observed. The bands 900–890 and 930  $\text{cm}^{-1}$  characterize the valence oscillations of N-O bond in hydroxamic and amidoxime groups, respectively.

Table 1

Influence of conditions of the treatment of the CG complexite samples with flame retardants on a decrease in the flammability

No.	Sample of fiber	Flame retardant	Batch of fiber, g	Treatment time, s	OI, %	
					Before the treatment	After the treatment
1	Complexite CG	Methylphosphonamide	0.50	120	17.5 [5]	24.7
2	Complexite CG	phosphoric acid	0.50	120	17.5 [5]	25.1
3	Complexite CG	phosphonic acid	0.45	120	17.5 [5]	24.9
4*	Complexite CG	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O Mo(VI)	0.50	3600	17.5 [5]	28.7 [5]
5	Complexite CG-Mo(VI)	phosphoric acid	0.47	120	26	29.2

Note: \*Sample 4 was obtained using procedure [5], their physical-chemical and sorption qualities are also described there

In the IR spectra of sample 1 of CG complexite (Table 1) after the treatment with flame retardant and washing, the peaks of valence oscillations of groups of methylphosphonamide are observed: P=O (1,250 cm<sup>-1</sup>), P-O-C (~1,320 cm<sup>-1</sup>). At the same time, band broadening at lower frequencies is observed in the OI spectra of modified CG complexite, which is probably the result of the formation of a bound OH group formed as a result of the chemical interaction of methylphosphonamide with a fiber. In addition, the existence of phosphorus in the structure of modified phosphoric acid complexite CG (sample 2) is proved by the bands in the region of 1,490 cm<sup>-1</sup>.

5.2. Results of studying the morphology of fiber samples

Examples of scanning electron microphotographs are shown in Fig. 1.

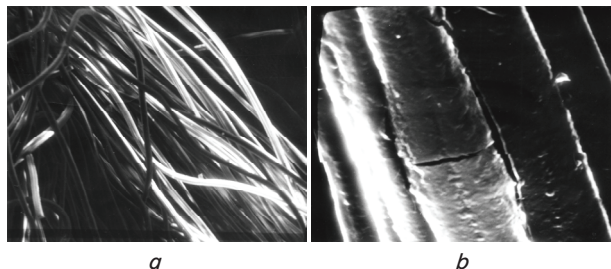


Fig. 1. Scanning electron microphotographs of CG complexite fiber: a – without treatment with flame retardant (sample 1), b – complexite sample treated with phosphoric acid (sample 3). Magnification x1,000 and x2,000, respectively

On the scanning electron microphotography of the sample of CD fiber before the modification by the flame retardant, there is a typical striped morphology (Fig. 1, a). Electronic microphotographs of the sample of CG complexite treated with flame retardant phosphoric acid have a different kind of surface.

5.2. Results of studying thermal properties

The changes in the character of the thermal destruction in argon medium and in the air of the samples of CG complexite and CG complexite saturated with the ions of Mo(VI) with subsequent modifications with flame retardant by phosphoric acid are shown in Fig. 2–4.

The given curves of thermal destruction of modified CG complexite samples in the argon medium and in the air medium indicate a different nature of the curves of the weight loss of fiber samples at different temperature intervals.

Table 2 gives the kinetic parameters of the processes of the destruction of samples of modified fiber.

The differences in the character of the destruction of the modified samples of CG complexite at the first stage of the reaction of thermal destruction are proved by calculated values of *n* and *E* (Table 2), where magnitude *n* is the order of a heterogeneous reaction, and magnitude *E* is the energy of activation of a heterogeneous reaction [19]. The heat of the processes of thermal dissociation of the samples of CG fiber modified by flame retardant is calculated according to the method described in paper [19].

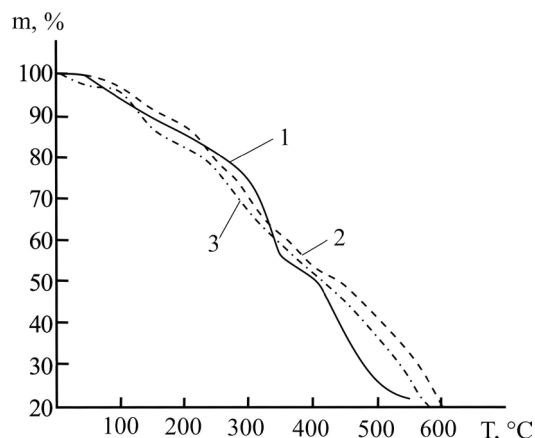


Fig. 2. Curves of thermogravimetric analysis (TG) in the air medium of modified samples of CG complexite when treated: 1 – with phosphoric acid, 2 – with the ions of Mo(VI), 3 – CG complexite with Mo(VI) ions in phosphoric acid

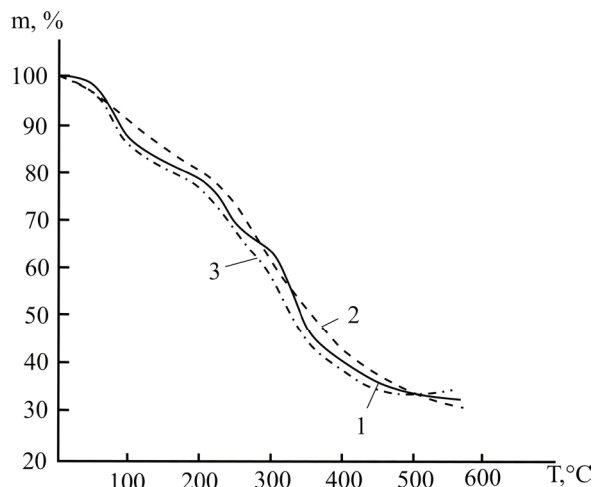


Fig. 3. Curves of thermogravimetric analysis (TG) in argon medium of modified samples of CG complexite when treated: 1 – with phosphoric acid, 2 – with Mo(VI) ions, 3 – of CG complexite with Mo(VI) ions in phosphoric acid

Kinetic parameters of the processes of destruction of samples of modified CG fiber in air and argon media

Sample	Temperature interval °C	% weight loss on DTG	<i>E</i> , kcal/mol	<i>n</i>	$\Delta H$ , kcal/mol
Air medium					
CG+phosphoric acid	300–340	14.0	30.5	0.58	20.5
CG+phosphoric acid	295–305	13.4	28.5	0.52	14.2
CG-Mo(VI)	240–290	14.2	9.7	0.42	12.8
CG-Mo(VI)+phosphoric acid	225–270	14.0	9.0	0.38	11.8
Argon					
CG+phosphoric acid	290–330	20.0	26.2	0.60	18.7
CG+phosphoric acid	290–320	20.0	24.0	0.50	14.0
CG-Mo(VI)	240–290	16.3	12	0.36	12.4
CG-Mo(VI)+phosphoric acid	220–265	16.0	8.6	0.36	11.1

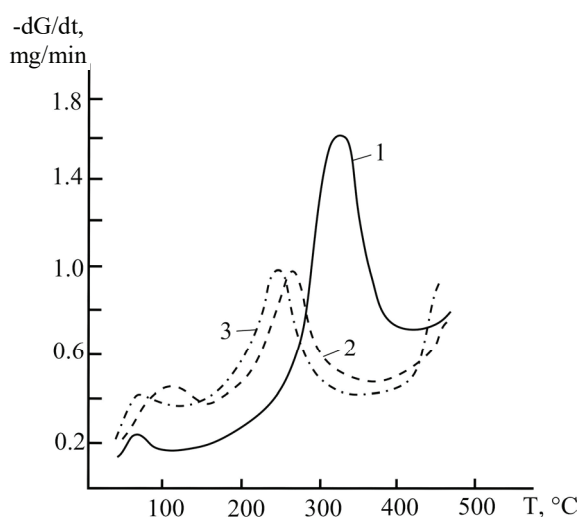


Fig. 4. Curves of differential-thermogravimetric analysis (DTG) in air medium of modified samples of CG complexite when treated: 1 – with phosphoric acid, 2 – with Mo (VI) ions, 3 – CG complexite with Mo(VI) ions in phosphoric acid

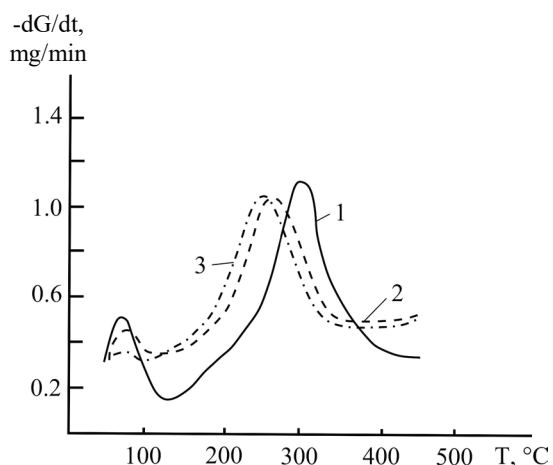


Fig. 5. Curves of differential-thermogravimetric analysis (DTG) in the argon medium of modified samples of CG complexite when treated: 1 – with phosphoric acid, 2 – with Mo(VI) ions, 3 – CG complexite with Mo(VI) ions in phosphoric acid

**Table 2 5. 3. Results of studying mechanical properties**

Rupture load, relative lengthening of the samples of modified CG complexite (Table 3) were evaluated before and after the modification by flame retardant, according to the procedure given in paper [20]. The relative error of the data on rupture load data was 1–2 %, and the error of the data on lengthening readings was 1 mm.

At a decrease in the flammability of samples of CG complexite fibers due to their modification with flame retardant, the strength properties of the samples worsen insignificantly.

Table 3

Mechanical properties of modified samples of CG complexite fiber

Sample of fiber	Rupture load, sN	Sample lengthening, %
CG	38	19
CG+methylphosphonamide	36	18
CG+phosphoric acid	36	18
CG+phosphoric acid	36	17
CG-Mo(VI)	33	14
CG-Mo(VI)+phosphoric acid	34	16

**6. Discussion of results of studying the samples of CG complexite with decreased flammability**

Conditions of treatment with flame retardant (Table 1) of the samples of CG complexite influence a decrease in fiber flammability. Since the oxygen concentration in the air is 21 %, the OI magnitude that is lower than 21 % indicates that a sample supports combustion in the atmosphere. The studies show that the OI magnitude, depending on the method of treatment of the fiber samples with flame retardant, varies from 23.6 to 29 vol. % (Table 1). If the OI magnitude makes up more than 21 %, the material has self-attenuating properties [3]. In this case, sample 5 has the highest value. The CG complexite has in the fiber matrix the free amidoxime groups that do not participate in complex formation with the molybdenum (VI) ion and the residual number of hydroxamic groups that do not interact with molybdenum ions (VI) in acidic medium. Thus, sample 5 consists of three types of flame retardants: nitrogen (amidoxime groups of CG complexite), phosphorus (treatment with phosphoric acid) and Mo (VI) [5–7]. Comparison of the OI magnitudes of samples 2 and 5 (Table 1) and sample 5 with the sample obtained during the treatment by phosphonic acid (5) indicates a slightly greater decrease in the flammability of modified cellulose complexite in the case of flame retardant of phosphoric acid.

The IR-spectra of the samples indicate the existence in its structure of the CG complexite, treated with flame retardant of phosphorus, phosphonic acids, bands of valence

oscillations characteristic of phosphorus. At the same time, the complex formation of hydroxamic groups of Mo (VI) ions was established earlier.

The change in the morphology of the sample of CG complexite before and after the modification by the flame retardant is proved by the example of scanning electronic microphotographs (Fig. 1). The surface of the fiber in Fig. 1, *a* appears smooth. Much rougher fibers in the form of a bundle of final fibers are more visible after the fire protective impregnation (Fig. 1, *b*). An example of the sample of the CG fiber, previously impregnated with the fire protective composition, shows the existence of a morphological change on the surface compared to Fig. 1, *a*.

The process of thermal destruction of modified samples of the CG complexite is affected by the medium. Fig. 2–5 shows the data of thermal studies of the samples of modified CG complexite in the air medium (Fig. 2, 4) and in the argon medium (Fig. 3, 5).

It follows from Fig. 2 that in all cases (curves 1–3) the rate of the weight loss by samples 1–3 changes, depending on the introduced flame retardant. The curves of thermal destruction for the samples containing molybdenum (VI) are different from curve 1. In the sample, modified by both molybdenum (VI) and phosphonic acid (curve 3), the rate of weight loss in the temperature interval of 100–340 °C is clearly higher. One of the reasons for this character of thermal destruction of samples of the CG complexite fiber may be the interaction of molybdenum (VI) with the products of fiber decomposition.

The thermal destruction of fiber samples in argon medium has a similar character (Fig. 3). At the same time, the decomposition of all samples begins at lower temperatures. Curve 3 (Fig. 3) in the temperature range of 100–500 °C lies below curves 1 and 2. That is, the weight losses of the samples of fibers modified by molybdenum (VI) ions occur at lower temperatures compared to curve 1. Thus, the introduction of the flame retardant into the CG complexite affects the process of destruction of the samples. At the same time, the introduction of molybdenum significantly reduces the thermal stability of fibers. It is likely that the processes of thermal destruction can be catalyzed by metals both in the air medium and in the argon medium.

For all examples of the fiber samples, the temperatures responsible for the beginning of decomposition processes correspond to the points of inflection of the straight lines constructed on certain areas of thermogravimetric TG curves. In this case, in samples 2 and 3, they are at lower temperatures compared to sample 1, Table 2, (Fig. 4, 5). The curves of DTG destruction of fiber samples in two media are different. Oxidative processes in the presence of oxygen probably play a major role in the temperature range of more than 350 °C. The processes of thermal destruction are also associated with the processes of decomposition of the matrix of fiber and functional groups introduced into a macromolecule of the CG complexite. Explanation of the obtained dependences has certain difficulty and requires additional research.

The kinetic parameters of the destruction of the studied samples of cellulose fiber were calculated using the method of [19] from the data of the curves of differential thermogravimetric (DTG) and thermogravimetric (TG) analysis. Table 2 shows the values of activation energy, the order of reaction, pre-exponents in the Arrhenius equation, based on the parameters of the differential thermogravimetric curve alone.

The results of the data (Table 2) show a decrease in the magnitude of the order of reaction  $n$  of thermal decompo-

sition at the transition from the sample of the CG fibers, treated only with acids, to the samples of CG complexite, containing molybdenum (VI).

In this case, the values of activation energies  $E$ , kcal/mol, and the enthalpy of the process  $\Delta H$ , kcal/mole decrease as well. Especially low values of these magnitudes were obtained for the sample of CG complexite, which has the highest OI values (Table 2), containing both phosphorus and molybdenum (VI).

The results of the effect of fire protective treatment of the CG complexite on the mechanical properties allowed establishing that, depending on the composition of flame retardants, rupture load decreases by 6–11 %, lengthening of samples – by 6–16 %. Similar data were obtained in paper [2].

It is likely that during the interaction of CG complexite with flame retardants, inter-chain bridges are formed in the fiber phase during the formation of complexes, as a result of which the polymer matrix becomes more rigid. This is due to the shrinkage of the samples of CG complexite fibers, compaction of their structure in the process of modification (Fig. 1, *a*). This reduces the thermal resistance of modified fibers, possibly due to the initiation by metal ions of the process of destruction of the matrix and functional groups of the CG complexite.

Thus, the introduction of molybdenum (VI) ions into the CG complexite, as well as the subsequent treatment of samples with flame retardant, decrease the thermal stability of objects, but the resulting OI values increase (Table 1). The obtained results expand the database on the creation of cellulose-based fire-protected materials. In addition, the use of flame retardants of a different nature and more diverse methods of research of the obtained modified objects would make it possible to expand and deepen the interpretation of the obtained results.

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## 7. Conclusions

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1. The methods for fire protection, in which the samples of modified CG complexite have decreased flammability, were developed. The sample of modified CG complexite with molybdenum (VI) ions, treated with phosphoric acid is the most fire protected with the magnitude of oxygen index of 29 vol. %. It contains three types of flame retardants: nitrogen (amidoxime groups of CG complexite), phosphorus (treatment with phosphoric acid) and molybdenum (VI). The obtained data of IR-spectra indicate the chemical interaction of flame retardants with the CG complexite.

2. The introduction of flame retardant into the CG complexite affects the morphology of the modified fiber and the process of thermal destruction of the samples. The scanning electronic microphotographs show the existence of a morphological change in the surface at modification of the CG complexite samples with flame retardant. The introduction of flame retardants into CG complexite affects the process of thermal destruction of the samples in the air and argon media. At the same time, the introduction of molybdenum (VI) significantly reduces the thermal stability of fibers. It is likely that the processes of thermal destruction can catalyze metals both in the air medium and in the argon medium. We found a decrease in the magnitude of the order of reaction  $n$  of thermal decomposition during the transition from the sample of the CG fiber, treated only with acids, to the samples of the CG fiber containing molybdenum (VI) up to 0.38. In this case, the values of activation energies  $E$ , kcal/mol, and the enthalpy of the process  $\Delta H$ , kcal/mol also decrease.

3. Fire protective treatment of CG complexite affects the mechanical properties of fibers. Depending on the composition of flame retardants, rupture load decreases by 6–11 %, lengthening of samples – by 6–16 %. This is due to shrinkage of the fiber samples of CG complexite, compaction of their structure in the process of modification.

#### References

1. Salmeia, K., Gaan, S., Malucelli, G. (2016). Recent Advances for Flame Retardancy of Textiles Based on Phosphorus Chemistry. *Polymers*, 8 (9), 319. doi: <https://doi.org/10.3390/polym8090319>
2. Beshshaposhnikova, V., Mikryukova, O., Zagoruiko, M., Shteinle, V. (2018). Research of fire-protective modification influence on the structure and properties of blended fabrics. *Materialy i tehnologii*, 1 (1), 37–42. doi: <http://doi.org/10.24411/2617-1503-2018-11007>
3. Syrbu, S. A., Burmistrov, V. A., Samoilov, D. B., Salikhova, A. H. (2011). Development fire proof composition for textile materials. *Tehnologii tehnosfernoy bezopasnosti*, 5 (39), 1–7.
4. Khaidarov, I., Ismailov, R. (2020). The study of fire resistance of cellulose materials physically modified with flame retardant suspensions. *Universum: Tehnicheskie nauki*, 6 (75).
5. Korovnikova, N. I., Oliynik, V. V. (2015). Ways to give Fire resistant cellulose-based fibers. *Problemy pozharnoy bezopasnosti*, 37, 116–119. Available at: [https://nuczu.edu.ua/sciencearchive/ProblemsOfFireSafety/vol37/Ppb\\_2015\\_37\\_22.pdf](https://nuczu.edu.ua/sciencearchive/ProblemsOfFireSafety/vol37/Ppb_2015_37_22.pdf)
6. Korovnikova, N. I., Oliynik, V. V. (2016). Reducing fire hazards fibers based on cellulose and polyacrylonitrile. *Problemy pozharnoy bezopasnosti*, 40, 108–111. Available at: <https://nuczu.edu.ua/sciencearchive/ProblemsOfFireSafety/vol40/korovnikova.pdf>
7. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.-M., Dubois, P. (2009). New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Materials Science and Engineering: R: Reports*, 63 (3), 100–125. doi: <https://doi.org/10.1016/j.mser.2008.09.002>
8. Horrocks, A., Eivazi, S., Ayeshe, M., Kandola, B. (2018). Environmentally Sustainable Flame Retardant Surface Treatments for Textiles: The Potential of a Novel Atmospheric Plasma/UV Laser Technology. *Fibers*, 6 (2), 31. doi: <https://doi.org/10.3390/fib6020031>
9. Liu, Y., Pan, Y.-T., Wang, X., Acuña, P., Zhu, P., Wagenknecht, U. et. al. (2016). Effect of phosphorus-containing inorganic–organic hybrid coating on the flammability of cotton fabrics: Synthesis, characterization and flammability. *Chemical Engineering Journal*, 294, 167–175. doi: <https://doi.org/10.1016/j.cej.2016.02.080>
10. Abou-Okeil, A., El-Sawy, S. M., Abdel-Mohdy, F. A. (2013). Flame retardant cotton fabrics treated with organophosphorus polymer. *Carbohydrate Polymers*, 92 (2), 2293–2298. doi: <https://doi.org/10.1016/j.carbpol.2012.12.008>
11. Carosio, F., Alongi, J., Malucelli, G. (2012). Layer by Layer ammonium polyphosphate-based coatings for flame retardancy of polyester–cotton blends. *Carbohydrate Polymers*, 88 (4), 1460–1469. doi: <https://doi.org/10.1016/j.carbpol.2012.02.049>
12. Castrejón-Flores, J. L., Reyna-Luna, J., Flores-Martinez, Y. M., García-Ventura, M. I., Zamudio-Medina, A., Franco-Pérez, M. (2020). Characterizing the thermal degradation mechanism of two bisphosphoramidates by TGA, DSC, mass spectrometry and first-principle theoretical protocols. *Journal of Molecular Structure*, 1221, 128781. doi: <https://doi.org/10.1016/j.molstruc.2020.128781>
13. Zhao, P., Li, X., Zhang, M., Liu, S., Liang, W., Liu, Y. (2014). Highly flame-retarding cotton fabrics with a novel phosphorus/nitrogen intumescent flame retardant. *Korean Journal of Chemical Engineering*, 31 (9), 1592–1597. doi: <https://doi.org/10.1007/s11814-014-0095-2>
14. Korovnikova, N. I., Oliynik, V. V. (2014). Fire-retardant properties of fibrous materials based on cellulose. *Problemy pozharnoy bezopasnosti*, 35, 122–126. Available at: [https://nuczu.edu.ua/sciencearchive/ProblemsOfFireSafety/vol35/korovnikova\\_olejnik.pdf](https://nuczu.edu.ua/sciencearchive/ProblemsOfFireSafety/vol35/korovnikova_olejnik.pdf)
15. Korovnikova, N., Dubyna, O. (2017). Research into complexing properties of polyacrylonitrile complexite in the mixtures of water-dioxane. *Eastern-European Journal of Enterprise Technologies*, 5 (6 (89)), 63–69. doi: <https://doi.org/10.15587/1729-4061.2017.110135>
16. Korovnikova, N., Dubyna, O., Oliinik, V. (2019). Features of complex formation of a fibrous complexite with nickel ions in water–dioxane mixtures. *Eastern-European Journal of Enterprise Technologies*, 2 (6 (98)), 15–22. doi: <https://doi.org/10.15587/1729-4061.2019.162359>
17. Miroshnik, L. V., Korovnikova, N. I., Shabadash, Y. V. (2006). Stability of copper(II) complexes with cellulose complexite in water-dioxane mixtures. *Russian Journal of Inorganic Chemistry*, 51 (4), 649–655. doi: <https://doi.org/10.1134/s0036023606040255>
18. Silva-Santos, M. C., Oliveira, M. S., Giacomini, A. M., Laktim, M. C., Baruque-Ramos, J. (2017). Flammability on textile of business uniforms: use of natural fibers. *Procedia Engineering*, 200, 148–154. doi: <https://doi.org/10.1016/j.proeng.2017.07.022>
19. Piloyan, G. O., Bortnikov, N. S., Boeva, N. M. (2013). The Determination of Surface Thermodynamic Properties of Nanoparticles by Thermal Analysis. *Journal of Modern Physics*, 04 (07), 16–21. doi: <https://doi.org/10.4236/jmp.2013.47a2003>
20. Meraldi, J., Aubry, J., Cizek, V., Ribiere, J., Schneider, A. (2000). Pat. No. US-0544249. Cellulose fibers with improved elongation at break, and methods for producing same. Available at: <https://scienceon.kisti.re.kr/srch/selectPORSrchPatent.do?cn=USP2001076261689&dbt=USPA>