

NEW TYPES OF FLAME RETARDANTS BASED
ON PHOSPHATE DERIVATIVESM. L. YERITSYAN ^{1*}, A. M. ARUSTAMYAN ^{1**}, I. N. SIREKANYAN ^{1***},
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One of the main problems of nature conservation and protection of the environment is the reducing of flammability of natural and synthetic materials as well as products based on them. In order to obtain non-combustible materials such as flame retardants, monosodium salt of orthophosphoric acid, urea, thiourea and their monomethylol derivatives, as well as N-monomethylol acrylamide were used in this work. The reaction for the synthesis of the mentioned compounds was carried out in the presence of a small amount of water. During the reaction between urea and monosodium salt of orthophosphoric acid, ammonia and CO₂ were released. In the case of the reaction of thiocarbamide with the monosodium salt of orthophosphoric acid, in addition to ammonia and CO₂, hydrogen sulfide is partially released, the formation mechanism of which is presented in the work.

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Keywords: flame retardants, urea, thiourea, N-monomethylol acrylamide.

Introduction. In terms of application, the creation of new types of flame retardants with high fireproof efficiency and the ability to combine with natural and synthetic compounds and composite materials based on them is extremely important in solving fire protection problems of a wide profile. There are many references devoted to flame retardants and their functional derivatives, which are of great applying importance. Thus, works [1–4] deserve special attention, where the authors of [1] describe the synthesis of flame retardants obtained by the interaction of phosphorus-containing compounds with aminoaldehyde resins. The paper [2] presents the mechanism of the flame retardant action of a phosphorus-containing fire retardant during the combustion of wood materials. The effect of aminophosphates in extinguishing a fire during the combustion of plates made from chipboard and fibreboard is quite convincingly shown in [3]. As it follows from the mentioned above, the research in the field of synthesis of new, more efficient compounds based on phosphates with fireproof properties is of both theoretical and practical interest. In the present work, new monomeric and polymeric phosphates based on the interaction of mono- and disubstituted salts of orthophosphoric acid with urea and thiourea derivatives were synthesized. Particularly, N-monomethylol derivatives of urea and thiourea were used: H₂N–C(O)–NHR, H₂N–C(S)–NHR, where R={–H or –CH₂OH}.

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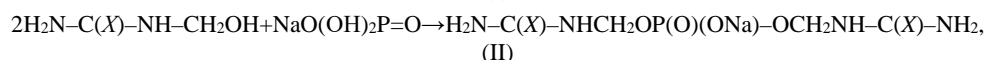
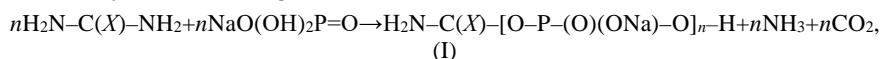
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Results and Discussion. The interaction of urea and thiourea, as well as their monomethylol derivatives, with the monosodium salt of orthophosphoric acid can be represented by the following reactions:



where in the case of urea (X is oxygen) products (Ia) and (IIa) are synthesized, and in the case of thiourea (X is sulfur) products (IIb) and (IIIb), respectively. Below are the names of the synthesized products:

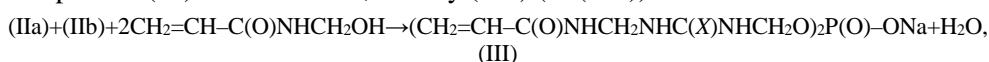
(Ia) – monosodium salt of carbamate polyphosphate,

(Ib) – monosodium salt of thiocarbamate polyphosphate,

(IIa) – monosodium salt of biscarbamidylmethylene phosphate,

(IIb) – monosodium salt of bistiocarbamidylmethylene phosphate.

Further, by reacting compounds (IIa) (or (IIb)) with methylolacrylamide, compounds (III) were obtained, namely (IIIa) (or (IIIb)):



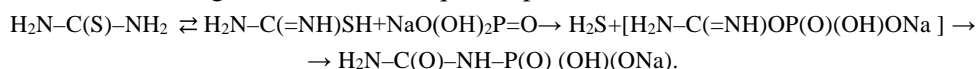
where in the case of reactant (IIa) the product (IIIa) is obtained, which is the monosodium salt of biscarbamidylmethylene carbamidyl phosphate, and in the case of (IIb) the product (IIIb), which is the monosodium salt of biscarbamidylmethylene thiocarbamidyl phosphate.

Elemental composition and absorption regions of functional groups in the IR spectra of the synthesized compounds

Compounds	Absorption regions of functional groups, ν, cm^{-1}	Elemental composition, % (found / calculated)		
		C	P	Na
(Ia)	1030 ($-\text{O}-\text{P}(\text{O})-\text{O}$), 1540, 1610, 1695 ($>\text{N}-\text{C}(\text{O})\text{O}-$)	7.5 / 7.36	18.9 / 19.02	14.0 / 14.11
(Ib)	1030 ($-\text{O}-\text{P}(\text{O})-\text{O}$), 1370 ($>\text{C}=\text{S}$), 1600 ($>\text{N}-\text{C}(\text{O})\text{N}<$), 1726 ($>\text{N}-\text{C}(\text{S})\text{O}-$)	6.5 / 6.7	17.4 / 17.32	12.7 / 12.85
(IIa)	1025–1035 ($-\text{O}-\text{P}(\text{O})-\text{O}$), 1680–1530 ($\text{H}_2\text{N}-\text{C}(\text{O})-\text{NH}-$), 889 ($-\text{CH}_2$)	18.0 / 18.18	11.8 / 11.74	8.6 / 8.4
(IIb)	1030 ($-\text{O}-\text{P}(\text{O})-\text{O}$), 1320 ($>\text{C}=\text{S}$), 1420 ($\text{H}_2\text{N}-\text{C}(\text{S})-\text{NH}-$)	16.3 / 16.22	10.4 / 10.47	7.8 / 7.77
(IIIa)	1030 ($-\text{O}-\text{P}(\text{O})-\text{O}$), 1590 ($\text{H}_2\text{N}-\text{C}(\text{O})-\text{NH}-$), 1640–1655 ($\text{CH}_2=\text{CH}-$), 1695 ($-\text{C}(\text{O})-\text{NH}-$), 2890 ($-\text{CH}_2$)	33.6 / 33.49	7.1 / 7.21	5.4 / 5.35
(IIIb)	1030 ($-\text{O}-\text{P}(\text{O})-\text{O}$), 1370 ($>\text{C}=\text{S}$), 1420 ($\text{H}_2\text{N}-\text{C}(\text{S})-\text{NH}-$), 1655 ($\text{CH}_2=\text{CH}-$), 1695 ($-\text{C}(\text{O})-\text{N}<$), 2900 ($-\text{CH}_2-$)	31.2 / 31.17	6.8 / 6.71	5.1 / 4.98

The Table below presents the data of elemental analysis and absorption regions of functional groups in the IR spectra of the synthesized compounds.

The reaction of synthesis of compound (Ib) is accompanied by a slight smell of hydrogen sulfide, and in the IR spectrum of compound (Ib) a weak band was found in the region of 1600 cm^{-1} , which characterizes the absorption of the urea unit obtained according to the reaction sequence presented below:



It should be noted that the compounds synthesized and presented above can be used as flame retardants in the composition of adhesives and varnish coatings based on butadiene-acrylonitrile rubbers, polyacrylic latexes, etc.

Experimental Part. The IR spectra of the synthesized compounds were taken on a NICOLET/FT-IR NEXUS spectrophotometer. The following compounds were used for research:

- urea and thiourea after recrystallization from ethyl alcohol;
- 37% formaldehyde aqueous solution (formalin);
- monosodium salt of phosphoric acid after recrystallization from an aqueous solution (mono-NaOPA);
- 40% aqueous solution of monomethylolacrylamide;
- $\text{Ni}[(\text{-O}-\text{C}(\text{O})\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}]$ “analytical grade”;
- N-monomethylolcarbamide prepared by the method described in [5];
- N-monomethylolthiocarbamide prepared by the method described in [6].

Preparation of Carbamate Polyphosphate Monosodium Salt (Ia).

The reactor was charged with 39.6 g (0.33 mol) of mono-NaOPA, 19.8 g (0.33 mol) of carbamide, 2.49 g (0.01 mol) of $\text{Ni}[(\text{-O}-\text{C}(\text{O})\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}]$ and 20 mL of water. The synthesis reaction was carried out at a temperature of 127–132.5°C and constant stirring for 30 min. As a result of it, NH_3 and CO_2 were released. Then the reaction mass was cooled to 60–70°C, 39 g of water preheated to 60°C was added, and the mixture was stirred until complete dissolution of the product. Then the content of the flask was put into receiver flask, where the product (Ia) precipitated. The precipitate was filtered off, repeatedly washed with ethyl alcohol and dried under vacuum at the temperature of 70–80°C to constant weight. Yield is 73%.

Preparation of Thiocarbamate Polyphosphate Monosodium Salt (Ib).

The reactor was charged with 39.6 g (0.33 mol) of mono-NaOPA, 25.8 g (0.33 mol) of thiocarbamide, 2.49 g (0.01 mol) of $\text{Ni}[(\text{-O}-\text{C}(\text{O})\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}]$ and 20 mL of water. The synthesis and isolation of the product (Ib) are similar to the product (Ia), described in detail above. In addition to NH_3 and CO_2 , a small release of H_2S was observed during the reaction. The monosodium salt of thiocarbamate polyphosphate (Ib) is pale brown in color and decomposes above 275°C. Yield is 69.5%.

Preparation of Monosodium Salt of Biscarbamide Methylphosphate (IIa).

The reactor was charged with 39.6 g (0.33 mol) of mono-NaOPA, 29.7 g (0.33 mol) of N-monomethylolcarbamide and 50 mL of water. The reaction mixture was vigorously stirred at pH 5–8. The reaction was carried out at a temperature of 60–65°C for 1.5 h with constant stirring. Then the water was removed under low pressure, leaving a white precipitate. It was repeatedly washed with ethyl alcohol under pressure 1.5–3 mm Hg at 70–75°C until constant weight. The synthesized compound

(IIa) is soluble in water, partially in methyl alcohol and dimethyl sulfoxide. The decomposition starts at 265°C. Yield is 82%.

Preparation of Monosodium Salt of Bisthiocarbamide Methylenphosphate (II b). The reactor was charged with 39.6 g (0.33 mol) of mono-NaOPA, 39.98 g (0.33 mol) of thiocarbamide and 50 mL of water. The synthesis and isolation of the product (IIb) are similar to the product (IIa) described above. Monosodium salt of bisthiocarbamide methylenphosphate (IIb) is pale brown in color and decomposes above 245°C. It dissolves in water and partially soluble in alcohols.

Preparation of N-methylolacrylamide. The reactor was charged with 14.2 g (0.2 mol) of acrylamide and 6.3 g (0.21 mol) or 17.0 mL of formaldehyde aqueous solution. The reaction was carried out at pH 9.0 with constant stirring for 3.5 h at 70°C. Quantitatively, a 37% aqueous solution of N-monomethylolacrylamide was formed, which was used in further syntheses. Water was removed under low pressure, and the white precipitate was repeatedly washed with chloroform and dried at 30–35°C (under a residual pressure of 1.5–2 mm Hg) to constant weight. The resulting white powder has a melting point of 74.5°C and is highly soluble in water, alcohols and esters.

Preparation of Sodium Salt of Biscarbamidyl Methylencarbamide Phosphate (IIIa). The reactor was charged with 10.1 g (0.1 mol) of N-monomethylol acrylamide (27.3 mL 37% aqueous solution of monomethylol acrylamide), 20 mL of water and 43.0 g (0.1 mol) of compound (IIa). The reaction was carried out at pH 9.0 with constant stirring for 3.5–4 h at 60°C. Then water was removed under low pressure, and the final content of the reactor, which was a white precipitate was repeatedly washed with acetone and chloroform and dried at 30–35°C (under a residual pressure of 1.5–2 mm Hg) to constant weight. Yield is 79%. The synthesized product easily dissolves in water and partially dissolves in ethyl and methyl alcohols. Thermal polymerization occurs at temperature above 115°C.

Preparation of Monosodium Salt Bisacrylamide Methylthiocarbamate Phosphate (III b). The reactor was charged with 10.1 g (0.1 mol) of N-monomethylol acrylamide (27.3 mL 37% aqueous solution of monomethylol acrylamide), 20 mL of water and 46.2 g (0.1 mol) of compound (IIb). The reaction and isolation of the dark brown product was carried out according to the previous procedure for the synthesis of the product (IIIa). The yield of the synthesized product (IIIb) is 67.5%. It dissolves easily in water and alcohols. Thermal polymerization takes place above 120°C.

Conclusion. New monomeric and polymeric phosphates based on the interaction of mono- and disubstituted salts of orthophosphoric acid with urea and thiourea derivatives were synthesized. The synthesized compounds can be used as flame retardants in the composition of adhesives and varnish coatings based on butadiene-acrylonitrile rubbers, polyacrylic latexes, etc.

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ՆՈՐ ԱՆՏԻՊԻՐԵՆՆԵՐ ՖՈՍՖԱՏՆԵՐԻ ԱԾԱՆՑՅԱԼՆԵՐԻ ՀԻՄԱՆ ՎՐԱ

Բնական և սինթետիկ միացությունների, ինչպես նաև դրանց հիման վրա պատրաստված իրերի այրման ունակության նվազեցումը բնապահպանության և շրջակա միջավայրի պաշտպանության կարևորագույն խնդիրներից մեկն է: Սույն աշխատանքում անտիպիրենների, որպես նմանատիպ չայրվող միացությունների, ստացման համար օգտագործվել են օրթոֆոսֆորական թթվի մոնոնատրիումական աղը, կարբամիդը, թիոկարբամիդը և դրանց հիման վրա ստացված մոնոմեթիլոլային ածանցյալները, ինչպես նաև N-մոնոմեթիլոլակրիլամիդը: Մինթեզի ռեակցիան տարվել է ոչ մեծ քանակությամբ ջրի առկայությամբ: Օրթոֆոսֆորական թթվի մոնոնատրիումական աղի հետ կարբամիդի փոխազդեցության արդյունքում անջատվում է ածխաթթու գազ և ամոնիակ: Օրթոֆոսֆորական թթվի մոնոնատրիումական աղի հետ թիոկարբամիդի փոխազդեցության դեպքում, բացի ածխաթթու գազից ու ամոնիակից նաև որոշ քանակությամբ ծծմբաջրածին է անջատվում, որի առաջացման մեխանիզմը ներկայացված է սույն աշխատանքում:

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НОВЫЕ АНТИПИРЕНЫ НА ОСНОВЕ ПРОИЗВОДНЫХ ФОСФАТОВ

Снижение горючести природных и синтетических материалов, а также изделий, изготовленных на их основе, является одной из главнейших задач охраны природы и защиты окружающей среды. В настоящей работе для получения таких несгораемых продуктов, как антипирены, были использованы моносодиевая соль ортофосфорной кислоты, карбамид, тиокарбамид и их монометилольные производные, а также N-монометилол акриламид. Реакция синтеза проводилась в присутствии небольшого количества воды. В ходе реакции карбамида с моносодиевой солью ортофосфорной кислоты выделяется аммиак и CO₂. В случае реакции тиокарбамида с моносодиевой солью ортофосфорной кислоты кроме аммиака и CO₂ частично выделяется сероводород, механизм образования которого представлен в работе.