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# *Study of a Method for Producing a Flame Retardant Based on Epichlorohydrin*

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**Abstract – The article presents the results of new studies conducted in the direction of shaving of methods for producing flame retardant based on epichlorohydrin. Some results of practical research are given. Attention is paid to the most common and effective way to reduce the combustibility of polymeric materials. The results of initial observations and practical studies of the properties of halogen-containing flame retardants are presented.**

**The article is devoted in general to the current problems of science and technology for studying the properties of obtaining flame retardants based on epichlorohydrin and modern methods for producing flame retardants.**

**Keywords – Method, Flame Retardant, Epichlorohydrin, Polymeric.**

Currently, a large number of compounds and mixtures thereof are known that have flame retardant properties. However, the ever-increasing demands on their quality, availability and cheapness determine the need for targeted improvement of existing and the search for new flame retardants and their compositions that are highly effective, easily obtained from available raw materials and economical both from the point of view of their synthesis and use.

Progress in the creation, industrial production, use of polymers and products made of them, along with clear advantages over traditional materials, has a negative side due to the release of harmful volatile impurities into the human environment and human activity at all stages of their production and use, as well as high combustibility and toxicity of thermal decomposition products of the majority of produced polymers [1].

Modification of polymers is a way to change the structure and properties of macromolecules, allowing to reduce the combustibility of materials. Any change in the chemical structure of a polymer substance under the influence of chemical and physical agents can significantly affect the properties of the finished material.

The most common and effective way to reduce the flammability of polymeric materials is the use of flame retardants. Along with the subdivision of flame retardants into groups according to the mechanism of action of the material, there are several types of classifications: by type of substances that slow down combustion, as intended, and others. In our opinion, the most complete of them is classification by the active element or grouping in a flame retardant with a libo-modifying agent, according to which They are divided into: 1. halogen-containing compounds; 2. phosphorazot-, antimony-, bismuth-containing flame retardants; 3. combustion retardants containing boron, silicon, aluminum and magnesium hydroxides. By volume, the flame retardant market makes up about 30% of all polymer additives produced, second only to pigments and dyes. The annual growth of aluminum hydroxide production is estimated at 3%, phosphorus-containing flame retardants - at 7% and bromine-containing flame retardants - at 8% [2].

Almost all halogen-containing compounds are combustion inhibitors. The effectiveness of halogen-containing flame retardants increases in the series F <Cl <Br <I [6]. Most often, chlorine & and bromine-containing compounds are used as flame retardants, as they provide the best price / quality ratio. Bromine-containing flame retardants are much more effective than chlorine-containing flame retardants, since their combustion products are less volatile. In addition, chlorine-containing flame retardants produce chlorine in a wide temperature range, therefore, its content in the gas phase is low, and bromine-containing flame retardants decompose in a narrow temperature range, thus ensuring an optimal concentration of bromine in the gas phase. The fluorine and iodine compounds are not used as flame retardants, since the fluorine compounds are ineffective, and the iodine compounds have low thermal stability during processing [3].

The action of halogen-containing flame retardants mainly occurs in the pre-flame and surface zones, to a lesser extent, in zone pyrolysis. Moreover, as a result of thermal transformations of the material and combustion retardants, halogenated hydrocarbon particles can be formed along with hydrogen halides and halogens, which, in turn, inhibit the combustion processes of materials, combustible halogen-containing compounds having low flash points and self-ignition. in addition to hydrogen halides, haloalkyls, halogenated, halogenbenzenes are formed [4].

Subsequent monitoring revealed that the personnel of the fire brigades observed chronic poisoning by dioxins, which were formed during the combustion of polymers, which included polybrominated diphenylethers (PBDFE) as flame retardants.

PBDEs are mostly resistant organic pollutants, are able to accumulate in the human body at dangerous concentrations, and exhibit hepato-, nephro-, gonadotoxic properties. Tetra- and hexa-PBDFE are the dominant forms that enter the human body with contaminated food.

It should be emphasized that toxicological studies of bromine-containing flame retardants are carried out very intensively in many countries of the world, as this opens up new details of the toxic effect on the human body and the uniformity of ecotoxicity of such global persistent organic environmental pollutants as dioxins, which are close to the considered group of flame retardants in their biological properties, toxicokinetics and pathogenesis of poisoning [5].

All flame retardants (retardants) are divided into 3 large groups [26] .1. The additives included in the first group chemically interact with the polymer. They are used mainly for fire protection of thermosets. Organophosphorus compounds are usually introduced into epoxy resins, and bromine-containing additives, for example, dibromneopentyl glycol, are introduced into polyester and polyurethane resins during their synthesis. It contains up to 60% bromine, is characterized by high thermal stability and chemical resistance, and is a highly effective flame retardant. 2. Intumescent additives stop the polymer from burning at the initial stages of ignition, i.e., at the stage characterized by the highest release of combustible gaseous products and intense smoke formation. 3. Additives of the third type are mechanically mixed with the polymer. They are used for thermoplastics, thermosets and elastomers.

Organophosphorus flame retardants satisfy most of the requirements of existing and new fire fighting technologies. They are practically colorless, are liquid and soluble products that exhibit excellent technological properties, especially in liquid systems such as polyols or resin compositions, and also exhibit valuable secondary properties, in particular, lower viscosity or improved compatibility of additives with the polymer.

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Thus, the above literature shows that the synthesis of new nitrogen and phosphorus compounds and the study of their physicochemical and flame retardant properties is of great scientific and practical interest. The use of flame retardants changes the behavior of flammable materials during a fire, reducing or suppressing their combustibility [7] .

Fire retardants can change the reaction of a substance to combustion, giving the substance fire-resistant properties, which leads to a slowdown in the rate of combustion upon ignition. Fire retardants provide invaluable time to save people from buildings in fire. Due to the recently increased interest in environmental pollution and the harm to human health, halogen-based flame retardants are constantly being replaced with more environmentally friendly phosphorus and nitrogen-containing flame retardants [8].

In this work, we carried out studies on the synthesis of nitrogen and phosphorus-containing flame retardants. Epichlorohydrin, urea, melamine, ammonium dihydrogen phosphate, phosphoric acid, morpholine were chosen as objects of study.

The influence of various technological parameters on the process of polycondensation of phosphoric acid and urea was studied. The interaction of urea with phosphoric acid proceeds in the liquid phase with vigorous stirring and heating of the reaction mass:

$$NH_2CONH_2 + (HO)_3PO \longrightarrow NH_2C(O)NH \cdot P(O) \cdot (OH)_2 + H_2O$$

By conducting a number of laboratory experiments, the optimal dilution rate was selected. It was found that at atmospheric pressure and 90 ° C and a molar ratio of urea: phosphoric acid: water 2.3: 1: 5 allows you to get a homogeneous reaction mass.

A study of the kinetics of the reaction shows that the reaction is characterized by a low speed. In this regard, we conducted studies to accelerate the polycondensation reaction. The reaction rate of urea with phosphoric acid was determined by the time the pH of the reaction medium reached 4. At this value of the acidity of the medium, approximately 50% of the conversion of the starting reagents is achieved; therefore, this parameter is chosen for the convenience of measurements. It was found that the intensity of mixing does not affect the reaction rate, i.e. the reaction is not complicated by diffusion inhibition and proceeds in the kinetic region. With increasing temperature from 70 to 90 ° C, the reaction rate increases (figure). An increase in the concentration of urea contributes to an increase in the rate of polycondensation. However, an excess of urea creates the conditions for its deposition at low temperatures.

We also obtained oligomeric flame retardant by condensation of urea with phosphoric acid in a melt at a temperature of 130-135 oC. The synthesis of the oligomer in the melt eliminates the hydrolysis of the original urea. The molar ratio of urea and phosphoric acid during the synthesis process is (1.5-2.5): 1, which corresponds to an atomic ratio of N / P from 3 to 5 and the yield is 95-98%. The resulting flame retardants are soluble in water and some organic solvents.

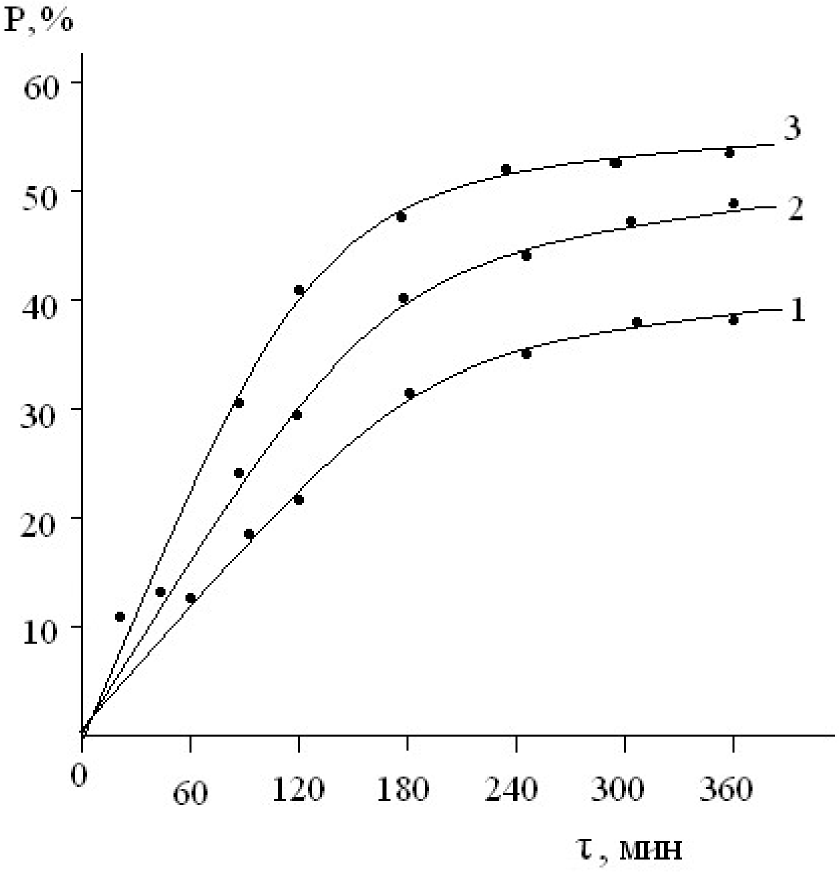
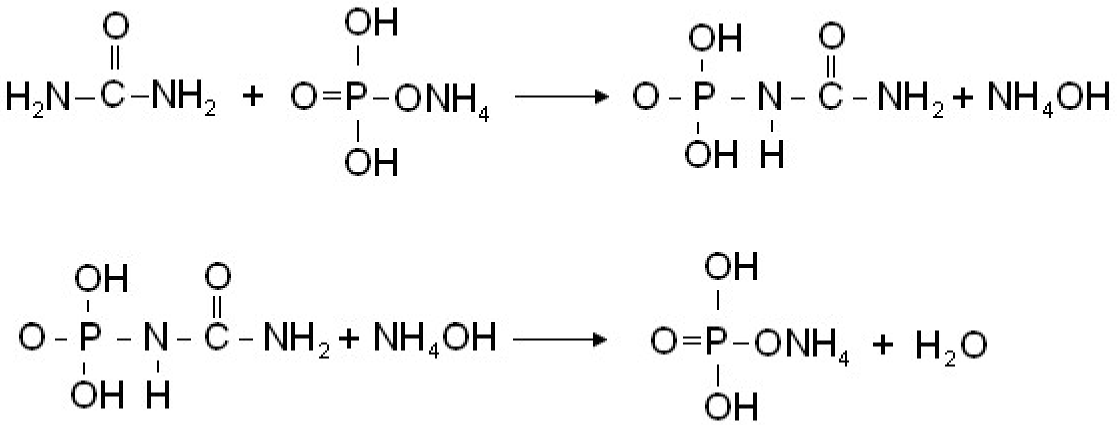



Fig. 1 Kinetics of polycondensation of phosphoric acid with urea at temperatures, ° C: 1 - 70, 2 - 80, 3 - 90.

The methods of elemental analysis and IR spectroscopy were used to study the structure of oligomers obtained by the joint polycondensation of urea and phosphoric acid. The method of viscometry was used to study the influence of synthesis conditions on the value of intrinsic viscosity.

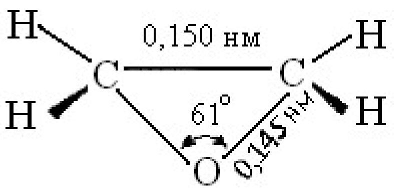
The reaction of the interaction of urea with ammonium dihydrogen phosphate in the melt was studied. It was experimentally established that a by-product of this reaction is ammonium hydroxide NH4OH, upon heating of which ammonia is formed. To interact with ammonium hydroxide, phosphoric acid was introduced into the reaction zone. As a result of the reaction, ammonium dihydrogen phosphate is formed, which is involved in the synthesis of flame retardant. The general scheme for the synthesis of a flame retardant based on urea with ammonium dihydrogen phosphate can be represented by the following scheme:

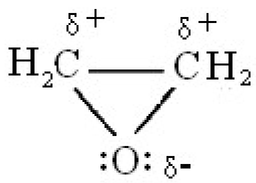


Thus, the binding of the released NH4 + ion to phosphoric acid ensures its use as a reagent for endogenously feeding the synthesis components with additional ammonium phosphate and a more complete course of the total condensation reaction.

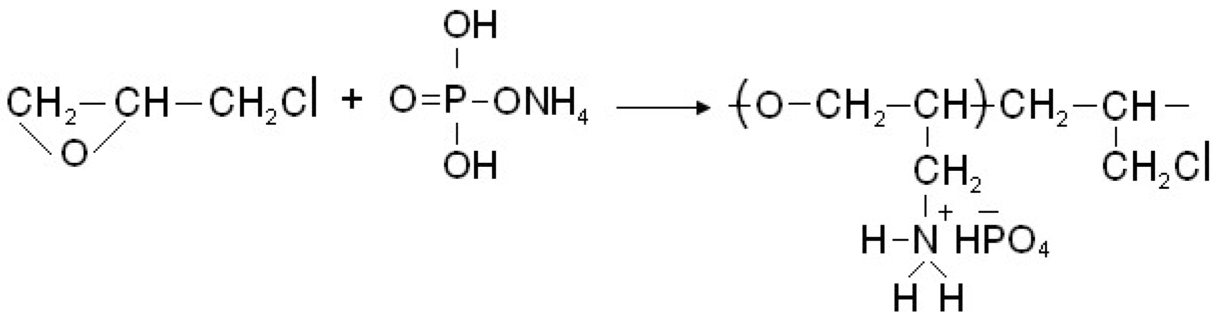
Next, we synthesized oligomeric flame retardants by polymerization of epichlorohydrin with a phosphorus-containing compound. Ammonium dihydrogen phosphate was used as the phosphorus-containing compound.

The epichlorohydrin molecule contains two active groups — the epoxy group and the C – Cl bond. The epoxy cycle is an almost regular triangle with significantly deformed valence angles. Therefore, only partial overlap of atomic orbitals occurs and the bond energy decreases:




The polymerization process was carried out by stirring at temperatures of 20-40 ° C. The structural formula of the synthesized compound based on epichlorohydrin with ammonium dihydrogen phosphate can be represented as follows:



The influence of various technological factors on the polymerization process was studied: the ratio of the starting reagents, the nature of the solvent, and temperature.

The study of the influence of the ratio of the starting reagents on the yield of the oligomeric product shows that with an increase in the ratio of ammonium dihydrogen phosphate

In order to study the fire-retardant properties of the synthesized products on cotton fabrics, we impregnated the fabrics with an aqueous composition containing 25-30% urea-based flame retardant with phosphoric acid followed by extraction (25-30%). Then it was dried at 50-60 oC and subjected to heat treatment at 140-150 oC for 5 minutes. It was found that the use of the specified flame retardant increases the effect of incombustibility of the fabric.

Thus, a synthesis of flame retardants based on urea with phosphoric acid and epichlorohydrin with ammonium dihydrogen phosphate was carried out. The condition of the synthesis process is studied. Based on the synthesis products, a new effective flame retardant has been developed.

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