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Аннотация. В настоящее время изучены и проанализированы преимущества и недостатки соединений сурьмы, галогенсодержащих соединений, фосфорсодержащих консервантов, а также гидроксидов алюминия и магния. Рассмотрены различные механизмы замедления процессов горения. Показано, что бромсодержащие антипирены более эффективны по сравнению с хлорсодержащими. Они разлагаются в узком температурном диапазоне. Кроме того, пластмассы, содержащие бромсодержащие антипирены, легко перерабатываются благодаря высокой термостойкости.

Ключевые слова: фосфат аммония, сульфат аммония, борная кислота, силикаты, хлорид аммония, синергисты, ретардер, смазочный материал.

Annotatsiya. Hozirgi vaqtda surma birikmalari, galogen birikmalari, fosfor saqlovchi konservantlar, shuningdek alyuminiy va magniy gidroksidlarining afzalliklari hamda kamchiliklari o‘rganilib, tahlil qilingan. Yonish jarayonlarini sekinlashtirishning turli mexanizmlari ko‘rib chiqilgan. Brom saqlovchi olovga chidamli qo‘shimchalar xlor saqlovchi qo‘shimchalarga nisbatan samaraliroq ekani aniqlangan. Ular qisqa harorat oralig‘ida parchalanadi. Bundan tashqari, brom saqlovchi olovga chidamli qo‘shimchalar mavjud plastmassalar yuqori issiqlikka chidamliligi sababli oson qayta ishlanadi.

Kalit so‘zlar: ammoniy fosfat, ammoniy sulfat, bor kislotasi, silikatlar, ammoniy xlorid, sinergistlar, retardator, moylovchi modda.

Abstract. Currently, the advantages and disadvantages of antimony compounds, halogen compounds, phosphorus-containing preservatives, as well as aluminum

and magnesium hydroxides have been studied and analyzed. Various mechanisms for slowing down combustion processes have been considered. Bromine-containing flame retardants have been shown to be more effective than chlorine-containing flame retardants. They decompose in a short temperature range. In addition, plastics containing bromine-containing flame retardants are easily recycled due to their high heat resistance.

Keywords: ammonium phosphate, ammonium sulfate, boric acid, silicates ammonium chloride, synergists, retarder, lubricant.

INTRODUCTION.

Currently, there is no sector of the economy in the world where polymer materials and products based on them have not penetrated. The level of their use is one of the most important indicators of the level of scientific and technological development of the country. The growth of industry and production leads to high design requirements for the types and properties of polymers used in the automotive, construction and household sectors. Therefore, it is important to modify polymers, improve their physical and mechanical properties, and obtain composite materials that meet a number of requirements by adding additives without changing their chemical composition.

Currently, research in the field of using modifiers with individual and multifunctional effects is an important direction in improving the quality of anti-corrosion coatings and refractory materials. It is necessary to conduct scientific research on the dependence of the colloidal-chemical, physico-chemical, technological and operational properties of composite materials obtained to date on the nature and composition of the modifiers, on the production and creation of technology for obtaining polymer composites with convenient and inexpensive special properties based on local raw materials, and on expanding their areas of application.

In recent times, not flame retardants themselves, but their mixtures are being used. Flame retardants include (1, 2):

- fire retardants (ammonium phosphate, ammonium sulfate, boric acid, silicates, ammonium chloride);
- synergists – substances that enhance the effect of inhibitors;
- stabilizers that adjust the consumption of retardant.

Flame retardants prevent the material from burning once the flame retardant content in the material reaches an appropriate level. Under the influence of flame, various chemical and physical processes occur in this material, preventing ignition [3-4].

All means that increase fire resistance properties are divided into fire-protective coatings and compounds that penetrate the material being processed.

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The first category includes varnishes, pastes, paints and various types of greases, the second category includes fire-protective impregnations.

Combustion is a very complex physicochemical process, which includes chemical destruction reactions, formation and carbonization reactions, chemical formation reactions and oxidation products of gaseous products during combustion, and physical heat transfer processes [5]. In practice, reactions lead to two main types of products: gaseous substances (combustible and non-combustible) and solid products (carbon and mineral). As a result of the reaction in the pre-combustion zone, soot and others are formed.

Thermal degradation of polymers releases volatile compounds. These are radicals that form free radicals, which are the CC and CH groups, and react with oxygen. The rate of fire and the spread of fire depend on the formation of HO• radicals. Such reactions, which lead to the formation of CO2 and H2O, are highly exothermic reactions, which are accompanied by the release of a large amount of heat. This heat, in turn, causes the fire to spread further and accelerate oxidation reactions.

Mechanism of action of flame retardants

There are several mechanisms for retarding combustion using flame retardants [6]:

- inhibition of free radical formation processes. The introduction of substances containing halogens (chlorine, bromine, fluorine, iodine), nitrogen, phosphorus and boron helps to slow down combustion. Under the influence of high temperatures, flame retardants decompose, forming highly active NO• halogen radicals.

- the formation of a protective layer on the polymer surface, impervious to oxygen or insulating from further heating. The mechanism of action of a number of flame retardants (silicates and aluminosilicates, metal borates, phosphates, their organic derivatives) is that they form protective layers that prevent the combustion process.

These layers are composed of non-volatile residues (mainly metal oxides) and are inorganic decomposition compounds. Flame retardants form dense and durable surface protective layers, preventing the spread of flammable substances. Such flame retardants include barium meta-borate, zinc borate, ammonium tetrafluoroborate [7, 8].

Flame retardants containing phosphorus compounds reduce the oxygen absorption of materials. An example of such flame retardants is diammonium phosphate. One of the effective inhibitors that slow down combustion processes is considered to be organic phosphorus compounds, the effect of which is explained as follows [9, 10, 11]:

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- The pyrolysis process of polymers containing phosphorus compounds is accompanied by the formation of phosphoric acid and its anhydrides, which catalyze its dehydration and dehydrogenation.

- The release of non-combustible gases that prevent the combustion zone from being supplied with oxygen. The mechanism of action of halogen compounds that retard the combustion of polymers as flame retardants is as follows: Ammonium bromide or chloride decomposes into ammonia, hydrogen chloride and bromine at temperatures above 200°C and 250°C. Hydrogen chloride and hydrogen bromide in the gaseous state reduce combustion. In addition, the proportion of oxygen in the gas phase decreases, which in turn slows down combustion.

- Destruction processes that occur as a result of the decomposition or interaction of flame retardants and their absorption of heat with other substances lead to a decrease in the temperature of the ignition point of the material. A large group of substances used as flame retardants decompose endothermically, forming non-combustible products. These include aluminum hydroxide, magnesium, zinc hydroxides, hydrated metal carbonates, urea and other substances. The mechanism of action of such flame retardants is associated with a physical effect on the heat balance of the combustion process.

- Additional thermal energy is required to heat the powdered fillers to prevent the spread of fire.

The introduction of non-combustible fillers into the polymer composition allows you to reduce the amount of combustible components in the materials. For this purpose, dispersed fillers (chalk, sand) and fibrous fillers (glass fibers, asbestos) can be used. Of great importance in this regard are potassium or sodium silicates, the materials coated with which burn with great difficulty. For this purpose, the material is repeatedly coated with a silicate solution, to which a small amount of chalk, bone ash, mineral paint or other crushed, insoluble mineral substances is added. Materials treated with these flame retardants do not burn with a flame, but can only warp under the influence of heat.

Flame retardant synergistic mixtures

It should be noted that the mechanism of action of flame retardants is not characterized by a single effect, it is a more complex process. The simultaneous presence of two or more mixtures significantly inhibits the formation of fire. The combined effect of two substances is called synergism.

Currently, the most effective flame retardant is antimony oxide, which is combined with halogen-containing organic compounds (optimal molar ratio Sb / Cl = 1/3). This mixture has a synergistic effect [12]. The mechanism of action of this mixture is as follows. During the combustion of the polymer, hydrogen

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chloride, released from the halogen-containing organic compounds, interacts with antimony oxide to form antimony oxychloride, which in turn can decompose into antimony trichloride:

$$Sb_2O_3 + 2HCl = 2SbOCl + H_2O$$
$$5SbOCl = Sb_4O_5Cl_2 + SbCl_3\ (245–280^oC)$$
$$4Sb_4O_5Cl_2 = 5Sb_3O_4Cl + SbCl_3\ (410–475\ ^oC)$$
$$3Sb_3O_4Cl = 4Sb_2O_3 + SbCl_3\ (475–565\ ^oC)$$

The antimony oxide formed in the final stage is a powder filler that helps slow down the combustion. The gaseous antimony trichloride limits the supply of oxygen to the material zone. Antimony oxide is not carcinogenic to the human body.Halogen-containing flame retardants. The effectiveness of halogen-containing flame retardants of the same type is characteristic of the series J > Br > Cl > F. The highest effectiveness is shown by the carbon-halogen bond with the lowest energy . The effectiveness of halogen-containing compounds is determined by how easily the SG bonds dissociate. The effectiveness of flame retardants depends not only on the amount of halogen, but also on the number of radicals to which it binds. Chlorinated paraffins (CnH_2n+2-x Clx, where n=10–30; x=1–7) containing up to 70% bound chlorine are used as halogen-retaining aliphatic compounds. Often, aromatic chlorine or bromine-containing compounds are used, for example, decabromodiphenyloxide, ($S_{16}N_{10}Br_{10}O$), tetrachlorophthalic anhydride ($C_8Cl_4O_3$).

Aromatic chlorine or bromine compounds are used less frequently. For example, decabromodiphenyl oxide ($S_{16}N_{10}Br_{10}O$), tetrachlorophthalic anhydride ($C_8C_{l4}O_3$) are among them. Aromatic compounds are more stable and therefore reduce flammability less. Fluorine and iodine compounds are not used as flame retardants: fluorine compounds are less effective and iodine compounds have very low thermal stability.

In recent years, the use of chlorine has been significantly reduced due to public pressure and organizations concerned about its toxicity. Bromine-containing flame retardants do not emit toxic compounds (dioxins and furans). In terms of nomenclature and scope of application, bromine-containing flame retardants are much more numerous than chlorine-containing compounds. Bromine-containing flame retardants are more effective than chlorine, and their combustion products are also less volatile.

In addition, chlorine-containing flame retardants release chlorine over a wide temperature range, so the amount of chlorine in the gas phase is very low, while bromine-containing flame retardants decompose over a short temperature range, ensuring an optimal concentration of bromine in the gas phase. According to recent data , the high thermal stability of flame retardants containing bromine

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compounds in the polymer composition allows for easy recycling of polymer raw materials.

Polybrominated diphenyl oxide and its derivatives are suitable for many plastics other than expanded polystyrene. Currently, due to pressure from environmental organizations, the number of such compounds is decreasing. Dibrominated neopentyl glycol and its derivatives are used in the synthesis process to obtain polyester resins containing 60% bromine. They have high chemical and thermal stability; highly effective flame retardant; resistant to light. In addition, they are used in the production of rigid polyurethane films.

Phosphorus-containing flame retardants

Phosphorus-containing flame retardants can be organic or inorganic [13 , 14 , 15]. They are active in the gas or condensed phase, and sometimes in both . Phosphorus compounds act in the gas phase by generating RO• radicals. The scavengers of the active H• and OH• radicals contribute to the spread of the flame.

The nomenclature of phosphorus-containing compounds is very wide, they can be divided into 2 groups : halogen-containing and halogen-free compounds.

Advantages of halogen-containing and phosphorus-containing compounds:

- during the decomposition process, it forms halogen radicals, that is, it forms the usual N• and ON• radicals characteristic of halogens;
- as is typical for halogens, the above activated radicals form H• and OH•;

The second group includes red phosphorus, water-soluble inorganic phosphates, insoluble ammonium phosphate and polyphosphates, organophosphates, phosphonates, as well as phosphine oxides.

Red phosphorus is an excellent flame retardant for heterochain polymers (polyethylene terephthalate, polycarbonate, etc.). In particular, red phosphorus is used as a flame retardant in the production of electrical products made of polyamide, which is specially processed. However, its use is limited due to its toxicity and red color.

During the processing of high-grade polyethylene raw materials, which are also produced at Shurtan Gas Chemical Complex LLC, a certain amount of technological waste, i.e. secondary raw materials, is generated. After polymer products are used for various purposes, their shelf life expires and they are crushed and repeatedly processed as secondary products. In order to reduce the flammability properties of polymer materials obtained as secondary products, we used a number of flame retardants. For this purpose, the following grades of polyethylene were used: PE I-0525, PE I-0760, PE F-0220, PE F-0320.

The results obtained (Table 1) show that the flammability characteristics of materials obtained from secondary PE of the above brand correspond to class V-0 according to the UL94 standard.

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Table 1.

Formulations developed to reduce the flammability of PE

No.	Chemical name	Recipe-1	Recipe-2	Recipe-3	Recipe-4
1	PE I-0525	43.7	8	10.7	30
2	PE I-0760	0	50	43	38.7
3	PE F-0220	0	5.7	5	0
4	PE F-0320	5	0	5	0
5	APF (ammonium polyphosphate)	30	25	28	30
6	Fiberglass, 17 microns	20	0	0	0
7	Talk	0	10	7	0
8	PE WAX ethylene bis stearamide	0.3	0.3	0.3	0.3
9	Fire resistance according to UL94 Standard, Class V -0 compliant	V-0 (1.6mm)	V-0 (1.6mm)	V-0 (1.6mm)	V-0 (1.6mm)

Metal hydroxides.

Aluminum hydroxide is used in the production of elastomers, thermosets, and thermoplastics. It decomposes at temperatures between 190 and 230°C and particle sizes between 0.25 and 3 μm. The main applications are in the production of butadiene-styrene latex, carpet coatings, non-flammable elastomer cables, conveyor belts, roofing materials, and hoses. The highest efficiency is achieved when aluminum hydroxide is incorporated into oxygen-retaining polymers (polyethylene terephthalate, polybutylene terephthalate, and polyamide).

Magnesium hydroxide is a white powder with particle sizes ranging from 0.5 to 5 μm. To achieve a fire retardant effect, it is added in an amount of 50-70% by weight of the polymer. Magnesium hydroxide is more expensive than aluminum hydroxide, but has high heat resistance (up to 300°C). It is mainly added to polymers based on polypropylene, acrylonitrile butadiene styrene plastics and polyphenylene oxide. It is not recommended for use in thermoplastic polyesters (polyethylene terephthalate, polybutylene terephthalate), as it accelerates the destruction of polymers.

Metal hydroxides decompose at high temperatures with the release of water. This decomposition reaction is endothermic, which causes the material to cool to a temperature below its ignition temperature. The formation of water helps to dilute the combustible gases released by the reaction, weakening the effect of

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oxygen and reducing the rate of combustion. The effectiveness of hydroxides is directly proportional to their amount in the polymer matrix [16].

Zinc borate can also be used for fire protection of materials based on PVC, polyolefin, polyamide, elastomer and epoxy polymers. Halogen-containing compounds can be used in combination with antimony oxide, and halogen-free compounds - in combination with metal hydroxides or red phosphorus.

CONCULUSION. An Among the flame retardants described above, the most effective in terms of volume of use (more than 40% of all flame retardants) are aluminum and magnesium hydroxides. This is explained by the fact that they are cheap, technologically convenient to process and environmentally friendly. A properly selected polymer composition based on them is non-flammable and inexpensive, and only a small amount of smoke can be released during decomposition. Therefore, the use of metal hydroxides as flame retardants is constantly growing. Flame retardants are special substances used to increase the fire resistance of combustible materials. They slow down or completely prevent the rapid burning of polymers, wood, fabrics, plastics and other organic materials. Flame retardants affect the combustion process of the material, reducing heat release, limiting the formation of flammable gases and creating a protective layer. As a result, the ignition temperature of the material increases and the risk of fire decreases.

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