SYNTHESIS OF OLIGOMERIC FLAME-RETARDANT GRADE AK-1 BASED ON COPPER PHTHALOCYANINE PIGMENT AND STUDY OF PHYSICOCHEMICAL PROPERTIES

[1]Akramjon Sadikov, [2]Fayzulla Nurkulov, [3] Jahongir Fayziev
[1]PhD student, Tashkent research institute of chemical technology
[2]DSc, prof., Tashkent research institute of chemical technology
[3] PhD, associate professor, Tashkent research institute of chemical technology
https://doi.org/10.5281/zenodo.8150213

Abstract. *In this article, the properties of the obtained oligomeric fire-retardant AK-1 based on phthalocyanine pigments are studied. IR spectral and differential thermogravimetric analyzes of oligomeric fire-retardant AK-1 are considered. The advantage of the resulting flame retardant is that it is used in the process of dyeing fabrics. Existing connections were studied and what changes are observed in these connections under the action of heat. This is evidenced by the results of the differential thermogravimetric analysis.*

Keywords: *phthalocyanine, macrocyclic coltso, flame retardant, IR spectrum, thermogravimetric analysis, differential thermal analysis.*

Introduction. Phthalocyanines (Pc) are a class of photoactive compounds whose unique physicochemical properties are being studied in many areas of modern science. Metal complexes - phthalocyaninates (MPc) - are products of large-scale industrial synthesis (over 80 thousand tons per year), while most of them are traditionally used as pigments in the composition of color printing inks, paints and varnishes, for dyeing plastics and synthetic fibers [1; S. 191-202]. In recent years, increasing the fire-resistant properties of natural textile materials has become increasingly important. This is due to the fact that these textile materials are distinguished as combustible by the inclusion of factors such as rapid ignition, flame spread, the release of various fumes and gases. Nevertheless, textile materials are widely used in everyday life, in buildings and structures, in transport and as means of special protection [2; 153-R., 3; 201-207-R.].

Recently, due to the increasing use of new polymeric materials and fabrics in the decoration of buildings, the toxicity and density of smoke generated during combustion have increased [4; 3–123-R.]. In order to reduce this risk, a number of countries are preparing or adopting regulations and laws prohibiting the use of flammable fabrics, primarily workwear, decorative, covering and wallpaper, curtain fabrics [5; 152-R.]. Types of refractory fibers created on the basis of modern methods: Phenylon, Arselon, Nomex, Rusar, Arlana, Kevlar, Arimid, etc. [6; 100 -125 - R.].

In the production of flame retardants based on melamine, they are divided into: pure melamine, melamine derivatives (boric, cyanuric, phosphoric acids or salts of organic and inorganic acids, for example, pyro-, polyphosphoric acid) and melamine homologues. Due to endothermic decomposition, they are heated at a temperature of 250-400°C. During decomposition, melamine releases ammonia and forms cyclic compounds called melon, melam, melem, which make up the surface layer of the skin [7; 579-589-R., 8; 138-149-R., 2; 153-R.].

Methods and materials. Synthesis of flame retardants AK-1 based on phthalocyanine pigment was carried out as follows:

Orthophosphoric acid	45 %
Urea	50 %
Copper phthalocyanine pigment	5 %

Phosphoric acid (45%), phthalocyanine pigment (5%) and urea (50%) were placed in a vessel equipped with a temperature controller, a reflux condenser and a mechanical stirrer. The reaction was continued for one hour while the temperature of the flask was maintained at 130°C. A pale blue viscous product was obtained in 90% yield.

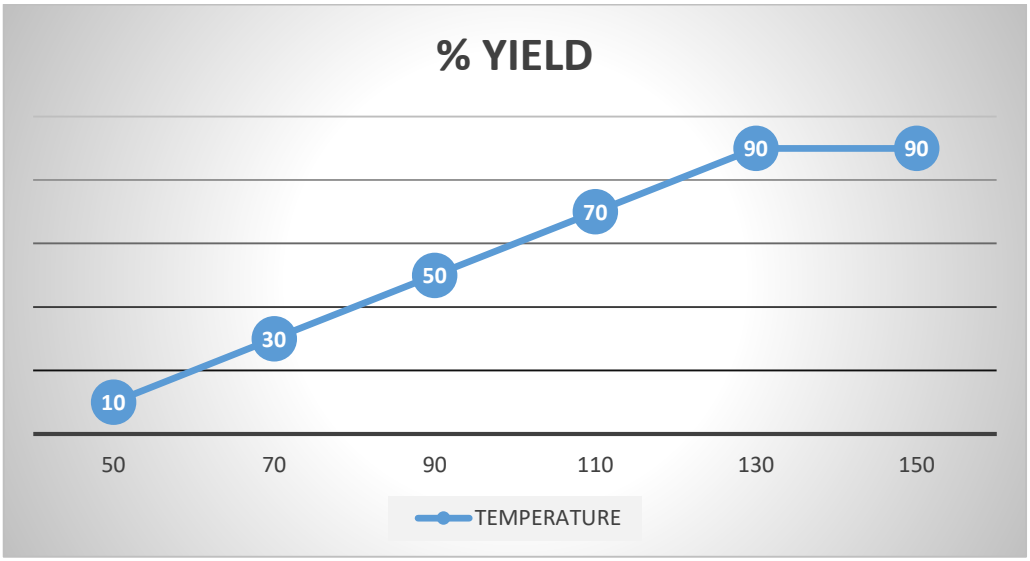

Figure 1. Reaction yield as a function of temperature

The yield of these AK-1 grade oligomeric flame retardants is affected by temperature, time, and the ratio of components, as well as the use of a catalyst. The highest yield of flame retardant AK-1 is 90%, the process takes place under optimal conditions of 130°C for 1 hour. Oligomeric flame retardants AK-1 have been successfully obtained and their physicochemical properties have been analyzed.

Table 1

Physical and chemical properties of flame retardant oligomeric AK-1

1	Appearance	Thick, viscous, light brown.
2	pH	6-7
3	Density (25°C), г/см^3	1,18
4	Mass fraction of volatile substances, %.	0,01
5	Solubility	Soluble in water at a temperature 50°C

The IR spectrum of this oligomeric flame retardant shows that the absorption lines in the region of 1697.36 cm^{-1} of the IR spectrum indicate the presence of free groups -$CONH_2$, and the absorption lines in the region of 2300-2450 cm^{-1} indicate the presence of secondary groups -CONH. Absorption bands in the region of 898.83 cm^{-1} confirm the presence of –NH_2 groups. In addition, in the range of 721.38-763.81 cm^{-1}, intensities containing metal-containing compounds, i.e., a metal phthalocyanine bond, appear in the IR spectrum. At the same time, in the regions of 1056.99-1274.94 cm^{-1}, phosphorus bonds can be observed, as well as bonds belonging to the P=O and P-O-C groups.

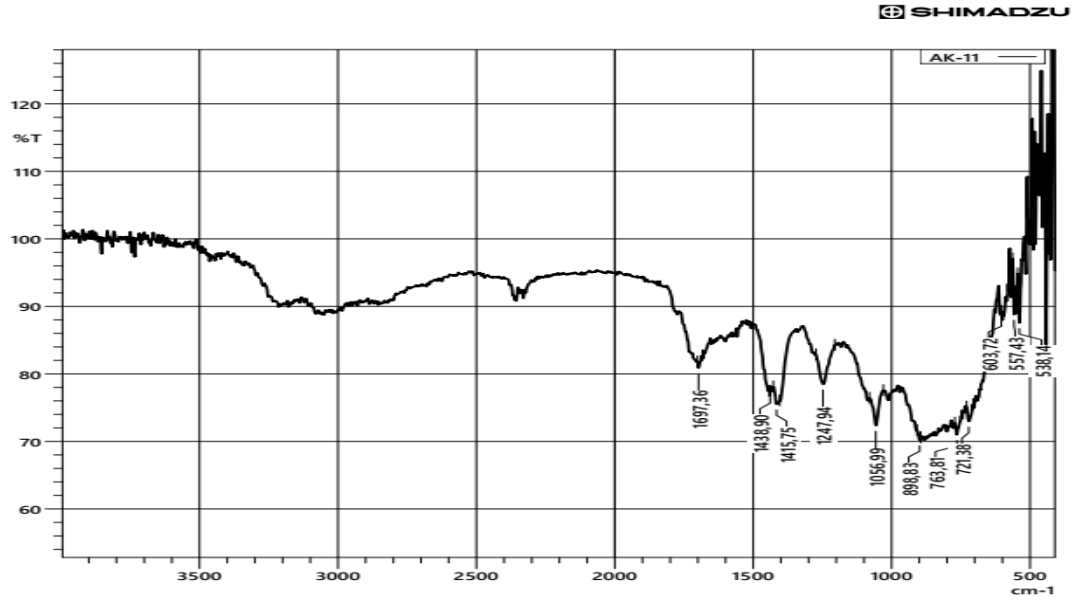

Figure 2. IR spectrum of proprietary AK-1 oligomer

The structure of the synthesized oligomeric flame retardants was studied by IR spectroscopy and the presence of metal phthalocyanine in the fire resistance of textile materials treated with oligomeric flame retardants. The partial progress of the reaction depending on the composition of the obtained oligomeric flame retardants was determined based on the above reaction and results.

The viscosity of the resulting flame retardant oligomer was determined by importance on a VPZh-1 viscometer. Viscometer diameter 0.55 mm.

Table 2

Viscosity of flame retardant AK-1 (т-45^0 C)

№	Substance ratio	%Solution concentration	Solution flow time (min)	η_{otn}	η_{ud}	η_{pr}	η_{log}	η_{hv}
1	AK-1	0	4.89					
2	1:1:0,01	1	5.10	1.050	0.050	0.3	0.95	0,7
		0,5	5.5	1.140	0.140	0.57	0.52	
		0,25	7.7	1.50	0.55	1.1	1.15	
3	1 : 1: 0,02	1	5.5	1.1	0.1	0.4	1.25	1,4
		0,5	5.8	1.2	0.2	0.8	1.55	
		0,25	5,1	1,1	0,15	0,75	1,54	

A derivatogram of a sample of an oligomeric fire-retardant composition of the AK-1 brand, consisting of 2 curves, is presented. An analysis of the thermogravimetric analysis (TGA) curve (curve 1) shows that the TGA curve of flame retardant AK-1 mainly passes in the temperature range of intensive decomposition 3. The 1st decomposition interval corresponds to a temperature of 31.26-250.32°C, the 2nd the decomposition interval corresponds to a temperature of 250.32-456.93°C, the 3rd decomposition interval corresponds to a temperature of 456.93-801.62°C. (Fig. 3).

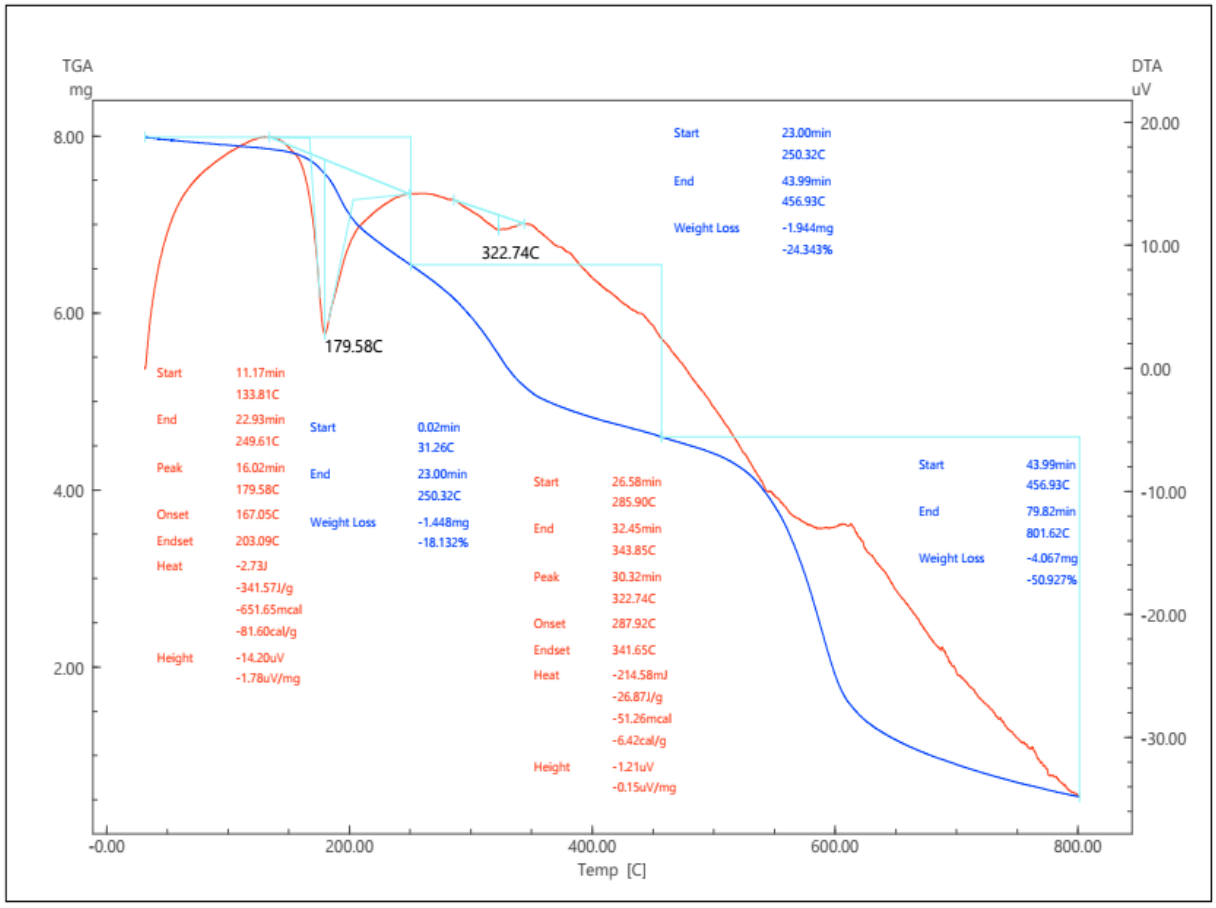

Figure 3. Derivatogram of flame retardant grade AK-1.
1 - curve of thermogravimetric analysis (TGA); 2 - curve of differential thermal analysis (DTA);

The analysis shows that the loss of the mass of the nucleus occurs during the 1st decay between 31.26-250.32 oC, when 18.132% of the mass of the nucleus is lost. Decomposition 2 takes place at 250.32-456.93 oC, with the loss of 24.343% of the mass. The 3rd decomposition occurs at 456.93-801.62 °C, while 50.927% of the mass is lost. The weight loss of the studied oligomeric flame retardants due to temperature effects in time is associated with various processes: with an increase in weight due to partial oxidation, decomposition of primary composites is observed, decomposition of the substance begins, the second decomposition occurs with the release of volatile substances contained in oligomeric flame retardant composites, and the decomposition of other substances accelerates as a result of an increase in temperature.

Conclusion. In the IR spectrum of the synthesized oligomeric fire retardant based on copper phthalocyanine, intense bands appear in the range of 721.38–763.81 cm–1, which contain metal-containing compounds, i.e. phthalocyanine bonds of copper. In this case, phosphorus bonds can be observed in the ranges of 1056.99-1274.94-1415.75 cm-1, and the bonds of the P=O and P-O-C and P-O-Pc-Cu groups give the synthesized oligomer its flame retardant properties, i.e. e. gives the property of fire resistance. According to thermogravimetric analysis, the mass loss was 50.927% at a temperature of 801.62 0C. This synthesized flame retardant based on oligomeric copper phthalocyanine is recommended for special clothing, which is considered to be a product of the textile industry.

REFERENCES

1. Wöhrle D., Schnurpfeil G., Makarov S. G., Kazarin A., Suvorova O. N. Practical applications of phthalocyanines – from dyes and pigments to materials for optical, electronic and photo-electronic devices // Макрогетероциклы. 2012. № 5 (3). С. 191-202.
2. Текей Ергенгул. Разработка новой технологии огнестойкой отделки целлюлозных текстильных материалов//Алматинский технологический университет. Диссертация на соискание степени доктора философии (PhD) Алматы-2019. С.153.
3. Таусарова Б.Р., Абдрахменова Г.С., Биримжанова З.С. Применнеие полиэтиленполиамина и гидрофосфат калия для придания огнезащитных свойств целлюлозным текстильным материалам // Химический журнал Казахстана.-2016.-№2.-С.201-207.
4. Horrocks A.R., Kandola B.K., Davies P.J., Zhang S., Padbury S.A. Developments in flame retardant textiles // Polymer Degradation and Stability.-2005.-№88.-P.3–123.
5. Зубкова Н.С. Огнезащитные химические волокна // Полимеры («Полимерные материалы XXI века»): матер. Междунар. Конф. – М., 2007. С. 152.
6. Laoutid F., Bonnaud L., Alexandre M., Lopez-Cuesta J., Dubois P.H. New prospects in flame retardant polymer materials: from fundamentals to nanocomposites // Materials Science and Engineering.-2009.-№63.-P.100–125.
7. Alongi J., Colleoni C., Rosace G. Malucelli G. Phosphorus- and nitrogen doped silica coatings for enhancing the flame retardancy of cotton: synergisms or additive effects // Polym. Degrad. Stab.-2013.-P.579–589.
8. Alongi J., Carosio F., Malucelli G. Current emerging techniques to impart flame retar- dancy to fabrics: an overview// Polym. Degrad. Stab. 106.-2014.-P. 138–149.