Improving the fire resistance of PVC plastic: the introduction of ammonium octamolybdate

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Abstract. An efficient method for the synthesis of ammonium octamolybdate with a quantitative yield has been developed. Compounds based on PVC plastic and octamolybdate are obtained. It was found that the introduction of ammonium octamolybdate in PVC plastic leads to an increase in the fire resistance of the compound and to a decrease in smoke formation during its combustion. At the same time, the mechanism for reducing smoke emission during PVC plastic combustion in the presence of ammonium octamolybdate consists in its catalytic action in the conversion of soot particles into various oxidized forms. It is shown that PVC plastics containing ammonium octamolybdate have elevated oxygen index and coke residue.

1. Introduction

One of the large polymer materials that is widely used in industry is polyvinyl chloride (PVC) [1, 2]. In particular, the volume of production of PVC and composites based on it in our country is more than 140 thousand tons per year [3]. At the same time, the fields of application of PVC and composites based on it are extremely extensive. Thus, PVC in significant amounts is used as insulation, filling and sheathing of electrical wires and cables [3, 4]. In the absence of flammable ingredients such as combustible plasticizers, PVC with a limiting oxygen index of about 37 does not ignite in air under normal conditions [2]. However, the majority of soft materials based on PVC, which are cable plastics, use different plastics, which leads to an increase in the flammability of these materials [5]. At the same time, the burning and smoldering of cable PVC plastic compounds is accompanied by the formation of a significant amount of smoke, which has a toxic effect on all living things in the environment [6]. In this regard, developers who deal with the problem of increasing fire resistance and reducing smoke generation during the burning of PVC plastic compounds face the problem of searching for and creating effective additives - flame retardants [7-11]. In this regard, molybdenum compounds can be quite promising and effective dyes suppressors [12-21].

The purpose of this work was to increase the fire resistance of PVC plastic, the introduction of ammonium octamolybdate, as well as to evaluate its effect on smoke formation during the combustion of plastic. The choice of ammonium octamolybdate rather than ammonium heptamolybdate is due to...
the fact that thermal decomposition of ammonium octamolybdate occurs at elevated temperature, accompanied by the formation of a significant amount of coke.

2. Experimental

In this work, ammonium octamolybdate (OMA) was used as a flame retardant to increase the fire resistance and reduce the smoke produced during PVC burning. OMA was obtained according to the following procedure. Thus, ammonium heptamolybdate (GMA), purified from impurities, was dissolved in distilled water. Then the solution was heated to a temperature of 90-95 °C and an aqueous suspension MoO3 was added to it, also heated to a temperature of 90-95 °C. At this temperature, the reaction mixture was stirred for 3–5 h until all of the molybdenum trioxide dissolved. The reaction scheme can be represented as follows: \((\ce{NH4})_6\ce{Mo7O24} + \ce{MoO3} \rightarrow (\ce{NH4})_4\ce{Mo8O26} + 2\ce{NH3} + \ce{H2O}\).

The resulting solution was evaporated to a volume of 300-400 ml using a rotary evaporator. Then the solution was left at room temperature until precipitation. After that, the precipitated white crystals were filtered off, washed with a small amount of water, and dried in a vacuum cabinet at a temperature of 70 °C to constant weight.

Synthesized OMA in PVC-plastic was introduced by dispersing it at the stage of hot mixing (mixer DIOSONAD-49074 Germany) of the main components in the preparation of plastic [15]. Then the mixture was extruded using a twin-screw extruder with a screw diameter of 20 mm at a temperature of 140 - 165 °C. The content of OMA in plastic was 3÷10 mass. %. Then, the ex-laborers were granulated and used to make the appropriate test specimens.

The duration of burning compounds was determined according to GOST 21207-81 and UL-94. The test specimens were bars of 100×10×4 mm.

The oxygen index (OI) was determined by the GTS 12.1.044-89 on the instrument of the company Noselab ast. Fire testing model Oxygen Index (Italy). The samples were bars with a length of 100×10×4 mm.

Coke residue (CR) was determined as follows. Samples based on the original and OMA-containing PVC plastic were kept at a temperature of 800 °C in a muffle furnace for one hour. Then, the difference in the mass of sample weights was found before and after keeping in a muffle furnace, and the coke residue (%) was calculated.

To determine the amount of heat released and the specific volume of smoke produced during combustion of plasticates, studies were performed on a calorimeter (made in Italy) according to ISO 5660-1: 2002. Compound samples (plates with dimensions of 150 × 150 × 2.0 mm) based on the original I40-13A, p.8/2 PVC compound and modified 10 wt.% OMA were exposed to a heat flux of 35 kW/m². The flame was at a distance of 6,4 mm from the sample.

3. Results and discussion

In the work to compare the efficacy of OMA used PVC plastic stamps 40-13A, p. 8/2 and a compound based on it and OMA. Studies have shown that PVC plastic I40-13A, p.8/2 burns while in the flame zone (OI = 26%). During removal from the flame zone, the sample stopped burning after 10 seconds. At the same time, in the process of burning PVC plastic of the brand I40-13A, p.8/2, a significant amount of smoke is emitted. In turn, PVC plastic, containing OMA, when burning out of the flame zone, stopped burning almost immediately.

The increase in fire resistance of PVC plastic with the introduction of OMA is also confirmed by the determination of the OI values of the samples (see table). So it can be seen from the table that in PVC KI plastic compound increases markedly with the introduction of OMA. This behavior of the compounds is due to the decomposition of OMA and the release of non-combustible products into the flame zone [23].

It is important to note that in the process of burning in the fiery zone of PVC plastic compounds containing OMA, the amount of smoke is much less produced than in the case of burning PVC plastic of the I40-13A, p.8/2 type. The increase in fire resistance and the slight formation of smoke during the burning of PVC plastic compounds containing OMA are associated with changes in the process and
mechanism of combustion of the material. It is known [22, 24], that molybdenum-containing compounds effectively influence the combustion processes of polymeric materials.

It should be noted that in the obtained composites, due to the decrease in the thermal effect of the combustion process and the catalysis of the coking process, the amount of coke residue after the destruction of PVC plastic compounds should be greater. As shown by the results of thermal studies of PVC plastic compounds containing OMA, the additive contributes to an increase in the coke residue \((\text{CO})\) in comparison with PVC plastic from the I40-13A brand, p.8/2 (see table).

The formation of a larger number of CR during combustion of samples was confirmed by photos taken from the surface of PVC plastics exposed to flame. The photos showed that during the burning of PVC plastic with the addition of OMA, the surface was covered with a dense coke crust. The resulting dense crust will prevent the flow of combustible products of destruction of plastic in the flame zone.

Table 1. The influence of OMA on CR and OI PVC plastic

| Indicator          | 0      | 3      | 5      | 8      | 10     |
|--------------------|--------|--------|--------|--------|--------|
| Coke residue, %    | 3      | 4      | 6      | 7      | 8      |
| Oxygen index (OI), %| 26     | 28     | 29     | 30     | 31     |

As noted above, a significant amount of plastic-fixer is used in PVC plastics [2, 4], which leads to an increase in the flammability of the material. So, when burning standard I40-13A PVC compound, a significant amount of smoke is formed.

Con-calorimetric studies have shown that the introduction of OMA in PVC plastic leads to a significant change in the entire process of burning material. In particular, to determine the effect of OMA on the resistance to burning of PVC plastic, a calculation was made of the rate of heat generation using the results of a calorimetric analysis. The results of research are shown in figure 1 and 2.

![Figure 1](image_url)

**Figure 1.** The dependence of the rate of heat generation on the time of combustion of the samples:
1 - PVC plastic compound I40-13A; 2 - PVC plastic + 10% OMA.

From figure 1 it can be seen that the introduction of OMA in PVC plastic leads to a significant change in the rate of heat generation during the combustion of the material. In particular, at the initial moment of the combustion process of the initial PVC compound and the sample containing OMA, the
heat-fission rate is almost the same. However, then the heat release rate for PVC plastic containing OMA is significantly reduced. Such behavior of PVC compound with OMA is explained by the fact that in the initial stage of material burning a solid coke crust forms on its surface, which effectively prevents the process of heat generation.

It is important to note that when samples are burned, the total amount of heat released for PVC plastic, containing OMA, is significantly lower than for standard plastic. This effective reduction of heat generation is obviously due to the fact that OMA is working mostly in the solid phase of plastic, catalyzing various processes. Firstly, the structural fragments of the polymer with the trans-configuration of macromolecules are formed [25]. The formation and presence of such sufficiently stable structures in PVC macromolecules inhibits the further process of polymer dehydrohalogenation, reducing the possibility of the formation of aromatic elements [26, 27]. Secondly, the processes of coking and charring are activated, leading to the formation of a crust-resistant crust. This is evidenced by the presence of a single peak on the heat release rate curve for PVC plastic with OHM (Fig. 1). Such a stable crust will effectively interfere with the process of heat generation and the output of various products of plastic decomposition. As a result, under equal conditions of combustion of two PVC plastic compounds, the initial sample (PVC plastic of the I40-13A brand, р.8/2), unlike the plastic compound containing OMA, will contribute to the further spread of the burning zone.

The results of an estimate of the amount of smoke produced during the burning of I40-13A, p.8/2 PVC and OMA plastic compound (Fig. 2) also indicate a reduction in smoke. As can be seen from Figure 2, the amount of smoke produced when burning plastic compound containing OMA is significantly lower than when burning PVC plastic of the brand I40-13A, p. 8/2. Such a decrease in the amount of smoke emitted during the burning of PVC plastic containing OMA confirms the effectiveness of the use of OMA. In particular, the reduction of smoke can be explained by the oxidative effect of OMA on soot particles [28], which are formed during the decomposition of the material in its combustion zone, i.e. OMA effectively demonstrates its ability to eliminate carbon particles of smoke by the reaction: \( C + H_2O \rightarrow CO + H_2 \).

![Figure 2](image-url)  
**Figure 2.** The dependence of the rate of smoke emission on the time of combustion of the samples: 1 - PVC plastic board brand I40-13A; 2 - PVC plastic + 10% OMA the specific area of extinguishing
In this case, the oxidation processes, obviously, proceed through the metal carbonyl intermediate compounds. It is for this purpose that molybdenum is used in the form of OMA, which reacts at the required temperatures.

It should be noted that the insignificant amount of smoke that is formed during the burning of PVC plastic compound containing OMA (Fig. 2) has a significantly lower temperature by 15 - 20 °C, in comparison with the standard material.

4. Conclusions

Thus, the obtained with quantitative yield ammonium octamolybdate. In this case, the introduction of ammonium octamolybdate in PVC plastic compound leads to an increase in fire resistance, as well as to a decrease in the speed and amount of heat released. These changes in the properties of PVC plasticate are due to the fact that ammonium octamolybdate has a catalytic effect on the formation of structures of macromolecules resistant to dehydrohalogenation and a strong coke crust on the surface of the compound, which prevent the flow of combustible products of destruction of the material into the flame zone. In addition, octamolybdate ammonium can effectively oxidize soot produced when burning PVC plastic, preventing the process of smoke generation.

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