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Regulation of the Processes of Chemical Interaction of Flame Retardants in the Pre flame Zone of the Condensed Phase: A Method to Form New Fire-Resistant Polymeric Compositions

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Investigations of primary interactions between the components of antimony–halogen mixtures in the condensed phase are used to elucidate processes and causes which inhibit combustion of polymers.

KEY WORDS Fire resistance, flame retardants, antimony oxide, antimony halogenide.

RESULTS AND DISCUSSION

It is difficult to increase the fire resistance of known and create new almost non-flammable composite materials because of the absence of information about the mechanism of action of flame retardants and about the processes which produce the determining effect on the inhibition of burning. Such information is hard to obtain because of the multicomponent character of the systems, the presence of a polymeric matrix and the multistage character of the processes proceeding in both the condensed and the gas phases.¹

It is universally accepted that during the course of interaction between the components of a synergistic Sb_2O_3 -based mixture and halogen-containing organic compounds antimony halogenide, which is an effective inhibitor of radical processes in the gas phase, is formed. However, the initial stages of this interaction and the influence of the nature of the polymer and the halogen-containing additive on them have not been investigated. It is not clear how the interaction of flame retardants in the condensed-phase influences the gas phase of burning inhibitors. The proposed schemes of the processes have not been confirmed by experiment. Up to now there have been no complex studies of the quantitative and qualitative composition of the gaseous and solid products of thermal decomposition and burning of polymeric compositions containing the same synergistic mixtures.

To elucidate the causes of different efficiency of the same flame retardants in polyolefins and to find and purposefully regulate the processes which most essentially contribute to the burning inhibition, we have studied the nature and the quantitative composition of solid and gaseous products of thermal decomposition and burning of polyolefin compositions with synergistic SbO_3 -based mixtures and halogen-containing organic compounds. To find the common characteristics or differences in the mechanisms of inhibiting action of flame retardants in polymers of various classes, we have studied the transformations of antimony-halogen-containing synergistic mixtures in foam polyurethane, polystyrene and chlorosulfured polyethylene.

It has been found by direct measurement of the temperature gradient in a burning polymer using thermocouples separated by different distances that in the polymer mass depending on the sample thickness, at a distance of 4 mm from the burning surface a temperature of 100–200°C is reached and the temperature of the burning polyolefin surface is ~515°C.² Consequently, in the near-surface zone of the condensed-phase at a sufficient distance from the burning surface the conditions for polymer, halogen-containing additive thermolysis and for interaction of the products of destruction with one another and with antimony oxide are created.

Mass-spectrometry in combination with chromatographic studies of gaseous products of thermolysis of polyethylene and polypropylene compositions with antimony oxide and hexabrominecyclododecane $\text{C}_{12}\text{H}_{18}\text{Br}_6$ (HBCD) in the 300–500°C temperature range have revealed that whatever the nature of the polymer in the gas phase the same products are detected, and their quantity is almost equal. At the same time we have found that there are considerable differences in both the quantitative and the phase composition of solid products of thermal decomposition and burning of polyolefin compositions containing the same synergistic mixtures. Depending on the type of the flame retardant and polymer in the condensed phase, the following products are contained in different amounts and combinations: Sb_2O_3 , antimony oxyhalogenides and halogenides, and metal antimony.³ These products result from the interaction between the synergistic mixture components, and each of these processes leading to the formation of one product or another makes a certain contribution to the inhibition of burning. This contribution can be estimated by comparing data on the quantitative composition of each of the products above with the efficiency of the synergistic mixture in a given polymer.

Let us see how the entry of volatile compounds of antimony into the gas phase changes depending on the nature of the polymer and halogen-containing additive by the example of polyolefin compositions containing Sb_3O_3 , HBCD or chlorinated paraffin $\text{C}_{27}\text{H}_{31}\text{Cl}_{25}$ (CP). The curves of time loss of antimony of heat treatment of compositions with HBCD have induction periods (Figure 1(a)) and in the polypropylene composition the induction period remains at 300°C. The induction period is also observed at heat treatment of a polypropylene composition with CP (Figure 2(a)). X-ray phase analysis of solid products of thermolysis has revealed that presence of induction periods on the curves of the dependence of the degree of antimony volatilization on the duration of heat treatment for HBCD and CP results from various causes. In the first case, the interaction of the synergistic mixture components occurs mainly with the formation of antimony oxyhalogenide while in the

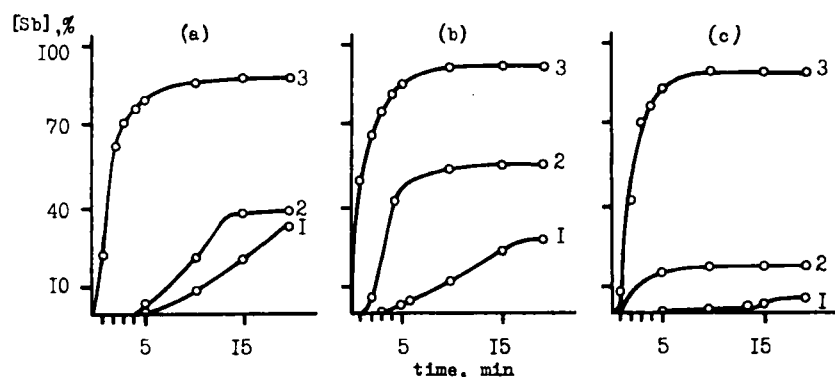


FIGURE 1 The degree of antimony volatilization versus the duration of heat treatment of (a) PP:HBCD:Sb₂O₃, (b) PELD:HBCD:Sb₂O₃, and (c) PEHD:HBCD:Sb₂O₃ compositions. Temperature: (1) 250, (2) 300, and (3) 500°C.

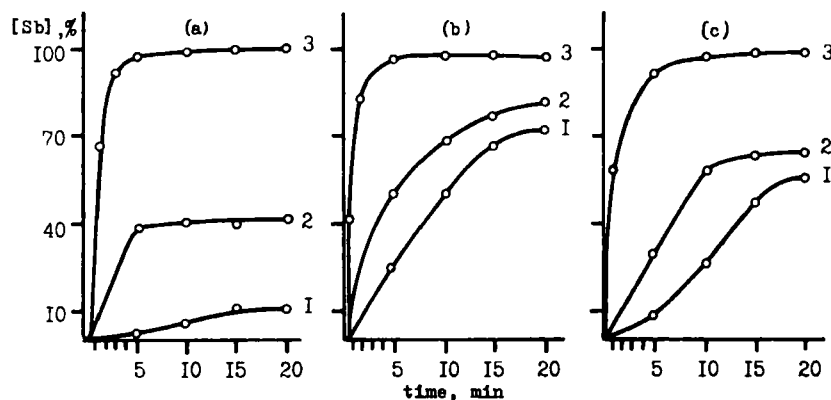


FIGURE 2 The degree of antimony volatilization versus the duration of heat treatment of (a) PP:CP:Sb₂O₃, (b) PELD:CP:Sb₂O₃, and (c) PEHD:CP:Sb₂O₃ compositions. Temperature: (1) 300, (2) 350, and (3) 500°C.

composition with CP the induction period is due to the formation of metal antimony as a result of which different quantities of volatile antimony compounds go into the gas phase.

By comparing the fire-extinguishing efficiency in polyolefins of synergistic mixtures with CP (PELD \geq PEHD $>$ PP) and HBCD (PP \gg PELD $>$ PEHD) with antimony oxide and the data on the phase and quantitative composition of combustion products it is shown¹ that the efficiency of synergistic mixtures is higher in the cases where in the drops antimony oxyhalogenide prevails and lower when the drops have a high content of metal antimony.

Thus, for antimony-halogen-containing synergistic mixtures used for decreasing the combustibility of various polymers we have for the first time shown by the example of polyolefins at the quantitative level that the efficiency of flame retardants is largely determined by the character of the primary interaction of synergistic mixture components in the condensed phase, namely, by the conditions of con-

jugation of parallel and sequential processes in the condensed-phase, which, in turn, determines how much volatile antimony halogenide—effective inhibitor of radical processes—will go to the gas phase. It has been found that the character of this interaction depends to a great extent on the nature of both the polymer and the halogen-containing additive. Similar studies using PPU-, PS- and CSPE-based polymeric compositions containing antimony–halogen synergistic mixtures have shown that in the products of thermal decomposition and burning the same products as in polyolefins are detected, which points to the characteristic of interaction between the components of the mixtures under study.⁴ This fact gives us reason to suppose that common approaches for increasing the efficiency of antimony–halogen-containing antipyrenes in both carbo- and heterochain polymers are possible.

To confirm experimentally the suppositions about the possibility of increasing the efficiency and decreasing the antipyrene content, we purposefully changed the direction and varied the rate of primary reactions of interaction between the synergistic mixture components proceeding from the fact that the most important of these processes is the interaction of halogenohydrogen with Sb_2O_3 with the formation of antimony halogenide or oxyhalogenide and metal antimony.

Effective formation of antimony oxyhalogenide was achieved by varying the Sb-halogen ratio from 1:3 used in real polymeric compositions to 1:2 and 1:1. It has been found by X-ray analysis that as the concentration of the halogen-containing component in the mixture decreases, the content of antimony oxyhalogenide in the products of heat treatment increases. The fire-extinguishing efficiency of mixtures Sb_3O_3 : chlorinate paraffin at the ratio $\text{Sb}:\text{Cl} = 1:2$ passes through the maximum despite the fact that the highest content of antimony oxyhalogenide was observed in a mixture with equal contents of antimony and halogen. This fact is explained by the shortage of halogenohydrogen in the mixture $\text{Sb}:\text{Cl} = 1:1$ at the stage of antimony halogenide formation.

The interaction between the synergistic mixture components can be shifted to oxyhalogenides without affecting the formation of halogenohydrogen if oxides or hydroxides of metals are introduced into the composition. Indeed, the use of calcium oxide, aluminum, titanium, silicon or magnesium hydroxides makes it possible to decrease the antimony oxide content in a base polymer composition by 30–40% without affecting the fire resistance. It should be noted that neither individual oxides and hydroxides nor their mixtures with halogen-containing organic compounds in amounts used as additives to synergistic mixtures displayed the fire-extinguishing effect.

Hydrated titanium oxide (HTO) compared to the other oxides and hydroxides used in the work made it possible to maximally decrease the antimony oxide content (to ~40%) without affecting the fire resistance of the composition.

It is seen from comparison of the data (Table I) on quantitative content of the products formed in the condensed-phase at combustion of base polymer compositions and with a reduced content of Sb_2O_3 that in the presence of HTO in the combustion products a considerable decrease (2–5 times) in the metal antimony content with a fairly high content of antimony oxyhalogenide is observed. It should be noted that the total content of antimony in solid combustion products of com-

TABLE I
Composition of solid-phase combustion products of polyolefin compositions

Composition	X-ray anal.	Whole cont. Sb %	Sb in Sb_2O_3 %	Sb in $Sb_2O_3Br_2$ %	Sb met. %	Br %	Whole cont. Ti %	$TiOBr_2$ %	TiO_2 %
PEHD-HBCD- Sb_2O_3 78%-15%-7%	Sb met.	25	0	4	21	4	—	—	—
PP-HBCD- Sb_2O_3 78%-15%-7%	$Sb_2O_3Br_2$, Sb_2O_3 init., Sb met.	34	14	16	4	11	—	—	—
PEHD-HBCD- Sb_2O_3 -HTO 73%-20%-5%-2%	Sb met., TiO_2	14	5	5	4	9	100	30	70
PP-HBCD- Sb_2O_3 -HTO 73%-20%-5%-2%	Sb_2O_3 init., TiO_2	14	2	10	2	18	88	38	50

positions with HTO is much lower than the level which would correspond to a simple decrease in the Sb_2O_3 content in the initial composition.

To explain what occurs in the condensed phase on partial substitution of Sb_2O_3 by HTO, let us consider the data of the X-ray phase and quantitative chemical analysis obtained by a comparative study of the products of thermal decomposition and combustion of base compositions containing Sb_2O_3 and HBCD and of these same compositions with a reduced content of antimony oxide in the presence of HTO. Simultaneously, we investigated the products formed at interaction of Sb_2O_3 with HBCD and HBr in the 200–500°C temperature range. X-ray analysis has revealed that beginning with 200°C, as HBr is passed over HTO and in the HBCD-HTO mixture thermolysis products, a previously unidentified phase is formed, which as established by chemical analysis, is titanium oxyhalogenide. We have detected the lines of this phase in the products of the heat treatment of polymer compositions where partial replacement of antimony oxide by HTO was carried out. When the temperature is raised to 300°C, the titanium oxyhalogenide thus formed decomposes with the formation of TiO_2 (anatase), as evidenced by the data of the X-ray phase analysis of the thermolysis products of a HTO mixture with HBCD without a polymer and in a polymer.

Thus, for the first time, as a result of purposeful regulation of the character and rate of the interaction between the components of an antimony–halogen-containing synergistic mixture in the condensed phase, a high fire resistance of polyolefin compositions with a reduced content of antimony oxide has been established. It has been found by quantitative chemical and X-ray phase analysis that at the initial stages of interaction of flame retardants (200–250°C) hydrated titanium oxide combines with halogenoxygen to form mainly antimony oxyhalogenide, and then, as the temperature is increased and titanium oxyhalogenide decomposes, the halogen formed interacts with the oxide with the formation of antimony halogenide. The possibility of the proceeding of such a reaction is shown by an example of a synergistic mixture Sb_2O_3 -decabromidinephenyl-oxide ($\text{C}_{12}\text{Br}_{10}\text{O}$) where the formation of volatile antimony halogenides without participation of halogenoxygen was observed. Besides, in the polymer melt at titanium oxybromide thermolysis the formation of halogenoxide, which at interaction with oxyhalogenide also leads to the formation of antimony halogenide, is possible.

In investigating the peculiarities of interaction between the components of synergistic mixtures in the condensed phase, one should take into account the influence of the polymer nature on these processes, namely, the peculiarities of its thermolysis and structuring. By an example of a synergistic Sb_2O_3 -HBCD mixture, in investigating the quantity of the gel-fraction formed at heating in the 200–350°C range, we obtained data which throw light on the cause of different efficiency of this synergistic mixture in polyethylene and polypropylene. It was previously found⁵ that the formation of antimony oxybromide $\text{Sb}_4\text{O}_5\text{Br}_2$ occurred in a polypropylene composition at a temperature lower by 100°C than in a polyethylene composition. Such a difference in the rate of interaction between the components of a synergistic mixture can be caused by the different states of the polymeric matrices in the preflame zone of the condensed phase, namely, it has been established that the quantity of the gel-fraction in the polyethylene composition heat treatment products

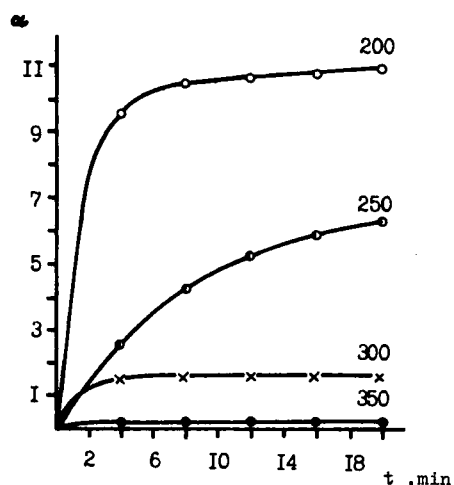


FIGURE 3 Quantity of the gel-fraction in the products of heat treatment of the PP:HBCD:Sb₂O₃ composition.

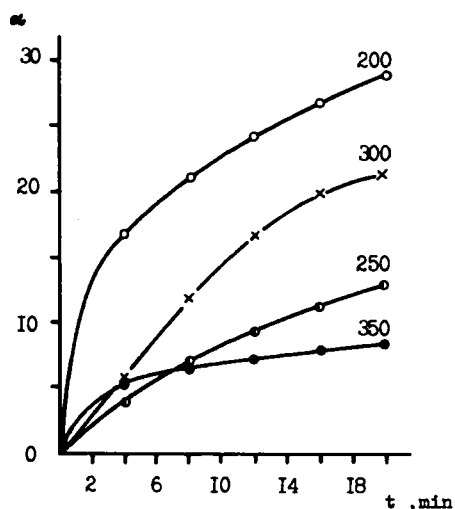


FIGURE 4 Quantity of the gel-fraction in the products of heat treatment of the PP:HBCD:Sb₂O₃ composition.

is greater by a factor of 2–4 than in the products of heat treatment of the polypropylene composition (Figures 3 and 4), which, perhaps, is just responsible for the different mobility of the reaction mixture components.

In investigating the solid-phase products formed at thermal decomposition and combustion of polystyrene, polyurethane compositions and CSPE-based compositions, it has been shown that the character of the processes of interaction between the Sb-halogen-containing mixtures in carbo- and heterochain polymers is the same, which makes it possible to use recommendations on increasing the efficiency of additives in polyolefins for polymers of other classes.

Thus, thorough investigations of the peculiarities of the primary processes of

interaction between the components of antimony-halogen-containing synergistic mixtures in the condensed phase have helped to elucidate the processes which produce the determining effect on the inhibition of polymer combustion and identify the causes responsible for different efficiencies of the same synergistic mixtures in different polymers. It has been shown that depending on the rate and character of the primary processes of interaction between flame retardants, different amounts of the effective inhibitor of radical processes, antimony halogenide, goes to the gas phase. We have obtained direct experimental proof of the possibility of increasing the efficiency and decreasing the content of antimony-halogen synergistic mixtures by purposeful regulation of the processes of interaction between flame retardants in the condensed phase. As a result of the investigations, compoundings of a number of polymer compositions with a reduced content of flame retardants without affecting the fire-resistance have been developed. We have established a common character of the mechanism of action of Sb-halogen-containing synergistic mixtures in carbo- and heterochain polymers, which makes it possible to extend these approaches to other classes of polymers.

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