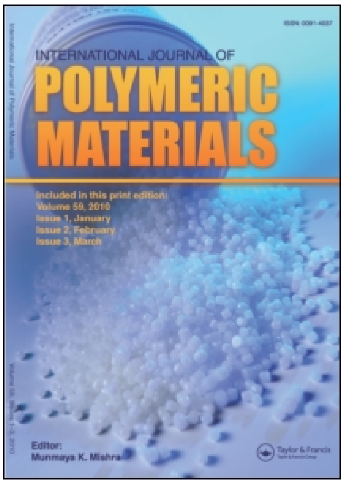

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N. A. Khalturinskij[a]; O. N. Tsirekidze[a]
[a] Institute of Synthetic Polymeric Materials, Moscow, Russia

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Influence of Antimony Compounds on Epoxide Composition Flammability

N. A. KHALTURINSKIJ and O. N. TSIREKIDZE
Institute of Synthetic Polymeric Materials, 82 Profsoyuznaya Street, Moscow, Russia

The effect of antimony compounds on flame resistance of epoxy compounds is investigated.

KEY WORDS Antimony compounds, epoxies, flame resistance.

INTRODUCTION

This paper presents our investigations of the burning process and physico-chemical transformations of epoxide compositions filled with such compounds as antimony trichloride, triphenylstibine or antimony trioxide. It has been shown that antimony trioxide inhibited burning in the condensed phase, thereby increasing coke output. Antimony trichloride and triphenylstibine are the inhibitors of the gaseous phase, having negligible effect. We have studied the optical properties of epoxide compounds and the production of coke in pyrolysis. It has been demonstrated that an introduction of antimony trioxide substantially influenced said properties and that the inhibitory mechanism of epoxide composition burning provided by the antimony trioxide included, in addition to other factors, a modification of these properties.

Polymeric materials are commonly used today. Their rate of production growth is higher than that of many other products. They are of practical value the polymers but the same time they have a major shortcoming—the tendency to catch fiare under the action of different heat sources including low-powered ones. The problem is to lower the flammability of synthetic and natural high molecular weight compounds as well as composition materials prepared from them. It becomes more relevant because the high production and utilization rates of such materials are accompanied by damage due to fires that occur as a result of polymer flare up and burning. However, a practical solution of this problem does not yet exist. The empirical approach to designing low-flammable materials dominates over other approaches.

The main ways of reducing the degree of flammability of polymeric materials include:

1. The use of different salt hydrates and compounds that upon destruction release inert substances. As a result, heat balance will be disturbed by the increase in heat destruction and flame temperature.
2. The use of different organic and inorganic flammability inhibitors that change the destruction mechanism. On the one hand, such inhibitors shift the balance of the flame substances by means of the decrease in the portion of the forming volatile destruction products. On the other hand, the inhibitors provide conditions that allow the low thermal conductivity coke "cap" to be formed on the burning surface. It occurs due to the change in the rheological properties of high-temperature pyrolysis products and gasification speed during the destruction.
3. The use of gas-phase burning inhibitors, for example, halogen containing compounds that change the reaction mechanism of preflame and flame zones. In addition, these inhibitors reduce the burning degree of destruction products. On the one hand, such mechanisms reduce heat production in the flame and, on the other hand, they increase radiant heat loss by increasing the production of soot.
4. The filling of the polymer matrix by inert substances to increase induction period and ignition energy.

Antimony trioxide is the most commonly used burning inhibitor. The compound belongs to the category of so-called synergistic inhibitors, that is compounds used in combination with other substances to lower the flammability and, as a rule, it is used in combination with halogen containing compounds. The majority of articles concerned with the influence of antimony trioxide on polymer flammability point out an extremely low effectiveness of this compound when used without halogens. The formation of intermediate compounds inhibiting burning in the gaseous phase, as halogens do, may be responsible for a possible synergetic mechanism existing between antimony and the halogens.

Little[1] was the first to propose the inhibitory mechanism of polymer burning by antimony trioxide and halogen containing compounds. The author concluded that the formation of antimony oxyhalide inhibiting the burning process in the gaseous phase is a cause of the synergism. But as further data concerning polymer products of pyrolysis with synergetic additives was obtained, it was concluded that the antimony halide formation dominated the oxyhalides.[2,3]

Agrawal and co-workers[4] studied the thermal behavior of antimony trioxide in air and in inert gas atmospheres. It has been shown that Sb_2O_3 was oxidized into Sb_2O_4 in the air with temperatures of 510–600°C. In the inert atmosphere, Sb_2O_3 did not undergo change up to a temperature of 430°C. When the temperature reached 550°C evaporation began, and the higher the temperature the more rapidly this process runs. Antimony trioxide of cubic structure has been found in the vapor, and antimony trioxide of orthorhombic structure has been found in the remainder. These investigations show that the thermal behavior of antimony trioxide during polymeric material burning can be complex enough.

According to Pitts' study,[5] the formation of antimony chloride occurred as a series of the following reactions:

$$\mathrm{Sb_2O_3 + 2HCl - 2SbOCl/s/ + H_2O}$$

$$\mathrm{5SbOCl - Sb_4O_5Cl_2/s/ + SbCl_3/g/} \qquad 250\text{–}280^{\circ}\mathrm{C}$$

$$\mathrm{4Sb_4O_5Cl_2 - 5Sb_3O_4Cl/s/ + SbCl_3/g/} \qquad 410\text{–}475^{\circ}\mathrm{C}$$

$$\mathrm{3Sb_3O_4Cl - 4Sb_2O_3/s/ + SbCl_3/g/} \qquad 475\text{–}565^{\circ}\mathrm{C}$$

$$\mathrm{Sb_2O_3/s/ - Sb_2O_3/l/} \qquad 658^{\circ}\mathrm{C}$$

On the contrary, Lum and and co-workers[6] found that $SbCl_3$ is formed immediately from the following reactions:

$$\mathrm{Sb_2O_3/s/ + 6HCl - 2SbCl_3/g/ + 3H_2O.}$$

Bendou and Cullis[7,8] considered that the appearance of an antimony halide in the burning zone causes the formation of aerosol Sb_2O_3 and atomic halogen. Antimony trioxide acts as a catalyst of free-radical recombination and atomic halogen causes the formation of a hydrogen halide known as a burning inhibitor.

On the other hand, the study in Reference 9 supposes that halogens are only transport mechanisms for the antimony transference from condensed to gaseous phases.

The study in Reference 10 provides detailed investigation of processes that take place in the polyolephine condensed phase during burning inhibition by antimony trioxide and halogen compounds.

It has been demonstrated that metallic antimony is formed during the pyrolysis of such compositions. The occurrence of metallic antimony appears to be a consequence of antimony halide reduction by hydrogen, and halogen additives promote the release of hydrogen.

In a further study in Reference 11 it has been shown that the efficiency of the inhibiting mixture was higher during Sb_4O_5Br pyrolysis and lower when the amount of metallic antimony was increased. The authors concluded that the formation and accumulation of Sb_4O_5Br cause $SbBr_3$ to gradually enter into the gaseous phase. As a result, the lesser part of antimony tribromide interacts with radicals ineffectively in the condensed phase.

On the other hand, according to the study in Reference 12 oxyhalides and antimony halides can act as dehydrogenating agents in the condensed phase, increasing the coke remainder. The growth of coke remainder leads to an increase in polymer rate gasification and flame heat production, thereby decreasing flammability.

Thus, the experimental data available at present are discrepant enough and do not allow us to make a final conclusion concerning the inhibition properties of antimony antipyrens. The purpose of this study is to investigate certain characteristic properties of antimony compounds and refine the burning inhibitory mechanism of antipyrens.

MATERIALS AND SUBSTANCES

The subject of inquiry was epoxy resin ED-20 (diglycidyl ether of isopropylic acid) hardened by polyethylene in stoichiometric proportion. The fillers were antimony trioxide (TU 48-14-1-82), antimony trichloride (TU 6-09-636-76) and triphenylstibine synthesized by the technique described in the study in Reference 13.

To prepare test specimens the needed amount of antimony trioxide and trichloride was added to liquid epoxy previously stirred at room temperature. The mixture was scrupulously stirred again until finely dispersed mass occurs. The triphenylstibine was added to the epoxy heated to 60°C and then dissolved in it. After cooling, a hardener was added. The prepared composition was filled in the forms and hardened. Extra hardening of test specimens then followed during 3 hours at a temperature of 80°C.

EXPERIMENTAL TECHNIQUES

We used the oxygen index (GOST 21793-76), the method of high-temperature pyrolysis[14] and the spheric model of diffusion burning.[15] These standard techniques allow us to assess the flammability inhibition effectiveness of the compositions in question.

To investigate processes that decrease the polymer inflammability in more detail we used other original methods as well.

ASSESSMENT OF THE EFFECTIVENESS OF ANTIMONY TRICHLORIDE

The most comprehensive assessment of the effectiveness of the gas phase inhibitor action has been developed for halogen containing compounds.[16-18] The majority of experimental methods used at present provide only a comparative quality characteristic of inhibitors. Therefore, we developed the method that allows us to describe antipyren behavior in the gaseous phase numerically.

The purpose of our experiment was to determine the oxygen indices for the epoxy composition when burning in a binary gas mixture (O_2, N_2) or a gas mixture containing three components—O_2, N_2 and antimony trichloride (nitrogen was partially replaced by antimony trichloride with the same rate of oxygen flow). The experimental unit modified for determination of the oxygen index. It had a bottom and walls insulated by asbestos and was additionally heated to reduce heat loss and temperature gradient of flow along the diameter and height of the tube. This gradient did not exceed 10°C. The inhibitor was evaporated from an electrically heated vessel placed at the bottom of the unit. The power of the heater was controlled by an autotransformer. During the experiment antimony trichloride entered the gas flow where it was evaporated and then condensed to an aerosol. The gas mixture (O_2, N_2) consumption indicated the concentration of antimony trichloride in gas flow.

The total heat balance of polymer burning in binary gas mixture (O_2, N_2):

$$\dot{m} \times q \times a = \dot{m} \times C_{p1} \times (T_s - T_O) + \dot{m} \times C_{p2} \times (T_f - T_s) + \dot{m}_{O_2} \times C_{p_{O_2}} \times (T_f - T_O) + \dot{m}_{N_2} \times C_{p_{N_2}} \times (T_f - T_O) + Q_{\text{loss}} \quad (1)$$

and in three component gas mixture (O_2, N_2 and $SbCl_3$):

$$\dot{m} \times q \times a = \dot{m} \times C_{p1} \times (T_s - T_O) + \dot{m} \times C_{p2} \times (T_f - T_s) + \dot{m}_{O_2} \times C_{p_{O_2}} \times (T_f - T_O) + \dot{m}_{N_2} \times C_{p_{N_2}} \times (T_f - T_O) + \dot{m}_{SbCl_3} \times C_{p_{SbCl_3}} \times (T_f - T_O) + Q_{\text{loss}} \quad (2)$$

where $\dot{m}$ is the mass rate of polymer gasification; $\dot{m}_{O_2}$, $\dot{m}_{N_2}$ and $\dot{m}_{SbCl_3}$ are the injection rates of oxygen, nitrogen and antimony trichloride in flame zone; C_p is the specific heat; q is the polymer burning heat; a is the stoichiometric coefficient; T_O, T_S, and T_f are the temperatures of polymer, pyrolysis surface and flame, respectively; C_{p_1} and C_{p_2} are the specific heat of polymer and products of pyrolysis.

Then, during comparative determinations of the oxygen index in experiments with binary and three-component mixtures under similar oxygen rates and conditions when the temperatures in formulas (1) and (2) do not differ markedly at the limit of burning, the specific heat of antimony trichloride can be defined as:

$$C_{p_{SbCl_3}} = \frac{(\dot{m}_{1N_2} - \dot{m}_{2N_2}) \times C_{p_{N_2}}}{\dot{m}_{SbCl_3}}. \quad (3)$$

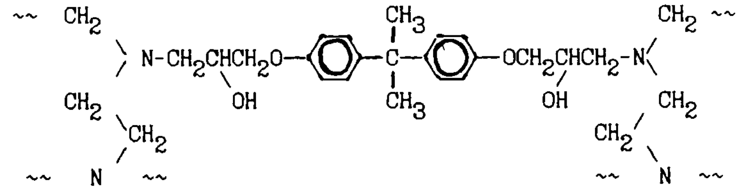
If calculated, specific heat will be in agreement with the standard, and antimony trichloride would behave as an inert diluter in the flame. The exceeding of a calculated value over a standard value could show a contribution of antimony trichloride in the polymer flame inhibition.

We define the relation between antimony trichloride concentrations in condensed and gaseous phases. Let the amount $\dot{m}$ of pyrolysis products be gasified from the polymer surface per unit of time. Then, the molar flow of antimony trichloride entering the burning zone is defined as:

$$\dot{\nu}_{SbCl_3} = \frac{\dot{m} \times [SbCl_3]}{\mu_{SbCl_3}}$$

where $[SbCl_3]$ is the mass concentration of antimony trichloride in polymer composition; μ_{SbCl_3} is the molecular mass of antimony trichloride.

The fragments of epoxide polymer space formula hardened by the amine binding agent has the following structure:



Thus, in stoichiometric flame at a limit of burning 1 g of the epoxide polymer pyrolysis products needs in 0.08 oxygen mols in the burning zone. Taking into account the burning degree of epoxide polymer, around 45%, the total amount of oxygen and nitrogen entering the burning zone can be expressed as follows:

$$\dot{\nu}_{O_2} + \dot{\nu}_{N_2} = \frac{0.036 \times \dot{m} \times (1 - [SbCl_3])}{OI}.$$

Then, the relation between concentrations of antimony trichloride entering from atmosphere and polymer composition is:

$$[SbCl_{3g}] = \frac{\dfrac{\dot{m} \times [SbCl_3]}{\mu_{SbCl_3}}}{\dfrac{\dot{m} \times [SbCl_3]}{\mu_{SbCl_3}} + \dfrac{0.036 \times \dot{m} \times (1 - [SbCl_3])}{OI}}$$

where $[SbCl_{3g}]$ is the volume concentration of antimony trichloride in the gaseous phase; $[SbCl_3]$ is the mass concentration of antimony trichloride in the composition. After transformation the equation can be rewritten as follows:

$$[SbCl_{3g}] = \frac{[SbCl_3] \times OI}{[SbCl_3] \times OI + 0.036 \times (1 - [SbCl_3]) \times \mu_{SbCl_3}}. \qquad (4)$$

Thus, the technique allows us to evaluate quantitatively the gas-phase antipyren using formula (3) and to compare its effectiveness when charring from condensed and gaseous phases using formula (4).

METHODS FOR DETERMINATION OF POLYMER COMPOSITIONS AND COKE AND THEIR INFLUENCE ON HEAT LOSS FROM SURFACES

The processes that occur during polymer burning, in general, can be subdivided as running in gaseous and condensed phases. But even so, they are in indissoluble connection and influence each other. For this reason the given external effects on polymers are used (temperature, rate of heating, graduated energy) during the investigations of inhibitor influence on the condensed phase.

Heat transfer from the flame to the surface of burning polymer occurs by conduction, convection and radiation. The role of radiation during diffusion burning has been noted in the study.[19] The authors investigated the relation between the burning rate of fuel and its characteristic size under conditions of natural convection. It has been shown that when site burning diameter was 20 cm or more the mechanism of heat transmission between flame and fuel changed from convection to radiation.[20] In the study[21] the flame radiant power of burning cylindrical epoxide samples with a diameter of 25 mm has been measured. It has been shown that the flame radiant power reaching the polymer surface was a substantial factor even near the limit of burning.

The represented data prove the important role of radiant heat transmission in polymer burning as well as the necessity to investigate the behavior of both the polymers and the coke under radiation.

A number of studies concerned the role of overradiation from the burning polymer surface. Reference 22 contains data on burning of fuel bars with dimensions of 30 × 30 cm in air under natural convection. It was shown that the radiant heat loss from the polymer surface can reach up to half the energy transferred from the flame to the polymer surface. Based on data obtained in the condensed phase during wood burning under conditions of the flat countercurrent flame and ventilation by oxidating mixture, the authors concluded that radiant heat loss from the surface to the environment is substantial enough.

It is known that the heat transfer from a surface of a body into the environment depends on both temperature and optical properties of the material (e.g., blackness, reflection ability). Heat loss from bodies at the same temperatures can be different by several-fold. Thus, considering a mechanism of heat loss increasing from the coke surface when an inhibitor is made a part of the composition, it is necessary to study the optical properties of polymer composition and formation of coke in pyrolysis.

The data in the literature on the subject show that there is not a clear conception concerning the influence of optical properties on the flammability of polymer materials (the reports usually consider one of the factors, for example, overradiation from a surface without regard to others). Our study represents the attempt of a comprehensive approach to this problem.

The experimental unit (Figure 1) was used to investigate the influence of inhibitor on the composition's optical density. The furnace (CUOL 0.4.4)—an extended source allowed to produce radiant heat with spectrum close to absolutely black-body radiation—was used. During the experiment the polymer film (2) was placed

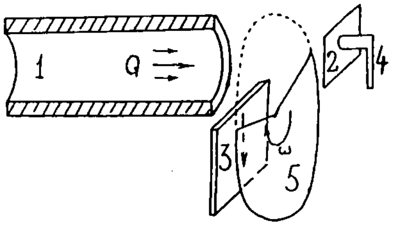


FIGURE 1 The experimental unit for polymer and coke film optical density investigations under heat radiation: (1) furnace; (2) polymer film; (3) cover; (4) radiation detector; (5) modulator.

in front of the furnace (1) heated to 1200°C. Then, the cover (3) was opened and the detector of radiation (4)—an optical thermocouple telescope with spectrum range of 0.4–25 mcm—measured energy transmitted through a test specimen. Under the action of radiant heat, the polymer film was gradually pyrolyzed and the layer of coke was formed. The modulator (5)—as a rotatable semicircle—separated the energy transmitted through the polymer from that emitted from the heated polymer film and coke. The rate of modulation was of the order of 1 Hz. An oscillograph registered radiation data. Thus, during polymer pyrolysis the unit was allowed to measure a part of the radiant heat transmitted through a film with given thickness and coke formed as a result of the pyrolysis.

The investigations of heat loss from the polymer surface and the coke were carried out in the unit shown in Figure 2. It included the radiation panel (1)—gas burner GIIBL—the cover (2) for modulation of radiation transmitted from the panel to a polymer under study (3), which was the layer of material 20 mm thick. The detector of radiant heat (4)—barretter BMK with operating spectrum range of 0.4–20 mcm—was placed in close proximity to the test polymer. The operating range of the detector overlapped radiation of the panel and hot coke in the visible and infrared bands of the spectrum. The heating of the barretter caused by neighboring hot surfaces shifted zero level of signal. To fix this shift the modulator (6) with a modulation frequency of 2 Hz was used. It closed the entrance window of the barretter within a specific time interval. Since the gasifying products of pyrolysis contaminated the entrance window made from KBr monocrystal its surface was systematically cleared and polished.

Gas flow passed to the burner was controlled by a gauge. The level of radiant heat transmission from the panel was measured by the moderate level indicator of radiant heat (IMO-2N) with an operating band spectrum of 0.4–50 mcm. To measure the surface temperature of the polymer and the coke during heating and pyrolysis a platinum-platinorodium thermocouple was inserted into the test specimen at a depth of 0.2 mm.

It has been found that the morphology of coke formation and the heat loss from the coke surface substantially depended on experimental conditions, namely, environmental oxygen concentration. To provide the conditions similar to burning pyrolysis the polymer surface after forming of a thin coke layer was cleared during

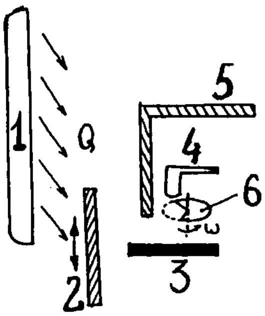


FIGURE 2 The experimental unit for study of heat loss from polymer and coke film surfaces under heat radiation: (1) radiation panel; (2) cover; (3) polymer under study; (4) radiation detector; (5) heat screen; (6) modulator.

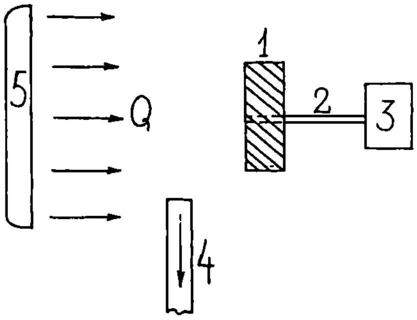


FIGURE 3 The experimental unit for investigations of antimony trioxide influence on epoxide composition pyrolysis under heat radiation: (1) polymer sample; (2) straw; (3) electronic balance; (4) cover; (5) radiation panel.

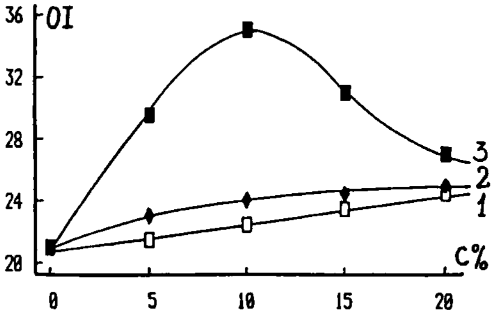


FIGURE 4 The dependence of epoxide composition oxygen index (OI) on filler concentrations for: (1) antimony trichloride; (2) triphenylstibine; (3) and antimony trioxide.

the experiment and the optical properties of coke forming further on the surface were studied (the coke formation at the surface took place in the vapor of pyrolysis products). A signal from the barretter and the thermocouple came to oscillograph N-043. In the experiment we used the registration point on the metallic plate covered by nielloid platinum with a diffusion reflection coefficient of 50%.

The experimental unit for study of antimony trioxide influence on the pyrolysis of epoxide composition under the action of radiant heat is shown in Figure 3. The polymer sample (1) was placed on straw (2) fixed in the electronic balance (3). Then, the cover (4) of the radiation panel (5) was opened and the pyrolysis began. During the experiment we registered polymer mass loss under given heat radiant emittance.

Figures 4–6 illustrate correspondingly the oxygen index, the relation between the stationary gasification rate and temperature gradients between environment and composition (the method of high-temperature pyrolysis) and the influence of inhibitor on temperature profiles in the flame (the spheric model of diffusion burning). Antimony trichloride and triphenylstibine were ineffective inhibitors of epoxide composition burning and did not provide a substantial increase in the oxygen index. Both compounds accelerated the gasification. This can be attributed to their low heat of evaporation in comparison with the heat of gasification and the destruction of starting polymer. This assumption was confirmed by the decrease

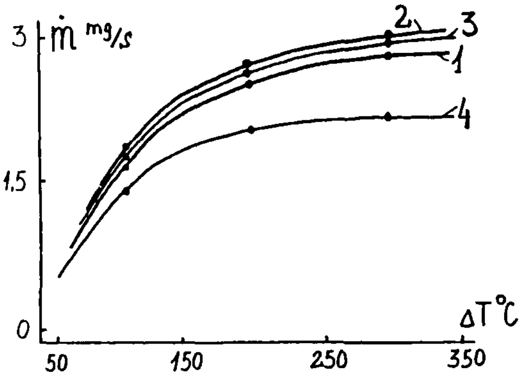


FIGURE 5 The dependence of high-temperature pyrolysis stationary rate on temperature gradient between polymer composition and environment for: (1) starting composition; (2) compositions with 20% antimony trichloride; (3) 20% triphenylstibine; (4) and 10% antimony trioxide.

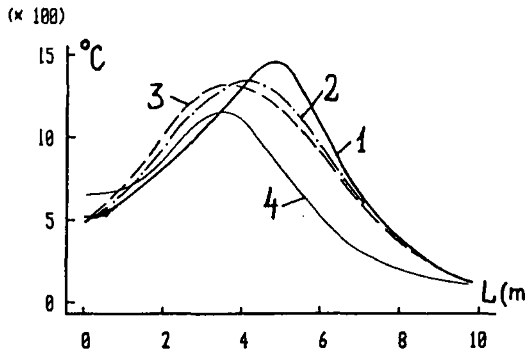


FIGURE 6 The temperature profiles in gaseous phase of (1) starting epoxide composition and (2) compositions with 20% antimony trichloride; (3) 20% triphenylstibine and (4) 10% antimony trioxide. Environment oxygen concentration.

in surface temperature of pyrolyzing composition (Figure 6) after the addition of such inhibitors. At high concentrations of these compounds we could observe an increase in flame shine that appears to be explained by the chemical inhibition of gas-phase reactions. Antimony trichloride decreases the viscosity of melt by its dilution. The increase in this compound led to the faster melt run off of the burning surface of composition.

Thus, taking into consideration the data obtained we concluded that antimony trichloride and triphenylstibine enter the gaseous phase in the burning. Nevertheless, the problem remained unsolved and called for further study whether chemical inhibition or only inert dilution play the main role in the process.

An unexpected result was that the antimony trioxide without halogens effectively inhibits the burning of epoxide composition, increasing the oxygen index by more than 15 units. Using the spheric model of diffusion burning it was shown that antimony trioxide produces a steady rise in coke remainder after the finishing of gasification. But when measuring the oxygen index at high concentrations of this compound we observed a slow down of polymer destruction below the formed coke "cap" and an increasing rate of coking close to the flame edge that facilitated flame spread along the surface not yet pyrolyzed. Figure 5 shows that introducing antimony trioxide greatly decreases the stationary pyrolysis rate in comparison with starting composition and makes it only slightly dependent on the variation of heat flows. With burning (Figure 6) the temperature of the coke "cap" increased markedly, which must have resulted in a rise in that loss from the surface and decreased heat flows that reached the pyrolyzing polymer placed below the coke layer. It seems to be a physical mechanism of flammability decrease. The causes promoting the rise of heat loss from a surface will be described below.

Figure 7 shows the oxygen index dynamics of epoxide composition when antimony trichloride entered the gaseous phase of burning polymer from the environment. High temperatures (150 ± 10°C) of the flow and the polymer caused the decrease in the oxygen index under nitrogen and oxygen flow burning. The concentration of antimony trichloride in the range of 0–0.6 vol.% in gas flow caused a linear increase in the oxygen index. The further rise in concentration resulted in a beyond-cutoff situation. Calculated according to Formula (3) for the linear segment of the curve, the specific heat was 500 J/mol·°C. This magnitude was almost greater than that in Reference 1 by a factor of 10.[23] Thus, the action of antimony trichloride in the gaseous phase consists exactly of flame chemical inhibition and does not in inert dilution.

At first sight we can consider antimony trichloride as an efficient gas-phase inhibitor (being introduced in the gaseous phase it increases the oxygen index by more than 10 units; the effect of the inhibitor exceeds the specific heat by a factor of 10). On the other hand, this discrepancy can be eliminated by the assessment of its concentrations in the gaseous and condensed phases according to Formula (4). The calculated data show that even high concentrations of antimony trichloride in the composition are in agreement only with the starting part of the curve presented in Figure 7.

Figure 8 presents experimental data on the oxygen index of epoxide polymers containing antimony trichloride and data calculated using Formula (4) (Figure 7). The closeness between experimental and calculated data on the oxygen index shows that the gas-phase inhibition of composition flammability by antimony trichloride dominates over the condensed-phase inhibition.

The measured data on polymer and coke optical densities are presented in Figures 9 and 10. Measurement of 0.4-mm thick films was performed. The figures show

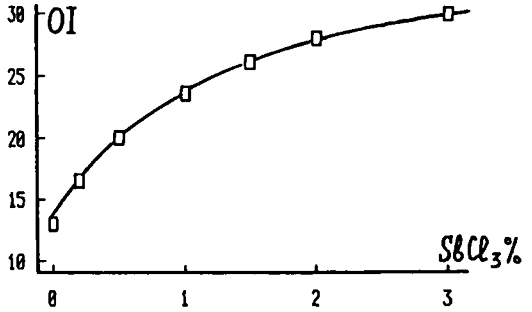


FIGURE 7 The dependence of epoxide composition oxygen index on antimony trichloride volume concentration in leak-in gas.

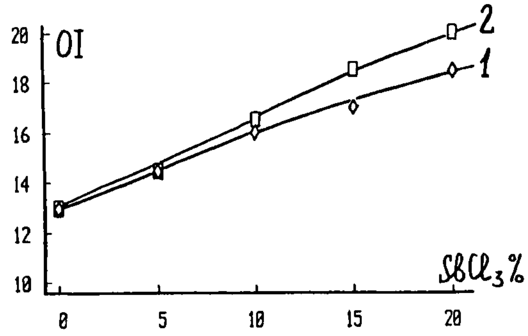


FIGURE 8 The comparison of epoxide polymer burning inhibitory effect after the introduction of antimony trichloride (1) in the composition and (2) in the gaseous phase with correction on its concentration in condensed phase.

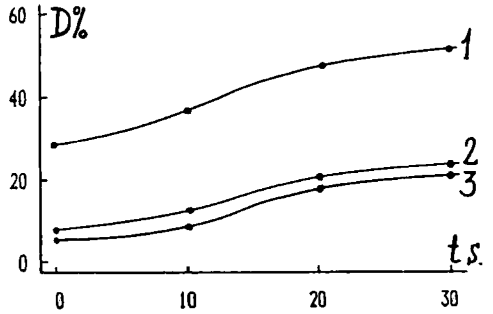


FIGURE 9 The dynamics of radiant fraction passing through pyrolyzing polymer film. (1) Starting epoxide composition; (2) compositions with 10% Sb_2O_3; and (3) 20% Sb_2O_3. (Film thickness = 0.4 mm.)

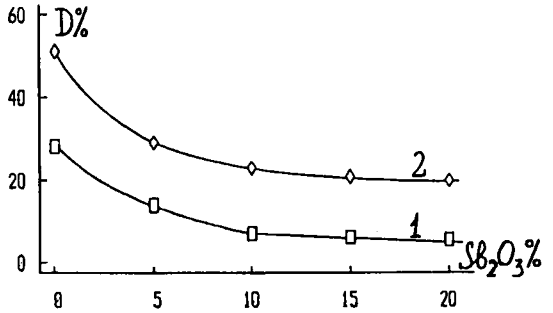


FIGURE 10 Antimony trioxide influence on the optical density of (1) epoxide composition and (2) coke. (Film thickness = 0.4 mm.)

that introduction of antimony trioxide caused a rise in the optical density of the coke "cap." The coke formed during the pyrolysis of polymer film (0.4 mm thick) without additives let more than 50% of the radiant energy of the furnace escape but as the concentration of antimony trioxide in the polymer film reached 20%, this value decreased to 20%.

Based on our measurements we concluded that, in addition to the radiant heat

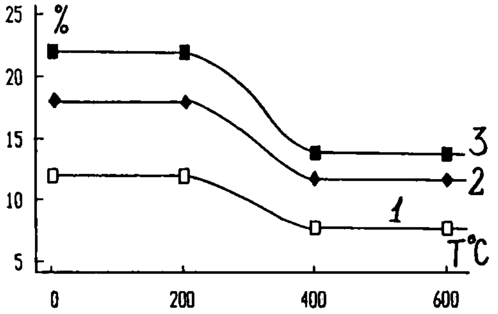


FIGURE 11 The influence of antimony trioxide on reflective heat loss from polymer composition and coke surfaces. (1) Starting epoxide composition; (2) compositions with 10% Sb_2O_3; and (3) 20% Sb_2O_3. (The intensivity of dropped heat radiation is 2.0 W/cm^2.)

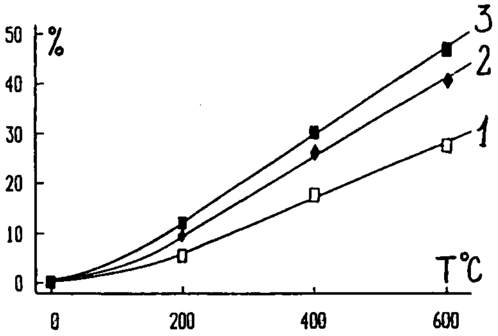


FIGURE 12 Antimony trioxide influence on radiant heat loss from polymer composition and coke surfaces. (1) Starting epoxide composition; (2) compositions with 10% Sb_2O_3; and (3) 20% Sb_2O_3. (The intensivity of dropped heat radiation is 2.0 W/cm^2.)

loss from the coke surface, loss by reflection from it also plays a substantial role. Figure 11 illustrates the measured fraction of decreasing heat radiation reflected from the polymer and coke surfaces. The introduction of antimony trioxide in composition (up to 20%) increased the reflecting ability of the polymer from 12 to 22%. A decrease in the reflection coefficients at temperatures of 300–400°C was a result of coke formation on the polymer surface.

The measured fractions of overradiant heat from polymer and coke surfaces during heating and pyrolysis are illustrated in Figure 12. The introduction of antimony trioxide caused an increase in radiant heat loss due to the increased optical density of the coke, which is in agreement with data presented in Figures 9 and 10.

Figure 13 shows the integral heat loss (radiation plus reflection) from the polymer surface during radiant pyrolysis. The introduction of antimony trioxide increased the heat loss from the coke "cap" surface at the same surface temperature and could reach 70% of the energy supply.

It should be noted that when the concentration of antimony trioxide was increased in the composition the difference in heat loss between inhibited and noninhibited compositions was greater than that depicted by Figure 13. This can be explained

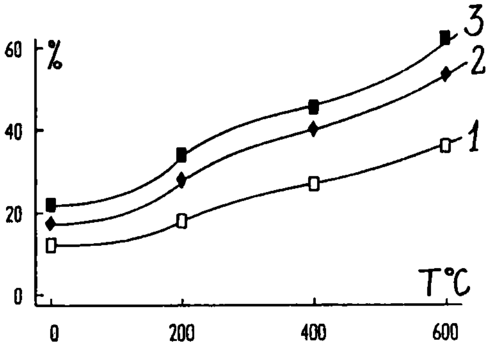


FIGURE 13 Antimony trioxide influence on total heat loss from polymer composition and coke surfaces. (1) Starting epoxide composition; (2) compositions with 10% Sb_2O_3; and (3) 20% Sb_2O_3. (The intensivity of dropped heat radiation is 2.0 W/cm^2.)

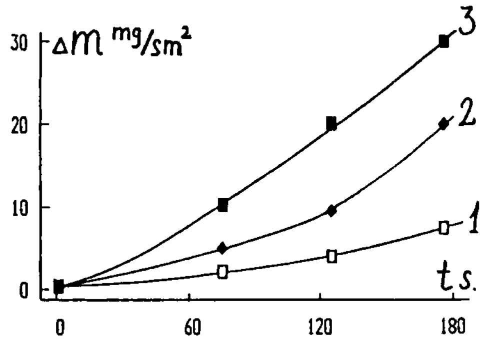


FIGURE 14 The early mass loss of test specimens under heat radiation for (1) starting epoxide composition; (2) compositions with 10% Sb_2O_3; and (3) 20% Sb_2O_3.

by the increased optical density of the coke. Because of this situation, at the same energy supplied to the surface, the temperature of the coke containing antimony trioxide will be higher than that forming in pyrolysis of the polymer composition without additives. These proposals are corroborated by the data on stationary temperatures of coke surfaces forming on epoxide balls containing antimony trioxide (Figure 6).

Figure 14 shows the mass loss of composition during radiant pyrolysis. As indicated in Figure 14 the increase in the percentage of antimony trioxide caused a rise in the rate of composition mass loss at the coking step. Nevertheless, after the coke "cap" is formed on the surface the stationary gasification rate of the composition with antimony trioxide was reduced. (When the power density was 1.0 W/cm·s the introduction of antimony trioxide (20%) in composition lowered the gasification rate from 1.2 mg/cm^2·s (starting polymer) to 0.3 mg/cm^2·s. To define the stationary gasification rate the polymer surface was cleared after the thin coke layer formed due to the above-mentioned cause and the measuring was performed during polymer pyrolysis in destruction product vapors.)

Based on the data obtained we can concern ourselves with the extremal relationship between the oxygen index of composition and the percentage of antimony trioxide in it to two acting factors: on the one hand, the introduction of antimony trioxide increased the heat loss from the "cap" surface; on the other hand, the time needed for the beginning of pyrolysis decreased at the expense of the elevation of the composition's optical density.

It would also be advantageous to note that the nature of heat flows run from the coke to the pyrolyzing polymer. During the inhibition of epoxide composition flammability by antimony trioxide, as was above mentioned, we observed a great expansion of formed coke "cap" on the flame way (the expansion of test specimens even with dimension of the order of 1 cm reached approximately 0.7 mm). Thus, the gaseous layer that exists between the coke and the polymer of burning composition contained antimony trioxide, and it increased in the process of polymer burn-out. The simple calculation based on the temperature gradient between the coke and the pyrolyzing polymer surface of 100°C and the coke blackness of 0.4 shows that heat transfer via conduction through gas in the layer will dominate over radiant heat transfer at layer thickness less than 0.1 mm even with overestimated thermal conductivity of 0.01 kcal/m·s°C. At gas layer thickness on the order of 1.0 mm the entire heat exchange will approximately equal the radiant one. But the data on layer thickness are somewhat overestimated since there is a direct moving of pyrolysis products from the polymer surface to the coke. So, if the conduction heat exchange between the forming coke and the composition exists near the flame edge, then further it will be replaced by the radiant one.

Thus, we have studied in detail the influence of antimony compounds on the physical processes occurring in polymer pyrolysis and burning and have shown the following:

1. The gas-phase inhibition by antimony compounds is ineffective and does not substantially reduce epoxide composition flammability.
2. The antimony trioxide, itself, can be an effective burning inhibitor.
3. The inhibitory mechanism of polymer composition flammability was defined, which consists of changing of the optical characteristics of polymer compositions and coke and gives rise to the elevation of heat loss from burning surface. To put this mechanism in action in the case of soot flames we must seek the production of coke which has a high reflection coefficient especially in the spectrum range where the radiation maximum of flame occurs. Since the full reflection is almost not achievable, the coke must be opaque to radiant heat from the flame in addition to having high reflection properties.

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