

Halogen-Modified Impact Polystyrenes: Quantification of Pre flame Phenomena

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Synopsis

A novel flash thermolysis technique was developed and used to elucidate factors which control pre flame phenomena in halogen-modified impact polystyrenes. The interrelation between the flux of fuel from impact polystyrene, the flux of flame quenching agents from decabromodiphenyl oxide and metal oxides, and the formation of char was quantified in flash thermolysis experiments at $>500^{\circ}\text{C}$. The results were correlated with the performance of materials in a standard flammability rating test. In contrast to existing theories of flame retardancy via aromatic halide-antimony trioxide systems, it was found that polymeric free radicals generated during the burning process participate in the halogen release mechanism. The temperature for the halogen release is proportional to the bond strengths of the matrix resin. The specific role of polybutadiene in halogen-modified impact polystyrene was recognized to include impact modification, halogen release synergism, and the reduction of dripping tendencies during burning.

INTRODUCTION

The use of brominated aromatics such as brominated diphenyl oxide in the reduction of the flammability of plastics has been known since 1933.^{1,2} The increase of the flame-quenching efficiency of organic halides by the admixture of antimony trioxide into the flammable matter was dealt with in mechanistic studies.^{3,4} The present paper concerns the synergistic interaction of antimony trioxide with aromatic halides in a polymeric environment. More specifically, it describes the role of thermolyzed polystyrene and polybutadiene in the scission of the aromatic bromine bond. Research focused on the following pre flame phenomena: the flux of combustible volatiles, the flux of flame quenchers, and the degree of carbonification of the heat-exposed resin. An attempt was made to correlate the pre flame reaction characteristics of a material with its performance in a common flammability rating test, namely, the Underwriters' Laboratory Bulletin 94 V test specifications.

Additional attention is paid to the onset of dripping during the flammability test, to the temperature at which halides are released, and to the nature of the char. The material balance of thermolyzed decabromodiphenyl oxide/antimony trioxide-modified impact polystyrene is presented.

Insight into the pre flame phenomena of burning impact polystyrene was gained by the rapid thermolysis of the composite in a metal bath, by material balance data, mass spectrometry, NMR, and IR analysis.

EXPERIMENTAL

Measurement of the Internal Temperature of Test Specimens

A thermocouple of 0.025-in. cross section was centered between two IPS specimens of 4 in. \times 0.05 in. \times 0.075 in. which were then heat fused. The tip of the thermocouple was thereby centered 0.075 in. inside the fused \sim 0.150 in. \times 0.05 in. \times 4 in. test specimen and 0.075 in. from the base. The thermocouple was connected to a recorder capable of responding to a temperature rise of 700°C in 4.0 sec.

Sample specimens of the resin systems were constructed as described above. Resin A: 84% IPS, 16% polybutadiene; resin B: 69% IPS, 13% polybutadiene, 12% tetrabromophthalic anhydride, 5% Sb_2O_3 , 1% $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; resin C: 66% IPS, 13% polybutadiene, 14% NH_4Cl , 5% Sb_2O_3 , 2% $\text{NH}_4\text{H}_2\text{PO}_4$.

Thermolysis in the Metal Bath

A cylindrical stainless steel container with a cross section of 4.5 in. and height of 6.5 in. was filled with Wood's metal and supported in a welded iron ring. Two thick layers of asbestos were used to insulate the mantle of the cylinder, which was heated by a Mecker burner. A thermocouple was inserted in a stainless steel needle in the bath and used to record the temperature of the bath. Several 0.25-in. layers of asbestos formed the cover of the cylinder.

Well-mixed and preweighed samples of the reactants to be studied were charged into a thin walled test tube of 1 in. \times 8 in. The material temperature was monitored with a thermocouple which was protected by a thin glass capillary. Stainless steel tubes were used for flash thermolysis at temperatures $>560^\circ\text{C}$.

The tubes were immersed 4 in. into the bath as shown in Figure 1. Above the immersion zone was a condensation zone filled with a 2-in. layer of glass wool, followed by a 2-in. zone containing pH paper and small gas inlet and outlet tubes. The condensation and pH paper zone was cooled with a rapid air stream.

The batch temperature was recorded at 3-min intervals and the glass tube was raised for visual inspection of the batch for \sim 3 sec. The release of bromine or acid was registered from the color change of wet pH paper. After the experiment, the glass test tube was cut at a height of 4 in. The residue was carefully collected and weighed and the char yield thus recorded. The glass wool which held the condensate was weighed, extracted several times with benzene, dried, and reweighed. The condensates were reclaimed by evaporation of the benzene. The residue and the condensate were analyzed for bromine, antimony and organic moieties.

Underwriters' UL-94 Vertical Flammability Test⁵

The test specimens were prepared to meet the dimensional requirements for the UL-94 vertical test specifications.

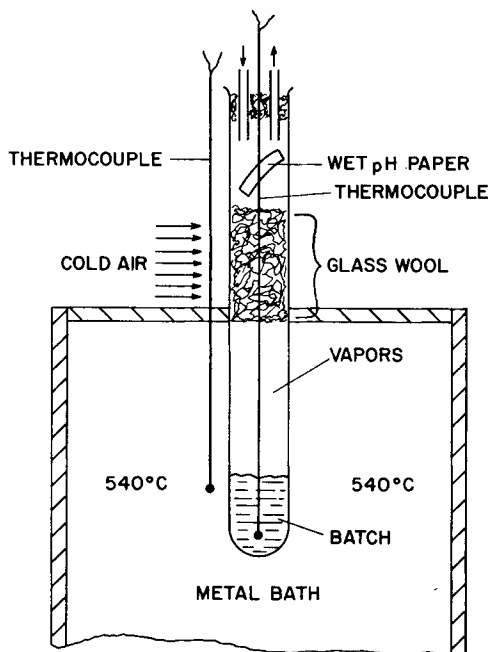


Fig. 1. Reactor for thermolysis of resins and flame retardants.

A sample specimen 5 in. \times 0.5 in. \times 90 mil is mounted in a vertical position and ignited using a $\frac{3}{4}$ -in. Bunsen burner flame. After 10 sec, the flame is removed and the specimen allowed to extinguish. The 10-sec ignition process is repeated again and the rating determined by the extinguishing characteristics, as follows. Flaming droplets are allowed to fall on cotton.

Vertical Extinguishing Group 0 (V-0). Extinguishment in a vertical bar test in 5 sec or less average; no single burn value plus afterglow greater than 10 sec; no flaming dripping.

Vertical Extinguishing Group 1 (V-1). Extinguishment in a vertical bar test in 25 sec or less average; no single burn value plus afterglow greater than 30 sec; no flaming dripping.

Vertical Extinguishing Group 2 (V-2). Same as V-1 except that flaming dripping occurs.

RESULTS AND DISCUSSION

Temperature Profile During the UL-94 V Test

Impact polystyrene (IPS)⁶ is a composite consisting of a flammable, continuous polystyrene phase (PS) and a flammable, dispersed polybutadiene rubber phase (PB). The heats of combustion of PS and PB are 4400 cal/g and 4500 cal/g, respectively. Upon exposure to the UL-94 V test specimen to a Bunsen burner blue flame of $\frac{3}{4}$ -in. or 2.0-in. height, ignition generally takes place at $\sim 245^\circ\text{C}$.⁷ The temperature of the test specimen increases and dripping may occur.

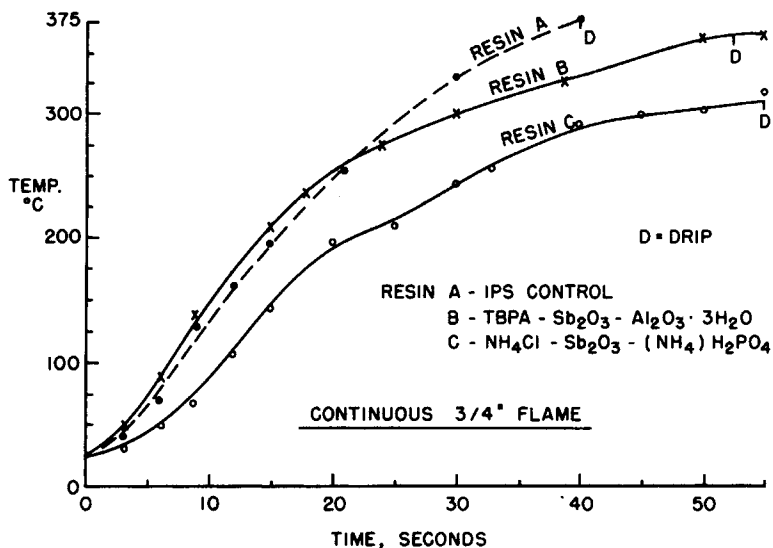


Fig. 2. Temperature profile in IPS test specimens: continuous $\frac{3}{4}$ -in. flame.

Figure 2 shows the temperature profile of an IPS control and two halogen-modified IPS (HM-IPS) as monitored with an implanted thermocouple during continuous exposure to the $\frac{3}{4}$ -in. flame. The IPS control dripped after 40 sec; the thermocouple, which was 75 mil inside the vertical exposed end of the test specimen, registered 375°C at this point. The internal heat-up rate of resin B (tetrabromophthalic anhydride, $\text{Sb}_2\text{O}_3\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ modified IPS) is equal to that of the control up to 260°C. At this temperature, endothermic (dehydration of $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$) and flame quenching (release of halogen) phenomena decrease the heat-up rate. Dripping occurred after 52 sec of exposure to the $\frac{3}{4}$ -in. flame. The inorganic flame retardants (NH_4Cl , Sb_2O_3 ,

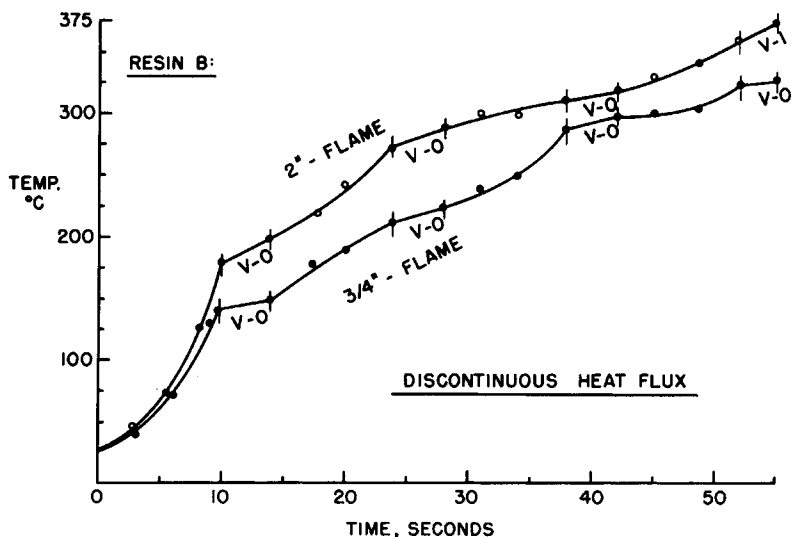


Fig. 3. Temperature profile in IPS test specimens: UL-94, vertical test.

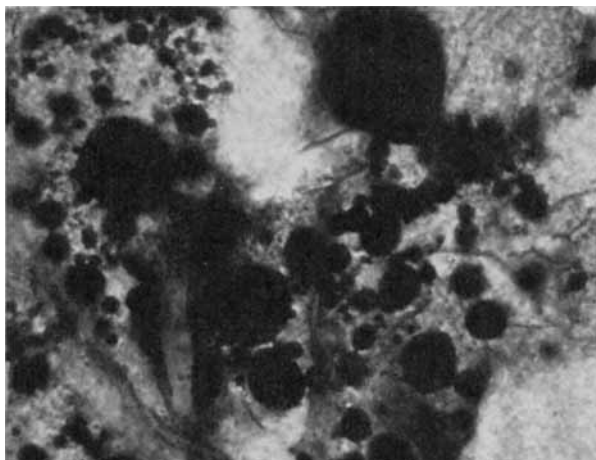


Fig. 4. HM-IPS: Flamed 3 sec. Note: Pockets of degrading flame retardants and polymer. Magnification: 400 \times .

$\text{NH}_4\text{H}_2\text{PO}_4$) in resin C reduce the internal temperature of the test specimen during exposure to a flame, and dripping was observed after 55 sec; the internal temperature registered only 310 $^\circ\text{C}$ when dripping occurred.

An essential feature of the UL-94 V test is the discontinuation of the flame exposure after 10 sec. Figure 3 depicts the internal temperature profile of resin B with discontinuation periods of 4 sec. It can be seen that the tetrabromophthalic anhydride, Sb_2O_3 , $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ combination is a highly effective flame retardant package. As seen in Figure 3, the composition passes the V-0 requirements after four exposures to a $\frac{3}{4}$ -in. flame (note that only two exposures are required in the V-0 test specification). The internal temperature increase resulting from a discontinuous 2-in. flame is nearly the same as the continuous heat flux of the $\frac{3}{4}$ -in. flame (Fig. 2, resin B). Microscopic inspection of the resin B showed the char structure was produced 8 to 10 mil into the specimen.

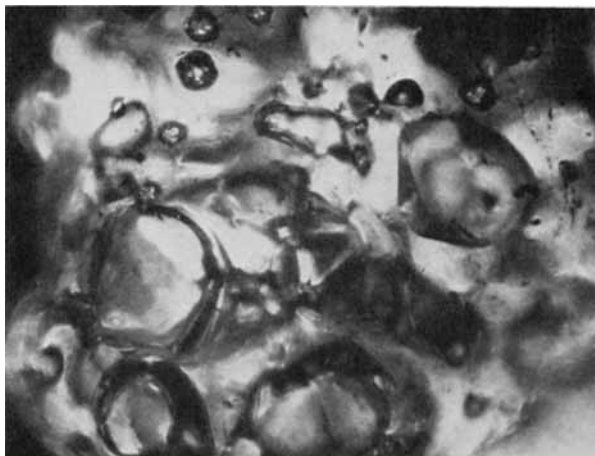


Fig. 5. HM-IPS: Flamed 6 sec. Note: Microfoam bubbles. Magnification: 400 \times .

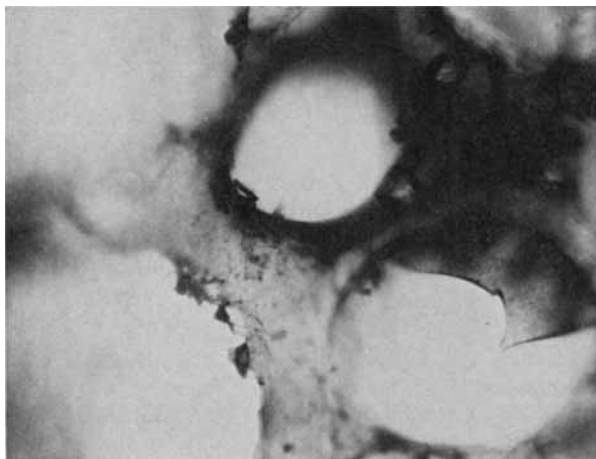


Fig. 6. HM-IPS: Flamed 105 sec. Note: Fractured microfoam lamella. Magnification: 100X.

The very thin charred layer of microfoam lamellas which encases the end exposed to the flame constitutes a thermal insulation and fuel barrier. These microlamellas burst during the flame test and discharge volatiles into the flame zone. Up to 10% of the total Sb_2O_3 concentration is transported to the flame by this mechanism involving the bursting of microbubbles.

Figures 4 to 6 characterize the surface of flamed HM-IPS (decabromodiphenyl oxide/ Sb_2O_3 -modified impact polystyrene).

The information gained from the above study of the temperature profile during the UL-94 V test was used to guide the subsequent study on preflame phenomena. While the internal temperature levels off at 300–400°C, it should be noted that the flame temperature can reach 800–1000°C. Thus, chemical and physical phenomena occurring within these temperature ranges are of interest.

The Effect of Additives on the Melt Flow of PS

The danger of spreading fire by flame dripping is considerable. Therefore, UL-94 V tests include the melt rheological behavior of the test specimens. The dripping characteristic of UL-94 V test specimens was determined by prolonged exposure to the $\frac{3}{4}$ -in. flame. Flammable test specimens were ignited and allowed to burn until the first drop fell, whereas continued 10-sec exposures to a $\frac{3}{4}$ -in. flame were employed for V-0, V-1, or V-2 grades of halogen modified IPS.

Table I reveals that polybutadiene or graft polymers of styrene onto polybutadiene is the major antidrip component in IPS. Sb_2O_3 , which slightly enhances dripping in PS, clearly depresses drip in the presence of PB and is able to compensate for the adverse effect of DBDPO (mp = 285°C, bp = ~425°C) on dripping in the system. It is interesting to note that within this experiment the Lewis acid ZnBr_2 ⁸ did not cleave PS fast enough to affect the onset of dripping. In contrast, PB rubber in IPS was obviously adversely attacked by ZnBr_2 since the time to drip was decreased by a factor of about 2.

TABLE I
Effect of Additives on Dripping^a

PS additive	Time to drip, sec	IPS additive	Time to drip, sec	UL-94 status
—	24	—	55	non-V
10% Sb ₂ O ₃	19	1% ZnBr ₂	35	non-V
20% Sb ₂ O ₃	20	10% DBDPO	35	non-V
1% ZnCl ₂	23	5% Sb ₂ O ₃	62	non-V
2% ZnBr ₂	26	10% DBDPO/5% Sb ₂ O ₃	74	V-0
5% PB ^b	56			
10% PB	110	10% DBDPO/5% Sb ₂ O ₃ /	86	V-0
20% PB	no drip	1% ZnO		

^a UL-94 V test specimens, 10-sec ignition, 3/4-in. flame.

^b Polybutadiene: 35% cis-1,4; 55% trans-1,4; 10% 1,2 addition.

The Limits of IPS/DBDPO/Sb₂O₃ Systems

The minimum additive levels of DBDPO and Sb₂O₃ in IPS to pass the three UL-94 flammability categories are shown in Figure 7. The known synergistic effect of Sb₂O₃^{3,4} is clearly demonstrated. Examination of the data reveals that the useful additive limits for the three classifications differ over a narrow range. The area of commercial interest has been framed. Incorporation of flammable oil or lubricant may drastically affect the flammability status of the final HM-IPS.

Effects of Metal Oxides on Halogen Release

The control of the release of flame quenchers during the UL-94 test is of paramount importance for the efficiency of flame retardants.⁹ To study the release of flame quenchers, intimate mixtures of finely powdered aromatic

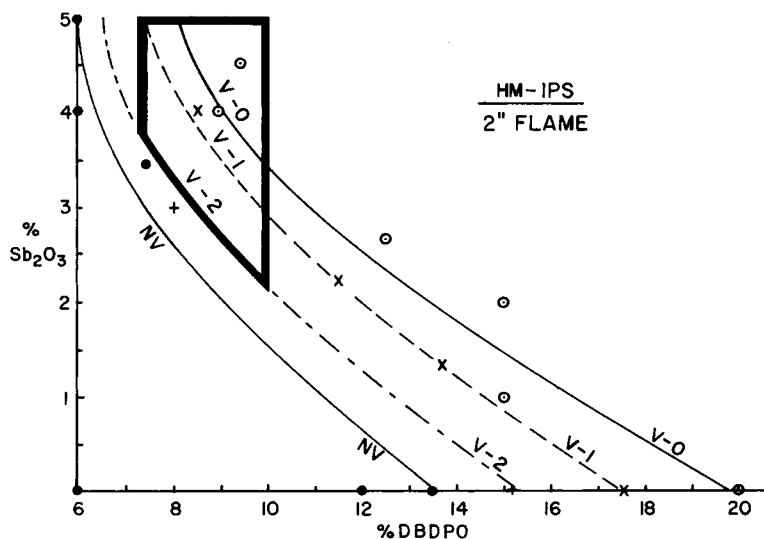
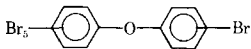


Fig. 7. The limits of the DBDPO-Sb₂O₃ synergism in a given IPS resin.

TABLE II
Effect of Metal Oxides on Halogen Release from DBDPO^a

Sb ₂ O ₃ ^b	MgO ^c	ZnO ^d	Release temperature, °C	Release rate
—	—	—	485	very slow
+	—	—	450	fast
—	+	—	485	very slow
+	+	—	455	very slow
—	—	+	430	very slow
+	—	+	450	very fast

^a 3.0 g Decabromodiphenyl oxide, 

^b 1.0 g Sb₂O₃.

^c 0.5 g MgO.

^d 0.5 g ZnO.

bromides and metal oxides were flash thermolyzed. The release temperature of halogen was registered with pH paper as described in the experimental section. The results (Table II) on the thermolysis of decabromodiphenyl oxide demonstrate the control of halogen release by combinations of metal oxides. The following generalization has been formulated from studies on a number of systems: (1) Sb₂O₃ increases the rate of halogen release from aromatic bromides. (2) MgO decreases the rate of release of halogen from Sb₂O₃/aromatic bromine systems. (3) Very fast, nearly explosive release is induced by Sb₂O₃ and ZnO combinations.

The steps of the interaction of Sb₂O₃¹⁰ and the halogen donor which finally produce volatile SbBr₃ and SbOBr are not fully documented. Visual inspection revealed that liquid decabromodiphenyl oxide is immediately adsorbed by Sb₂O₃ to produce a viscous, doughlike melt. At 455°C, this melt decomposes to a thin, brown liquid with strong volatility and forms a high-gloss, brittle solid upon cooling.

The degree of degradation of the halogen donor by the various metal oxides was reflected in the nature of the char (Table III). These observations correlate with the results presented in Table II, namely, Sb₂O₃ and Sb₂O₃/ZnO have an accelerating effect on DBDPO decomposition whereas MgO has a retarding effect on Sb₂O₃.

We have shown that by the judicious choice of metal oxide combinations, one can markedly affect the rate and temperature of release of volatile halogen moieties.

TABLE III
Char of Thermolyzed Neat DBDPO

Metal oxide	Residue
—	gray, rigid, no foam
Sb ₂ O ₃	black, rigid, no foam
Sb ₂ O ₃ -MgO	gray, rigid, no foam
Sb ₂ O ₃ -ZnO	black, fragile, foam

Thermolysis of Polystyrene and Polybutadiene

The thermal cleavage of PS and PB initiates and maintains the flux of combustible volatiles from the IPS test specimen to the flame. The literature^{11,12} describes a graduated decomposition from $\sim 320^{\circ}\text{C}$ to $\sim 380^{\circ}\text{C}$ for PS and 360°C to $>440^{\circ}\text{C}$ for an unspecified type of PB.

In our flash thermolysis studies, no exothermic reactions were observed during the thermolysis of PS. Figure 8 shows the growth of gas bubbles observed during the melt degradation of PS in the temperature range of $30\text{--}415^{\circ}\text{C}$.

It can be seen that at $>330^{\circ}\text{C}$, PS forms a foam which ultimately leads to dripping.

During the thermolysis of 4.5 g PS and 1.5 g Sb_2O_3 at a heat-up rate similar to that in Figure 8, no bubbles were observed. A slightly opaque dope was formed at 260°C . At 450°C , the resin was carbonized to brittle pitch. Sb_2O_3 has no significant effect on the rate of decomposition of PS, but prevents large bubbles and catalyzes char formation. In contrast to PS, the thermolysis of PB (microstructure: 35% *cis*-1,4, 55% *trans*-1,4; 10% 1,2 addition) is highly exothermic at 355°C . Up to this temperature, PB does not liquefy. Within 30 sec, the internal temperature rises to 440°C and the PB rubber changes to a thin, amber liquid. IR analysis confirmed the formation of cyclized products. There was no effect of Sb_2O_3 on the rate of thermolysis of this polybutadiene. The highly exothermic reaction took place at 355°C and the low molecular weight cyclized products refluxed violently. Considerable amounts of Sb_2O_3 were transported into the condensation zone of the test tube but no acid was released; the characteristic odor of 4-vinylcyclohexene was apparent.

The Effect of the Polymers on Halogen Release

The previous thermolytic experiments (Table II) documented the catalytic action of some metal oxides on DBDPO in lowering of the halogen release temperature and increasing release rate. There was added interest generated when the relationship between polymer bond strength and the halogen release was discovered during a systematic flash thermolysis investigation of halogen/antimony modified commodity resins. The results from several mixtures of polymer/DBDPO and polymer/DBDPO/ Sb_2O_3 , which were thermolyzed under argon or in air, are listed in Table IV. The data (Table IV) show a strong effect of the polymer type on the release of halogen from DBDPO. Within these experiments, air had no significant effect on the onset of halogen release. Sb_2O_3 increases the rate of halogen release from DBDPO but does not markedly affect the release temperature. Polybutadiene lowers the halogen release temperature of the DBDPO/ Sb_2O_3 system by

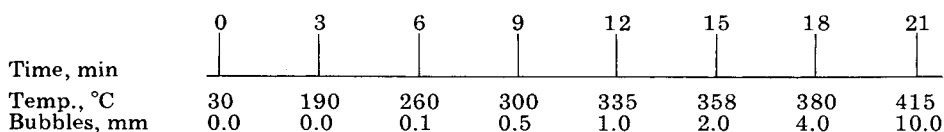
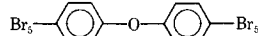


Fig. 8. The growth of bubbles in polystyrene.

TABLE IV
Effect of Polymer on Halogen Release from DBDPO

Polymer ^a	DBDPO ^b	Sb ₂ O ₃ ^c	Release temperature, °C	Release rate
PB	+	—	355	fast
	+	+	340	very fast
IPS	+	—	375	fast
	+	+	370	very fast
PS	+	—	410	fast
	+	+	400	very fast
HDPE	+	+	400	fast

^a 4.5 g Polymer.

^b 3.0 g Decabromodiphenyl oxide, 

^c 1.5 g Sb₂O₃.

100°C, IPS by 75°C, PS and polyethylene by 50°C. The coincidence of the isomerization of PB to brittle, cyclic products of very low molecular weight at 355°C and the release of acid from PB/DBDPO/Sb₂O₃ at 355°C suggests a free-radical attack of the fragments of PB on the aromatic C–Br bonds. Inspection of the bond strengths^{13,14} of the polymers involved (Table V) indicates that PB will undergo homolytic cleavage more readily than PS or PE, which correlates with the experimental results.

Precedence for the attack of aliphatic radicals on aliphatic carbon–halogen bonds already exists in the literature.^{15,16} However, the accelerated release of halogen from bromides via polymer radical intermediates in flame retardant compositions has never been previously reported. Model experiments summarized in Table VI demonstrate free radical-induced halogen release occurred at temperatures which are drastically lower than the interaction of DBDPO with Sb₂O₃ at 455°C. An elegant proof for the scission of the aromatic C–Br bond by $\sim\text{CH}_2\cdot$ radicals was obtained through the reaction of finely powdered 2.2-paracyclophane with DBDPO under argon. Wet pH paper turned red quickly when the mixture reached 235°C and the white surface of DBDPO turned brown at the onset of the reaction.

We propose this interaction mechanism with a polymer:

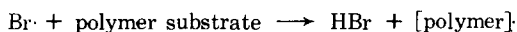
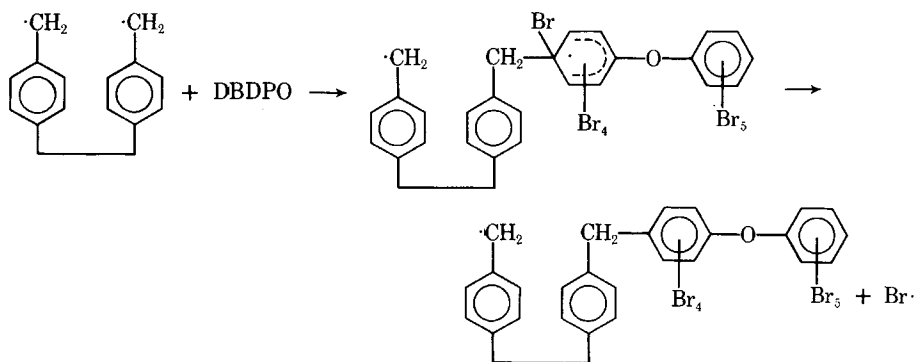


TABLE V
 Bond Strengths in HM-IPS

Compound	kcal/mole	Compound	kcal/mole
Polybutadiene		Polystyrene	
C ₄ —C ₁	43	Chain C ₇ —H	74
C ₁ —H; C ₄ —H	75	Chain C ₈ —H	75
C ₁ —C ₂ ; C ₃ —C ₄	83	Chain C ₇ —C ₈	80
C ₂ H; C ₃ —H	89	Ring C—C ₇	87
C ₂ =C ₃	145	Ring C—H	102
DBDPO		Ring C=C	145
Ring C—Br	~78	Polyethylene	
Ring C—O—C ring	85	C—C	80
Ring C=C	145	C—H	87

The observation that paracyclophane accelerates the release of halogen from DBDPO provides insight into an unsolved problem which exists in the flame retardant literature. It has been reported^{17,18} that paracyclophane and alkyl analogs markedly increase the flame retarding efficiency of cycloaliphatic bromine/antimony oxide additives in polypropylene. For example, polypropylene containing 1 phr each of 1,2-dibromo-1,2-bis(3,4-dibromocyclohexyl)ethane (Br₆BCE) and antimony oxide was rated as burning in the ASTM D-635-63 test; polypropylene containing 1.25, 0, and 2.0 or 0.8, 0.2, and 0.8 phr of Br₆BCE, Sb₂O₃ and paracyclophane, respectively, were rated nonburning. In light of the data presented in Table VI, the effect of paracyclophane is interpreted as due to the accelerated release of HBr and alkyl halides to the flame front. In effect, paracyclophane is acting similar to antimony oxide with the difference that the temperature for HBr release from paracyclophane-containing systems is lower.

Flash Thermolysis: Material Balance of Polymers and Additives

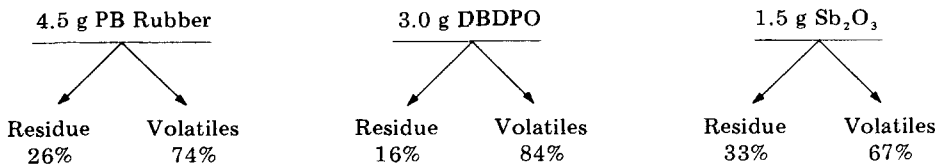
The microscopic inspection of HM-IPS test specimens after the UL-94 V test (exposure to a flame for 20 sec) defined the charring zone as approximately 8–10 mils deep. This char layer has a profound effect on the flammability characteristics of the IPS system as discussed earlier. Therefore, meaningful material balance data were retrieved from HM-IPS at charring heat, i.e., at >500°C, to gain better insight into the charring process.

 TABLE VI
 Free-Radical Attack on Aromatic C—Br

Peroxide	Halogen release temperature, °C
None	485
Dibenzoyl peroxide ^a	120
Dicumyl peroxide ^a	145
Di- <i>t</i> -butyl peroxide ^a	175
2,2-Paracyclophane ^b	235

^a 1.0 g DBDPO + 0.2 g peroxide.

^b 4.0 g DBDPO + 1.0 g 2,2-paracyclophane.



Average Thermolysis Phenomena Rates Over the 55-Second Period

Fuel Flux = 3.6 g/min

Quencher Flux = 3.8 g/min

Total Residue = Rate of Char Formation = 2.4 g/min

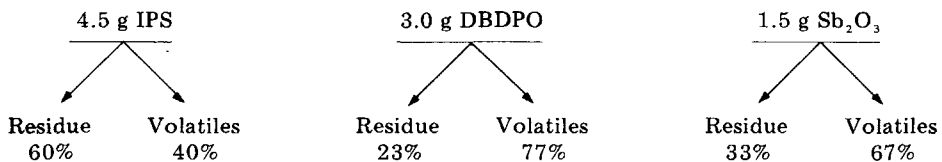
Fig. 9. 550°C/55 sec flash thermolysis: material balance.

The immersion of a finely powdered mixture of the polymers, DBDPO and Sb₂O₃, into the metal bath at 550°C simulated the thermal conditions in which preflame phenomena occur. Explosive discharge of polymer fragments, aromatic halide fragments, and Sb₂O₃ or SbBr₃ (mass spectroscopy) took place 55 sec after the immersion of PB/DBDPO/Sb₂O₃ at ~355°C and after 115 sec for IPS/DBDPO/Sb₂O₃ at ~375°C. The material balance diagrams for these systems are given in Figures 9 and 10. The analysis for Br and Sb in the char and the condensate, and the weights of the char and the condensate established the material balance. It can be seen in Figures 9 and 10 that the total fuel flux over the respective thermolysis periods is smaller than the flux of flame quenchers.

NMR analysis of the tarry condensates grouped the thermolysates in benzene, alkylene-benzene, methylbenzene, aliphatic methylene, and aliphatic moieties containing end-methyl and a large amount of cyclohexane. Mass spectroscopy of the tar showed that the majority of volatile fragments of DBDPO had a mass of ~720, hence DBDPO lost ~3 Br atoms.

The release of halogen from an IPS/DBDPO/Sb₂O₃ composite (IPS/DBDPO/Sb₂O₃ = 87/9/4) was also conducted in metal tubes at 570°C immersion temperature. After only 4 sec, while the sample temperature reached 380°C, an explosive release of acid occurred. Thus, in a burning situation, it can be anticipated that the halogen release mechanism will activate at about this temperature.

The material balance data in Figures 9 and 10 explain why the IPS/DBDPO/Sb₂O₃ = 87/9/4 composite meets the UL-94, V-0 specification. The



Average Rates over the 115-Second Period

Fuel Flux = 0.9 g/min

Quencher Flux = 1.7 g/min

Total Residue = Rate of Char Formation = 2.2 g/min

Fig. 10. 550°C/115 sec flash thermolysis: material balance.

short-term reduction of the flammability of IPS, which is caused by a short-term, high rate of quencher flux, is advantageous in incipient fire situations. At raging fire conditions, at $>500^{\circ}\text{C}$ in the composite, a rapid depletion of DBDPO and Sb_2O_3 takes place and the above-mentioned HM-IPS will burn.

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